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To previous and current co-workers.

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Preface

When Wiley-VCH approached me with the suggestion that I edit a textbook on metal–metal complexes, I was, at first, not convinced. Published in 2005 and already in its third edition, *Multiple Bonds Between Metal Atoms*, edited by F. Albert Cotton, Carlos A. Murillo, and Richard A. Walton, presents a comprehensive treatment of the area. However, time moves on, and so does science. Many advances have occurred in the intervening decade, and some entirely new areas of metal–metal chemistry have emerged while old ones have been reinvigorated. It was felt that a textbook to update the area was warranted and that its scope had to encompass the newfound breadth as well as depth of the area. Thus, the decision was made to cover all areas of the Periodic Table rather than just the d-block. This then raises the question of the structure of the book. Do we cover by group number? Do we cover by ligand class? Do we cover by structural motif? The options are varied, and each has its pedagogical advantages and disadvantages. In the end, the decision was made to generally treat each class by group number with the exception that s-block metal–metal bonds could be covered in one chapter. The result is a book of 15 chapters, which starts with a general overview of metal–metal bonding before dealing with individual groups.

In every chapter, authors have endeavored to be as comprehensive as possible, although an encyclopedic treatment is simply not possible due to the sheer volume of the literature and so a balance had to be struck. The authors have attempted to highlight important compounds and demonstrate important concepts and reactions. Inevitably the level of attention varies between areas and we apologize in advance for the inadvertent omission if the reader cannot find their favorite compound. Each chapter mentions important molecules at the genesis of each area but focuses principally on research published since 2005 as repetition of the above-mentioned treatise would be pointless. While attempts were made to harmonize the general structure of chapters, it had to be recognized that each area has its own specialties and by retaining individual author styles each chapter remains fresh to the reader. This approach has resulted in some duplications, but it is felt that this provides the reader with more than one perspective of a given area and thus provides the pedagogically useful comparisons that are to some extent lost when categorizing metal–metal compounds by group numbers.

To produce a book in this area with the necessary breadth and depth is a formidable challenge for anyone, and in order to achieve this feat in any reasonable timescale, to not render the book obsolete before it is published, it was necessary to call on the help of others. This book project has been very fortunate that a number of authors have enthusiastically answered the call to arms. They vary from rising stars to established leaders of their fields, but importantly are all experts and have written from positions of authority. One particularly pleasing aspect is that several authors from *Multiple Bonds Between Metal Atoms* have found the time to contribute to this book, thus providing a link from what has gone before to now. I wish to take this opportunity to thank all the authors for their invaluable contributions and the editorial staff at Wiley-VCH for their patience.

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1

Introduction and General Survey of Metal–Metal Bonds

John E. McGrady

1.1

Introduction

The interactions between metal ions continue to challenge our understanding of the nature of the chemical bond. The first decade of the new millennium has been a particularly productive period, with a number of landmark discoveries including the ultrashort $\text{Cr}^{\text{I}}\text{--Cr}^{\text{I}}$ bonds [1], the $\text{Mg}^{\text{I}}\text{--Mg}^{\text{I}}$ and $\text{Zn}^{\text{I}}\text{--Zn}^{\text{I}}$ dimers of Jones [2] and Carmona [3], respectively, and the distannynes [4] and diplumbynes [5], the heavier analogs of acetylene. Moreover, metal–metal bonded systems are increasingly finding applications in fields as diverse as molecular electronics [6], organometallic catalysis [7], and even in enzyme-mediated transformations [8]. The pioneering work in the field dates back almost exactly half a century and is inevitably associated with Cotton and the quadruple bond in $[\text{Re}_2\text{Cl}_8]^{2-}$ [9–11]. Since that time, the three transition series have proved the most fertile source of metal–metal bonds, largely because the presence of $(n+1)s$, $(n+1)p$, and nd orbitals in the valence region offers an unrivaled potential for strong interactions. Nevertheless, the transition metals make up fewer than half of the known “metallic” elements, and metal–metal bonds in discrete molecular systems are becoming increasingly well established for the s -, p -, and even the f -block elements [12].

In general, the formation of bonds between metals is a delicate balancing act: on the one hand the valence orbitals involved must be sufficiently diffuse to afford substantial diatomic overlap, on the other, competitive binding of additional ligands must be avoided. In fact, much of the recent progress in the field has come through the elegant design of sterically encumbered ligands that block access of additional ligands to the metal coordination sphere. The intrinsic strength of the bond between two metals depends on many factors, including the number of available electrons and the radial and angular properties of the valence orbitals involved. The angular properties determine the local symmetry of the overlap between metal-based orbitals: σ , π , δ , the latter being unique to systems with valence orbitals with $l > 1$ (i.e., d or f orbitals, Figure 1.1). While undoubtedly iconic in the context of metal–metal interactions, δ bonding is typically very weak and the components with σ and π symmetry dominate the overall bond strength. The radial properties of the orbitals control many of the important periodic trends: radial distribution functions for the valence orbitals in exemplary s -, p -, d -, and f -block elements (Mg, Sn, Cr, and Eu, respectively) are collected in Figure 1.2. In the main groups, the valence ns and/or np orbitals are generally well extended relative to core orbitals and so the equilibrium geometry affords near-optimal overlap. The more diffuse nature of orbitals with higher principal quantum number then leads to reduced overlap and hence to relatively weaker bonds in the heavier members of the group: the multiple bonds in distannenes and distannynes are classic examples. The inert-pair effect also means that metal–metal bonding in the heavier post transition metals is increasingly dominated by np orbitals, the ns character accumulating in nonbonding lone pairs. In the transition series (exemplified by Cr in Figure 1.2), in contrast, the radial maxima of the valence nd orbitals lie in the same region as those of the filled ns and np core, and so diatomic overlap is intrinsically small. In this case, an increase in principal quantum causes a greater fraction of the

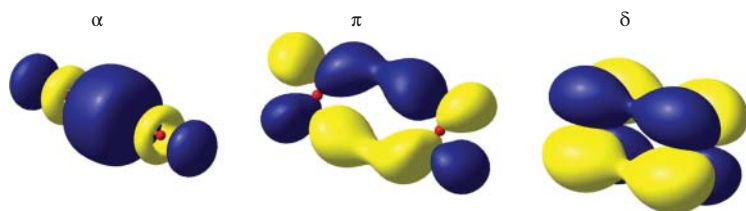


Figure 1.1 σ , π , and δ overlap of d orbitals between two arbitrary metal centers.

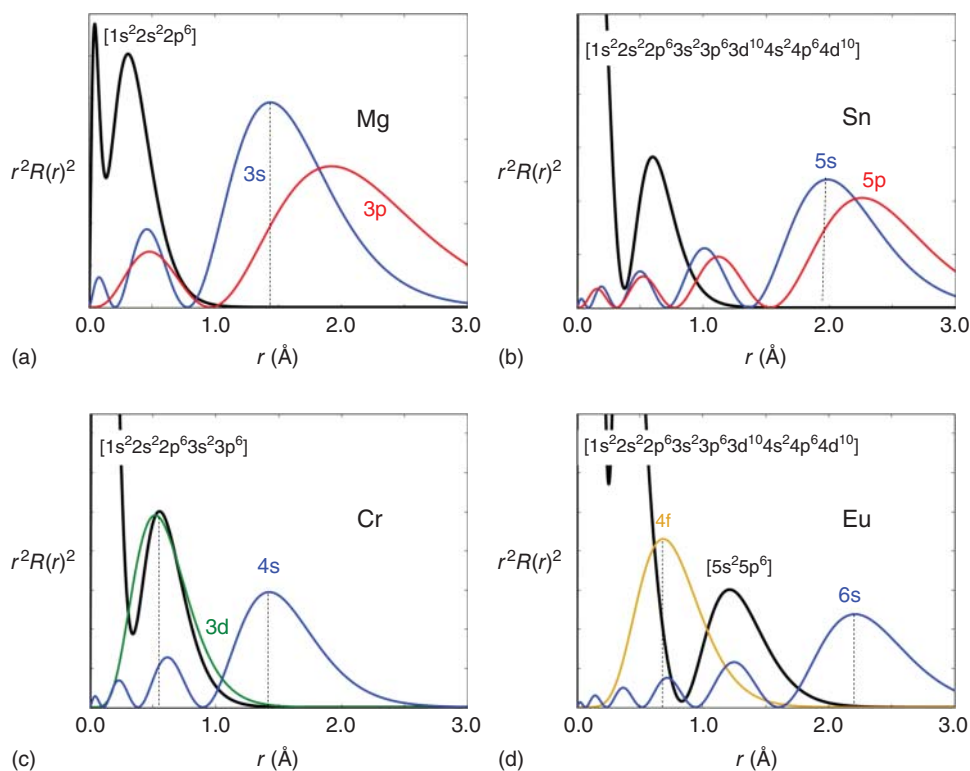


Figure 1.2 Radial distribution functions of the valence orbitals in the (a) s-(Mg), (b) p-(Sn), (c) d-(Cr), and (d) f-(Eu) blocks of the periodic table. Black lines correspond to the core density.

nd orbital to protrude outside the core and so d-d overlap increases, rather than decreases, down a group. The trend in bond strengths is therefore precisely the opposite of that in the main group: metal–metal bonding becomes stronger in the heavier transition metal elements. The lanthanide and actinide series (Eu in Figure 1.2.) can be regarded as extreme versions of the transition elements, with the nf orbitals now lying almost entirely inside the radial maxima of filled $(n+1)s$ and $(n+1)p$ and unavailable to participate in effective bonding interactions.

It is important to emphasize from the outset that metal–metal bonds present a substantial challenge to electronic structure theory, particularly where diatomic overlap is weak and the electrons are highly correlated. The chromium dimer, Cr_2 , for example, is a notoriously difficult case and has been the subject of debate for decades [13]. Some progress toward a quantitative understanding of these correlation effects has been made through Complete Active Space Self Consistent Field (CASSCF) and related wavefunction-based techniques, but much of our qualitative understanding

of metal–metal bond remains based on single determinant methods. While such methods are necessarily deficient in the limit of weak overlap, they have the considerable advantage of affording a transparent molecular orbital–based picture. Density functional theory (DFT) is the tool of choice in most modern research laboratories, but the early contributions made using Extended Hückel theory, most notably by the Hoffmann school, should be acknowledged [14]. The emphasis in this introduction is firmly on qualitative overlap arguments that have, typically, followed hard on the heels of the synthesis of new types of compound. The coverage reflects the structure of the periodic table, with metal–metal bonds mediated primarily by *s* orbitals discussed first, followed by the *d*, *f*, and *p* blocks. The purpose of this introductory chapter is to provide a periodic framework for the discussion of specific classes of metal–metal bonds that appear in subsequent chapters.

1.2

Metal–Metal Bonds Involving *s* Orbitals

The chemistry of groups 1 and 2 is characterized almost exclusively by the +1 and +2 oxidation states, respectively, leaving little scope for direct covalent interactions between the metals. Exceptions occur in the relatively electronegative lighter elements, Li and Be, where the occupied bonding orbitals carry substantial metallic character. A textbook case is the electron-deficient Li_4Me_4 tetramer, where the bonding orbitals have both Li–Li and Li–C bonding character and the Li–Li distance is rather short at 2.56 Å [15]. Examples of unsupported metal–metal bonds in subvalent Mg^{I} species emerged only in the 1980s when species such as HMg–MgH and ClMg–MgCl were characterized in inert matrices [16]. The first species containing direct $\text{Mg}^{\text{I}}\text{–Mg}^{\text{I}}$ bonds ($\text{Mg–Mg} = 2.8508(12), 2.8457(8)$ Å) to be isolated were reported only in 2007 by Jones and Stasch (Figure 1.3) [2]. The Mg–Mg bonding is dominated by the Mg 3*s* orbital (>90%), with homolytic bond dissociation energies in the region of ~ 45 kcal mol^{−1}. The radial disparity between the very diffuse 3*s* valence orbital and a relatively compact [*1s*²*2s*²*2p*⁶] core (shown in Figure 1.2) means that the electron density in the bond is somewhat isolated from the nuclei [17–19], and these dimers are very effective two-electron reducing agents [20].

The potential for extending this chemistry to heavier members of group 2 seems rather limited, primarily because the high energy of the *ns* orbitals makes the interception of the M^{I} oxidation state increasingly challenging. Moreover, the radial maxima become even more diffuse, making the putative M–M bonds very weak. For example, Ca–Ca bonds have been computed to be almost 1 Å longer than their Mg counterparts, with bond dissociation energies lowered by 50% [21]. On the opposite side of the first transition series in group 12, however, penetration through the nd^{10} core stabilizes the (*n* + 1)*s* orbital and contracts its radial maximum, making bonds mediated by the *s* orbitals accessible once again. Prior to 2004, the chemistry of Zn–Zn bonded species was limited to reports of the Zn_2^{2+} cation in Zn/ZnCl₂ melts [22] and the spectroscopic characterization of the dihydride HZn–ZnH in inert matrices [23]. Carmona's report of the structure of dizincocene ($\text{Cp}^*\text{Zn–ZnCp}^*$), with a Zn–Zn separation of 2.3050(3) Å and two parallel Cp* rings, represents the first structurally characterized example of its kind (Figure 1.3) [3]. The nature of the Zn–Zn bond in Zn_2^{2+} and related species had been extensively discussed well before Carmona's seminal discovery [24], but the realization that $\text{Cp}^*\text{Zn–ZnCp}^*$ was a stable chemical entity prompted a number of theoretical investigations [25]. Much like the Mg–Mg bond, the Zn–Zn bond in dizincocene is mediated primarily by overlap of the *s* orbitals (4*s* in this case), which make up $\sim 90\%$ of the character of the HOMO: symmetry allowed mixing with the *p_z* and *d_{z²}* orbitals is minimal [26]. Compared to the Mg–Mg bonds, however, the contraction of the 4*s* orbital leads to much shorter and stronger (65 kcal mol^{−1} vs 45 kcal mol^{−1}) bonds. Numerous other Zn–Zn bonded species have emerged in the decade since Carmona's report, primarily with chelating nitrogen-based ligands [27], and these compounds have even found use as reagents in chemical synthesis [28]. The nature of the Zn–Zn bonding appears to be relatively similar

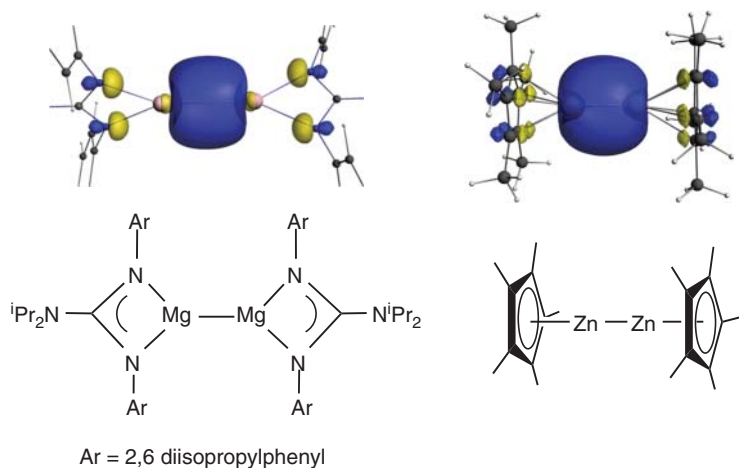


Figure 1.3 HOMOs of $((\text{Ar})\text{NC}(\text{N}^i\text{Pr}_2)\text{N}(\text{Ar}))\text{Mg}-\text{Mg}((\text{Ar})\text{NC}(\text{N}^i\text{Pr}_2)\text{N}(\text{Ar}))$ and $\text{Cp}^*\text{Zn}-\text{ZnCp}^*$.

in all cases, although linear coordination to a strong σ -donor ligand in $\text{ArZn}-\text{ZnAr}$ ($\text{Ar} = \text{C}_6\text{H}_3-2,6-(\text{C}_6\text{H}_3-2,6-^i\text{Pr}_2)_2$) [29] results in a somewhat longer Zn–Zn bond (2.3591(9) Å) with more extensive s/p_z mixing, the latter making up $\sim 30\%$ of the Zn character in the HOMO.

The heavier dications Cd_2^{2+} and Hg_2^{2+} are relatively common structural motifs in both the solid state and melts [30], but discrete molecular analogs of the Zn–Zn bonded systems are scarce because coordination of ligands tends to induce disproportionation to M^0 and M^{II} . In fact, the first structurally characterized complex of Hg_2^{2+} , the silyl complex $\text{Hg}_2[\text{Si}(\text{SiMe}_2\text{SiMe}_3)_3]_2$ with an Hg–Hg separation of 2.6569(1) Å, was described only in 1999 [31]. Alongside $\text{ArZn}-\text{ZnAr}$, the Cd–Cd [32] and Hg–Hg [33] analogue presented the first opportunity to compare trends in bonding down group 12 within an isostructural series. The Cd–Cd bond appears to be rather similar to the Zn–Zn analog, with dominant $5s$ character mixed with some $5p_z$. In the mercury congener, however, relativistic stabilization of the $6s$ orbital reduces the $5d_{z^2}/6s$ separation, and $\sim 5\%$ d_{z^2} character is present in the Hg–Hg bonding HOMO. In conjunction with the lanthanide contraction, the result is that the Hg–Hg bond (2.5738(3) Å) is marginally shorter than its Cd–Cd analog (2.6257(5) Å) despite the presence of 32 extra electrons in the core shells.

The predominance of the +3 oxidation state in aluminum chemistry means that, like the group 1, 2, and 12 analogs, homometallic covalent Al–Al bonds are relatively scarce. A number of subvalent Al^{I} and Al^{II} species have, however, been synthesized, including the first molecular Al–Al bond in $\text{Al}_2(\text{CH}(\text{SiMe}_3)_2)_4$ (Al–Al = 2.660(1) Å) [34]. Even lower oxidation states of Al are generally stabilized through the formation of pseudo-spherical clusters such as the tetrahedral Al^{I} species, Cp_4^*Al_4 [35] and the remarkable icosahedral “superhalide” ion, $[\text{Al}_{13}]^-$ [36]. The latter is observed in gas-phase experiments, where it is notably resistant to reaction with oxygen compared to neighboring members of the $[\text{Al}_n]^-$ series. The stability of the $[\text{Al}_{13}]^-$ cluster can be understood using a delocalized “jellium” model, where the 40 valence electrons are confined in an approximately spherical positive potential generated by the nuclei and the core $1s$, $2s$ and $2p$ electrons (Figure 1.4). The degeneracies in the energy level ordering shown in Figure 1.4 ($1a_{1g} < 1t_{1u} < 1h_g < 2a_{1g} < 2t_{1u} < 1g_u = 1t_{2u} < 2h_g$) are reminiscent of a superatomic ordering sequence $1s < 1p < 1d < 2s < 2p < 1f < 2d$, reflecting the approximate spherical symmetry of the confining potential.

In contrast to the now relatively extensive metal–metal bonded chemistry of subvalent Mg, Al, and Zn, homometallic bonds involving the $6s$ and $7s$ orbitals of the lanthanide and actinides elements are rare (diatomic overlap between the $5f$ orbitals in U_2 and other cases is discussed later). Their absence is largely a consequence of the relatively low second and third ionization energies (compared to Al), which reduce the stability of the +1 and +2 oxidation states. Examples

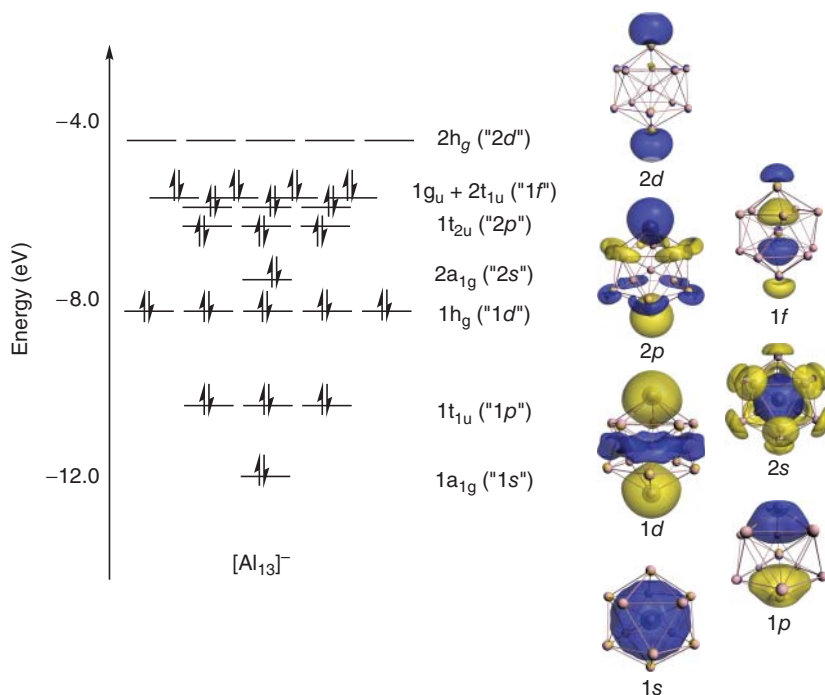


Figure 1.4 The icosahedral $[Al_{13}]^-$ cluster: a "superhalide."

of metal–metal bonds are limited to heterobimetallic cases where the lanthanide acts as a Lewis acid in combination with strongly Lewis basic transition metal fragments such as $[Fe(CO)_4]^{2-}$ or $[Ru(Cp)(CO)_2]^-$. In $(Cp)_2Lu(thf)-Ru(Cp)(CO)_2$, for example, the interaction between the metals is primarily electrostatic (Lu–Ru 2.995(2) Å) [37], the HOMO having <10% Lu character. A similar electrostatic picture emerges even in adducts of the earlier lanthanide ions such as Nd^{III} , where the f shell is higher in energy and only partly filled [38]. The more diffuse $5f$ orbitals of the actinides allow higher oxidation states to be accessed and, in principle, also allow the f orbitals to participate directly in the bonding. Substantial charge transfer from an $Al(\eta^5-C_5Me_5)$ unit to U^{III} has been reported in $(\eta^5-C_5H_4-SiMe_3)_3U-Al(\eta^5-C_5Me_5)$ [39], and there is even some evidence for weak π overlap involving the $5f$ orbitals in the U–Re bond in $\{[N(CH_2CH_2NSiMe_3)_3]URe(\eta^5-C_5H_5)_2\}$ and the U–Ga bond in $\{[Tren^{TMS}]U\{Ga(NArCH_2)_2\}(THF)\}$ [40]. The role of the $5f$ orbitals is, however, a relatively minor component of the bonding in all cases.

1.3

Metal–Metal Bonds Involving d Orbitals

Over the past 50 years, the three transition series have been responsible for the vast majority of metal–metal bonded species, and an enormous number of dimers and larger clusters are now known. In addition to providing a unique insight into the nature of the chemical bond, these clusters have been exploited for their catalytic potential [7], and a biological role for a Ni–Fe bond in Ni–Fe hydrogenases has even been proposed [8]. Transition metal–metal bonds may be broadly classified into two types: "supported" bonds that have ligands that bridge the two centers and "unsupported" bonds that do not. In the supported class, the relative importance of metal–metal and metal–ligand interactions is often difficult to delineate because any single molecular orbital may feature contributions from both. On the other hand, the presence of bridging ligands confers great flexibility, simply because the

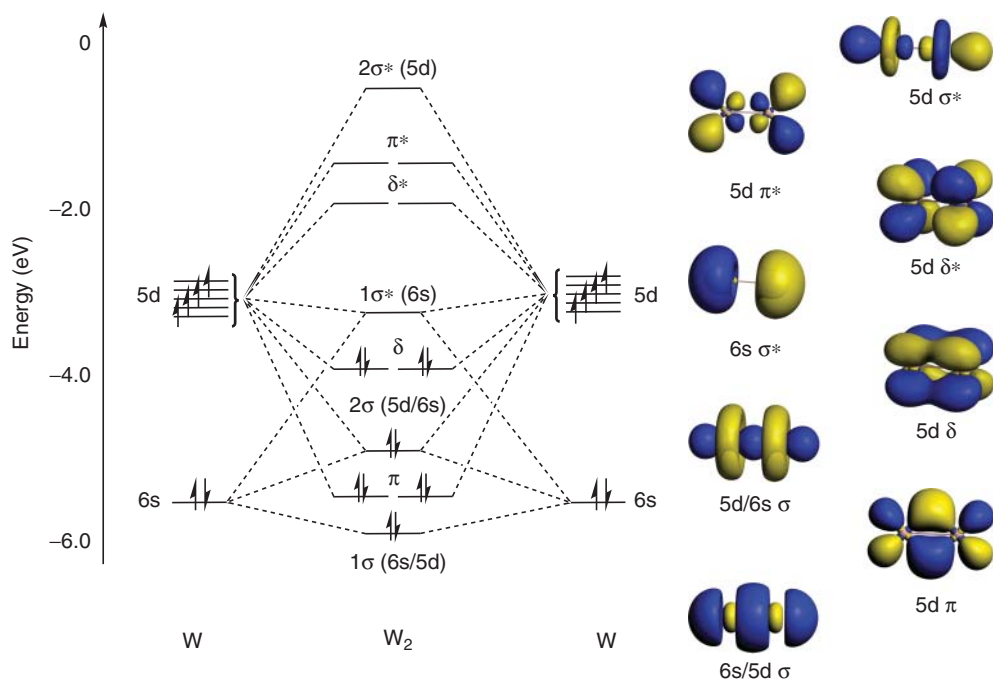


Figure 1.5 The singlet ground state of sextuply bonded W_2 .

cluster does not rely solely on the metal–metal bond for its integrity. The limit of negligible direct overlap of the metal orbitals corresponds to the extensive class of exchange-coupled clusters, which lie outside the remit of this book. There are, however, a few intermediate cases where the metal–metal bond is partially formed, and even cases where distinct bonded and nonbonded isomers can be isolated [41, 42].

A survey of the electronic structure of the naked transition metal diatomics, M_2 , serves to highlight many of the key periodic trends that emerge in their more chemically relevant ligated analogs. The diatomics encompass a wide range of metal–metal bond types, from strong multiple bonding to weak magnetic coupling, and they have been used as a testing ground for successive generations of theoretical methods. The elements near the center of the transition series are the most interesting from a bonding perspective as they offer the potential for extreme high bond orders, up to six in the dimers of the group VI metals Cr_2 , Mo_2 , and W_2 . The molecular orbital array for W_2 , the heaviest member of the series, illustrated in Figure 1.5 illustrates the basic features of the sextuple bond: the doubly degenerate π and δ components are supplemented by *two* distinct orbitals with σ symmetry, 1σ and 2σ , each with mixed $5d_{z^2}/6s$ character. 2σ represents a conventional σ bonding orbital, in so much as the dominant $5d_{z^2}$ character is concentrated along the internuclear axis. In 1σ , in contrast, the dominant $6s$ character concentrates the overlap in a cylindrical region around the axis, reducing electron–electron repulsions with the 2σ component. The $5d_{z^2}/6s$ hybridization is closely related to the Orgel/Dunitz mechanism used to account for the preference for linear coordination in complexes of the coinage metals [43].

The formal bond order of 6 in W_2 reflects the structure of the molecular orbital diagram but is clearly simplistic in that it fails to take into account the very different contributions of the σ , π , and δ components to the overall bond strength. In the case of the δ bonds in particular, the weak overlap leads to a small HOMO–LUMO gap, and the single determinant description of the electronic structure that is implicit in the molecular orbital diagram can be inadequate. Within the constraints of single determinant methods such as DFT, the weakness of the δ bond (and, to a lesser extent, the π

component) manifests itself in a tendency toward symmetry breaking, wherein electrons of opposite spin localize on different centers. For example, Bauschlicher's study of Cr_2 revealed net spin densities of ± 2.7 at opposite centers, reflecting the strong tendency of the electrons in both the δ and π bonds to localize [44]. The potential energy surface for Cr_2 also highlights a link to the main group species discussed previously. A minimum at the equilibrium separation of 1.67 Å allows for substantial 3d–3d overlap, but a plateau is also present in the region of 2.5 Å, a result of residual overlap between the more diffuse 4s orbitals. The bonding in this region is in fact very reminiscent of that in the Mg_2^1 and Zn_2^1 dimers, in so much as 4s–4s overlap is the dominant feature: the three systems differ only in the size of the spherically symmetric 3d cores: d^0 , d^5 , and d^{10} for Mg_2^1 , Cr_2^0 , and Zn_2^1 , respectively. Multiconfigurational character also becomes apparent in CASSCF calculations, where the effective bond orders of 5.2, 5.2, and 4.52 for W_2 , Mo_2 , and Cr_2 , respectively, highlight the weakness of the δ component, particularly in the lightest member of group 6 [45]. In Mn_2 , the five 3d electrons on each center are again weakly antiferromagnetically coupled, but both in- and out-of-phase combinations of the 4s orbital are now doubly occupied. Mn_2 can therefore be viewed as an analog of an inert gas dimer, where the bonding is dominated by van der Waals' forces, and the Mn–Mn separation in the $^1\Sigma_g^+$ ground state has been estimated at 3.64 Å [46]. Perhaps unsurprisingly this situation presents a substantial challenge to DFT, and computed Mn–Mn separations ranging from 1.6 to 3.5 Å have been reported [47].

The increasing strength of bonds involving *nd* orbitals down a group is a general feature of transition metal chemistry, the origins of which lie in the more diffuse nature of the 4d and 5d orbitals relative to *s* and *p* orbitals with the same principal quantum number: the greater exposure of the *nd* orbital increases diatomic d–d overlap from its very low value in the first transition series. A quantitative understanding of periodic trends, however, also requires an appreciation of the changes in electron–electron repulsion as the bond is formed. In the limit of very weak bonding (for example, as in the Mn_2 case), the individual atoms adopt local high-spin configurations, thereby minimizing electron–electron repulsions. The sharing of electron density in covalent bonds necessarily equalizes the spin densities at the two atoms, causing an increase in electron–electron repulsion. Thus, covalent bonding represents a compromise between overlap, which lowers the kinetic energy and so favors bond formation and the competing increase in electron–electron repulsions. The latter are largest in the compact 3d orbitals, and so in addition to the weak overlap, the lighter elements experience a greater increase in electron–electron repulsion upon formation of a covalent bond. A detailed analysis suggests that the two factors contribute approximately equally to the overall trend to stronger metal–metal bonds in the heavier transition elements [48, 49].

An introduction to metal–metal bonding in the transition metals would be incomplete without a discussion of the iconic quadruple bond in $[\text{Re}_2\text{Cl}_8]^{2-}$. This molecule represents a major landmark in inorganic chemistry, simply because the δ component of the bond was entirely without precedent in the main group. The quadruple bond has subsequently become synonymous with the field of metal–metal bonding, and its structure and properties have been extensively reviewed, most prominently in the seminal textbook “*Multiple Bonds Between Metal Atoms*.” [50] The short Re–Re separation and eclipsed nature of the ReCl_4 units in an anion formulated as $[\text{Re}_2\text{Cl}_8]^{4-}$ (in “(pyH)(H)ReCl₄”) were in fact first noted by Kuznetsov and Koz'min in 1963 [10], but a subsequent study of the potassium compound $\text{KReCl}_4 \cdot \text{H}_2\text{O}$ by Cotton and Harris revealed a dianion with an Re–Re distance of 2.241(7) Å, now correctly formulated as $[\text{Re}_2\text{Cl}_8]^{2-}$ [9]. Very soon afterward, Cotton presented the first electronic rationale for the structure [11], and the essential features of this model underpin all the more sophisticated treatments that have been reported in the subsequent half century. Cotton's model, summarized in Figure 1.6, shows how the electronic structure emerges naturally from perturbations to the diatomic developed in Figure 1.5. The combination of the high oxidation state (Re^{III}) and the square-planar ligand field removes the 6s and $5d_{x^2-y^2}$ orbitals from the valence manifold, leaving only $5d_{z^2}$, $5d_{xz}$, $5d_{yz}$, and $5d_{xy}$ available to form the Re–Re bond. The σ , π , and δ linear combinations that result from diatomic overlap give rise to a $\sigma^2\pi^4\delta^2$ ground-state configuration with a

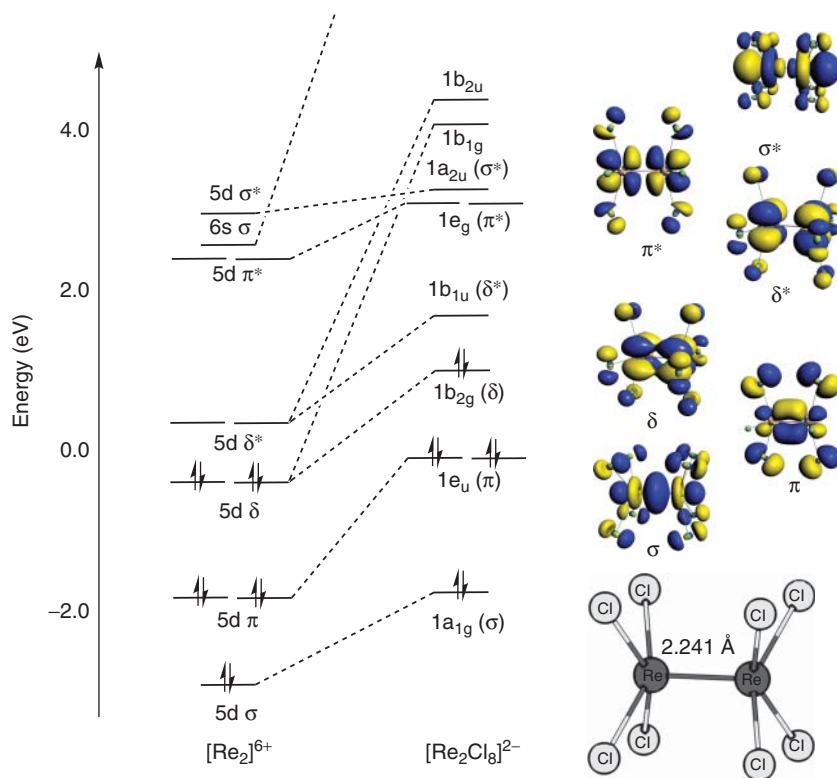


Figure 1.6 The quadruple bond in $[Re_2Cl_8]^{2-}$ (the midpoint of the δ/δ^* pair is taken as an arbitrary zero of energy).

formal bond order of 4.0. The δ overlap between the d_{xy} orbitals can account for the adoption of the fully eclipsed conformation, although it has also been argued that hyperconjugation between Re–Cl σ and Re–Cl σ^* orbitals contributes to the conformational preference [51].

While the basic features of Figure 1.6 were established by Cotton's 1965 paper, attempts to quantify the strength of the δ bond had to await the emergence of more sophisticated theoretical models [52]. A 1994 CASSCF calculation on $[Re_2Cl_8]^{2-}$ using an (8,8) active space including the Re–Re σ , π , and δ orbitals along with their antibonding counterparts [53] indicated that the lead $\sigma^2\pi^4\delta^2\delta^{*0}\pi^{*0}\sigma^{*0}$ configuration makes up only ~63% of the total wavefunction. This conclusion is consistent with the symmetry breaking apparent in DFT-based studies of the same system [54, 55]. More recently, (8,8) and (12,12) active spaces (the latter including the Re–Cl σ and σ^* orbitals) have been used to optimize the geometry of $[Re_2Cl_8]^{2-}$, the resulting Re–Re bond length being in good agreement with X-ray data [56, 57]. The occupations of the δ and δ^* orbitals in the CASSCF wavefunction (~1.5 and ~0.5, respectively) confirm the weakness of the δ bond.

While $[Re_2Cl_8]^{2-}$ is certainly the iconic quadruply bonded molecule, a number of isoelectronic analogs have also been reported including the rhenium bromide [58] and iodide [59], as well as the lighter $[Tc_2X_8]^{2-}$ congeners ($X = Cl, Br$) [60] and the group VI tetraanions $[Mo_2X_8]^{4-}$ and $[W_2X_8]^{4-}$ [61]. In the osmium analogs, $[Os_2X_8]^{2-}$ ($X = Cl, Br$), where the presence of two additional electrons in the δ^* orbital [62, 63] annihilate the δ bond, the OsX_4 units adopt the more sterically favored staggered conformation. The weakness of the δ component of the metal–metal bond also gives rise to somewhat counterintuitive structural changes upon one-electron reduction of $[Tc_2Cl_8]^{2-}$. Both $[Tc_2Cl_8]^{2-}$ (formal bond order 4.0) and $[Tc_2Cl_8]^{3-}$ (formal bond order 3.5) have been structurally

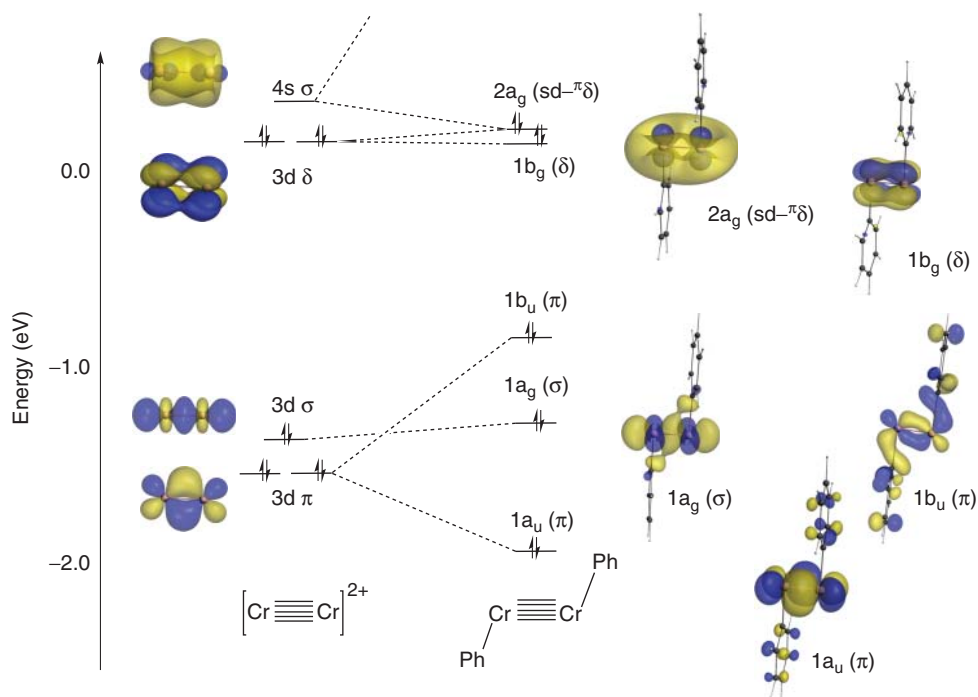


Figure 1.7 Ultrashort Cr–Cr quintuple bonds: correlation of frontier orbitals in $[\text{Cr}_2]^{2+}$ and *trans*-bent isomers of Ph-CrCr-Ph (the δ orbital is taken as an arbitrary zero of energy).

characterized, and although bond lengths depend on the identity of the cation, a trend toward shorter Tc–Tc bonds in the trianions can be discerned (2.117(2) vs 2.151(1) Å) [64]. This appears, at first sight, to be surprising as 50% of a δ bond is lost upon reduction. This minor loss of stabilization is, however, more than offset by enhanced overlap in both the σ and π components as a result of the radial expansion of the metal-based 4d orbitals upon reduction. This observation highlights a general theme that will underpin much of the subsequent discussion of bonding in both the transition series and the p-block: σ bonding plays by far the dominant structural role. Indeed, much of the complex structural chemistry to be outlined in the following paragraphs can be understood in terms of optimization of the σ framework, if necessary at the expense of the intrinsically weaker π or δ components of the bond.

Forty years on from the discovery of the quadruple bond in $[\text{Re}_2\text{Cl}_8]^{2-}$, the range of bond multiplicities in isolable molecules was further extended by Power's synthesis of the landmark compound Ar-CrCr-Ar ($\text{Ar} = \text{C}_6\text{H}_3-2,6-(\text{C}_6\text{H}_3-2,6\text{-}i\text{Pr}_2)_2$), with a quintuple bond between the metals (Figure 1.7). [1] The Cr–Cr separation of 1.8351(4) Å is extremely short, and the structure is strongly *trans*-bent, with C–Cr–Cr angles approaching 100°. Subsequent work showed that the Cr–Cr distance could be tuned over a narrow range (1.8077(7)–1.8351(4) Å) by variation in the aromatic substitution pattern [65], the lowest of these values being shorter than the shortest known Cr–Cr quadruple bonds at that time (1.830(4) and 1.828(2) Å) [66]. Soon afterward, a number of closely related “ultrashort” Cr–Cr bonds emerged from the groups of Theopold [67], Kempe [68], and Tsai [69]. The earliest of these reports featured a Cr_2 unit supported by two diazadiene ligands [67], the Cr–Cr separation of 1.8028(9) Å being fractionally shorter than the shortest member of the Ar-CrCr-Ar family. Tsai and Kempe then published almost simultaneous reports of closely related species with even shorter Cr–Cr separations of 1.7397(9) and 1.749(2) Å, respectively, and the current record low of 1.7293(12) Å [70] is held by a complex with a guanidinate ligand architecture. Power's work inspired a number of theoretical studies of the quintuple bond [71–76], but its basic features had in fact been

set out some 25 years earlier by Hoffman and coworkers [77], albeit in the context of a perfectly linear L–MM–L, where the distinction between σ -, π -, and δ -symmetric orbitals is rigorous. The analysis of the bonding in Ar–CrCr–Ar is complicated by the *trans* bending, but nevertheless, one σ ($1a_g$ in Figure 1.7) two π ($1a_u$, $1b_u$), and one δ ($1b_g$) component are readily identified in the occupied manifold. The nature of the fifth component of the bond, $2a_g$, is less obvious: like the σ orbital, it is a basis for the totally symmetric representation of the C_{2h} point group, but nevertheless it has been argued that it should be identified loosely as a δ bond. The overlap between the two s/d_{z^2} hybrids is clearly very weak and the $2a_g$ orbital has been labeled as a “side-on δ bond” or “sd- $\pi\delta$ ” to emphasize its qualitative similarity to an orbital of pure δ symmetry [74]. The relationship to the naked $[\text{Cr}_2]^{2+}$ dimer shown in Figure 1.7 highlights the reasons why a *trans*-bent structure is energetically favorable. The naked dimer presents two orbitals of σ symmetry, $1\sigma_g$ and $2\sigma_g$, that could, in principle, accommodate the developing Cr–C bond (note that the positive charge stabilizes nd relative to $(n+1)s$), so unlike the case for W_2 , the $(n+1)s$ character is more pronounced in the vacant $2\sigma_g$). Approach along the Cr–Cr axis would destabilize the $1\sigma_g$ orbital and, therefore, compromise the strongest component of the Cr–Cr bond. A *trans*-bent approach, in contrast, introduces overlap with the cylindrical $2\sigma_g$ orbital as well as one component of the δ pair, and, therefore, has much less impact on the Cr–Cr interaction. The bending therefore allows the Cr–Ar σ bonds to be established without compromising the energetically most important σ component of the Cr–Cr bond. The driving force for a *trans*-bent structure is therefore the retention of the σ bonding framework: the concomitant destabilization of the π and δ components is of lesser importance. A broader survey of structural possibilities in the model compound HWWH indicates that the quintuple bond is in fact rather resilient, persisting across a wide range of isomers of the M_2L_2 unit, including not just the *trans*-bent structure but also *cis*-bent (C_{2v}), dibridged (D_{2h}), and mono-bridged (C_s) alternatives [76]. The qualitative bonding model that emerges from DFT has been confirmed by a CASPT2 study by Brynda *et al.* [73] where one σ , two π (one in-plane, one out-of-plane), and one conventional δ bond are included in the active space, along with the “sd- δ ” side-on δ bond [74]. The antibonding components of both the conventional and side-on δ bonds are substantially populated (0.50 electrons for the former, 0.31 electrons for the latter), leading to an effective bond order of 3.52, well below the idealized limit of 5.0. Nevertheless, the authors conclude that the formation of the Cr–Cr bond does involve five pairs of electrons from each PhCr unit, and, therefore, that the “quintuple” label is justified for bonds of this type. The details of the bonding in the ultrashort Cr_2 species reported by Theopold, Tsai, and Rempe have also been analyzed in some detail [78], and in general rather similar features emerge despite the increase in coordination number at the metal centers. In the dibridged amidinate (Tsai, Kempe), pyridylamide (Kempe), and diazabutadiene (Theopold) analogs and also the lantern $\text{Cr}_2(\text{LL})_3$ structure, the metal–ligand interaction is established primarily through the cylindrical s/d_{z^2} hybrid σ orbital of the naked dimer, which has maximum amplitude orthogonal to the Cr–Cr axis, along with one or two components of the δ bond. The Cr–Cr quintuple bond is then formed through one σ , two π , and one δ bond, supplemented either by a second degenerate δ component ($\text{Cr}_2(\text{LL})_3$) or a “side-on δ ” orbital of the type described above. [78]

Closely related to the M_2X_8 family are the so-called paddlewheel complexes, where the two metal centers are bridged by four chelating ligands. Within this diverse series, the metal–metal interactions fluctuate widely, from the very strong ($\text{Mo–Mo} = 2.093(1) \text{ \AA}$ in $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$) [79] to the very weak ($\text{Cu–Cu} = 2.6143(17) \text{ \AA}$ in $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$) [80]. The quadruple bond in $\text{Mo}_2(\text{OAc})_4$ is strikingly similar to that in isoelectronic $[\text{Re}_2\text{Cl}_8]^{2-}$ (Figure 1.6), with the typical $\sigma < \pi < \delta$ ordering of occupied orbitals. Higher valence electron counts demand occupation of the antibonding δ^* and π^* orbitals, and it is here that the contrasts with the homoleptic M_2X_8 species are most apparent. In the latter, each ligand carries two orthogonal doubly occupied p orbitals (lone pairs), which leads to the destabilization of both the π - and δ -symmetry orbitals on the M_2 unit. In the paddlewheel complexes, in contrast, only the p orbital orthogonal to the M–M axis remains available for π bonding to the metal, the other being involved in σ bonding within the ligand framework. As a result, only the δ -symmetry orbitals of the M_2 unit are destabilized by π -donation from the ligand, reducing and even, in some cases, inverting the $\delta^*-\pi^*$ separation (Figure 1.8). The near degeneracy of the δ^* and π^* levels

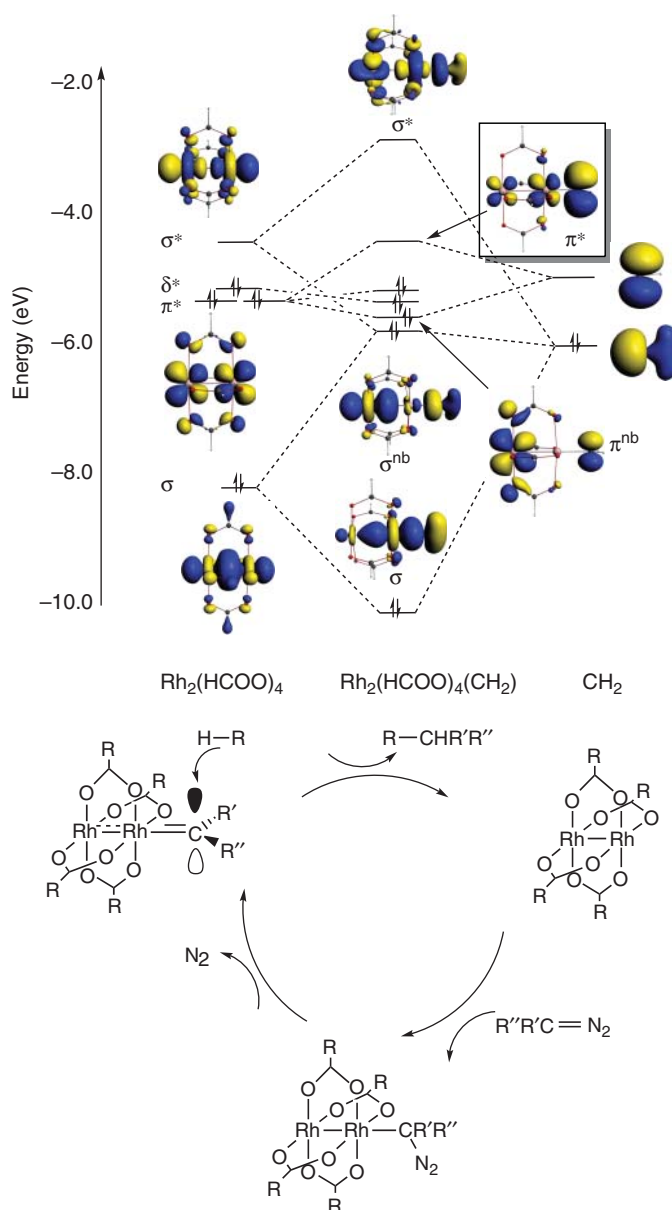


Figure 1.8 Relationship between electronic structure and catalytic activity in the dirhodium carbene complex $\text{Rh}_2(\text{HCOO})_4(\text{CH}_2)$.

in the paddlewheel complexes has a dramatic impact on their magnetic properties: while $[\text{Os}_2\text{Cl}_8]^{2-}$ has a $\sigma^2\pi^4\delta^2\delta^{*2}$ singlet ground state, isoelectronic osmium paddlewheel complexes are triplets with either $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*1}$ or $\sigma^2\pi^4\delta^2\pi^{*2}$ configurations [81].

A further increase in the *d*-electron count to 14 brings us to the dirhodium paddle wheels (Rh^{II}_2) that have found extensive use as catalysts for the decomposition of organic diazo compounds and the subsequent insertion of the carbene group into a C–H bond [7]. The complete occupation of the δ/δ^*

and π/π^* components of the manifold leaves a single Rh–Rh bond ($\sigma^2\pi^4\delta^2\delta^*\pi^4$) with Rh–Rh separations in the region of 2.4 Å. The consensus mechanism for catalysis involves the binding of the carbon of the diazo compound to one Rh center, followed by loss of N_2 to generate the key intermediate, a paddlewheel complex containing a linear Rh–Rh=CR₂ group. Electrophilic attack of the substrate C–H or C=C bond then leads to insertion of the carbene group. The utility of these paddlewheel complexes is related in part to the robust nature of the Rh₂L₄ unit, but also to the subtle interplay between Rh–Rh and Rh–C bonding, which must play a role because insertion into C–H bonds is not a typical reactivity pattern for mononuclear carbenes. By analogy to the Fischer carbenes, the Rh–C bond in the intermediate contains σ - and π -symmetry components generated by the transfer of electron density to and from the bimetallic unit, respectively. The Rh–Rh π^* orbital acts as a source of electron density to stabilize the Rh=CR₂ bond, which at the same time allows the Rh–Rh bond to develop some π character. The unique reactivity of the Rh₂ dimers appears to stem primarily from the three-center four-electron nature of the σ bonding in Rh–Rh=CR₂, which weakens the σ component of the Rh=C bond compared to monometallic analogs [82]. Alternatively, this phenomenon can be viewed in terms of the strong *trans* influence of the Rh–Rh bond. The weak, relatively long Rh=C bond in turn localizes the LUMO on the carbene unit (see boxed orbital in Figure 1.8), rendering the latter more susceptible to electrophilic attack. The potential for electron density to flow from the bimetallic core to the bound substrate and back again during the reaction cycle is clearly an important feature of the compound's reactivity.

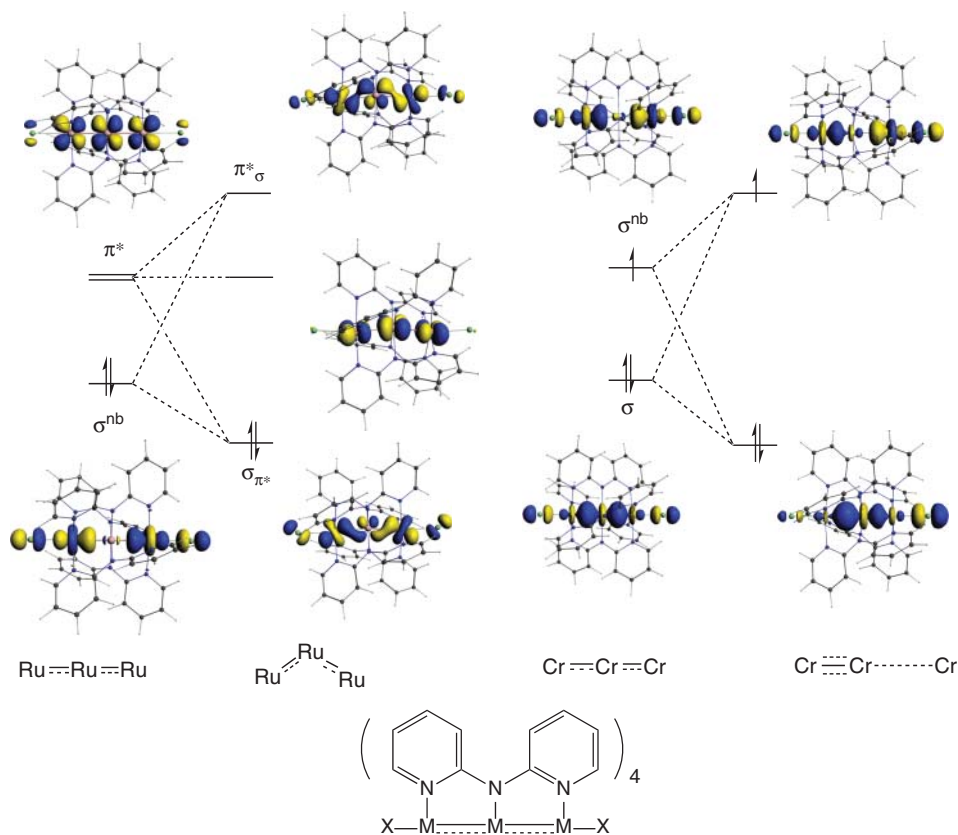


Figure 1.9 Origin of the bends and stretches in $Ru_3(dpa)_4X_2$ and $Cr_3(dpa)_4X_2$.

In recent years, there has been a concerted effort to extend the paddlewheel and related architectures to longer chains. Perhaps the most diverse of these are the so-called extended metal-atom chains (EMACs) developed by Peng, Cotton, and Berry [83, 84]. The archetypes are the trimetallic chains based on a helical array of four dipyriddyamide (dpa) ligands, $M_3(dpa)_4X_2$ (Figure 1.9). Complexes of this general formula are now known for much of the first transition series as well as many of the heavier transition elements. The four dipyriddyamido ligands provide a scaffold for strong multiple Mo–Mo bonds such as those in $Mo_2M'(dpa)_4X_2$ [85] ($M' = Mn, Fe, Co, Ni, Zn$) all the way through to the weak magnetic coupling present in the Ni_3 and Cu_3 analogs [86]. The synthetic strategies used to generate the dipyriddyamido ligands are readily extended to analogs with up to 11 nitrogen donor atoms, and metal-atom chains of this length have been reported [87]. The molecular orbital arrays of these chains show the same basic features as the bimetallic paddle wheels, with orbitals of σ , π , and δ symmetry made up of linear combinations of the d_{z^2} , (d_{xz}, d_{yz}) , and d_{xy} orbitals, respectively. The π and δ components overlap only weakly and form relatively narrow bands, while the σ components show a greater dispersion. This often leads to a densely populated region around the Fermi level, with π^* and δ^* orbitals lying very close in energy to nonbonding orbitals of σ symmetry. In such circumstances, second-order effects can lead to distinct low-symmetry distortions, which, in turn, have significant impact on the magnetic and electron transport properties [6]. In the triruthenium EMACs $Ru_3(dpa)_4X_2$, for example, a truly linear Ru_3 unit is found only when X is a strong σ donor ligand (CN^- or RCC^-): otherwise, a distinct bending at the central Ru atom occurs ($Ru-Ru-Ru \sim 170^\circ$) [85]. A closely related phenomenon occurs in the trichromium analogs, $Cr_3(dpa)_4X_2$, where again only strong σ donors such as CN^- and RCC^- yield truly symmetric structures. At the opposite extreme, $Cr_3(dpa)_4(NO_3)_2$ retains a linear Cr_3 unit ($Cr-Cr-Cr = 180^\circ$), but the $Cr-Cr$ separations themselves are now grossly asymmetric ($\Delta Cr-Cr = 0.71 \text{ \AA}$). Intermediate cases such as $Cr_3(dpa)_4Cl_2$ ($\Delta Cr-Cr = 0.22 \text{ \AA}$) [88, 89], and $Cr_3(dpa)_4(NCS)_2$ ($\Delta Cr-Cr = 0.25 \text{ \AA}$) are also known [90]. Both types of distortion can be understood in terms of the primacy of the σ bonding framework over the weaker π or δ components. In the Ru_3 case, the linear structure has a formal bond order of 3.0 (1.5 *per* $Ru-Ru$ bond), made up of $1\sigma + 2\pi$ components. Bending introduces mixing between the near degenerate σ^{nb} and π^* orbitals, increasing the σ character in the $Ru-Ru$ bonds at the expense of π [91]. In the Cr_3 case, second-order effects mix σ and σ^{nb} orbitals, driving an asymmetric stretch rather than a bend. The distortion generates one very strong $Cr-Cr$ bond along with an isolated Cr^{II} center ($S = 2$) [92]. Stronger σ donor ligands such as CN^- again dampen the second-order effects by destabilizing the σ^{nb} orbital: in effect, the formation of a short, strong $Cr-Cr$ σ bond becomes unfavorable because it compromises the strong *trans* $Cr-L$ bond.

One of the main motivations for the synthetic effort invested in these extended metal-atom chains is the search for molecular analogs of the semiconductor-based wires, diodes, and transistors that are the building blocks of present day computers. Peng, Chen, and coworkers have made extensive use of conductive atomic force microscopy (CAFM) and scanning tunneling microscopy (STM) techniques to establish important periodic trends in the conductance (G) across a range of EMACs [90, 93]. For example, conductivity increases in the order $Ni < Co < Cr$, irrespective of the chain length, suggesting a direct link between electronic configuration and current. By analogy with organic conductors, it is tempting to ascribe the higher conductance of the Cr chains to the presence of π interactions, but a detailed analysis of $Cr_3(dpa)_4(NCS)_2$ indicates that it is dominated by a channel of σ symmetry [94], which lies close the Fermi level of the electrode. The complex nature of the metal–metal bond clearly makes it difficult to extrapolate structure–property relationships from organic materials, but future progress will rely heavily on models that link transport properties to the underlying electronic structure.

Much like the paddlewheel structures, face- and edge-shared bioctahedral complexes (M_2X_9) are also found across much of the transition block, and they illustrate very elegantly many of the important periodic trends. Metal–metal separations span almost $1 \text{ \AA}$ in the nonachloride series alone, mapping out a continuum linking entirely nonbonded situations (as in $[Rh_2Cl_9]^{3-}$ and $[Ir_2Cl_9]^{3-}$, $M-M > 3.0 \text{ \AA}$) [95] to strong multiple bonds ($[W_2Cl_9]^{3-}$, $W-W = 2.4329(6) \text{ \AA}$) [96]. The qualitative features of the molecular orbital array for this class, established using extended Hückel theory and

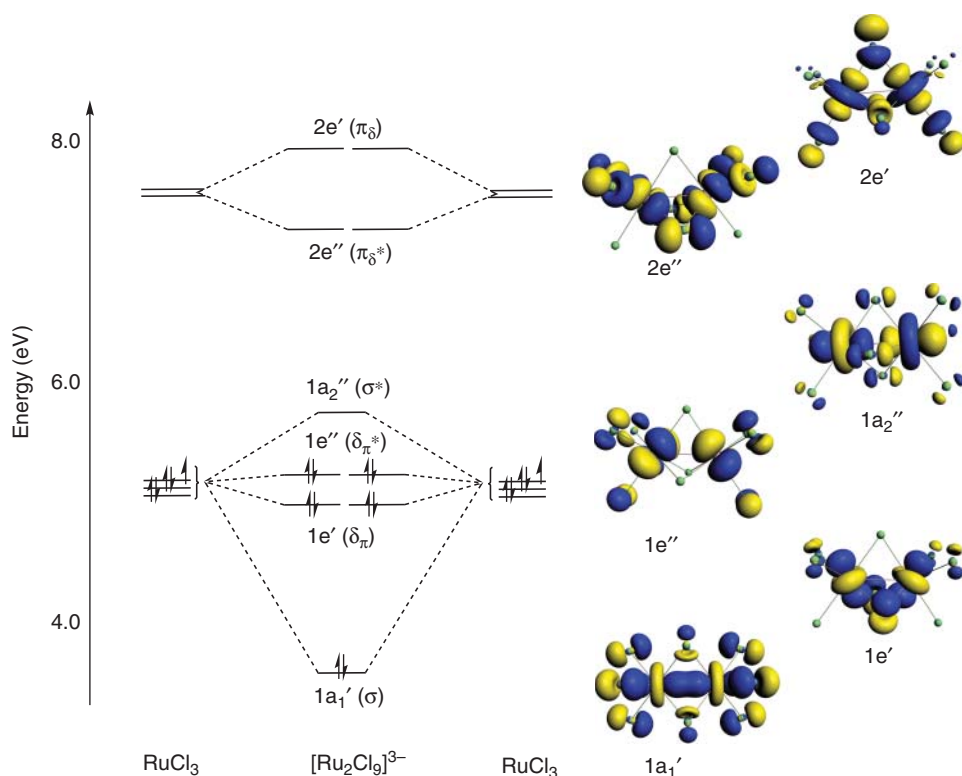


Figure 1.10 $[\text{Ru}_2\text{Cl}_9]^{3-}$, the archetype of the M_2X_9 family.

DFT methods [97–99], are summarized for the archetype $[\text{Ru}_2\text{Cl}_9]^{3-}$ ($\text{Ru}-\text{Ru} = 2.725 \text{ \AA}$) [100] in Figure 1.10. The threefold degenerate orbitals of a RuCl_3 fragment are conveniently quantized along the trigonal axis, leading to one level with σ symmetry (made up of d_{z^2}) and a degenerate pair with mixed π/δ symmetry ($2/3\pi + 1/3\delta$ in a perfect biotetrahedron). Combination of the two fragments then leads to σ , σ^* , δ_π , and δ_π^* levels, which can strongly mix with p orbitals of the three bridging halides. The isosurfaces shown in Figure 1.10 emphasize the important point that metal–metal and metal–ligand π bonding are antagonistic: the σ and δ_π orbitals are simultaneously Ru–Ru bonding and Ru–Cl antibonding. In cases where the Ru–Ru overlap is inherently weak, as for example in the upper π_δ set, the Ru–Cl antibonding character can invert the expected order, with the out-of-phase combination ($2e''$) lying lowest. In the closely related di-chloro bridged ruthenium dimer ($\text{CpClRu}_2(\mu\text{-Cl})_2$), the metal–metal and metal–ligand bonding is in fact so finely balanced that two distinct isomers with Ru–Ru distances that differ by $0.8 \text{ \AA}$ are found in the same crystal [41, 42]. In one, the Ru–Ru σ bond is optimized at the expense of a relatively weak terminal Ru–Cl interaction ($\text{Ru}-\text{Ru} = 2.930(1) \text{ \AA}$, $\text{Ru}-\text{Cl}_t = 2.418(2) \text{ \AA}$), while in the other the Ru–Cl bonding is optimized at the expense of the Ru–Ru interaction ($\text{Ru}-\text{Ru} = 3.752(1) \text{ \AA}$, $\text{Ru}-\text{Cl}_t = 2.365(2) \text{ \AA}$).

The effect of changing the electronic configuration can be extrapolated using the framework set out in Figure 1.10. Thus, a d^6d^6 configuration found, for example, in $[\text{Rh}_2\text{Cl}_9]^{3-}$, populates the σ^* orbital and eliminates the direct Rh–Rh bond. The equilibrium Rh–Rh separation of $3.121(5) \text{ \AA}$ then represents a balance between the confining influence of the three bridging ligands and the coulomb repulsion between the Rh^{3+} ions. At the opposite extreme, the d^3d^3 configuration in the $[\text{W}_2\text{Cl}_9]^{3-}$ anion depopulates the δ_π^* orbital, giving a formal bond order of 3. This anion was in fact one of the very earliest bimetallic complexes to be subjected to X-ray structural analysis, as far back as 1935: [97]

the structure clearly revealed the strong bonding between the metal atoms ($W-W = 2.4329(6) \text{ \AA}$), although its precise origins remained unclear for several decades. The very different contributions of σ , π , and δ components to metal–metal bond strength have been emphasized throughout this chapter, and the complexes of group VI provide a vivid illustration of this point. The very short $W-W$ bond in $[W_2Cl_9]^{3-}$ contrasts with the much larger separation of $3.12 \text{ \AA}$ in isoelectronic $[Cr_2Cl_9]^{3-}$ [101]. In the latter, the radially contracted $3d$ orbitals allow minimal diatomic overlap, irrespective of the symmetry of the interaction (σ or δ_π), and the result is almost complete localization of all the valence orbitals. The $[Mo_2Cl_9]^{3-}$ system is an intriguing intermediate case: the metal–metal bond length is highly dependent on the identity of the cation in the $A_3Mo_2Cl_9$ lattice, varying from $2.524 \text{ \AA}$ ($A = K^+$) to $2.734 \text{ \AA}$ ($A = \text{pipeH}^+$) [102]. The potential energy surface in this region is very flat and maps out a transition from a triply bonded situation typified by $[W_2Cl_9]^{3-}$ to one where the σ bond remains intact but the two δ_π components are lost. The triad of $[Cr_2Cl_9]^{3-}$, $[Mo_2Cl_9]^{3-}$, and $[W_2Cl_9]^{3-}$ therefore shows a progressive increase in the effective bond order from 0 through ~ 1 to ~ 3 . The isoelectronic $[Mo_2Cl_9]^{3-}$ and $[Re_2Cl_9]^-$ anions also provide an unusual example of a diagonal relationship in the transition metal block because the $Re-Re$ bond length of $2.704(1) \text{ \AA}$ [103] in the latter is also indicative of the presence of a single $Re-Re$ σ bond. The greater radial expansion of the $5d$ orbitals of Re relative to the $4d$ orbitals of Mo is clearly offset by the increased charge on the Re^{4+} cation, leading to a very similar balance between overlap and exchange energies. The one-electron reduction of $[Re_2Cl_9]^{1-}$ offers a further striking illustration of the points introduced earlier in the context of the $[Tc_2Cl_8]^{2-/3-}$ couple, where one-electron reduction caused a contraction in the bond (albeit a marginal one) despite a reduction in the formal bond order [64]. The $Re-Re$ bond length in $[Re_2Cl_9]^{2-}$ is $2.473(4)$, $0.23 \text{ \AA}$ shorter than in the monoanion, despite a reduction in the formal bond order from 3.0 to 2.5. The loss of half of a δ_π bond is structurally inconsequential, and the dominant factor is again the increase in σ bond strength associated with the expansion of the $5d$ orbitals on Re .

The difficulties in identifying an unambiguous metal–metal bond order when bridging ligands are present are further illustrated by a debate in the recent literature concerning the bonding in $Fe_2(CO)_9$ (Figure 1.11) [104, 105]. The 18-electron rule demands that such a bond is present, and, indeed, the $Fe-Fe$ separation of $2.523(1) \text{ \AA}$ appears consistent with this proposal. It is not clear, however, whether this short separation genuinely reflects a bonding situation, or simply the very small size of the bridging ligands. The local d^8 configuration fills the bonding (σ and δ_π) and antibonding (σ^* and δ_π^*) combinations as well as the $2e''$ (π_δ^*) orbital (Figure 1.11), giving a formal bond order of -2 – that is, a net antibond. Hartree–Fock calculations by Bauschlicher [106] and an analysis of the Laplacian of the charge density in $Fe_2(CO)_9$ by Poblet and coworkers [107] appear to corroborate the view that there is no direct $Fe-Fe$ bond present. Mealli and Proserpio argued, also on the basis of the extended Hückel theory and charge density analysis, that interaction of the $Fe-Fe$ σ^* orbital with a linear combination of CO π^* orbitals with a_2'' symmetry transferred some antibonding character from the $1a_2''$ orbital into the vacant manifold ($2a_2''$ in Figure 1.11), meaning that the $Fe-Fe$ bonding character in $1a_1'$ is in fact not completely offset by the antibonding character in $1a_2''$ [108, 109]. Despite these subtle differences, it seems clear that whatever interaction is present between the Fe centers, it is most certainly *not* a simple covalent sharing of two unpaired electrons on the metals as implied by the 18-electron rule. There are, in fact, many parallels between 34-electron $Fe_2(CO)_9$ and square-planar 16-electron species, not least the tendency of both to react with nucleophiles. The breakdown of the 18-electron rule in square-planar complexes occurs because the vacant p_z orbital fails to find an appropriate symmetry match among the linear combinations of ligand-based orbitals, and so is not used, either to form a bond or to accommodate metal-based lone pairs of electrons. The position of the equilibrium between 16-electron ML_4 and 18-electron ML_5 is then determined by the balance between electron transfer from a fifth ligand into the p_z orbital and repulsion with the filled d_{z^2} , which occupies the same region of space. In $Fe_2(CO)_9$, there are two vacant a_2'' -symmetric metal-based combinations (primarily linear combinations of $4s$ and $4p_z$) but only one occupied ligand-based combination of the same symmetry. Thus, one of the two metal-based orbitals remains “unused” in

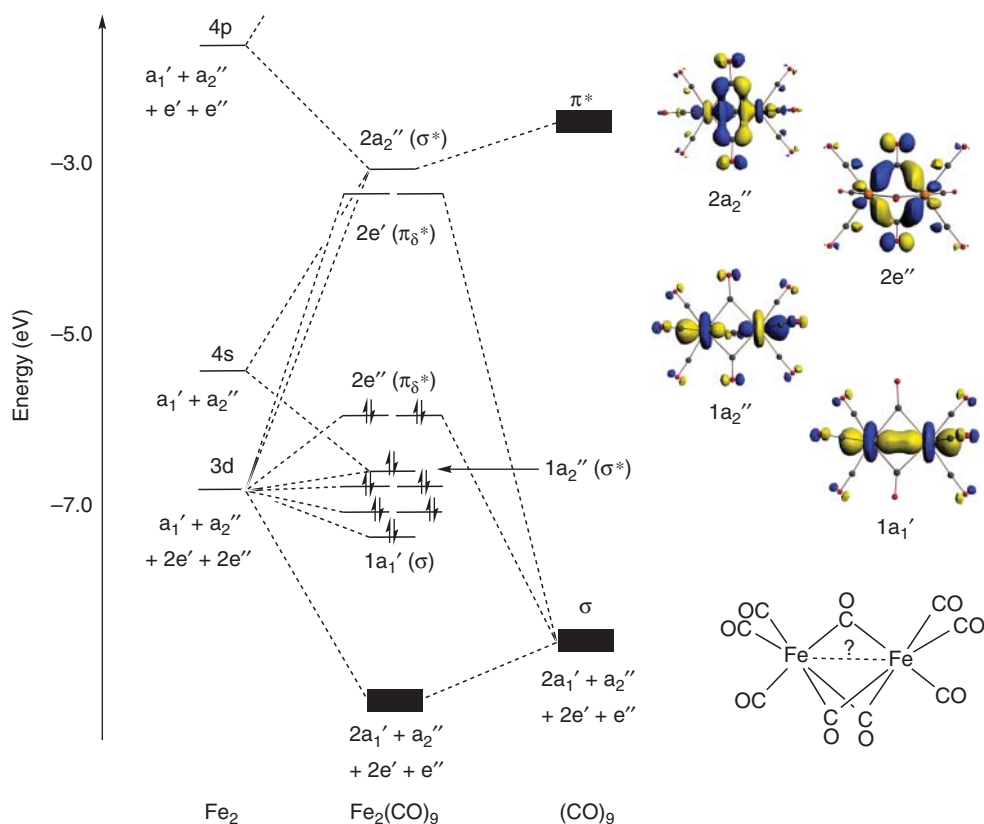


Figure 1.11 $\text{Fe}_2(\text{CO})_9$: bond or no bond?

the same sense that the p_z orbital remains unused in square-planar species. This simple symmetry-based analysis suggests that there is no need to invoke an Fe–Fe bond in $\text{Fe}_2(\text{CO})_9$, simply because the metal centers do not conform to the 18-electron rule.

1.4

Metal–Metal Bonds Between f Orbitals

The relatively weak d–d overlap in the transition series arises because the nd valence orbitals have radial maxima in the same region as their fully occupied ns and np counterparts. The situation is even more exaggerated in the lanthanide and actinide series where the nf valence orbitals are famously “core-like,” with radial maxima actually inside the fully occupied $\{(n+1)s, (n+1)p\}$ shells (see Eu in Figure 1.2). The result is that overlap between nf orbitals is negligible and instead strong interactions between ligands and the vacant $(n+2)s$ orbitals tend to favor highly coordinated monometallic complexes over metal–metal bonded dimers. Indeed, only the actinide series shows any significant homobimetallic chemistry and then only in inert matrices. The naked diatomic U_2 [110] has been characterized by vibrational spectroscopy, as have the hydrides U_2H_2 and U_2H_4 [111]. The electronic structure of the gas-phase diatomic U_2 highlights the complexity of the bonding in this region of the periodic table. A CASSCF study suggests that the ground state is a septet with a dominant configuration $(7s, 6d\sigma_g)^2(6d\pi_u)^4(6d\sigma_g)^1(6d\delta_g)^1(5f\delta_g)^1(5f\pi_u)^1(5f\phi_u)^1(5f\phi_g)^1$ and a total orbital angular

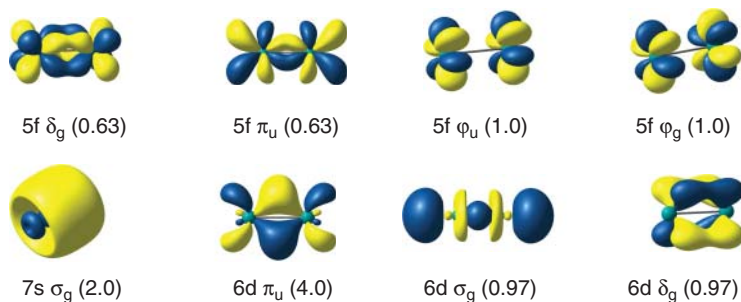


Figure 1.12 Occupations of orbitals in the septet ground state of U_2 (CASSCF).

momentum, Λ , of 11 (the $m_l = +1$, $+2$, and $+3$ components of π_u , δ_g , and ϕ_u , respectively, are occupied) (Figure 1.12) [112]. The formal bond order is therefore 5.0, just as in $ArCrCrAr$, but the nature of the quintuple bond is very different, being composed of three 2-center 2-electron bonds ($7s, 6d\sigma_g$ and doubly degenerate $6d\pi_u$) and four 2-center 1-electron bonds ($6d\sigma_g$, $6d\delta_g$, $5f\delta_g$, and $5f\pi_u$). The remaining two electrons in $5f\phi_u$ and $5f\phi_g$ make no net contribution to the bonding.

A very different type of quintuple bond is present in the putative plutonium compound $[Pu_2Cl_8]^{2-}$ (Pu(III), f^5), where the high oxidation state and the presence of a ligand field stabilizes the 5f shell relative to 6d and 7s [113]. The resulting $(\sigma + 2\pi + 2\delta)$ quintuple Pu–Pu bond is created primarily through 5f–5f overlap (Figure 1.13). This pair of quintuply bonded species U_2 and $[Pu_2Cl_8]^{2-}$ elegantly highlights the plethora of bonding possibilities when 7s, 6d, and 5f orbitals are near degenerate. A feature of Figures 1.12 and 1.13 is the presence of orbitals with ϕ symmetry (i.e., with *three* angular nodes that contain the internuclear axis), which are unique to atomic orbitals with $l > 2$. There is no net ϕ component to the bonds in either U_2 or $[Pu_2Cl_8]^{2-}$ because the bonding and antibonding combinations are equally occupied in both cases, but a ϕ component has been proposed in the U–U bond in the $^7A_{2u}$ ground state of the encapsulated species $U_2@C_{60}$ (Figure 1.14) [114].

1.5

Metal–Metal Bonds Between *p* Orbitals

Moving from the transition series to the p-block, we return to the typical main group situation where the valence orbitals (in this case *ns* and *np*) are radially diffuse relative to other occupied orbitals (*Sn*, Figure 1.2). The diatomic overlap in the lighter elements is therefore close to optimal and decreases as the principal quantum number increases. The result is a general reduction in bond strength in the heavier elements, precisely the opposite trend to that observed in the transition series. A second significant consideration in this region of the periodic table is the increase in the separation of the *ns* and *np* orbitals with atomic number, causing the *ns* orbital to become core-like (the inert-pair effect). The bonding interactions, conversely, are increasingly dominated by the *p* orbitals, driving a preference for bond angles approaching 90° rather than the larger values of 109.5° , 120° , or 180° favored when *s* and *p* contribute more equally. The impact of these periodic trends in the context of metal–metal bonds is exemplified by the heavier analogs of alkenes and alkynes, the first of which was Lappert's distannene $Sn(CH(SiMe_3)_2)_2$, with a $Sn=Sn$ bond length of $2.768(1)$ Å. [115] Prior to this, the so-called double-bond rule, the observation that multiple bonds were stable only between elements of the first long period [116], appeared to be universally valid. Other doubly ($Si=Si$ [117], $Ge=Ge$ [118], and $Pb=Pb$ [119]) and triply ($Sn\equiv Sn$ [4] and $Pb\equiv Pb$ [5]) bonded species have subsequently emerged, the latter only in the last decade. Like the CrCr quintuple bond described previously, their isolation owes much to the creative ligand design, and in particular to the steric bulk of the aryl ligands [120]. The status of the Sn and Pb dimers as doubly or triply bonded analogs of the alkenes or alkynes has been controversial because, much like the quintuply bonded $ArCrCrAr$,

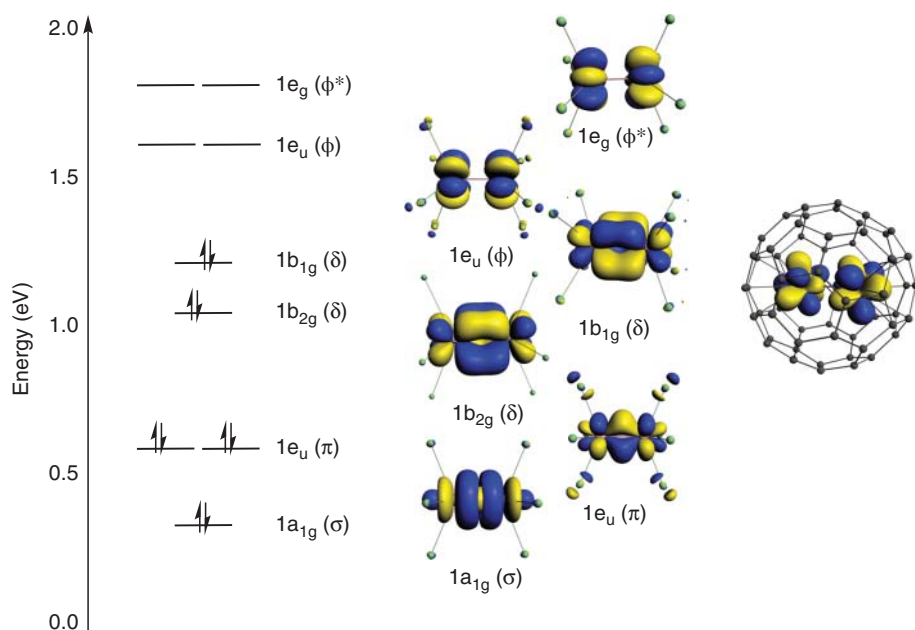


Figure 1.13 The quintuple bond in $[\text{Pu}_2\text{Cl}_8]^{2-}$ and ϕ overlap in $\text{U}_2@\text{C}_{60}$.

they are strongly “*trans*-bent.” [74] The identification of a formal bond order is therefore complicated by the lack of a rigorous symmetry-based distinction between orbitals of σ and π symmetry. The angle between the R_2M plane and the $\text{M}-\text{M}$ axis in the alkene analogs is $\sim 40^\circ$ (compared to a value of 0° for the planar alkene geometry) while the $\text{H}-\text{M}-\text{M}$ angle in the alkyne analogs is $\sim 125^\circ$ for the Sn systems and $\sim 95^\circ$ for the heaviest Pb system (Figure 1.14). Similarly, while the $\text{Sn}=\text{Sn}$ and $\text{Sn}\equiv\text{Sn}$ distances are marginally smaller than those in single-bonded analogs, the $\text{Pb}=\text{Pb}$ and $\text{Pb}\equiv\text{Pb}$ bonds are generally considerably longer than typical $\text{Pb}-\text{Pb}$ single-bonded distances. A number of theoretical models have emerged to explain these periodic trends in $\text{M}=\text{M}$ and $\text{M}\equiv\text{M}$ bonding, all of which have their roots in the increased radial and energetic separation of the ns and np valence orbitals on descending the group. In the planar isomer of the distannene $\text{Me}_2\text{Sn}=\text{SnMe}_2$, a conventional $\sigma + \pi$ picture of the double bond emerges, albeit with a small HOMO–LUMO gap separating the π and σ^* orbitals (Figure 1.14). This planar arrangement means that three σ bonds at each metal center utilize only two of the $5p$ orbitals, along with some $5s$ contribution, the third $5p$ orbital being used exclusively to establish the inherently weak π component of the bond. *Trans* bending allows mixing between the π^* and σ^* orbitals (a second-order Jahn–Teller distortion) to form a slipped $sp-//\pi$ bond, which ultimately becomes a nonbonding “resonating lone pair” (resonance structure II in Figure 1.14). The net effect of the *trans* bending is to sacrifice the intrinsically weak π component of the bond in order that the three σ bonds at each center ($\text{Sn}-\text{Sn} + 2 \text{ Sn}-\text{R}$) can be formed from three orthogonal p orbitals. In this context, the $\text{Sn}=\text{Sn}$ bond should be compared to the quintuply bonded ArCrCrAr , where *trans* bending similarly avoids the situation where the two strongest bonds ($\text{Cr}-\text{Cr}$ σ and $\text{Cr}-\text{C}$ σ) share the same orbital. Closely related arguments apply to the triply bonded distannynes and diplumbynes, where the *trans* bending affords two orthogonal σ bonds ($\text{E}-\text{E}$ and $\text{E}-\text{C}$) along with a lone pair with dominant ns character. The balance between the various resonance forms in the acetylene analogs is a delicate one, and, at least for the distannynes, a significant contribution from the diradical structure (II in Figure 11.4) has been proposed [121].

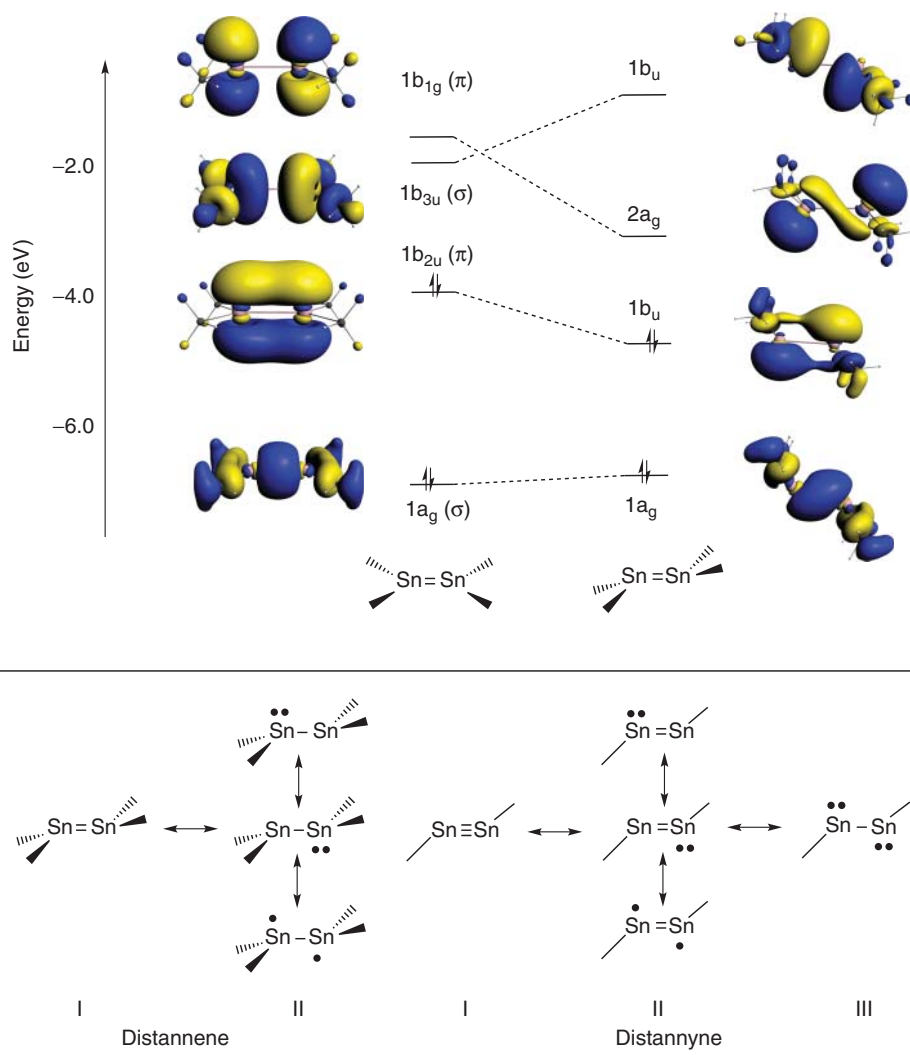


Figure 1.14 *trans* bending in distannenes and distannynes: correlation between planar (D_{2h}) and *trans*-bent (C_{2h}) limits.

1.6

Concluding Remarks

This introductory chapter tries to convey a sense of the diversity of interactions that fall under the broad umbrella of “metal–metal bonds.” The quadruple bond with which the subject is most readily associated represents only a small part of an active and expanding field. At one extreme, the last decade has witnessed the race to ever shorter and stronger multiple bonds while at the other, systems with single metal–metal bonds are finding applications in catalysis and even perhaps biology. There seems little doubt that the chemistry of metal clusters will continue to throw up surprises that challenge theory and that will, ultimately, give us a deeper understanding of the nature of the chemical bond.

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2

s-Block Metal–Metal Bonds

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2.1

Introduction

This chapter is organized into three main sections that describe historical aspects of and recent developments in the chemistry of compounds containing homo- and heteronuclear metal–metal bonds involving at least one group 1 or 2 metal. While a comprehensive coverage of the literature is not given in all sections, the comparatively small size of the field has allowed its relatively complete treatment, especially with respect to developments occurring for bimetallic systems over the last decade. These developments have been rapid and have given rise to a number of landmark results (e.g., the stabilization of magnesium(I) dimers), which ensure that the chemistry of s-block metal–metal bonded complexes has a bright future.

2.2

Group 1 Bimetallics

This section is confined to metal–metal bonded species involving two group 1 metals and excludes the study of larger metal clusters. The majority of the described molecular examples have been studied in the gas phase, at very low temperatures, or solely by theoretical methods.

2.2.1

Group 1 Diatomics and Related Species

The alkali metal diatomics [1–3] have been studied in the gas phase and/or at very low temperatures in the condensed phase, often supported by theoretical investigations. To date, all combinations of homo- and heterodiatom, $M-M$ or $M-M'$, molecules ($M, M' =$ group 1 metal) from Li to Cs have been experimentally observed (see Table 2.1) [4–26]. Data from Table 2.1 includes theoretical investigations into diatomics containing Fr and the not-yet-discovered element 119 (eka-francium), denoted as 119. In all of these molecules, the two metal atoms interact via single bonds, derived from s-orbital overlap, to yield molecules with an $X^1\Sigma_g^+$ ground state. The metal–metal bond lengths in the homonuclear dimers increase down the group from Li_2 to Cs_2 , and then calculations show them to contract for Fr_2 and 119_2 , due to relativistic effects [11–13]. The metal–metal bond dissociation energies decrease from Li_2 to Cs_2 and then increase again to 119_2 . The 119_2 metal–metal bond has been calculated to be similar in strength to that of K_2 due to relativistic effects on the $8s(119)$ orbital [13]. These studies also indicate that Cs is the most electropositive element in the periodic table [13].

The alkali metal diatomics are typically generated in high lying vibrational states and can be relaxed to absolute ground states for reaction studies on ultra-cold $M-M'$ ($M, M' = Li-Cs$) molecules. The dismutation of a heterodiatom species into two homodiatom molecules, according to the equation

Table 2.1 Homodiatomics (M_2) and heterodiatomics ($M-M'$) of the group 1 metals.

Compound	Bond length (Å)	BDE ^{a)} (kJ mol ⁻¹)	References
Li ₂	2.673	101.9	[4]
Na ₂	3.079	72.04	[5, 6]
K ₂	3.924	53.25	[7]
Rb ₂	4.210	47.77	[8]
Cs ₂	4.648	43.66	[9, 10]
Fr ₂	About 4.61 ^{b)}	About 42.1 ^{b)}	[11–13]
119 ₂	About 4.27 ^{b)}	About 53.4 ^{b)}	[13]
LiNa	2.885	85.00	[14, 15]
LiK	3.319	74.37	[16]
LiRb	3.461	70.91	[17]
LiCs	3.668	70.29	[18, 19]
NaK	3.499	63.09	[20]
NaRb	3.643	60.18	[21]
NaCs	3.851	59.27	[22]
KRb	4.068	50.46	[23]
KCs	4.284	48.68	[24]
RbCs	4.418	45.60	[25, 26]
RbFr	About 4.34 ^{b)}	About 43.9 ^{b)}	[12]
CsFr	About 4.53 ^{b)}	About 42.6 ^{b)}	[12]

a) BDE = bond dissociation energy.

b) Data from theoretical studies.

$2M-M' \rightarrow M-M + M'-M'$, has been calculated to be exoergic by approximately 3–8 kJ mol⁻¹ for Li–M and weakly endoergic (about 0.3–3 kJ mol⁻¹) for all other combinations, except the very weakly exoergic (about 0.1 kJ mol⁻¹) KRb [27].

Li₂ and Na₂ have been investigated by theoretical energy decomposition analyses [28]. The attractive bonding interactions in Li₂ are about one-third electrostatic in nature and two-thirds are due to the orbital term contribution. Pauli repulsion between both Li centers remains relatively low. Na₂ has equal electrostatic and orbital interactions and shows a comparably higher Pauli repulsion because its filled 2s core orbital is larger than the comparable 1s core orbital of Li. Furthermore, it has been found that the 3s orbital in Na₂ is only marginally polarized by bond formation, compared with the 2s orbital in Li₂. A so-called nonnuclear attractor (NNA) has been observed at the midpoint (3, –3 bond critical point) of the metal–metal bond for Li₂, LiNa, and possibly Na₂ and manifests as a weak local maximum of the diffuse electron density distinct from nuclear positions [29–32]. This rare feature is furthermore believed to be responsible for some of the properties of alkali metals [29, 30].

Molecular species of the general type L: → M–M (L: = neutral donor ligand, M = group 1 metal), and related species, have been detected in the gas phase and/or at very low temperatures, proposed as reactive intermediates, and/or studied using theoretical methods. For example, a range of organic heterocycles were co-condensed with Li vapor at 77 K to form “stable” σ- and/or π-bonded intermediates of the above type, prior to metallation of the heterocycle [33, 34]. A complex between disodium and dimethoxyethane (DME) has been generated in the gas phase and studied with photoionization mass spectrometry and theoretical methods. The latter suggest only a slight elongation of the Na–Na bond upon DME coordination [35]. Similar L: → M–M species have been proposed as intermediates in various reactions and have been mostly studied with computational methods. Examples here include intermediates in the reactions of metals with ammonia [36], for example, Li₂(NH₃)₂ [37] and the related Na₂(NH₃)_n[–] [38]. Moreover, some Li–Li bonded species have been considered

intermediates in the activation of N_2 by lithium [39]. The related molecules M_2CN ($M = Li, Na, K$) have been detected in the gas phase at elevated temperatures over mixtures of alkali metals and cyanide salts and studied by mass spectrometry and computations [40]. The favored structures can best be described as a complex of the M_2^+ ion and CN^- , and their dissociation into MCN and M is endoergic.

2.2.2

Stable Complexes with Group 1 Metal–Metal Bonding Interactions, and Related Species

No stable, well-defined complexes with group 1 metal–metal single bonds are known to date, though related alkali [41, 42] and electride [41, 43–45] compound classes with formal low oxidation state group 1 metals have been studied, and some alkali metal suboxide and subnitride materials are known [46].

Treating group 1 metals with suitable organic ligands (for example, cryptands or crown ethers) does not lead to ligand-stabilized M_2 molecules but can afford highly reactive ionized alkali complexes of the general formula $[L_nM^+][M^-]$ with the alkali (M^-) in the rare -1 oxidation state, or related electrides of the general formula $[L_nM^+](e^-)$ with electrons residing on “empty” anionic sites. Of the alkali, the sodide anion is most common, but they have been characterized for $M = Na-Cs$ (but not Li) [41, 42]. They contain large diamagnetic M^- anions with s^2 configurations. Sodide (Na^-) is approximately comparable in size to the iodide ion [42], and ceside (Cs^-) has an approximate ionic radius of $3.5 \text{ \AA}$ [42, 47]. Alkali complexes are generally thermally sensitive, but examples with Na^- and K^- stable at room temperature are known [48]. Alkalides can form weak dimers ($M = Na-Rb$) or polymeric chains ($M = Rb, Cs$) in the solid state with long $M^- \cdots M^-$ contacts [41, 42, 49] via $s^2 \cdots s^2$ closed-shell interactions [50]. For example, the sodide $[Ba(H_5\text{Azacryptand}[2.2.2])]Na \cdot 2\text{MeNH}_2$, **1**·2 MeNH_2 (see Figure 2.1) [51], synthesized from Ba and Na metal, $H_5\text{Azacryptand}[2.2.2]$, liquid NH_3 , and MeNH_2 at -60°C , shows weak $Na^- \cdots Na^-$ interactions ($4.17 \text{ \AA}$) in the solid state. These are approximately $1 \text{ \AA}$ longer than those found for the Na_2 molecule. The minimum on the potential energy curve for the sodide dimer has been calculated to be $3.92 \text{ \AA}$ [51]. Alkali complexes are highly reducing and reactive toward organic and inorganic substrates, and reactions generally occur via a stepwise two-electron transfer process [52]. Related electrides, for example, $[Cs(18\text{-crown-6})_2](e^-)$ [53, 54], can be obtained from similar experiments.

2.2.3

Stable Metal–Metal Bonded Complexes Involving One Group 1 Metal

Group 1 metals are the most electropositive elements in the periodic table, and thus bonds between them and other metals are highly polarized or ionic. For most examples, a lone pair of electrons

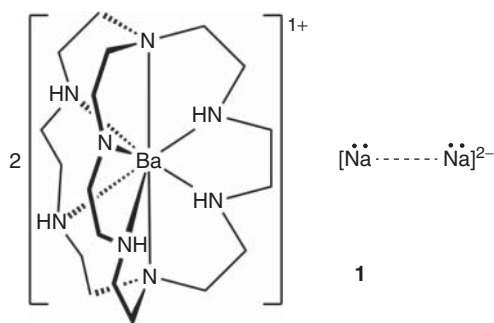


Figure 2.1 Compound **1**, including sodide–sodide interaction.

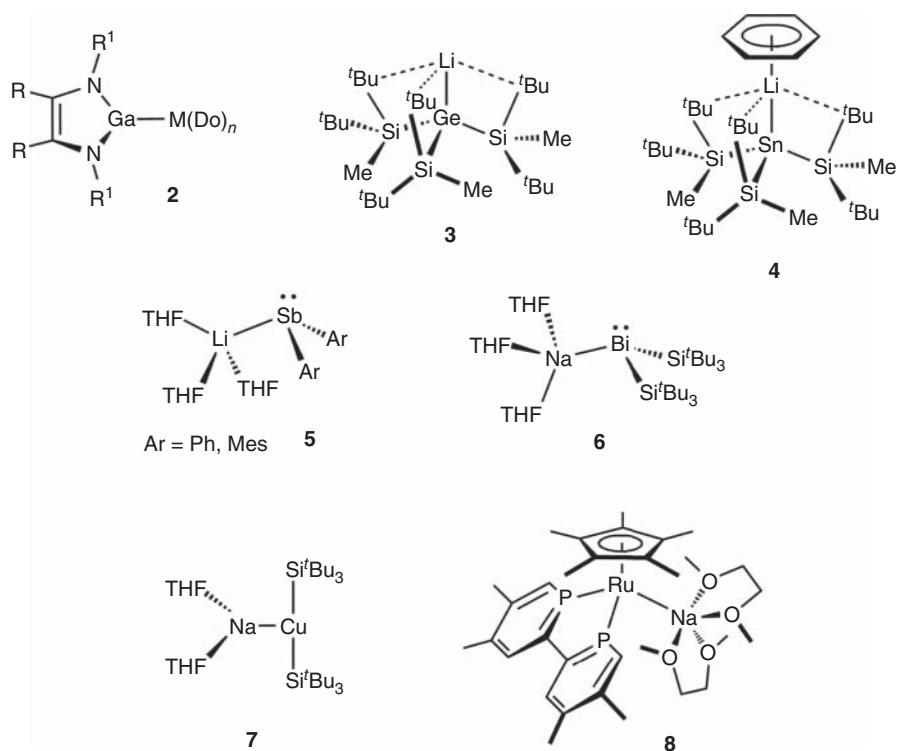


Figure 2.2 Examples of heterobimetallic complexes involving alkali metals.

resides on the central metal of an “-ate” complex that has a largely ionic contact with an alkali metal counterion, as described by the simplified model $\text{Do}_n\text{M}^+ \cdots [\text{:M}'\text{L}_m]^-$, where $\text{Do}_n = n$ neutral donor molecules, M = alkali metal, $\text{:M}'$ = metal center with lone pair, $\text{L}_m = m$ anionic ligands. Changes to the neutral donor environment, Do_n , for example, the addition of crown ethers and chelating tertiary amines, can lead to the formation of solvent-separated ion pairs without any significant alkali metal–metal bonding interaction, further highlighting the ionic nature of those contacts. Therefore, the properties and chemistry of the alkali metal–metal bonded complexes are largely governed by the characteristics of the non-alkali metal center. A brief overview of such complexes using examples with unsupported alkali metal–metal interactions, but excluding ring systems and larger clusters, is given here. Structurally characterized complexes with metal–metal bonds involving alkali metals and other metal atoms are limited to main group 13–15 metals, and some transition metal (TM) examples.

From group 13, a series of anionic five-membered gallium(I) heterocycles, that is, higher *N*-heterocyclic carbene (NHC) analogs, with contacts to alkali metal cations of the general formula **2** (see Figure 2.2, $\text{R}^1 = 2,6\text{-diisopropylphenyl}$, $t\text{Bu}$, etc.; $\text{M} = \text{Li}–\text{K}$, Do = ether or amine ligand) have been characterized [55]. These derivatives have been found to be extremely valuable in transfer reagent reactions that have accessed a wide range of gallium to metal bonded complexes, incorporating elements from across the periodic table [55]. In addition, a series of other contacts between alkali metal cations and group 13 metals have been characterized for a range of low oxidation state group 13 complexes [56, 57]. A related group 12 complex with $\text{Na} \cdots \text{Zn}$ contacts is known [58].

Most of the structurally characterized complexes with alkali metal–metal bonds contain group 14 metals. The majority of those interactions follow the general formula $\text{Do}_n\text{M}^+ \cdots [\text{:M}'\text{R}_3]^-$, where $\text{Do}_n = n$ neutral donor molecules, M = alkali metal, $\text{:M}'$ = group 14 metal, R = anionic organic

substituent [59–61]. These contain the $[:M'R_3]^-$ anion with Ge [59], Sn [60], or Pb [61] in the formal +2 oxidation state. For instance, the complexes $[R_3Ge-Li(THF)_n]$ ($R = tBu_2MeSi$; $n = 0, 3$, or 4) were structurally characterized, and the donor solvent-free ($n = 0$) example **3** shows a short $Ge \cdots Li$ interaction (2.518(7) Å) in the solid state [62]. The Ge geometry of the R_3Ge group in **3** is close to planar, in contrast to the THF solvated and ion separated examples ($n = 3$ and 4), which show a more pyramidal geometry around the Ge center [62]. A series of related R_3Sn derivatives has been synthesized, including the Li-bridged dimer $\{[R_3Sn(\mu-Li)]_2\}$ with long bridging $Li \cdots Sn$ interactions (2.985(7) and 3.143(7) Å), and the η^6 -benzene capped complex, $[R_3Sn-Li \cdots C_6H_6]$, **4** (see Figure 2.2) with a significantly shorter $Sn \cdots Li$ contact (2.771(4) Å) [63]. Structurally characterized $Ph_3Sn-Li(PMDETA)$ ($PMDETA = N,N,N',N'',N'''$ -pentamethyldiethylenetriamine) with $Sn-Li$ bonds of about 2.87 Å (mean value) shows unresolved $^{117,119}Sn-^7Li$ coupling ($J = 412$ Hz) that supports the retention of the $Sn-Li$ bond in solution [64]. Similarly, some alkali metal-group 15 metal bonded complexes are known, and several follow the general type $Do_nM^+ \cdots [:M'R_2]^-$, where $Do_n = n$ neutral donor molecules, $M =$ alkali metal, $:M' =$ Sb, Bi; $R =$ anionic organic substituent [65]. For example, $[(THF)_3Li-SbAr_2]$ **5** ($Ar = Ph, Mes$) shows some variation in the magnitude of the $Li \cdots Sb$ contacts, 2.881(4) Å ($Ar = Ph$) and 2.945(13) Å ($Ar = Mes$), depending on the organic substituent [66]. The related complex $[(THF)_3Na-Bi(Si^tBu_3)_2]$, **6** [67], with a $Na \cdots Bi$ contact of 3.11(1) Å, possesses an $Si-Bi-Si$ angle of 122.3(2)° that is some 20° more obtuse than the respective $C-Sb-C$ angles in complex **5**.

Significantly fewer unsupported and structurally characterized alkali metal-TM complexes are known, though they show similar motifs compared with their main group counterparts. For example, the cuprate complex $[(THF)_2Na-Cu(Si^tBu_3)_2]$, **7**, exhibits an almost linear $Si-Cu-Si$ fragment (175.26(5)°) and a $Na-Cu$ bond of 2.7393(18) Å [68]. The rare 2,2'-biphosphinine-coordinated Ru^0 complex **8** has been obtained from reduction of the corresponding Ru^{II} chloride complex with sodium naphthalenide in DME. This has a $Ru-Na$ bond of 3.072(2) Å in the solid state [69] and is effective in salt metathesis reactions with MeI or R_3SnCl ($R = Me, Ph$) to give substituted Ru^{II} complexes.

2.3

Group 2 Homobimetallics

The coverage of group 2 homobimetallics that is given here is largely restricted to the chemistry of isolable molecular compounds with metal-metal bonds. With that said, a brief summary of metal-metal bonded species that are only fleetingly stable in the gas phase, or at very low temperatures, is warranted and is addressed first. It should be noted that systems containing homonuclear group 2 metal-metal bonds are by definition low oxidation state compounds. A number of excellent recent reviews have covered the known chemistry in this area [70–75], and the reader should consult these for more detailed information.

2.3.1

Group 2 Diatomics and Related Species

Since the first spectroscopic observation of Mg_2 in 1970 [76], numerous experimental and theoretical studies have examined the structure and properties of the gas phase diatomics, M_2 ($M = Be-Ba$), in their ground and excited electronic states [1, 2, 77]. As might be expected for the nominally closed-shell (ns^2) metal atoms, the heavier dimers are known to exhibit weak van der Waals interactions (experimental dissociation energies, D_c : from Mg about 5 kJ mol⁻¹ to Ba about 19 kJ mol⁻¹) and very long $M-M$ interactions (from Mg 3.89 to Ba 4.88 Å) [76, 78–82]. In contrast, the bonding situation in the simplest diatomic, Be_2 , was a matter of some debate until 2009 when two studies laid the discussion to rest [83, 84]. While the atomic separation in ground state Be_2 (2.45 Å) is outside what would be expected for a covalent bond, it is at the short end of the van der Waals range. The $Be-Be$

bond is also anomalously strong ($D_e = 11.1 \text{ kJ mol}^{-1}$), which calculations suggest is due to a degree of covalent bonding arising from mixing of the energetically similar 2s and 2p orbitals [77, 83].

A variety of theoretical and some spectroscopic studies have been carried out on the ionized diatomics, $[\text{M}_2]^{n+}$ ($n = 1$ or 2), which typically show that the M–M interaction is strengthened relative to the neutral species [85–89]. A case in point here is the $[\text{Mg}_2]^{2+}$ dication, which is isoelectronic to Na_2 and has its magnesium centers formally in the +1 oxidation state. Calculations on this dication indicate that it should have a singlet ground state, $^1\Sigma_g^+$, with a Mg–Mg distance of $2.89 \text{ \AA}$, that is, close to those in isolated molecular Mg^{I} dimers (see below) [87]. Moreover, it was predicted to be a relatively long lived, metastable species in the gas phase, which was borne out by its experimental detection using mass spectrometry [88]. It is interesting to note that a variety of ternary hydride materials exhibit very short Mg–Mg interactions, for example, $2.754 \text{ \AA}$ for Mg_4IrH_5 [90]. These have been formulated as containing $[\text{Mg}_2]^{2+}$ units (e.g., $[\text{Mg}_2]^{2+}_2[\text{IrH}_3]^{2-}[\text{H}]^-_2$ for Mg_4IrH_5), as has superconducting MgB_2 in which the solid state Mg–Mg distance is $3.083 \text{ \AA}$ [91].

The neutral Be_2 fragment has been spectroscopically observed in solid argon matrices at about 30 K , albeit as complexes with the CO molecule, for example, planar $(\text{CO})_2\text{BeBe}(\text{CO})_2$ and linear $(\text{CO})\text{BeBe}(\text{CO})$ [92]. Although such compounds decompose at higher temperatures, a combination of infrared spectroscopic and theoretical analyses implies that their Be–Be interactions are significantly more robust than in Be_2 . In line with this are calculations that show $(\text{CO})_2\text{BeBe}(\text{CO})_2$ to have either a very short ($1.938 \text{ \AA}$) Be–Be double bond [93] or a Be–Be single bond, which forms part of a delocalized, multicentered bonding environment [94, 95]. Similarly, a recent computational study has shown linear and planar Be^0 complexes, $(\text{NHC})_n\text{Be}=\text{Be}(\text{NHC})_n$ ($n = 1$ or 2) to have short Be–Be bonds (about $n = 1$: $1.95 \text{ \AA}$, $n = 2$: about $2.10 \text{ \AA}$) that have some double-bond character but also exhibit a degree of $\text{Be} \rightarrow \text{C} \pi$ back-bonding [96]. The study proposed that such compounds could be synthetically achievable, whereas their Mg counterparts would likely not be.

2.3.2

Transient Group 2 Metal(I)–Metal(I) Bonded Dimers

Prior to 2007, no compound bearing a group 2 metal–metal covalent bond was known to be stable at anywhere near room temperature. This is not surprising when the results of prior, and subsequent, computational studies on simple metal(I) dimers, RMMR ($\text{M} = \text{Be–Ba}$, $\text{R} = \text{H}$, Cl , Cp , Ph , etc.), are taken into account. These investigations are too many to fully summarize here, but further details can be obtained from recent reviews [70–75]. However, it is instructive to consider the results of one study on PhMMPh , as an exemplar (see Table 2.2) [73]. These show the lighter molecules ($\text{M} = \text{Be–Ca}$) to be essentially linear with increasing M–M bond lengths. While their M–M bond dissociation energies are not large, they are not insignificant, especially for PhBeBePh and PhMgMgPh . This, combined with the fact that all three compounds are stable with respect to disproportionation in the gas phase,

Table 2.2 Calculated (BP86/TZVPP) geometrical parameters, M–M bond dissociation energies (BDEs)^{a)} and disproportionation energies (D_d)^{b)} for the group 2 metal(I) dimers, PhMMPh ($\text{M} = \text{Be–Ba}$).

M	M–M (Å)	M–M–C (°)	BDE (kJ mol^{-1})	D_d (kJ mol^{-1})
Be	2.09	177.7	286	137
Mg	2.87	178.9	167	25
Ca	3.81	179.0	89	48
Sr	4.12	138.1	70	22
Ba	4.53	116.8	—	–118

a) Dissociation to two MPh fragments in the singlet state.

b) For the gas phase reaction, $\text{PhMMPh} \rightarrow \text{MPh}_2 + \text{M}$.

suggests that PhMMPH ($M = \text{Be} - \text{Ca}$), and similar dimers, may be stable under ambient conditions. This is, of course, not the case because when the vaporization energies of the metals are taken into account, it is realized that all would spontaneously disproportionate to $M\text{Ph}_2$ and solid metal at room temperature. The heavier molecules ($M = \text{Sr}$ or Ba) have *trans*-bent structures, with PhSrSrPh having a weak and long Sr–Sr bond, while dissociation of the Ba–Ba bond of PhBaBaPh is exothermic, as is the disproportionation of the compound.

The results of this and other computational studies suggest that in the absence of substantial kinetic stabilization, no simple group 2 metal(I) dimer should exist at ambient temperature, but lighter examples may be transiently stable at lower temperatures. This is indeed the case, as the parent metal(I) dimers, HMMH ($M = \text{Be}$ [97], Mg [98], or Ca [99]), among other products, have been generated from the reaction of laser-ablated metal atoms with dihydrogen and have been trapped in solid noble gas or hydrogen matrices at temperatures of about 10 K. These compounds have been identified using a combination of infrared spectroscopy and theory. Similarly, the products obtained from the reaction of solid MgB_2 with HCl gas at 700 K were trapped in an inert gas matrix at 10 K and found to include ClMgMgCl and $\cdot\text{MgCl}$ radicals by IR and Raman spectroscopy, in combination with DFT calculations (e.g., $\nu_1[\Sigma_g] = 176 \text{ cm}^{-1}$ for ClMgMgCl). In this study, attempts were made to synthesize more stable magnesium(I) species, $\text{Cp}^*\text{MgMgCp}^*$ ($\text{Cp}^* = \text{C}_5\text{Me}_5^-$) and BrMgMgBr , which although stable to some extent in solution, decomposed to Mg metal above -60°C [100]. Subsequently, metastable solutions of $\text{BrMgMgBr}/\text{MgBr}$ containing NEt_3 or PEt_3 donors were shown to be stable below -40°C [101]. Reaction of these solutions with LiS^tBu , in an attempt to generate MgS^tBu radicals, instead led to the Grignard-like compound, $[(^t\text{BuMgS}^t\text{Bu})_4]$ among other products, via a redox decomposition of MgS^tBu . This result was said to provide some evidence for the formation of Grignard reagents, RMgX , via radicalic magnesium subhalide intermediates. Interestingly, diamagnetic magnesium(I) dimers, RMgMgX , have also been suggested to be intermediates in the formation of Grignard reagents. Theoretical studies have provided some weight to this proposal by showing that the insertion of an Mg atom into RMgX molecules is generally slightly exothermic [102, 103]. In this respect, Grignard-like reagents, for example, PhMg_4F , have been obtained from the reaction of Mg vapor and PhF and were claimed to be stable in solution under ambient conditions [104].

2.3.3

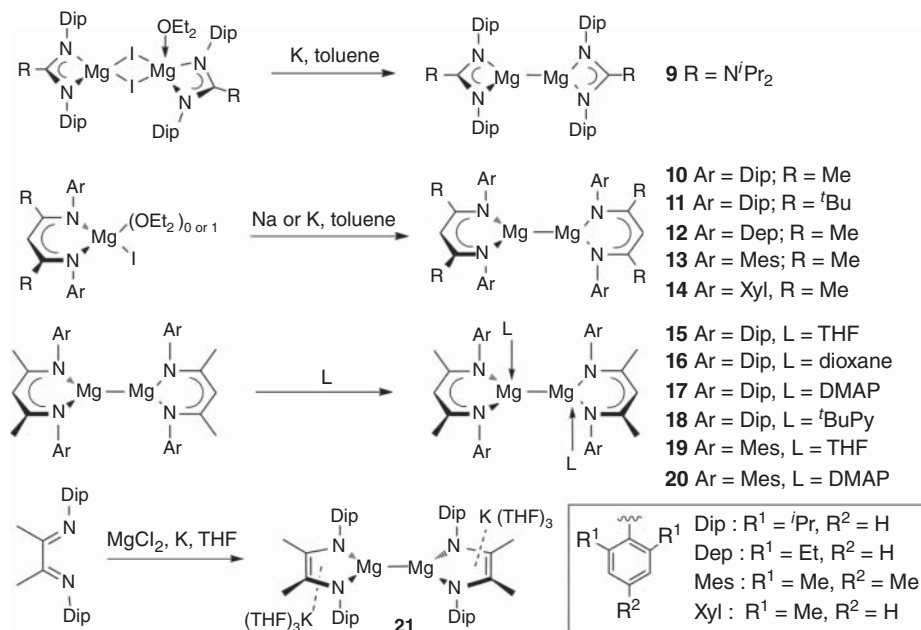
Isolable Group 2 Metal(I)–Metal(I) Bonded Dimers

2.3.3.1 Synthesis and Physical Properties

The results of the aforementioned computational studies suggested that the incorporation of very bulky ligands (R) into dimers of the type RMMR ($M = \text{Be}$, Mg , or Ca) could lead to their kinetic stabilization toward disproportionation to bulk metal and MR_2 under ambient conditions. Further, theory has shown that bidentate anionic ligands should provide additional stabilization to group 2 metal(I) dimers [70, 71, 73, 96, 100, 105]. In practice, however, the only dimeric metal(I) compounds to be isolated to date are those of magnesium, and, in all cases, bidentate amido-ligands chelate each metal center. It is of note that one stable calcium(I) compound, $[\{(\text{THF})_3\text{Ca}\}_2(\mu\text{-C}_6\text{H}_3\text{Ph}_3\text{-1,3,5})]$, has been reported, though this has an “inverse sandwich” structure with no significant Ca–Ca interaction [106].

Three ligand types have so far been utilized in the preparation of magnesium(I) dimers, namely, guanidinate, β -diketiminate (Nacnac), and 1,2-diamidoalkene (Scheme 2.1 shows all known examples). Of these, the yellow to orange β -diketiminate complexes (**10–14**) have been most studied [71, 107–110], while only one guanidinate (**9**) [107] and one 1,2-diamidoalkene complex (**21**) [111] have been reported. All three-coordinate guanidinato and β -diketiminato magnesium(I) compounds (**9–14**) were synthesized by the alkali metal (Na or K) reduction of magnesium(II) iodide precursor compounds, typically in good to high yields. Using substituents smaller than 2,6-xylyl at the N centers of β -diketiminate ligands in such reductions does not lead to stable magnesium(I) species. A case in

point here is the sodium metal reduction of $[(^{\text{Ph}}\text{Nacnac})\text{MgI}(\text{OEt}_2)]$ ($^{\text{Ph}}\text{Nacnac} = [(\text{PhNCMe})_2\text{CH}]^-$), which instead afforded the homoleptic magnesium(II) complex, $[(^{\text{Ph}}\text{Nacnac})_2\text{Mg}]$, presumably via disproportionation of an unstable Mg^{I} intermediate [110]. Moreover, the possibility of several of the magnesium(I) dimers actually existing as hydride-bridged magnesium(II) species, $[(\text{Nacnac})\text{Mg}(\mu\text{-H})_2\text{Mg}(\text{Nacnac})]$, has been ruled out by spectroscopic means and by the subsequent preparation of the Mg^{II} hydride complexes. These colorless compounds have significantly different properties from their Mg^{I} counterparts.



Scheme 2.1 Synthesis of magnesium(I) dimers.

The only 1,2-diamidoalkene complex, **21**, was prepared by reduction of a mixture of a bulky diazabutadiene ($\text{DAB} = \{\text{DipNCMe}\}_2$) and MgCl_2 with potassium metal [111]. The core of the pink complex encompasses doubly reduced DAB^{2-} ligands coordinated to the Mg_2^{2+} dication, thereby generating the dianionic fragment $[(\text{DAB})\text{MgMg}(\text{DAB})]^{2-}$. This exhibits π -interactions with two $[\text{K}(\text{THF})_3]^+$ counterions. In addition to reduction methodologies, a series of dark orange to red four-coordinate magnesium(I) Lewis base adducts (**15–20**) have been prepared in high yield by the treatment of the relevant three-coordinate dimer with ether or pyridine Lewis bases [108, 110]. The coordination of the ether molecules in **15** and **16** is only weak, as evidenced by the fact that it is readily reversed when solid samples of the adducts are placed under vacuum, heated under a dinitrogen atmosphere, or dissolved in aromatic solvents.

All of the three-coordinate guanidinato and β -diketiminato magnesium(I) dimers are remarkably thermally stable (see Table 2.3), which is perhaps best exemplified by compound **10**, which is stable at temperatures above 300°C . The compounds are not greatly air and moisture sensitive, though what sensitivity they exhibit is typically inversely proportional to the steric bulk of the ligand involved. These properties, combined with the ease of preparation and handling of magnesium(I) dimers, are lending them to increasing use as specialist reducing agents in both organic and inorganic synthetic methodologies (see the subsequent text).

Although no ambient temperature-stable Be^{I} or Ca^{I} dimers have been reported, it is worth mentioning that attempts to prepare them have been made by reductions of metal(II) halide

Table 2.3 Selected structural and physical data for dimeric magnesium(I) compounds.

Compound	Mg–Mg distance (Å)	C.N. _{Mg}	M.P. ^a (°C)	References
[{(Priso)Mg} ₂] 9	2.8508(12)	3	170–173	[107]
[{(DipNacnac)Mg} ₂] 10	2.8457(8)	3	301–303	[107]
[{(tBuNacnac)Mg} ₂] 11	2.847(2)	3	278–280	[110]
[{(DepNacnac)Mg} ₂] 12	2.8752(12)	3	121–124	[71]
[{(MesNacnac)Mg} ₂] 13	2.808(1)	3	201–203	[110]
[{(XylNacnac)Mg} ₂] 14	2.8212(11)	3	180–181	[71]
[{(DipNacnac)Mg(THF)} ₂] 15	3.0560(12)	4	68–71	[108]
[{(DipNacnac)Mg(dioxane)} ₂] 16	3.1499(18)	4	59–62	[108]
[{(DipNacnac)Mg(DMAP)} ₂] 17	3.1962(14)	4	159–160	[108]
[{(DipNacnac)Mg(^t BuPy)} ₂] 18	3.1260(15)	4	248–250	[108]
[{(MesNacnac)Mg(THF)} ₂] 19	About 2.89 ^b	4	86–89	[110]
[{(MesNacnac)Mg(DMAP)} ₂] 20	2.937(1)	4	142–143	[110]
[{[K(THF) ₃](DAB)Mg} ₂] 21	2.9370(18)	3	N/A	[111]

C.N._{Mg}: Mg coordination number; M.P.: melting point; and N/A: not available. [(DipN)₂CNⁱPr₂][−] (Priso);

[{ArNCMe)₂CH][−] (Ar = C₆H₃Et₂-2,6: ^{Dep}Nacnac, C₆H₃Me₂-2,6: ^{Xyl}Nacnac.

a) Typically denotes full decomposition.

b) Approximate value from a low-quality crystal structure.

complexes. For example, alkali metal reductions of [(^{Mes}Nacnac)BeI] and [{(^{Dip}Nacnac)CaI(OEt₂)₂}] (^{Mes}Nacnac = [(MesNCMe)₂CH][−]; ^{Dip}Nacnac = [(DipNCMe)₂CH][−]; Mes = mesityl, Dip = 2,6-diisopropylphenyl) both yielded complex product mixtures [110]. In contrast, the reduction of [(^{Dip}Nacnac)BeCl] with potassium metal was relatively clean and afforded two beryllium(II) compounds, in which the chelating ^{Dip}Nacnac lost or gained a hydrogen atom, thereby being transformed into dianionic diamido ligands in both cases. It was proposed this reduction reaction proceeded via reduction of the ligand, rather than beryllium, to give a radical intermediate, [(^{Dip}Nacnac)BeCl], which participated in subsequent hydrogen transfer reactions to give the observed products [112]. Related attempts to prepare low-valent Mg complexes via heating magnesium hydride clusters stabilized by bis(β-diketimate) ligands, viz. [(*para*)₃Mg₈H₁₀] (*para* = [{(DipNCMe)CH(MeCN)}₂](μ-C₆H₄-1,6)]^{2−}) [113] and [{NN(MgH)₂}]₂ (NN = [{(DipNCMe)CH(MeCN-)}₂]^{2−}) [114], to 200 and 175 °C, respectively, led to the elimination of H₂ and generation of red solids (cf. dehydrogenation of MgH₂ to give Mg(s) at about 300 °C). It was suggested that these solids could be the low-valent Mg–Mg bonded clusters, [(*para*)₃Mg₈] and [{NN(Mg₂)}]₂, though this has not been confirmed experimentally.

2.3.3.2 Structure and Bonding

All reported stable magnesium(I) dimers possess unsupported Mg–Mg bonds, coordinated by electronically delocalized bidentate ligands. Of the compounds listed in Table 2.3, the neutral three-coordinate compounds exhibit essentially planar Mg coordination environments with Mg–Mg distances in a fairly narrow range (2.808(1)–2.875(1) Å). Not surprisingly, the Mg–Mg separation (2.937(2) Å) in the dianionic complex, **21** [111], is markedly greater than in the neutral species, owing to coulombic repulsion. As long, or even longer, are the Mg–Mg bonds in four-coordinate adduct complexes, **15**–**20**. Indeed, their Mg–Mg bond lengths are greater than those of their uncoordinated counterparts by up to about 12%. This is remarkable, even when the increase in Mg coordination number in the adducts is taken into account, and implies that the potential energy surface about the equilibrium Mg–Mg bond distances in all the dimers is quite shallow. Theoretical [108] and experimental evidence [109] has supported this proposal (see later in the chapter). Despite

the apparent “deformability” of the Mg–Mg bonds in the three-coordinate dimers, these bonds do not appear to be readily susceptible to cleavage. Evidence for this comes from the fact that when solutions of two dimers in noncoordinating solvents are heated (to temperatures of up to 100 °C), there is no apparent “scrambling” of the Mg heterocycles between the dimers [110]. Therefore, there does not appear to be any significant dimer/monomer equilibria for the compounds in solution. The bond distances for all reported Mg^I dimers are comparable with the sum of two covalent radii for magnesium (2.82 Å) [115] and the Mg–Mg distance in the solid metal (3.20 Å) [116], but are significantly shorter than the metal separation in Mg₂ (3.89 Å) [1].

With respect to the nature of the bonding in neutral, three-coordinate guanidinate- or β-diketiminato-chelated magnesium(I) dimers, computational studies on model compounds have found that the Mg–Mg interaction is typically associated with the HOMO of the molecules. These single σ-bonds exhibit Wiberg bond indices of about 0.9, they have high (about 90%) *s*-character, and it is likely that there is a small barrier to rotation of the Mg heterocycles about the bonds [107, 108]. In comparison, calculations on a model of the dianionic complex, **21**, pointed to a significant *p*-orbital contribution (about 55%) to its Mg–Mg bonding molecular orbital (HOMO-2) [111]. Moreover, substantial π-bonding character was found for two nearly degenerate unoccupied orbitals near the electronic frontier of the guanidinate and β-diketiminato complexes (e.g., the LUMO and LUMO + 1 of a model of **9**; HOMO–LUMO gap of about 389 kJ mol^{−1} [107]). These data, in combination with calculated natural charges for the model complexes, imply that the magnesium(I) dimers should be viewed as consisting of covalently bonded dimagnesium dications, Mg₂²⁺, which are kinetically stabilized by ionic interactions with bulky anionic ligands.

The potential energy surface about the equilibrium Mg–Mg bond length of the parent β-diketiminato magnesium(I) complex, [{(H¹Nacnac)Mg}₂] (H¹Nacnac = [(HNCH)₂CH][−]), has been calculated, so as to shed light on the origin of the aforementioned elongation (by about 0.2 Å) of experimental Mg^I dimers upon coordination by ethers and pyridines [108]. This was found to be very shallow in that it requires only about 5.0 kJ mol^{−1} to elongate the bond by 0.20 Å. Similar to the uncoordinated model, [{(H¹Nacnac)Mg}₂], the THF adduct, [{(H¹Nacnac)Mg(THF)}₂], has very high *s*-character to its Mg–Mg bonds, with a bond order of 0.97.

An experimental charge density (ECD) study has been carried out on [{(D^{ip}Nacnac)Mg}₂] (**10**) using high-resolution single-crystal X-ray diffraction data in combination with theory [109]. The results of this study are consistent with prior computational investigations, in that **10** was shown to have average charges on its Mg and N centers of +1.15 and −1.20, respectively. Furthermore, a bond critical point was located almost midway along its Mg–Mg vector, which seemingly confirmed the presence of a covalent bond between the magnesium atoms. However, the electron density between the two atoms is quite diffuse, which is in keeping with the experimentally observed “deformability” of the bond. With that said, the results of a later study suggested that the nature of the Mg–Mg bonding in **10** might not be as straightforward as first thought. That is, further multipole modeling of the ECD data, along with supporting DFT studies, highlighted a nonnuclear local maximum of electron density distinct from nuclear positions (or an NNA), in a large region of the negative Laplacian between both Mg atoms in **10** [117]. This situation can be viewed as each Mg atom “binding” to the NNA, which itself can be considered a “pseudo-atom”. Compound **10** is the first example of a stable molecular compound displaying an NNA, which has previously only been observed for some elemental *s*-block metals and related unstable molecules such as Li₂ and Na₂.

2.3.3.3 Reactivity

Since the first report on isolable magnesium(I) dimers in 2007, their further chemistry has blossomed, especially with respect to their use as bespoke reducing agents in a variety of organic and inorganic synthetic methodologies. Almost all further chemistry of these compounds has come from β-diketiminato-coordinated examples, which possess a unique combination of properties that make them attractive alternatives for “traditional” reducing agents (e.g., magnesium metal, alkali metals,

and SmI_2) that are widely used in synthesis. These include their moderate air and moisture sensitivity, impressive thermal stability, and high solubility in many coordinating and noncoordinating organic solvents. In addition, the dimers can be prepared in good yields on multigram scales, are readily manipulated using standard techniques, are of low toxicity, and do not present any significant fire hazard. No data are yet available on the reduction potentials of magnesium(I) dimers, though the results of further reactivity studies suggest that they should be categorized as moderate to strong reducing agents. It is noteworthy that the reduction potential for the $\text{Mg}^{2+}/\text{Mg}^+$ couple has been reported at -2.05 V versus NHE [116], which may give some further indication of the reducing ability of magnesium(I) dimers.

Single-electron reducing agents such as alkali metals, SmI_2 [118], Mg/MgX_2 ($\text{X} = \text{Br}$ or I) [119], and even Grignard reagents [120] are of great importance to organic synthesis but can suffer from selectivity issues in that respect. Initial studies on the use of magnesium(I) dimers in organic synthesis have shown them to invariably act as highly selective, two-center/two-electron reducing agents (i.e., one electron per Mg center) in a variety of high-yielding transformations of unsaturated substrates to unprecedented product types. These include the single reduction of benzophenone to yield a ketyl radical [121], double reduction of the substrate (carbodiimides [107], anthracene [121], azobenzene [122], or cyclooctatetraene [122]) via its insertion into the Mg–Mg bond, reductive C–C bond forming reactions (some isonitriles, nitriles [123], and isocyanates [110, 122]), reductive N–N bond forming reactions (1-adamantylazide [110, 122]), reductive N–C cleavage reactions (some isonitriles [123]), or reductive C–C cleavage reactions (some nitriles [123]). In a similar vein, the reactivity of a Mg^{I} dimer, $[\{(\text{DipNacnac})\text{Mg}\}_2]$ (**10**) toward CO_2 has been explored. This leads to the quantitative reductive disproportionation of CO_2 , which could proceed via an initial reductive deoxygenation of CO_2 to give CO and $[\{(\text{DipNacnac})\text{Mg}\}_2(\mu\text{-O})]$, the latter of which subsequently reacts with CO_2 to yield $[\{(\text{DipNacnac})\text{Mg}\}_2(\mu\text{-}\kappa^2\text{-CO}_3)]$ [124]. Treating this complex with potassium metal regenerates the magnesium(I) dimer, **10**.

It is probable that the aforementioned reduction reactions proceed via an initial coordination of the substrate to one or both of the Mg centers of the dimer before its reduction or reductive coupling. Therefore, these reductions need to be carried out in noncoordinating solvents, as competitive coordination of a donor solvent (e.g., THF) at the Mg^{I} centers effectively blocks nucleophilic attack at those centers by the reaction substrate. For similar reasons, it has been found that the reactivity of β -diketiminato-coordinated Mg^{I} dimers toward unsaturated substrates is inversely proportional to the steric bulk of the β -diketiminate ligand involved.

With respect to the use of Mg^{I} reagents in inorganic/organometallic synthesis, they have shown most value as specialist reducing agents in the preparation of very low oxidation state p- and d-block element complexes. These are normally accessed via the reduction of “normal” oxidation state metal halide precursors with harsh and often insoluble reducing agents such as alkali metals, KC_8 , and alkali metal naphthalide solutions. Such reductions can be problematic, as they are often low yielding and can lead to “over-reduction” of the precursor complex, and/or other side reactions. The unique properties held by Mg^{I} dimers can minimize these problems and have allowed inorganic chemists access to an array of unprecedented complex types.

From group 13, Mg^{I} dimers have been utilized in the synthesis of the first neutral aluminum(II) hydride complex, $[\{(\text{NHC})(\text{H})_2\text{Al}\}_2]$, [125] the first TM complex of a diborene ($\text{RB}=\text{BR}$) [126], and a magnesium amidoborane complex [127]. Most success has come from group 14, which has seen the synthesis of the first Ge^0 and Sn^0 adduct complexes, $[(\text{NHC})\text{E}=\text{E}(\text{NHC})]$ ($\text{E} = \text{Ge}$ [128] or Sn [129]), the first monomeric germanium(I) radical, $[(\text{Nacnac})\text{Ge}]^\cdot$ [130], a variety of Si^{I} , Ge^{I} , and Sn^{I} dimers, $[\text{LEEL}]$ ($\text{L} = \text{mono- or bidentate ligand}$, $\text{E} = \text{Si}$ [131], Ge [131–133], or Sn [131, 134]), and two Si^{II} systems, which include one of the first stable acyclic silylenes, R_2Si : [135, 136]. From the d-block, important low oxidation systems that have been accessed include an unprecedented guanidinate-(guan) bridged Fe^{I} dimer, $[\{\text{Fe}(\mu\text{-guan})\}_2]$, which possesses the shortest known Fe–Fe bond [137], a related amidinato $\text{Mn}^{\text{I}}\text{–Mn}^{\text{I}}$ -bonded dimer [137], and a Zn^{I} dimer stabilized by a bulky diiminophosphinate ligand [138].

2.4

Group 2 Heterobimetallics

The report of homobimetallic Mg–Mg bonded complexes undoubtedly represents a significant landmark in the development of group 2 chemistry [107]. However, the first heterobimetallic group 2 metal–metal bonded complex predates this by more than 30 years [139]. Despite this, they are also few in number compared to body of TM–Metal bonded complexes and their chemistry remains underexplored. While cluster and zintl-phase complexes are known that potentially contain such interactions [140–145], they are not electron precise and will not be considered any further in this section.

2.4.1

Group 2–Transition Metal Complexes

Figure 2.3 illustrates the group 2–TM bonded complexes known to date, which have been structurally authenticated. The bond distances for the group 2–transition and group 2–main group metal complexes described here are listed in Table 2.4.

The first complex possessing a group 2–TM bond, $[\text{CpFeMgBr}(\text{DPPE})(\text{THF})_2]$ **22**, was reported by Felkin *et al.* in 1974 [139], synthesized by the reaction of $[\text{CpFeBr}(\text{DPPE})]$ with an excess of elemental Mg activated with $\text{BrCH}_2\text{CH}_2\text{Br}$ in THF. Compound **22** contains a four-coordinate Mg center with a distorted tetrahedral geometry with bonds to two THF ligands, Br and Fe. The Mg–Fe distance of 2.593(7) Å is within the sum of the respective covalent radii (2.73(8) Å) [115]. Jonas *et al.* [148] subsequently described $[\text{CpCo}(\eta\text{-C}_3\text{H}_5)\text{MgBr}(\text{THF})_2]$ **23** and $[\text{CpCo}(\eta\text{-C}_2\text{H}_4)(\text{Ph})\text{MgBr}(\text{TMEDA})]$ **24** with Mg–Co distances of 2.480(4) and 2.565(3) Å, respectively. They were synthesized by the reaction of $[\text{CpCo}(\eta\text{-C}_2\text{H}_4)_2]$ with the corresponding Grignard reagent RMgBr ($\text{R} = \text{C}_3\text{H}_5$ or Ph), resulting in transfer of the R-group to Co and concomitant Mg–Co bond formation. While both of the Mg–Co distances are within the sum of the respective covalent radii (2.67(8) Å) [115], the Mg–Co distance is substantially longer for **24**, presumably a consequence of the Mg–Ph interaction. In a similar manner, Wilke *et al.* found that reaction of $[\text{Ni}(\text{C}_2\text{H}_4)_3]$ with $[\text{MgMe}_2(\text{TMEDA})]$ afforded $[\text{Ni}(\eta\text{-C}_2\text{H}_4)_2(\mu\text{-Me})\text{Mg}(\text{Me})(\text{TMEDA})]$ **25** with a Mg–Ni bond distance of 2.615(1) Å [149, 164], that is, within the sum of the respective covalent radii (2.65(8) Å) [115], with a methyl group also bridging between these metal centers.

Also within group 10, Braunschweig *et al.* have reported the first structurally authenticated example of an electron-precise Be–TM bonded complex, $[\text{Pt}(\text{PCy}_3)_2\text{BeCl}_2]$ **26**, synthesized by the reaction of $[\text{Pt}(\text{PCy}_3)_2]$ with an excess of BeCl_2 , with a Be–Pt bond distance of 2.168(4) Å [146]. Complex **26** reacts with MeLi to form $[\text{Pt}(\text{PCy}_3)_2\text{Be}(\text{Me})\text{Cl}]$ **27** maintaining a Be–Pt bond (2.195(3) Å). Both of these Be–Pt distances are consistent with that expected for a direct interaction based on the sum of the respective covalent radii (2.32(6) Å) and represent the shortest group 2–TM interactions known to date, no doubt as a consequence of the very small covalent radius of Be [115]. The Be–Pt distance for **27** is longer than that for **26** and the Cl–Be–C angle (123.70(17)°) for **27** is wider than the Cl–Be–Cl angle (118.61(18)°) for **26**. DFT calculations on hypothetical models with smaller phosphine ligands gave shorter Be–Pt interactions and wider Cl–Be–X angles. The bond dissociation energies for **26** and **27** were calculated as 77.6 and 47.8 kJ mol^{−1}, respectively. The Be–Pt bonding formed by Lewis acid–base pairing has been demonstrated for other direct Pt(0)–main group metal interactions using the $\text{Pt}(\text{PCy}_3)_2$ moiety [165–169].

Green *et al.* synthesized polynuclear complexes $\{[\text{Cp}_2\text{Mo}(\text{H})]\{\mu\text{-Mg}_2\text{Br}_2(\text{R})\text{OEt}_2\}\}_2$ ($\text{R} = \text{Cy}$ **28** or $i\text{-Pr}$ **29**) via the alkane elimination reaction of $[\text{Cp}_2\text{MoH}_2]$ with the corresponding Grignard reagent in diethyl ether [150, 151, 170]. The Mg–Mo distances of 2.853(7) and 2.737(6), and 2.76(3) and 2.81(3) Å for **28** and **29** are consistent with metal–metal bonds based on the sum of the respective covalent radii (2.95(9) Å) [115]. The hydrides were not located in the Fourier difference maps and were believed to lie in the Mg–Mo–Mg plane within the ring. They have been positioned in Figure 2.3 in accordance

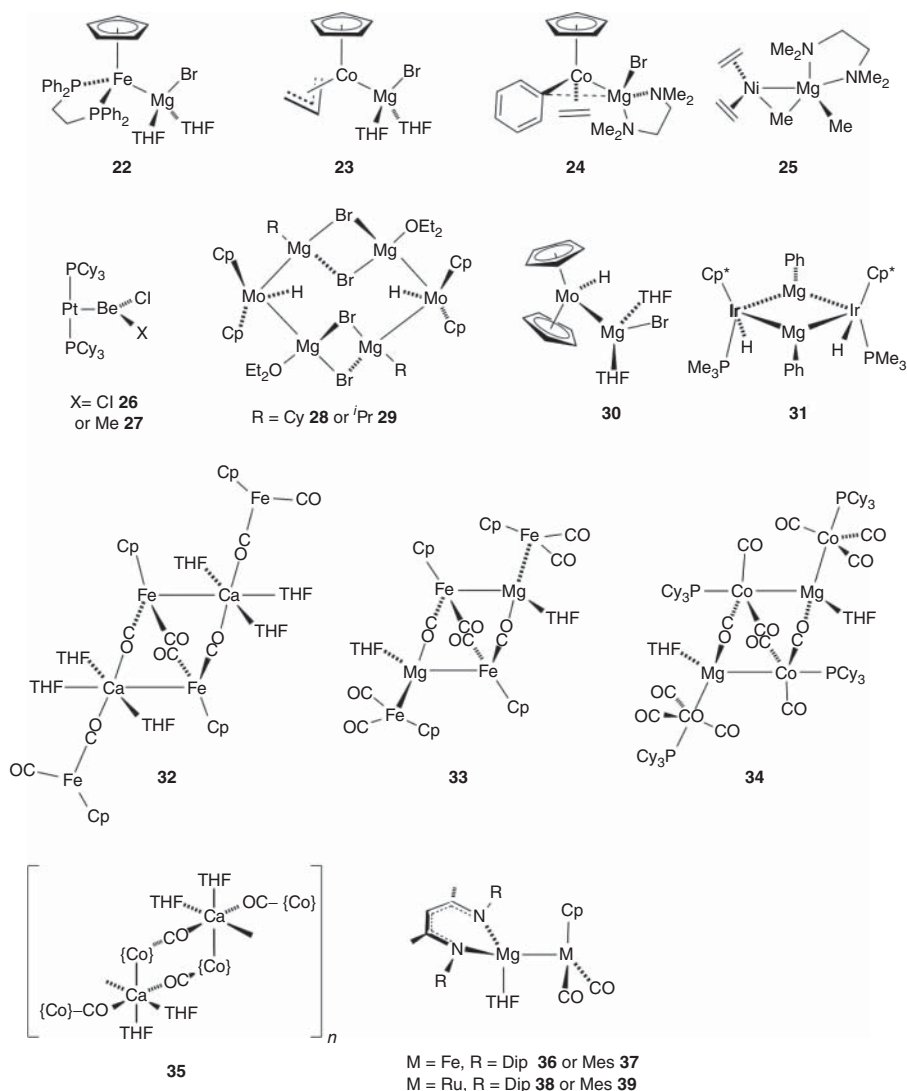


Figure 2.3 Group 2-transition metal bonded complexes. {Co} = Co(CO)₂(PCy₃).

with the original report. Complexes similar to **28** and **29** were synthesized using an analogous route with variation of the Grignard reagent RMgX (R = *n*Bu, Me, or Ph). Moreover, treatment of **28** and **29** with THF afforded monomeric [Cp₂Mo(H){MgBr(THF)₂}] **30**, reminiscent of Felkin's compound **22** [139], with an approximately tetrahedral Mg center having an unsupported Mg–Mo bond (2.732 Å) [152, 171].

Complexes **28**–**30** were described as having covalent Mg–Mo interactions on the basis of their reactivity with small molecules such as CO₂. However, the authors did state that these types of reactions are not exclusive to these metal–metal bonded systems, and, therefore, it could be the hydridic component, as opposed to the metal–metal bond, that is responsible for the reactivity observed for these complexes. Reactions between [Cp₂WH₂] and Grignard reagents RMgX (R = Me, *i*Pr, Ph) were also reported, affording products with similar properties to **28**–**30**, albeit lacking structural authentication.

Table 2.4 Group 2–transition metal and –main group metal bonded complexes.

Bond	Complex	Length (Å)	References
Be–Pt	[Pt(PCy ₃) ₂ BeCl ₂] 26	2.168(4)	[146]
Be–Pt	[Pt(PCy ₃) ₂ Be(Me)Cl] 27	2.195(3)	[146]
Mg–Fe	[CpFeMgBr(DPPE)(THF) ₂] 22	2.593(7)	[139]
Mg–Fe	[Mg{CpFe(CO) ₂ }(THF)] ₂ 33	2.6112(5), 2.5629(5)	M.P. Blake and P. Mountford (unpublished results)
Mg–Fe	[Mg(^{Dip} Nacnac){CpFe(CO) ₂ }(THF)] 36	2.6326(4)	[147]
Mg–Fe	[Mg(^{Mes} Nacnac){CpFe(CO) ₂ }(THF)] 37	2.5688(4)	M.P. Blake and P. Mountford (unpublished results)
Mg–Co	[CpCo(η-C ₃ H ₅)MgBr(THF) ₂] 23	2.480(4)	[148]
Mg–Co	[CpCo(η-C ₂ H ₄)(Ph)MgBr(TMEDA)] 24	2.593(7)	[148]
Mg–Co	[Mg{Co(CO) ₃ (PCy ₃) ₂ }(THF)] ₂ 34	2.6163(6), 2.5427(6)	M.P. Blake and P. Mountford (unpublished results)
Mg–Ni	[Ni(η-C ₂ H ₄) ₂ (μ-Me)Mg(Me)(TMEDA)] 25	2.615(1)	[149]
Mg–Mo	[Cp ₂ Mo(H){Mg(Cy)Br(OEt) ₂ }] ₂ 28	2.853(7)	[150]
Mg–Mo	[Cp ₂ Mo(H){Mg(ⁱ Pr)Br(OEt) ₂ }] ₂ 29	2.737(6)	[151]
Mg–Mo	[Cp ₂ Mo(H){MgBr(THF) ₂ }] 30	2.732	[152]
Mg–Ru	[Mg(^{Dip} Nacnac){CpRu(CO) ₂ }(THF)] 38	2.7075(3)	M.P. Blake and P. Mountford (unpublished results)
Mg–Ru	[Mg(^{Mes} Nacnac){CpRu(CO) ₂ }(THF)] 39	2.6430(3)	M.P. Blake and P. Mountford (unpublished results)
Mg–Ir	[Cp*Ir(PMe ₃)(H)MgPh] ₂ 31	2.660(2), 2.750(2)	[153]
Mg–Ga	[Mg{Ga(ArNCH) ₂ }(THF) ₃] 51	2.717(2), 2.727(1)	[154]
Mg–Ga	[Mg(^{Dip} Nacnac)(κ ¹ -TMEDA){Ga(ArNCH) ₂ }] 57	2.7470(7)	[155]
Mg–Ge	[Mg(GeMe ₃) ₂ (DME) ₂] 40	2.719(6)	[156]
Mg–Ge	[Mg{Ge(SiMe ₃) ₃ }(THF) ₂] 45	2.679(1)	[157]
Mg–Ge	[Mg{(GeR)(SiR) ₂ }(THF) ₃] 47	2.696(2)	[158]
Mg–Ge	[{N(Mes)C(Me)C(H)C(Me)Ge{N(Mes)}-[Mg(^{Mes} Nacnac)] ₂ (μ-Cl)] 50	2.7472(14)	[130]
Mg–Sn	[Mg{Sn(SiMe ₃) ₃ }(THF) ₂] 46	2.817(1)	[157]
Ca–Fe	[Ca{CpFe(CO) ₂ }(THF) ₃] ₂ 32	3.0185(6)	[159]
Ca–Co	[Ca{Co(CO) ₃ (PCy ₃) ₂ }(THF) ₂] _x 35	3.0450(9)	M.P. Blake and P. Mountford (unpublished results)
Ca–Ga	[Ca{Ga(ArNCH) ₂ }(THF) ₄] 52	3.1587(6)	[154]
Ca–Ga	[Ca{Ga(ArNCMe) ₂ }(THF) ₄] 53	3.1988(12)	[154]
Ca–Ga	[Ca{Ga(ArNCH) ₂ }(TMEDA) ₂] 54	3.228(1)	[155]
Ca–Ga	[Cp* ₂ CaGaCp*] 59	3.183(2)	[160]

Table 2.4 Group 2–transition metal and –main group metal bonded complexes.

Bond	Complex	Length (Å)	References
Ca–Ge	[Ca{Ge(SiMe ₃) ₃ } ₂ (THF) ₃] 42	3.022(2)	[161]
Ca–Ge	[Ca{(GeR)(SiR)} ₂ (THF) ₄] 48	3.038	[158]
Ca–Sn	[Ca(SnMe ₃) ₂ (THF) ₄] 41	3.2721(3)	[162]
Sr–Ga	[Sr{Ga(ArNCH) ₂ } ₂ (TMEDA) ₂] 55	3.324(1)	[155]
Sr–Ga	[Cp* ₂ Sr(THF)GaCp*] 60	3.4348(7)	[160]
Sr–Ge	[Sr{Ge(SiMe ₃) ₃ } ₂ (THF) ₃] 43	3.147(5)	[161]
Sr–Ge	[Sr{(GeR)(SiR)} ₂ (THF) ₄] 49	3.128	[158]
Ba–Ga	[Ba{Ga(ArNCH) ₂ } ₂ (TMEDA) ₂] 56	3.464(8)	[155]
Ba–Ga	[Ba{Ga(Dip-bian)} ₂ (THF) ₅] 58	3.6199(9)	[163]
Ba–Ga	[Cp* ₂ Ba(GaCp*) ₂] 61	3.5911(9)	[160]
Ba–Ge	[Ba{Ge(SiMe ₃) ₃ } ₂ (THF) ₄] 44	3.398(9)	[161]

Ar = Dip and R = SiMe^tBu₂.

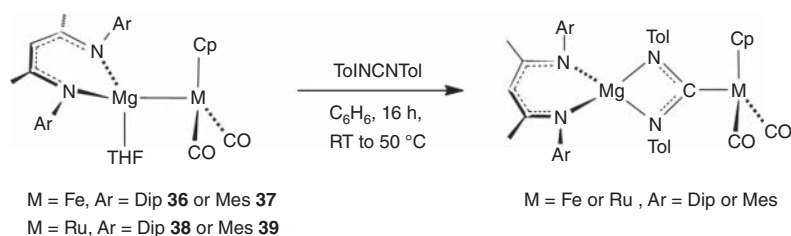
Another hydride complex, namely, [Cp*Ir(PMe₃)(H)(μ-MgPh)]₂ **31**, was reported by Bergman *et al.* in 1998 [153]. This was synthesized by protonolysis of [MgPh₂(THF)₂] with [Cp*IrH₂(PMe₃)] and contains the first example of structurally authenticated Mg–Ir interactions. Both Mg–Ir distances (2.660(2) and 2.750(2) Å) are consistent with a metal–metal bond based on the sum of the respective covalent radii (2.82(9) Å) [115]. Interestingly, none of the complexes **28–31** contain a potential TM (μ-H)Mg interaction between the metal centers.

In 2011, Blake, Mountford, and Kaltsoyannis reported [Ca{CpFe(CO)₂}₂(THF)₃] **32** [159], the first Ca–TM bonded complex, with two Ca–Fe bonds (3.0185(6) Å), comparable to the sum of the respective covalent radii (3.08(10) Å) [115]. Through crystallographic characterization of **32** and its isostructural and isomorphous ytterbium analog [Yb{CpFe(CO)₂}₂(THF)₃] **34**, the first direct comparison of group 2–TM and Ln(II)–TM (Ln(II) = divalent lanthanide) bonding was also achieved. Somewhat surprisingly, given the respective covalent radii (Ca = 1.76(10), Yb = 1.87(8) Å) and six-coordinate ionic radii (Ca = 1.00, Yb = 1.02 Å) [115, 172], the Ca–Fe distance is slightly longer than its Ca–Yb (2.9892(4) Å) counterpart. DFT analysis supported this, finding a slightly longer and weaker Ca–Fe interaction (2.984 Å, –134.9 kJ mol^{–1}) than the Yb–Fe (2.965 Å, –143.3 kJ mol^{–1}) one. Further DFT and AIM (atoms-in-molecules) analysis found little covalency in these bonds. The synthesis of **32** and [Yb{CpFe(CO)₂}₂(THF)₃] **34** was achieved via the reduction of [CpFe(CO)₂]₂ in THF with the corresponding metal amalgam. Use of magnesium as the reducing metal afforded [Mg{CpFe(CO)₂}₂(THF)₂] **33** (M.P. Blake and P. Mountford, unpublished results) with two Mg–Fe interactions (2.6112(5) Å) internal to and two external (2.5629(5) Å) to the illustrated eight-membered ring, consistent with the sum of the respective covalent radii (2.73(8) Å) and comparable in length to those in Felkin's **22** (2.593(7) Å) [115]. Compound **33** incorporates the first example of a group 2 element forming two metal–metal bonds to TMs. Both **32** and **33** reacted with MeI to give [CpFe(CO)₂Me].

Mountford *et al.* also reported the structures of [Mg{Co(CO)₃(PCy₃)₂(THF)}₂] **34** and [Ca{Co(CO)₃(PCy₃)₂(THF)}₂]_x **35**, synthesized from [Co(CO)₃(PCy₃)₂] by analogy to **33** and **32** (M.P. Blake and P. Mountford, unpublished results). The structure of **34** is similar to that of **33**, featuring an eight-membered ring containing two Mg–Co (2.6163(6) Å) bonds, with two additional Mg–Co (2.5427(6) Å) bonds external to the ring. These Mg–Co distances are slightly shorter than the sum of the covalent radii (2.67(8) Å) and are comparable to those in Jonas' **23** (2.480(4) Å) and **24** (2.565(3) Å) [115, 148]. Complex **35** also contains an eight-membered ring motif that is common to these structures, with two Ca–Co (3.0450(9) Å) bonds and two Ca(μ-OC)Co isocarbonyl linkages. Each Ca center has two additional Ca(μ-OC)Co linkages to neighboring [Co(CO)₃(PCy₃)]

moieties to afford a polymeric chain with alternating 8- and 12-membered rings, with and without Ca–Co bonding, respectively. Performing the analogous reduction with Sr amalgam afforded $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PCy}_3)_2(\text{THF})_3\}_x]$ (M.P. Blake and P. Mountford, unpublished results). As with **35**, the strontium congener has a polymeric structure containing 12-membered rings. However, rather than alternating with eight-membered rings containing metal–metal bonds, an intermediate arrangement was observed with side-on (η^2 -) carbonyl interactions to strontium. These interactions can be considered to be geometrically intermediate between metal–metal bonds and isocarbonyl linkages, with the $\text{Sr}\cdots\text{Co}$ distances (3.6263(4) Å) exceeding the sum of the respective covalent radii (3.21(10) Å) [115]. The ease with which Sr–Co bonding is disrupted serves to highlight the decreasing strength of group 2–Co interactions on descending group 2. DFT analysis of model complexes supported this by finding decreasing bond energies (Mg–Co , 220 > Ca–Co , 150 > Sr–Co , 130 kJ mol^{-1}).

In 2013, Mountford and Blake reported the synthesis of $[\text{Mg}^{\text{(Dip)Nacnac}}\{\text{CpFe}(\text{CO})_2(\text{THF})\}]$ **36** [147], by the reaction of $[\text{Mg}^{\text{(Dip)Nacnac}}\text{I}(\text{THF})]$ with $\text{K}[\text{CpFe}(\text{CO})_2]$. This monomeric compound possesses an unsupported Mg–Fe bond (2.6326(4) Å), shown to be very polar by AIM analysis. The Mg–Fe distance is within the sum of the respective covalent radii (2.73(8) Å) and again comparable with that for **22** (2.593(7) Å) and **33** (2.6112(5) and 2.5629(5) Å) [139]. Reaction of **12** with MeI gave $[\text{Mg}^{\text{(Dip)Nacnac}}\text{I}(\text{THF})]$ and $[\text{CpFe}(\text{CO})_2\text{Me}]$. More significantly, reaction of **12** with tolylcarbodiimide afforded $[\text{Mg}^{\text{(Dip)Nacnac}}\{(\text{NTol})_2\text{CFe}(\text{CO})_2\text{Cp}\}](\text{ToI} = 4\text{-C}_6\text{H}_4\text{Me})$, the first insertion of an unsaturated substrate into a group 2–TM bond (Scheme 2.2), calculated to be exergonic with $\Delta G_{298} = -25.2 \text{ kJ mol}^{-1}$. The structure of analogous $[\text{Mg}^{\text{(Mes)Nacnac}}\{\text{CpFe}(\text{CO})_2(\text{THF})\}]$ **37** has also been determined (M.P. Blake and P. Mountford, unpublished results), showing a slightly shorter Mg–Fe bond (2.5688(4) Å) compared to that for **36**. Tolylcarbodiimide was also successfully inserted into the Mg–Fe bond of **37** to give $[\text{Mg}^{\text{(Mes)Nacnac}}\{(\text{NTol})_2\text{CFe}(\text{CO})_2\text{Cp}\}]$. Attempts to synthesize the calcium analog $[\text{Ca}^{\text{(Dip)Nacnac}}\{\text{CpFe}(\text{CO})_2(\text{THF})\}]$ were unsuccessful, the target compound apparently decomposing in nondonor solvents to afford $[\{\text{Ca}^{\text{(Dip)Nacnac}}(\text{THF})\}_2\{\text{Cp}_4\text{Fe}_5(\text{CO})_8\}]$, among other products [147]. Mountford *et al.* also reported $[\text{Mg}^{\text{(Ar)Nacnac}}\{\text{CpRu}(\text{CO})_2(\text{THF})\}]$ (Ar = Dip **38** or Mes **39**) (M.P. Blake and P. Mountford, unpublished results). Consistent with their lighter congeners, **36** and **37**, the Mg–Ru distance is slightly shorter for Ar = Mes (2.6430(3) Å) than Dip (2.7075(3) Å), although both lie within the sum of the covalent radii (2.87(10) Å) [115]. Both complexes underwent reaction with ditolylcarbodiimide to afford structurally authenticated $[\text{Mg}^{\text{(Ar)Nacnac}}\{(\text{NTol})_2\text{CRu}(\text{CO})_2\text{Cp}\}]$ (Ar = Dip or Mes, Scheme 2.2).



Scheme 2.2 Reaction of heterobimetallic complexes with tolylcarbodiimide. (M. P. Blake and P. Mountford, unpublished results) [147].

Many complexes have been reported that could, at first sight, be considered to have group 2–TM bonds based on short intermetal distances. Although close contacts are an essential parameter in determining the presence of a metal–metal bond, this criterion cannot be relied upon on its own. In particular, the presence of bridging groups may reduce these distances without a direct interaction occurring. For example, the hydride-bridged $[(\text{Piso}^{\text{-H}})\text{Fe}(\mu\text{-H})\text{Mg}(\text{THF})^{\text{(Mes)Nacnac}}]$ reported by Jones *et al.* in 2012 has a $\text{Mg}\cdots\text{Fe}$ distance (2.7174 Å) that is less than the sum of the respective covalent radii (2.73(8) Å) [137]. However, both the Mg–H (1.98(2) Å) and Fe–H (1.50(2) Å) distances

are typical of those in the literature. This $\text{Mg}(\mu\text{-H})\text{Fe}$ interaction acts to shorten the $\text{Mg}\cdots\text{Fe}$ distance toward that expected for a direct interaction.

2.4.2

Group 2–Main Group Metal Complexes

Structurally authenticated complexes have been reported with bonds between group 2 and main group metals (Figure 2.4), prepared using reductive insertion, salt elimination, and Lewis acid–base pairing routes. Importantly, strontium– and barium–Main group metal bonded complexes are included in this cohort. Recall that electron-precise bonds between strontium or barium and a TM have yet to be structurally authenticated.

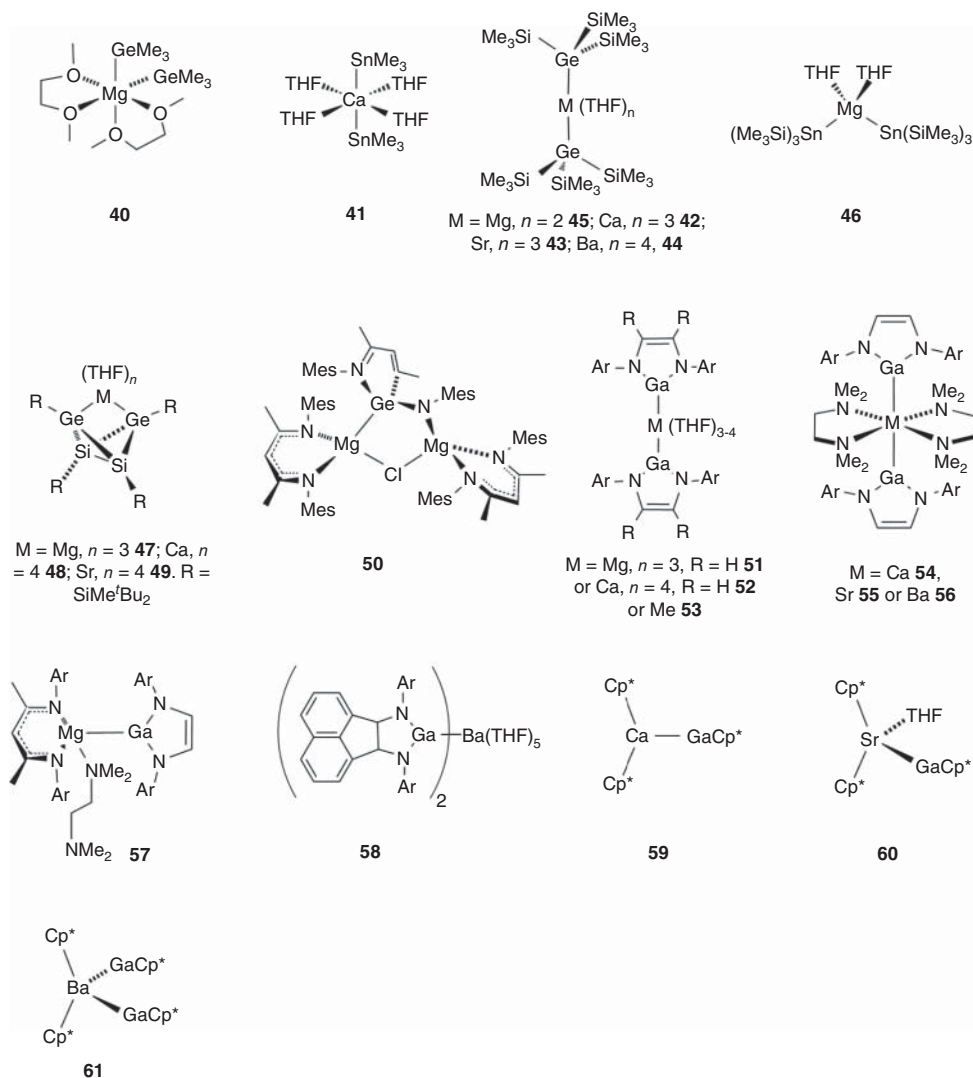


Figure 2.4 Group 2–main group metal bonded complexes. Ar = Dip.

Group 14 compound $[\text{Mg}(\text{GeMe}_3)_2(\text{DME})_2]$ **40** reported by Rösch *et al.* in 1984 was the first structurally authenticated complex in this category [156]. This was synthesized by the reaction of $[\text{Hg}(\text{GeMe}_3)_2]$ with elemental Mg in DME, and it contains two direct Mg–Ge interactions (2.719(6) Å), about 0.1 Å longer than the sum of the covalent radii (2.61(8) Å) [115]. The coordination geometry at Mg is approximately octahedral with a *cis*-arrangement of GeMe_3 groups ($\text{Ge–Mg–Ge} = 99.3(1)^\circ$). Given the near-identical Pauling electronegativities of Hg (2.00) and Ge (2.01) [173], this transmetalation reaction can be considered to involve a formal reduction of Ge(III) in $\text{Hg}(\text{GeMe}_3)_2$ to Ge(II) in **40**.

$[\text{Ca}(\text{SnMe}_3)_2(\text{THF})_4]$ **41**, reported by Westerhausen in 1994, represents the first structurally authenticated example of a calcium–Main group metal bond [162]. This was synthesized by the formal reductive insertion of elemental Ca into the Sn–Sn bond of Sn_2Me_6 . Like **40**, compound **41** has an approximately octahedral geometry at Ca, but with mutually *trans* Ca–Sn (3.2721(3) Å) bonds and equatorial THF ligands. The Ca–Sn distances are also significantly longer than the sum of the respective covalent radii (3.15(11) Å) [115].

Following on from Rösch and Westerhausen, Teng and Ruhlandt-Senge reported in 2004 the series of complexes $[\text{M}\{\text{Ge}(\text{SiMe}_3)_3\}_2(\text{THF})_n]$ ($\text{M} = \text{Ca}$, $n = 3$ **42**; Sr , $n = 3$ **43**; Ba , $n = 4$ **44**) [161]. In contrast to the reductive methods used for **40** and **41**, compounds **42–44** were synthesized by the salt elimination reaction of 2 equiv. of $\text{K}[\text{Ge}(\text{SiMe}_3)_3]$ with the corresponding MI_2 . Compounds **42–44** feature two group 2–Ge bonds with average distances of 3.022(2), 3.147(5), and 3.398(9) Å, respectively. These are comparable with those expected based on the sum of the respective covalent radii (2.96(11), 3.15(11), and 3.35(12) Å) [115]. The geometries of five-coordinate **42** and **43** are approximately trigonal bipyramidal and that of six-coordinate **44** is approximately octahedral. Comparing the O–M–O ($\text{M} = \text{group 2}$) angles for the axial THF ligands in approximately trigonal bipyramidal **42** and **43** with the Ge–Ba–Ge angle in approximately octahedral **44**, the extent of *trans*-angle compression (i.e., the deviation from the ideal 180°) increases on descending group 2 (155.1(2), 150.13(10), and $140.52(2)^\circ$). This is consistent with increasing bond lengths that permit a greater flexibility with reduced repulsion between the bulky groups, in addition to the increased ionic character that results in concomitantly weaker group 2 metal–Ge interactions.

In 2011, Castel *et al.* reported the structure of $[\text{Mg}\{\text{Ge}(\text{SiMe}_3)_3\}_2(\text{THF})_2]$ **45** [157], adding to the series of group 2–Ge complexes (**42–44**). The Mg–Ge distance (2.679(1) Å) is shorter than that for the heavier congeners as expected. An approximately tetrahedral geometry at the Mg center is observed, with the Ge–Mg–Ge angle ($130.82(3)^\circ$) deviating significantly from the ideal value of about 109.5° . In the same report, the structure of $[\text{Mg}\{\text{Sn}(\text{SiMe}_3)_3\}_2(\text{THF})_2]$ **46** was presented. As expected, the Mg–Sn distances (av. 2.817(1) Å) are longer than the Mg–Ge distances in **45**. However, the Sn–Mg–Sn angle is slightly changed ($130.83(8)^\circ$). Both **45** and **46** were synthesized by the reaction of MgBr_2 with 2 equiv. of $\text{K}[\text{M}(\text{SiMe}_3)_3]$ ($\text{M} = \text{Ge}$ or Sn) in THF.

In 2004, Sekiguchi *et al.* reported the series of complexes $[\text{M}\{(\text{GeR})(\text{SiR})\}_2(\text{THF})_n]$ ($\text{M} = \text{Mg}$, $n = 2$ **47**; Ca , $n = 4$ **48**; Sr , $n = 4$ **49**; $\text{R} = \text{SiMe}^t\text{Bu}_2$) [158]. Reduction of $[\text{Ge}(\text{R})\text{Si}(\text{R})\text{Cl}]_2$ with elemental Mg or Ca gave **47** and **48**, respectively. Alternatively, all three complexes **47–49** could be synthesized by the reaction of $[\text{K}(\text{THF})_2]_2[\text{Ge}(\text{R})\text{Si}(\text{R})]_2$ with the corresponding MI_2 . In these complexes, the group 2 metal occupies the bridgehead position to give two group 2–Ge bonds with five- (**47**) and six-coordinate (**48** and **49**) group 2 metal centers. The average Mg–Ge (2.696(2) Å), Ca–Ge (3.038 Å), and Sr–Ge (3.128 Å) distances are consistent with those expected based on the sums of the respective covalent radii (2.61(8), 2.96(11), and 3.15(11) Å) [115]. The hinge angles between the two GeSi_2 planes for **47** (98.9°), **48** (102.3°), and **49** (104.9°) reflect the increasing covalent radius of the group 2 metal.

Finally, with respect to group 2–Ge bonding, in 2011 Jones *et al.* reported $[\{\text{Mg}^{\text{Mes}}\text{Nacnac}\}_2(\mu\text{-Cl})\{\text{N}(\text{Mes})\text{C}(\text{Me})\text{C}(\text{H})\text{C}(\text{Me})\}\text{Ge}\{\text{N}(\text{Mes})\}]$ **50** as a ring-contraction product obtained from the low-yielding reaction of $[(^{\text{Mes}}\text{Nacnac})\text{GeCl}]$ with 0.5 equiv. of $[(^{\text{Mes}}\text{Nacnac})\text{Mg}]_2$ **13** [130]. Compound **50** contains a Mg–Ge bond (2.7472(14) Å) that is slightly longer than the sum of the covalent radii (2.61(8) Å), perhaps because of the rather strained five-membered ring, but comparable in length with that for **47** (2.696(2) Å).

We now turn our attention to group 2–group 13 complexes. The group 2–metal bond chemistry of these elements is exclusively associated with Ga, and, in addition, either based on Ga heterocyclic systems of the type $\text{Ga}(\text{ArNCR})_2$ or Cp^*Ga , a stable $\text{Ga}(\text{I})$ species in its own right. Jones *et al.* synthesized the first examples of group 2–Ga bonded complexes through the use of Ga heterocycles [154]. Reactions of $[\text{GaI}_2(\text{ArNCR})_2]$ ($\text{Ar} = \text{Dip}$; $\text{R} = \text{H}$ or Me) with an excess of elemental Mg or Ca in the presence of Hg gave $[\text{M}\{\text{Ga}(\text{ArNCR})_2\}_2(\text{THF})_n]$ ($\text{M} = \text{Mg}$, $n = 3$, $\text{R} = \text{H}$, **51**; Ca , $n = 4$, $\text{R} = \text{H}$ **52** or Me **53**). These represent the first structurally authenticated Mg–Ga and Ca–Ga bonded complexes. Attempts to prepare the Sr and Ba analogs were unsuccessful. Compound **51** has a distorted trigonal bipyramidal geometry with the gallyl ligands in equatorial positions ($\text{Ga–Mg–Ga} = 127.32(6)^\circ$), whereas **52** and **53** are very similar with octahedral geometries having mutually *trans* gallyl groups ($\text{Ga–Ca–Ga} = 180^\circ$). The Mg–Ga distances in **51** (2.7174(15) Å) are shorter than the Ca–Ga counterparts in **52** (3.1587(6) Å) and **53** (3.1988(12) Å), consistent with the change in covalent radius of the group 2 metal. These distances are again slightly longer than the sums of the respective covalent radii ($\text{Mg–Ga} = 2.63(8)$ and $\text{Ca–Ga} = 2.98(10)$ Å) [115]. The intramolecular parameters associated with the gallyl fragments were found to be intermediate between those previously reported for the non-bound and complexed cyclic anion [174–180], which is consistent with significant ionic character in these group 2–Ga interactions. DFT calculations for model complexes supported this conclusion.

Jones *et al.* have extended their use of gallium heterocycles to increase the number of group 2–main group bonds known [155]. Reaction of *in situ* generated $[\text{MI}_2(\text{TMEDA})_n]$ ($\text{M} = \text{Ca}$, Sr, or Ba) with 2 equiv. of $[\text{K}(\text{TMEDA})][\text{Ga}(\text{ArNCH})_2]$ ($\text{Ar} = \text{Dip}$) afforded $[\text{M}\{\text{Ga}(\text{ArNCH})_2\}_2(\text{TMEDA})_2]$ ($\text{M} = \text{Ca}$ **54**, Sr **55**, or Ba **56**). The presence of TMEDA in these reactions was found to be crucial to their success. These compounds have similar octahedral geometries with mutually *trans* gallyl groups and equatorial TMEDA ligands. The average M–Ga distances increase in the order $\text{M} = \text{Ca}$ (3.228(1) Å) < Sr (3.324(1) Å) < Ba (3.464(8) Å) as expected. It is unsurprising that the Ca–Ga distances in **54** are longer than in **52** or **53**, given the greater steric bulk around the Ca center in the former. The Mg analog could not be synthesized, and this was attributed to steric constraints about the smaller metal center. However, reaction of $[\text{K}(\text{TMEDA})][\text{Ga}(\text{ArNCH})_2]$ with $[\text{Mg}^{\text{(Dip)Nacnac}}\text{I}(\text{OEt}_2)]$ afforded $[\text{Mg}^{\text{(Dip)Nacnac}}(\kappa^1\text{-TMEDA})\{\text{Ga}(\text{ArNCH})_2\}]$ **57** containing a Mg–Ga bond (2.7470(7) Å), which is shorter than that in **51** (2.7174(15) Å).

Fedushkin *et al.* have also utilized Ga heterocycles to afford complexes with group 2–Ga bonds [163]. Reaction of digallane $[\text{Ga}(\text{Dip-bian})_2]_2$ with the respective group 2 metal in THF gave the complexes $[\text{M}\{\text{Ga}(\text{Dip-bian})\}_2(\text{THF})_n]$ ($\text{M} = \text{Mg}$, $n = 3$; Ca , $n = 4$; Sr , $n = 4$; Ba , $n = 5$ **58**). Of these, only **58** was structurally authenticated and found to have an average Ba–Ga distance of 3.6199(9) Å, substantially longer than that expected based on the sum of the covalent radii (3.37(11) Å) [115].

Shortly after Jones' initial report of group 2–Ga bonding in 2006 [154], Roesky reported a different approach based on $[\text{Cp}^*\text{Ga}]$ [160]. Reaction with the $[\text{Cp}^*_2\text{M}(\text{THF})_x]$ ($\text{M} = \text{Ca}$, Sr, or Ba) sandwich complexes afforded corresponding Lewis adducts $[\text{Cp}^*_2\text{CaGaCp}^*]$ **59**, $[\text{Cp}^*_2\text{Sr}(\text{THF})\text{GaCp}^*]$ **60**, and $[\text{Cp}^*_2\text{Ba}(\text{GaCp}^*)_2]$ **61**. The increasing average M–Ga distances (**59**, 3.183(2) < **60**, 3.4348(7) < **61**, 3.5911(9) Å) and coordination numbers reflect the increasing group 2 metal covalent radius, where that for Sr would appear to be intermediate between the requirement to afford a solvent-free complex observed for **59** and coordination of additional Cp^*Ga unit as for **61**. Attempts to calculate the Ca–Ga dissociation energy for **59** using DFT were unsuccessful. The authors concluded that this demonstrates the weak nature of the metal–metal interaction and proposed it was mainly based on van der Waals (dispersive) forces. Alternative MP2 calculations reproduced the bent metallocene structure but with a Ca–Ga distance that is 0.12 Å shorter than that observed experimentally. Consistent with the proposed weakness of these bonds, the group 2–metal distances in these three complexes are all longer than those predicted based on the sums of the respective covalent radii (Ca–Ga, 2.98(10); Sr–Ga, 3.17(10), and Ba–Ga, 3.37(11) Å) [115].

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3

Group 3, Lanthanide, and Actinide Metal–Metal Bonds

Benjamin Oelkers and Rhett Kempe

3.1

Introduction

The chemistry of rare earth (RE) metals, that is, the group 3 metals and the lanthanides (Ln), is strongly determined by their usual oxidation state +III. Mainly for samarium, europium, and ytterbium, +II can also be encountered in molecular compounds. In these cases, the formation of highly stable f-electron configurations (f^6 , f^7 , and f^{14} , respectively) plays a prominent role in stabilizing the divalent oxidation states. In a similar manner, compounds in the formal oxidation state +IV are formed with cerium, praseodymium, and terbium due to formation of f^0 , f^1 , and f^7 configurations though the last two are quite rare. A common feature of all these compounds is the resulting $s^0 d^0$ configuration, which results in the typical behavior of d^0 metal ions, as the f-electrons are deeply embedded in the electron shell and are thus not suitable for bond formation [1].

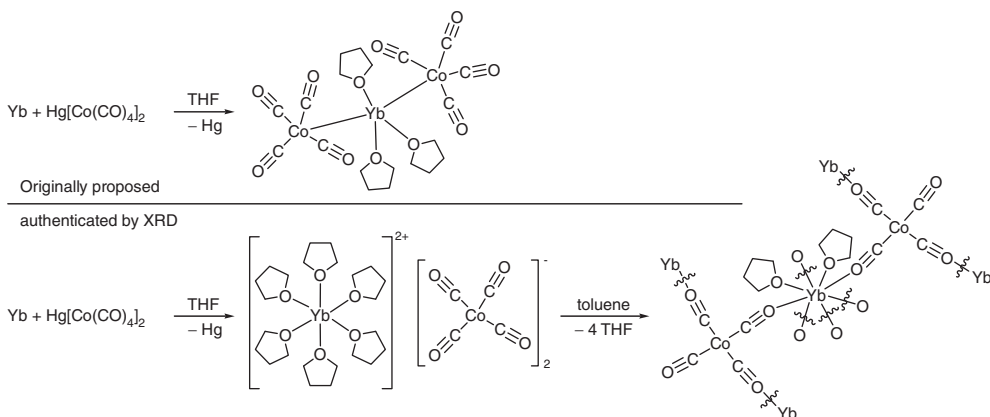
It is due to this electronic situation that rare earth metals are found to act as hard (divalent metal ions) or very hard (trivalent metal ions) Lewis acids in virtually all their compounds. In contrast to the somewhat related alkaline earth metals, where Mg^I dimers have been prepared recently [2] (*cf.* Chapter 2), no molecular compound with an unbridged RE–RE bond has been reported to date. Most compounds featuring formally short RE–RE distances in their respective solid-state structures are ligand-bridged dimers (or higher aggregates) with the lanthanide in the typical oxidation states as described earlier, for example, $[Cp^*Sc(bipy)(\mu-Cl)_2Sc(bipy)Cp^*]$ (the bipyridine ligands exist as radical anions in this compound) with $Sc \cdots Sc = 339.3(1)$ pm [3] (covalent radius = 170 pm [4]) and $[{(Me_3Si)_2N}Yb\{\mu-OC(CMe_3)_3\}_2Yb\{N(SiMe_3)_2\}]$ with $Yb \cdots Yb = 335.6(1)$ pm [5] (covalent radius = 187 pm [4]). In such cases, it is generally accepted that geometric constraints imposed by optimized ligand binding are responsible for short contacts between the metal atoms. There are, however, compounds known with at least some degree of interaction between the rare earth atoms, the largest and best studied group of which are metal-rich lanthanide halides. Their solid-state structures usually comprise (sometimes condensed) octahedral clusters that are often stabilized by interstitial atoms or atom groups and are usually bridged by halides [6].

Given the highly electropositive nature of the rare earth metals, the search for heterometallic compounds has to focus on combinations with nucleophilic main group metal (MM) or transition metal (TM) fragments in order to establish metal–metal bonding. As detailed reviews compiling all known compounds have appeared recently [7], we give a more feature-based account on this topic, describing typical preparations first, followed by reactivity, structural characterization, and finally theoretical insights into this unusual class of substances. The known metal–metal bonded compounds featuring actinides (An) as the f-element will be considered alongside those containing rare earth metals because the chemistry of both groups can in many cases be considered to be similar. It should be noted, however, that the higher tendency of early actinide 5f-electrons to take part in chemical reactions leads to a richer redox chemistry.

3.1.1

The Isocarbonyl Problem

This treatise focuses on compounds structurally authenticated by single-crystal X-ray diffraction (XRD) experiments. This restriction seems justified given a large body of early work claiming metal–metal bonds that could not be proved unequivocally or were even disproved in later studies. These problems arose in particular from carbonyl-containing transition metal fragments such as $[\text{Co}(\text{CO})_4]^-$ or $[\text{Fe}(\text{CO})_4]^{2-}$, which seemed the natural choice for strongly nucleophilic metalates due to the ability of carbonyl ligands to effectively stabilize low oxidation states via back-bonding. The proposed metal–metal bonded structure of the obtained products was often rationalized by IR spectroscopy as the main spectroscopic tool. However, XRD studies showed in a variety of instances that misleading assumptions could not be effectively excluded while solely relying on IR spectra. It was found that in many cases a different kind of linkage was established between the two metal centers, namely, isocarbonyl bridging. This can be understood by the very Lewis acidic and hard character of the RE fragments, which renders a connection with the hardest donor in the system (oxygen) comparable to, if not superior over, a bond to the softer transition metal atom. In other instances, no metal–metal bond was found at all, resulting in ionic structures. An instructive example of such assignments that had to be corrected after XRD analysis is shown in Scheme 3.1 [8].



Scheme 3.1 Erroneously proposed Yb–Co bonded complex (top) that was shown to be either ionic or isocarbonyl-bridged, depending on solvation (bottom).

3.2

Preparation

A range of different synthetic protocols has proved useful for the preparation of compounds with f-element–metal bonds. The list includes salt elimination, alkane or amine elimination, reductive cleavage of metal–metal bonds, and adduct formation, which are all briefly considered in the following section.

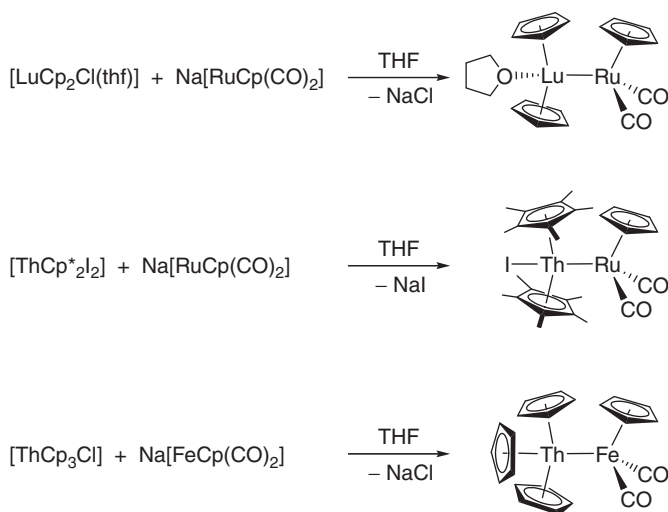
3.2.1

Salt Elimination

3.2.1.1 *f-Element–TM Bond Formation*

The first reaction to give a structurally authenticated RE–TM bonded complex was the salt elimination reaction of $[\text{LuClCp}_2(\text{thf})]$ and $\text{Na}[\text{RuCp}(\text{CO})_2]$, reported by Beletskaya and coworkers in 1990,

leading to $[\text{Cp}_2\text{Lu}(\text{thf})\text{RuCp}(\text{CO})_2]$ (Scheme 3.2, top) [9]. In a similar manner, the first unsupported An–TM bonds had been confirmed by XRD a few years earlier in a study of Sternal *et al.*, detailing the synthesis of $[\text{Cp}^*_2\text{Th}(\text{X})\text{RuCp}(\text{CO})_2]$ from $[\text{ThCp}^*_2\text{X}_2]$ and $\text{Na}[\text{RuCp}(\text{CO})_2]$ ($\text{X} = \text{Cl}, \text{I}$; Scheme 3.2, middle) [10]. This study was later supplemented by the synthesis of $[\text{Cp}_3\text{AnMCp}(\text{CO})_2]$ ($\text{An} = \text{Th}, \text{U}$; $\text{M} = \text{Fe}, \text{Ru}$; Scheme 3.2, bottom) using the same methodology [11].

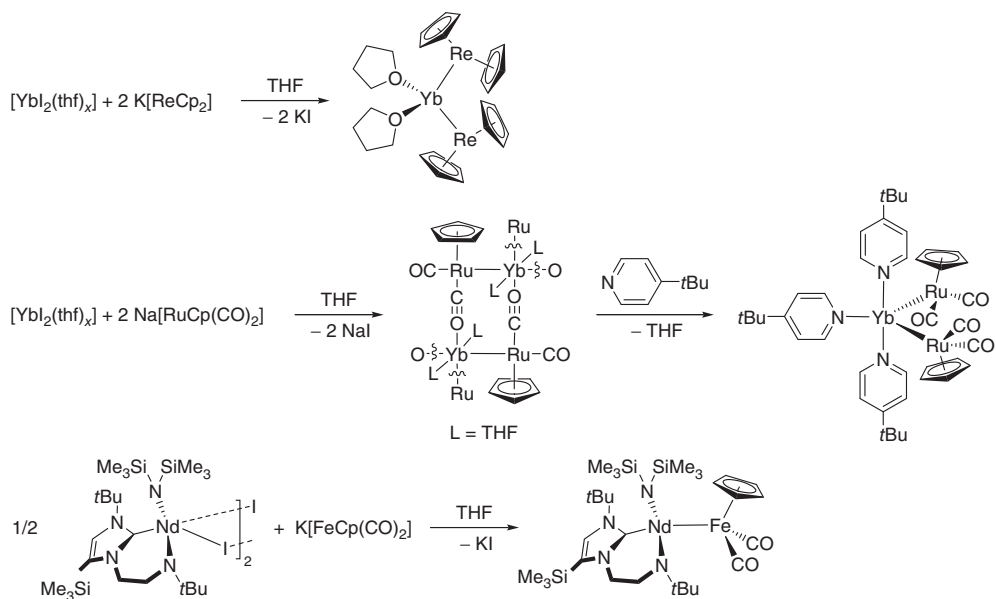


Scheme 3.2 Early salt elimination reactions forming f-element–transition metal bonds.

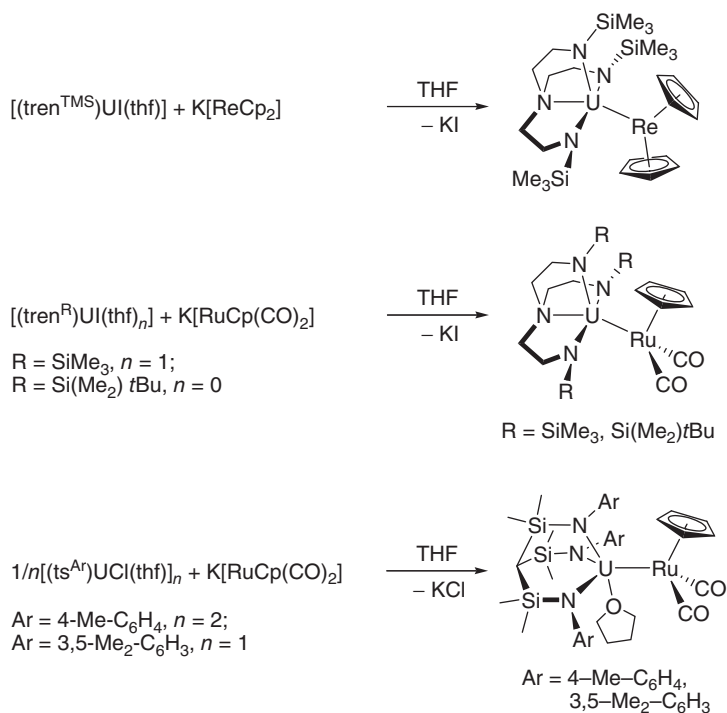
After these initial results, no further studies describing direct f-element–transition metal bonds were published for almost 20 years. This period of silence ended in 2008, when Kempe *et al.* showed alkane elimination (*vide infra*) to be a successful tool for the preparation of bismetallocenes $[\text{Cp}_2\text{RE}(\text{RE}(\text{Cp})_2)]$ ($\text{RE} = \text{Y}, \text{Yb}$) [12]. Within the series of reports following this finding, salt elimination still proved to be the potentially most versatile way of preparing RE/An–TM bonds. Divalent ytterbium was found to form two metal–metal bonds within the compounds $[(\text{thf})_2\text{Yb}(\text{ReCp}_2)_2]$ and $[(\text{py}^t\text{Bu})_3\text{Yb}\{\text{RuCp}(\text{CO})_2\}_2]$ ($\text{py}^t\text{Bu} = 4\text{-tert-butylpyridine}$). While the former was obtained directly by reaction of $[\text{YbI}_2(\text{thf})_x]$ with $\text{K}[\text{ReCp}_2]$, the latter was synthesized via salt elimination from $[\text{YbI}_2(\text{thf})_x]$ and $\text{Na}[\text{RuCp}(\text{CO})_2]$ followed by cracking of the isocarbonyl linkages in the primary polymeric product with 4-*tert*-butylpyridine (Scheme 3.3, top and middle) [13]. Using an iodo-bridged, NHC-stabilized dimer of neodymium and $\text{K}[\text{FeCp}(\text{CO})_2]$, a complex with an unsupported Nd–Fe bond was obtained (Scheme 3.3, bottom) [14].

In the field of An–TM chemistry, a number of U^{IV} compounds featuring trianionic tripod ligands were prepared, most of them via salt metathesis from either $\text{K}[\text{ReCp}_2]$ or $\text{K}[\text{RuCp}(\text{CO})_2]$ (Scheme 3.4) [15]. The employed chelating ligands that are based on tris(aminoethyl)amine (tren) or tris(aminodimethylsilyl)methane (ts) originate from efforts to stabilize the so-called early-late transition metal complexes of group IV metals (*cf.* Chapter 4) [16].

One of the limitations of the salt elimination strategy is the need for a polar solvent such as the commonly used tetrahydrofuran that promotes the reactions by providing at least partial solubility for the salt-like transition metalates. As was shown in detail for a Re–Lu system (*vide infra*), the stability of the bimetallic species may be low in ethers, sometimes leading to complete decomposition.



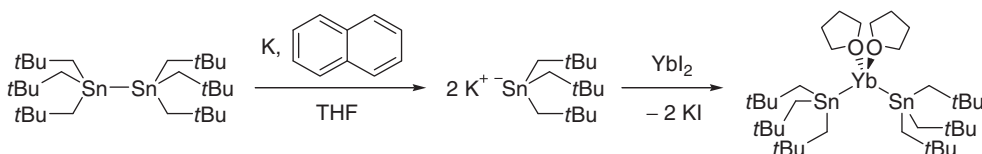
Scheme 3.3 Recent salt elimination reactions forming RE–TM bonds.



Scheme 3.4 Recent salt elimination reactions forming An–TM bonds.

3.2.1.2 f-Element–MM Bond Formation

While salt elimination is (to date) the most abundant reaction type in case of f-element–TM bond formation, for f-element–MM bonds, there has been a broader distribution of methodologies. However, the fragments R_3Sn^- and R_2Ga^- were shown to be well suitable for salt elimination strategies. Thus, the trimetallic complex $[(thf)_2 Yb\{Sn(CH_2tBu)_3\}_2]$ was prepared from YbI_2 and $KSn(CH_2tBu)_3$ (Scheme 3.5) [17]. It is interesting to note that the potassium stannide was obtained *in situ* from potassium naphthalenide and the respective distannane, which already demonstrates the possibility of reductive cleavage as a means of preparing metalate fragments suitable for f-element bonding. This principle is shown to be attractive for a number of other nucleophilic metal fragments as well.



Scheme 3.5 Ytterbium–tin bonds formed by salt elimination.

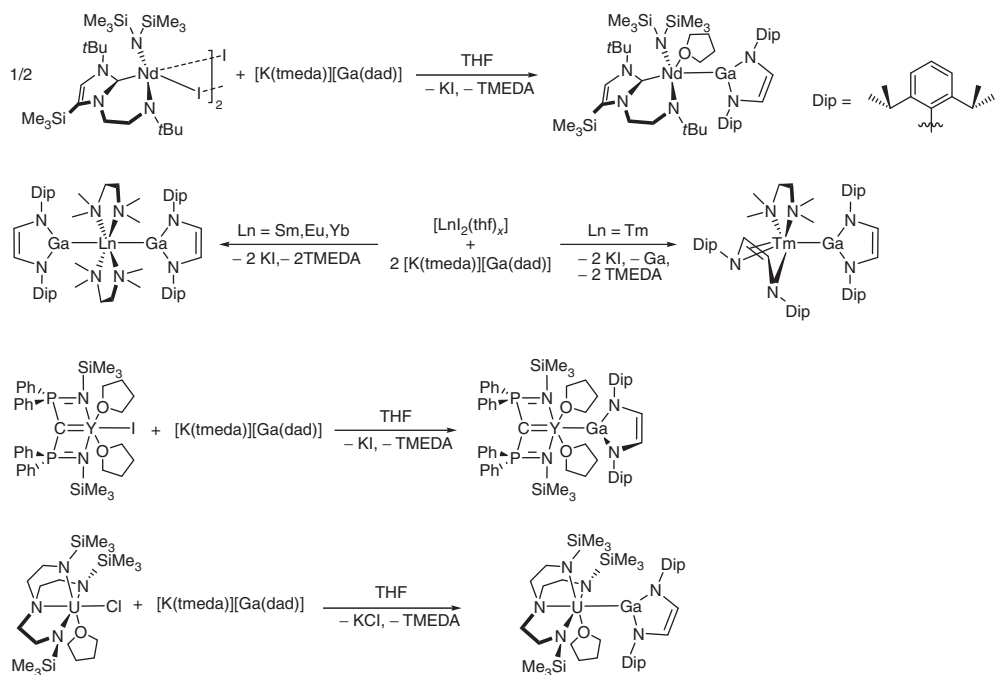
Concerning f-element–gallium bonds, anionic Ga^I fragments stabilized by doubly reduced 1,4-diazadienes (dad^{2-}) and 1,2-diiminoacenaphthenes ($bian^{2-}$) were utilized to great success. The first compound to be reported was a Nd–Ga complex, prepared from the above-mentioned NHC-bearing, iodo-bridged neodymium dimer, and $[K(tmeda)][Ga(dad)]$ (Scheme 3.6, top) [18]. A subsequent study showed that divalent lanthanide complexes are accessible in a similar manner through the preparation of $[(tmeda)_2Ln\{Ga(dad)\}_2]$ ($Ln = Sm, Eu, Yb$) from the respective lanthanide diiodides [19]. The analogous reaction with thulium diiodide proceeded unexpectedly in that partial reduction of the gallium precursor to metallic gallium was observed. The isolated product exhibits only one Ga moiety bound to Tm, and the coordination sphere is saturated by a side-on coordinated, doubly reduced DAD ligand (Scheme 3.6, second row). Using a tridentate dianionic iminophosphorano-derived ligand, Liddle, Jones, and coworkers stabilized a Y–Ga complex prepared from the same gallyl precursor (Scheme 3.6, third row) [20]. Uranium complexes with this structural motif were also shown to be accessible by the preparation of $[(tren^{TMS})U(thf)\{Ga(dad)\}]$ from the respective chlorido uranium complex (Scheme 3.6, bottom) [21].

As 1,4-diazadienes (DAD) and 1,2-diiminoacenaphthenes (BIAN) are closely related ligand classes with often similar redox behavior, it is reasonable to propose $[Ga(bian)]^-$ as a main group metal fragment also suitable for f-element bonding. It was indeed shown that La–Ga complexes can be obtained via salt metathesis using the gallyl precursor $[(Et_2O)_3Na\{Ga(bian)\}]$ and a bis(cyclopentadienyl) lanthanum chloride (Scheme 3.7, top) [22]. Complexes with divalent lanthanides Sm, Eu, Yb, and two gallyl fragments $[Ga(bian)]^{2-}$ were prepared by a similar reaction as in the case of $[Ga(dad)]^{2-}$ discussed earlier as well as by reductive cleavage of Ga–Ga bonds (*vide infra*) [23]. The reaction of samarium triiodide with $[(thf)_5K\{Ga(bian)\}]$ did not yield the corresponding trigallyl compound, but also led to the Sm^{II} complex due to the highly reductive nature of the anionic Ga^I precursor (Scheme 3.7, bottom).

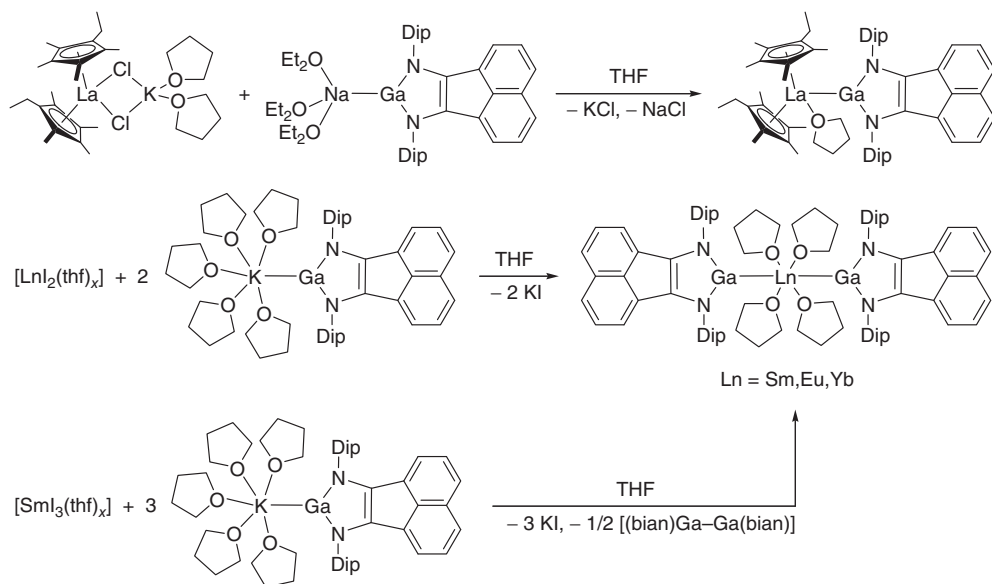
3.2.2

Alkane and Amine Elimination

Alkane and amine elimination routes are prominent in all fields of organometallic chemistry as they often combine homogeneous reaction behavior, even at low temperatures and in nonpolar solvents, virtually irreversible ligand exchange, and a strong entropic driving force. The main limitation of this strategy is usually the availability of suitable metal alkyls or amides. In the case of polar metal–metal bonding, however, another problem arises: in order to succeed, the respective nucleophilic metalate

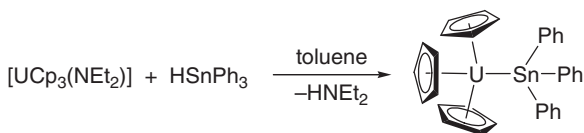


Scheme 3.6 f-Element–gallium bonds formed by salt elimination using DAD ligands.



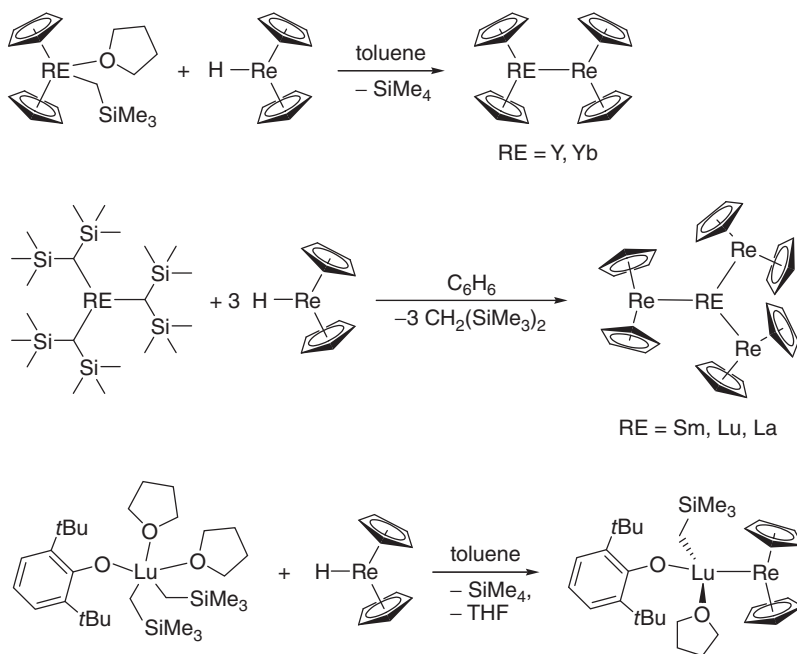
Scheme 3.7 f-Element–gallium bonds formed by salt elimination using BIAN ligands.

has to be provided in a protonated form with sufficient acidic character. It had already been demonstrated in 1986 that metal hydrides can fulfill these criteria by the reaction of $[\text{UCp}_3(\text{NEt}_2)]$ with HSnPh_3 , giving a U–Sn bonded complex with amine elimination (Scheme 3.8) [24].



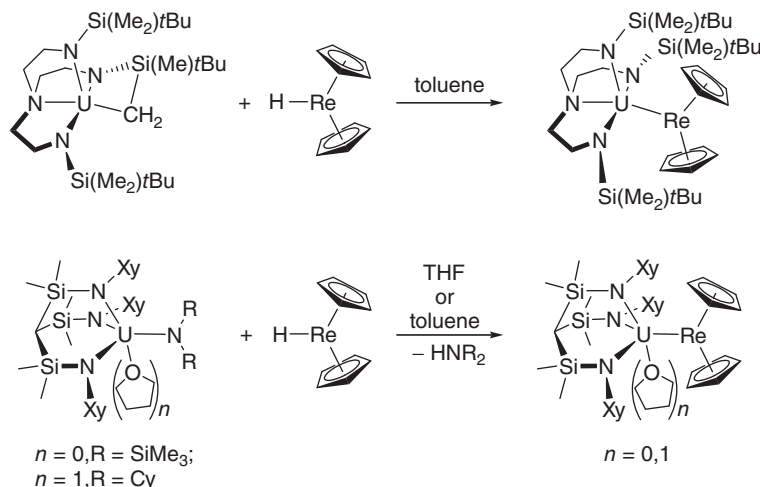
Scheme 3.8 Preparation of $[\text{Cp}_3\text{USnPh}_3]$ via amine elimination.

This result remained singular until 2008 when Kempe and coworkers proved alkane elimination to be a strong tool for the formation of RE–RE bonds by the preparation of bismetallocenes $[\text{Cp}_2\text{REReCp}_2]$ (RE = Y, Yb) [12]. These compounds were obtained from a reaction of monoalkyls $[\text{Cp}_2\text{RE}(\text{CH}_2\text{SiMe}_3)(\text{thf})]$ (RE = Y, Yb) with $[\text{Cp}_2\text{ReH}]$ (Scheme 3.9, top). Attempts to prepare complexes with three $[\text{ReCp}_2]^-$ ligands remained unsuccessful until the solvent-free starting material $[\text{RE}\{\text{CH}_2(\text{SiMe}_3)_2\}_3]$ (RE = Sm, Lu, La) was used. Upon applying these precursors with bulky alkyl substituents, the trisubstituted products $[\text{RE}(\text{ReCp}_2)_3]$ (RE = Sm, Lu, La) could be isolated in moderate to low yield (Scheme 3.9, middle) [25]. This result is particularly interesting because the central RE atom is solely coordinated by transition metal (i.e., rhenium) atoms, making these compounds an important step toward higher aggregates with metalloid behavior, which can be termed “molecular intermetalloids.” In order to investigate the side reactions observed when trying to attach more than one $[\text{ReCp}_2]^-$ ligand to a rare earth center via alkane elimination, the monoalkyl Lu–Re complex $[(\text{Ar}^{\text{tBu}2}\text{O})\text{Lu}(\text{CH}_2\text{SiMe}_3)\text{ReCp}_2]$ ($\text{Ar}^{\text{tBu}2}$ = 2,6-di-*tert*-butylphenyl) was synthesized and its reactivity explored (Scheme 3.9, bottom; *vide infra*) [26].



Scheme 3.9 RE–RE bonds formed by alkane elimination using $[\text{Cp}_2\text{ReH}]$.

This type of reaction that makes use of the well-known acidic character of $[\text{Cp}_2\text{ReH}]$ [27] was subsequently adapted to the formation of U–Re bonds via alkane and amine elimination. While in the first case a substituted tren ligand was applied in an elegant intramolecular alkane elimination [28], the second example stems from the amides $[(\text{ts}^{\text{Xy}})\text{U}(\text{thf})_n(\text{NR}_2)]$ ($n = 1$, $\text{R} = \text{Cy}$; $n = 0$, $\text{R} = \text{SiMe}_3$) (Scheme 3.10) [29]. Again, tripodal ligands were helpful in stabilizing the coordination sphere at uranium (*vide supra*).



Scheme 3.10 U–Re bonds formed by alkane or amine elimination using $[\text{Cp}_2\text{ReH}]$.

As these reactions seem quite straightforward and do not suffer from typical problems connected with salt metathesis as discussed in the preceding text, attempts were made to use other transition metal hydrides instead of $[\text{Cp}_2\text{ReH}]$. However, until now these experiments were found to lead to a different type of reaction, that is, CH-activation in the co-ligand periphery (for a detailed discussion *vide infra*). It can be concluded that the acidic character of the hydrides to be employed – or, in other words, a positive partial charge residing on the hydrogen atom – is of critical importance for alkane elimination reactions to give unsupported f-element–metal bonds.

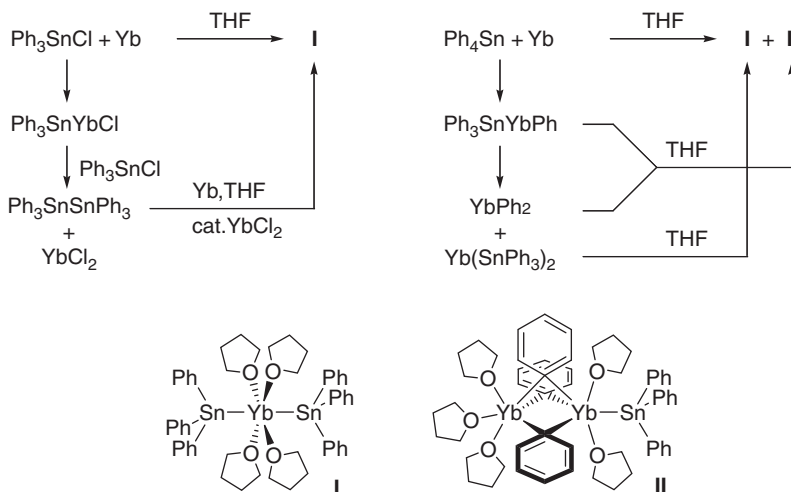
3.2.3

Reductive Cleavage of Metal–Metal Bonds

While the two above-mentioned strategies to achieve polar metal–metal bonding rely significantly on the exergonic nature of by-product formation, this type of reaction directly utilizes the highly electropositive nature of the RE elements. The oxidation of zero-valent RE is thus combined with the reduction of a homometallic M–M bond, resulting in reductive cleavage of the metal–metal bond and insertion of the rare earth metal. From the “viewpoint” of the RE, this is equivalent to an oxidative addition of the M–M bond. The two-electron nature of this reaction causes both a restriction to f-elements with stable divalent oxidation states and a certain similarity with reactions typical for group 2 metals.

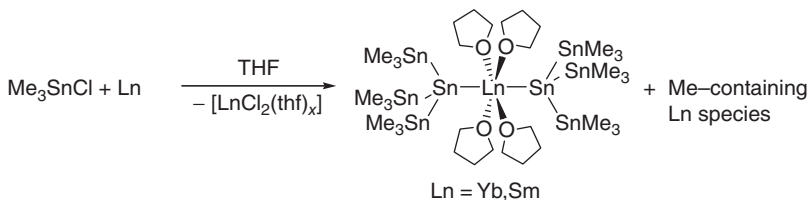
The first structurally authenticated examples of such reactions were reported in 1990 and already showed the potentially complicated behavior of such systems [30]: The target molecule, $[(\text{thf})_4\text{Yb}(\text{SnPh}_3)_2]$, was initially prepared from $\text{Ph}_3\text{SnSnPh}_3$ or (preferably) SnPh_4 and naphthalene ytterbium, which was referred to as $[\text{Yb}(\text{C}_{10}\text{H}_8)(\text{thf})_3]$ [31]. However, a later publication [32] stated that Yb activated by HgBr_2 (which forms ytterbium amalgam *in situ*) also yields this product when reacted with Ph_3SnCl and, surprisingly, PhSnCl_3 . Furthermore, ytterbium dichloride was found to

catalyze the reaction of $\text{Ph}_3\text{SnSnPh}_3$, which in turn was a primary product of the other reactions. In summary, the overall reaction pattern was deduced to be as shown in Scheme 3.11 (upper left part): ytterbium (in a sufficiently activated state) can insert into Sn–Cl bonds in a Grignard-like manner. Reductive coupling of two such reactive intermediates yields the observed distannane, which is subsequently subjected to another reductive bond cleavage, this time leading to the final Yb–Sn complex.



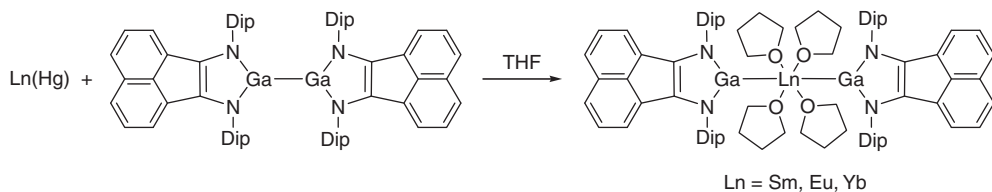
Scheme 3.11 Proposed reactions within the system activated ytterbium + Ph_3SnCl (top left)/ Ph_4Sn (top right) and XRD-authenticated products (bottom).

It should be noted that while PhSnCl_3 was suggested to give the same product via consecutive reductions of the Sn–Cl bonds, Ph_2SnCl_2 yielded a completely different XRD-authenticated product, namely, the ionic compound $[(\text{Ph}_3\text{Sn})_3\text{Sn}]_2[\text{Yb}_2\text{Cl}_2(\text{dme})_6]$ ($\text{DME} = 1,2\text{-dimethoxyethane}$). This example shows that crystal structure analysis is a very important part of such exploratory experiments as it is otherwise hardly possible to determine the correct connectivity of all incorporated atoms. This is further emphasized by the subsequent report on a significant by-product of the reaction between Yb and SnPh_4 , which was found to be $[(\text{thf})_3\text{Yb}(\mu\text{-Ph})_3\text{Yb}(\text{thf})_2\text{SnPh}_3]$ [33]. Its occurrence was rationalized as a result of scrambling and aggregation of the primarily formed anionic Ph^- and Ph_3Sn^- moieties with divalent ytterbium (Scheme 3.11, upper right part). In a later study, the reactivity of Yb and Sm toward Me_3SnCl was investigated [34]. The isolated products $[(\text{thf})_4\text{Ln}\{\text{Sn}(\text{SnMe}_3)_3\}_2]$ ($\text{Ln} = \text{Sm, Yb}$) are likely to be attributed to a sequence of reductive Sn–Sn coupling steps and oxidative addition of Sn–X bonds ($\text{X} = \text{Cl, C, Sn}$) toward Ln^0 (Scheme 3.12). The relatively high stability of tin in various oxidation states (attributable in part to readily formed di- and higher stannanes) is surely one of the determining factors leading to the diversity of observed reactions.



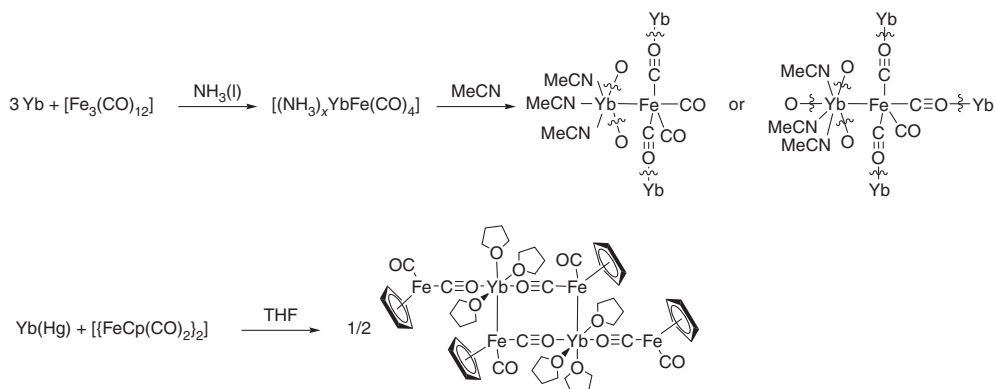
Scheme 3.12 Formation of $[(\text{thf})_4\text{Ln}\{\text{Sn}(\text{SnMe}_3)_3\}_2]$ ($\text{Ln} = \text{Yb, Sm}$) from Me_3SnCl .

Gallyl moieties stabilized by BIAN ligands were successfully used for f-element–Ga bond formation via salt elimination (*vide supra*). It was shown that dimeric Ga^{II} precursors can also be used to yield the same class of products via reductive Ga–Ga bond cleavage (Scheme 3.13) [23]. The related gallyl compounds stabilized by DAD ligands were, however, reported not to be accessible by this method, but accessible only by salt elimination [21].



Scheme 3.13 Reductive insertion of lanthanoids Sm, Eu, and Yb into Ga–Ga bonds.

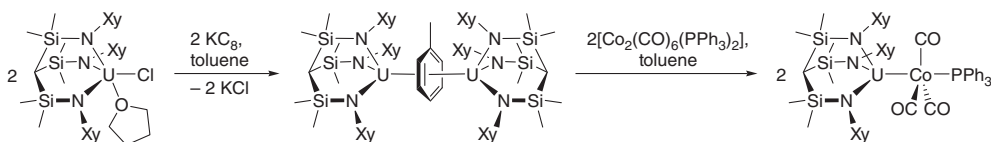
The reductive cleavage of TM–TM bonds is well known as a mean of preparing carbonyl-containing transition metalates. It seems therefore reasonable to investigate the behavior of suitable bi- or oligonuclear carbonyl complexes toward rare earth metals as reducing agents. While the formation of isocarbonyl-bridged compounds or ill-defined products prevented the expected formation of f-element–metal bonds in various cases (*vide supra*), this methodology proved successful in the reaction of ytterbium with $[\text{Fe}_3(\text{CO})_{12}]$ in liquid ammonia (Scheme 3.14, top) [35]. While the primary product could not be structurally characterized, it was possible to obtain two different crystalline products after ligand exchange with acetonitrile. Both compounds are polymeric and show isocarbonyl linkages in addition to Yb–Fe bonds, and they differ only in the degree to which CO bridging takes place. While the dianionic, sterically undemanding metalate $[\text{Fe}(\text{CO})_4]^{2-}$ was thus found to show both primary types of metal–metal interaction with f-elements (direct bonding and isocarbonyl linkage), the less CO-rich and sterically better shielded fragment $[\text{FeCp}(\text{CO})_2]^-$ could be expected to only yield unsupported Yb–Fe bonds. This assumption proved to be only partly correct, as the reaction of ytterbium amalgam with $[\{\text{FeCp}(\text{CO})_2\}_2]$ gave a dimeric product with Yb–Fe bonds as well as a reduced amount of CO bridges compared to the previous results (Scheme 3.14, bottom) [36]. It is interesting to note that the analogous calcium compound could be obtained in the same way using calcium amalgam.



Scheme 3.14 Formation of Yb–Fe bonds via reductive cleavage of Fe–Fe bonds.

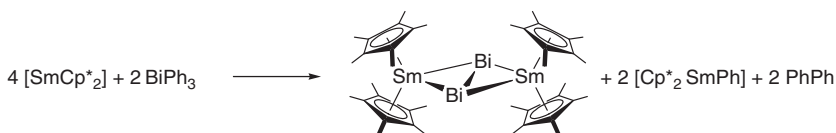
Another interesting candidate for reductive cleavage of metal–metal bonds was found in $[\text{Co}_2(\text{CO})_8]$, which should yield the nucleophilic metalate $[\text{Co}(\text{CO})_4]^-$ (isoelectronic to $[\text{Fe}(\text{CO})_4]^{2-}$)

upon reduction. In order to reduce the probability of isocarbonyl linkage, partial substitution of carbonyl ligands seems preferable. Thus, $[\text{Co}_2(\text{CO})_6(\text{PPh}_3)_2]$ was used in the preparation of a U–Co bonded complex [37]. However, this synthesis differs substantially from the others mentioned in this section because of the more sophisticated structure of the uranium-based reducing agent, that is, an inverse-sandwich diuranium complex (Scheme 3.15). From a synthetic point of view, it is interesting to note that in this case attempts to yield the same product via salt elimination failed.



Scheme 3.15 Formation of a U–Co complex via reductive Co–Co bond cleavage.

Although no metal–metal bonds are split by the following reaction, it shall be mentioned at this point because it relies on reduction of the main group metal precursor and oxidation of the lanthanoid fragment. To be precise, it was reported in 1991 that the reaction of $[\text{SmCp}^*_2]$ with BiPh_3 leads to the formation of $[\text{Cp}^*_2\text{Sm}(\mu\text{-}\eta^2\text{:}\eta^2\text{-Bi}_2)\text{SmCp}^*_2]$ (Scheme 3.16) [38]. This unexpected result can formally be described as a series of reductive Bi–C bond cleavages and a reductive Bi–Bi coupling and bears in this respect some resemblance to the in situ formation of $[\text{Sn}(\text{SnMe}_3)_3]^-$ ligands from Me_3SnCl as described earlier. In addition to showcasing the often unusual reduction behavior of $[\text{SmCp}^*_2]$ [39], this tetranuclear cluster compound is interesting because it allows direct comparison with the analogous dinitrogen complex $[\text{Cp}^*_2\text{Sm}(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)\text{SmCp}^*_2]$ [40].



Scheme 3.16 Reaction of $[\text{SmCp}^*_2]$ with BiPh_3 .

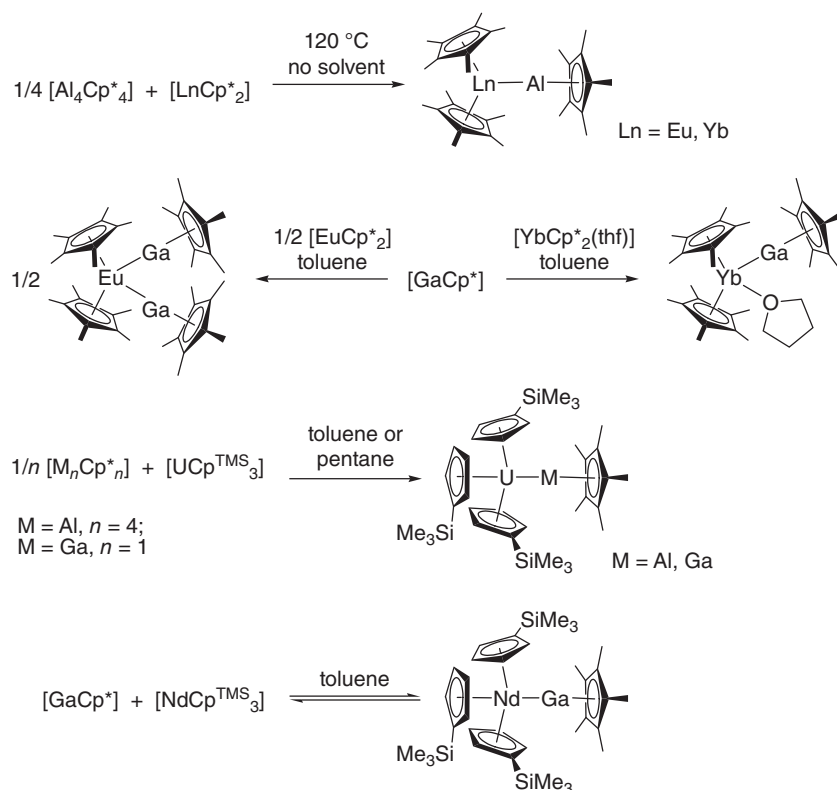
Reductive cleavage of metal–metal bonds by low-valent *f*-element precursors is an interesting alternative to the more common elimination routes as usually no intrinsic by-products are formed. The still ongoing development of binuclear transition metal complexes, for example, dimeric Zn^{I} and Ni^{I} compounds, delivers a wide range of interesting candidates for such reactions that have not been investigated in great detail so far. However, the possibility of undesired redox reactions is likely to limit the variety of actually successful candidates.

3.2.4

Adduct Formation

All heterobimetallic compounds described so far can formally be divided into a cationic *f*-element fragment and an anionic transition or main group metalate. This combination is useful to stabilize the desired complexes because of the Coulomb attraction between ionic species that contributes a large part of the overall binding energy in these highly polarized metal–metal bonds (*vide infra*). The combination of a neutral *f*-element complex and a neutral (nucleophilic) metal complex is thus predicted to be of limited stability. It is therefore not surprising that all but two known examples of such compounds rely on the group 13 metal fragments $[\text{AlCp}^*]$ and $[\text{GaCp}^*]$, both of which are known to be good neutral metal-centered nucleophiles [41].

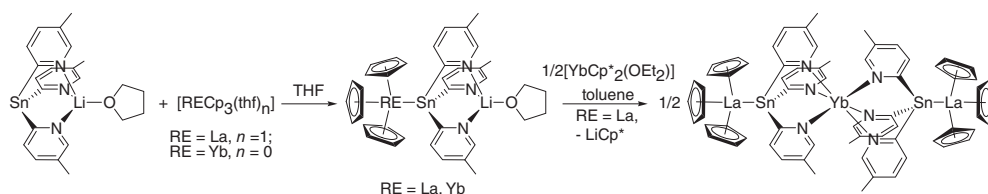
As shown in Scheme 3.17, all four of the possible dative combinations Ln–Al, Ln–Ga, An–Al, and An–Ga have been realized using homoleptic cyclopentadienyl complexes as *f*-element acceptors. It should be noted, however, that the stabilities of these compounds differ drastically: while $[\text{Cp}^*_2\text{LnAlCp}^*]$ (Ln = Eu, Yb) could only be obtained in a solvent-free reaction and is decomposed by aromatic hydrocarbons [42], the Ln^{II} complexes $[\text{Cp}^*_2\text{Eu}(\text{GaCp}^*)_2]$ and $[\text{Cp}^*_2\text{Yb}(\text{thf})\text{GaCp}^*]$ were prepared in toluene solution [43]. These two compounds also show the importance of sterics as two $[\text{GaCp}^*]$ ligands bind to $[\text{EuCp}^*_2]$, whereas only one can be attached to $[\text{YbCp}^*_2]$, which is most likely to be attributed to the smaller size of Yb^{2+} compared to Eu^{2+} . Using $[\text{U}(\text{Cp}^{\text{TMS}})_3]$, U–Al and U–Ga complexes could be isolated using the same strategy [44]. The analogous Nd^{III} compounds were found to be only existing in pronounced equilibria with the respective starting materials; however, a crystal structure of the slightly more stable gallium complex was obtained with co-crystallized $[\{(\text{Cp}^{\text{TMS}})_2\text{Nd}\}_2(\mu\text{-OH})_2]$ [44b]. The higher stability of the Ga complexes was rationalized by the fact that while $[\text{AlCp}^*]$ is a slightly better donor than $[\text{GaCp}^*]$, it is removed from the equilibrium by formation of its tetramer $[\text{Al}_4\text{Cp}^*_4]$, which strongly competes with *f*-element–Al bond formation.



Scheme 3.17 Adduct formation between $[\text{MCp}^*]$ ($\text{M} = \text{Al, Ga}$) and *f*-element moieties.

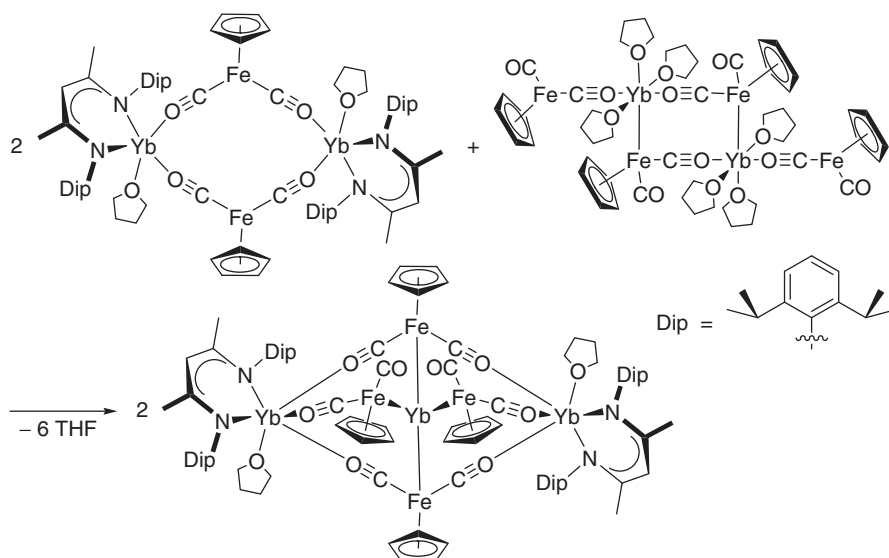
Another structurally authenticated example of an *f*-element–metal bond formed via adduct formation involves a tris(pyridyl)stannate (Scheme 3.18) [45]. The tripodal arrangement of the pyridyl substituents favors a chelating $\kappa^3\text{N}$ -coordination of lithium, which in turn allows the isolation of a formally neutral lithium salt of this monoanionic ligand that does not feature coordination of the anionic tin center to an acceptor. In this respect, the starting material could be regarded as being an intermediate between a neutral and an anionic donor. This figuratively explains the reaction depicted in Scheme 3.18, where the unused Sn^{II} donor (and not the chelating nitrogen atoms) forms a bond

toward fragments of the type $[\text{RECP}_3]$ ($\text{RE} = \text{La}, \text{Yb}$). It should be noted, however, that this preference seems to be of a rather delicate nature as the reaction of the same precursor with $[\text{LnCp}^*_2(\text{OEt}_2)]$ was reported to yield sandwich complexes $[\text{Ln}(\text{stannate})_2]$ ($\text{Ln} = \text{Eu}, \text{Yb}$) with $\kappa^3\text{N}$ -coordinated ligands [46]. Both coordination motifs were combined in a subsequent study by reacting the La–Sn bonded complex with $[\text{YbCp}^*_2(\text{OEt}_2)]$ to yield a pentametallic complex with retained La–Sn bonds (Scheme 3.18) [47].



Scheme 3.18 Adduct formation leading to RE–Sn bonds.

A reaction that can best be described as a combination of adduct formation and ligand rearrangement has been reported starting from the dimeric Yb–Fe bonded complex mentioned earlier (Scheme 3.19; *cf.* Scheme 3.14, bottom) [48]. The resulting complex features a Yb atom bonded to four $[\text{FeCp}(\text{CO})_2]^-$ fragments via the Fe atoms. Six of the carbonyl ligands form isocarbonyl linkages to two additional Yb atoms, a common structural feature of all systems with this carbonyl-containing transition metal fragment (*vide supra*).



Scheme 3.19 Adduct formation and ligand rearrangement in a Fe/Yb system.

3.3 Reactivity

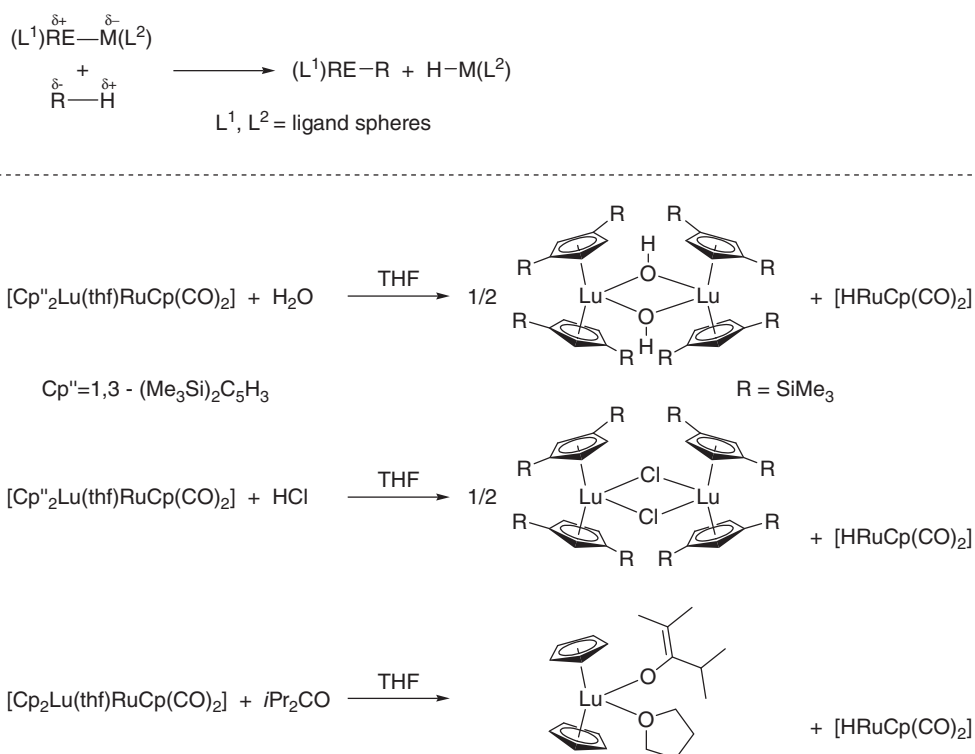
One of the major driving forces in the exploration of polar metal–metal bonds is the search for potentially new and unique reactivity that could lead to applications, for example, in catalysis. However,

the knowledge about the reactivity of f-element–metal bonds is still rather limited and has only been reported for a few of the structurally authenticated complexes described earlier. This is certainly caused by the very high reactivity of these compounds rendering not only the isolation but also selective follow-up reactions difficult.

3.3.1

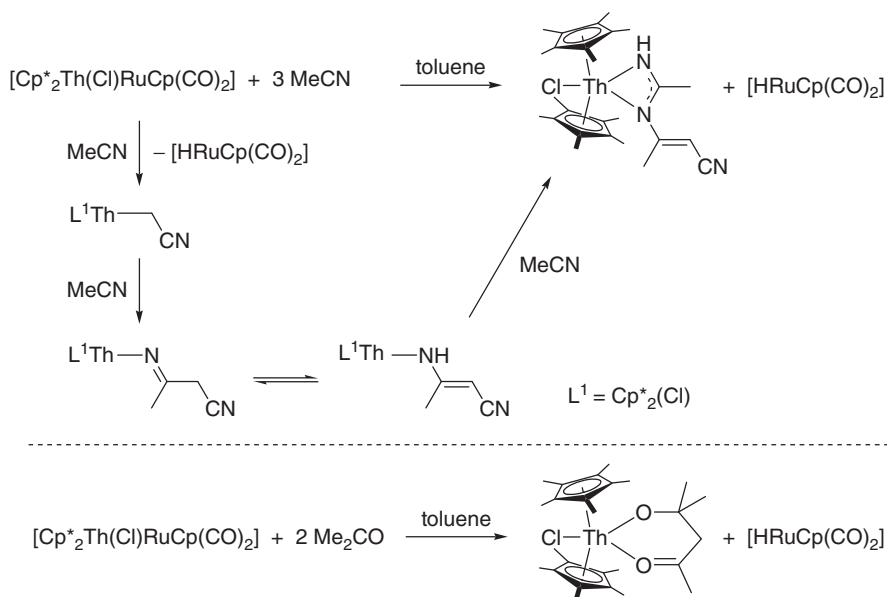
Deprotonation of Acidic Substrates

As f-element–metal bonds are usually highly polar (*vide infra*), it can be expected that they will react with acidic substrates forming f-element complexes of the substrate anion along with hydrides of the respective TM/MM fragment (Scheme 3.20, top). This assumption was confirmed in the reaction of $[(\text{Cp}^{\text{R}})_2\text{Lu}(\text{thf})\text{RuCp}(\text{CO})_2]$ ($\text{Cp}^{\text{R}} = \text{Cp}$, 1,3-(Me_3Si) $_2\text{C}_5\text{H}_3$) with HCl , H_2O , and the bulky ketone $i\text{Pr}_2\text{CO}$ [9], yielding the dimeric chlorido and hydroxido complexes as well as the enolate complex (Scheme 3.20, bottom).



Scheme 3.20 Deprotonation of acidic substrates by f-element–metal complexes.

While no reaction with additional ketone was reported for the latter compound as well as for the analogously formed enolate arising from $[\text{Cp}_3\text{ThMCp}(\text{CO})_2]$ ($\text{M} = \text{Fe}, \text{Ru}$) and acetone [11], the reactions of $[\text{Cp}^*_2\text{Th}(\text{Cl})\text{RuCp}(\text{CO})_2]$ with acetonitrile and acetone gave oligomerized substrates (Scheme 3.21) [49]. These reactions are likely to occur due to the initiating deprotonation of the respective methylene-active reactant followed by further nucleophilic attack(s) within the metal's coordination sphere. The striking difference between the products is presumably caused by the different steric bulk protecting the α -positions of the ketones and the metal centers, respectively.



Scheme 3.21 Oligomerization of methylene-active substrates in the f-element's ligand sphere.

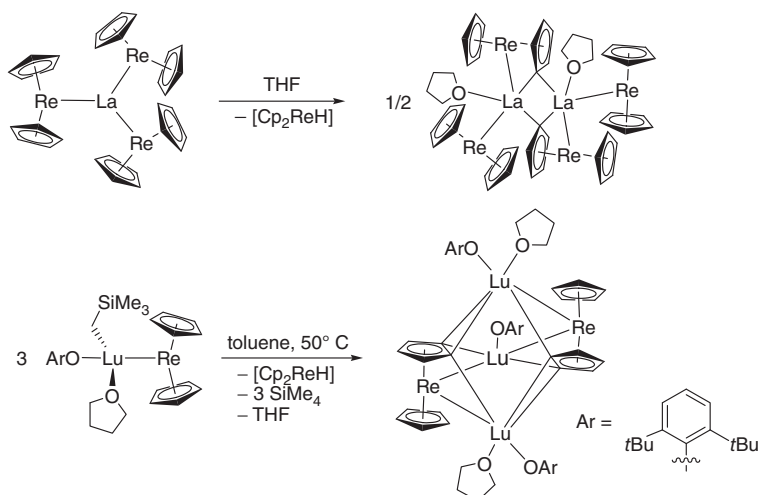
The reactions of $[(\text{thf})_2\text{Yb}\{\text{Sn}(\text{CH}_2t\text{Bu})_3\}_2]$ with 2 equiv. of Cp^*H and ArOH ($\text{Ar} = 2,6\text{-di-}t\text{-butyl-4-methylphenyl}$) have been investigated by NMR spectroscopy and yielded the complexes $[\text{YbCp}^*_2(\text{thf})_2]$ and $[\text{Yb}(\text{OAr})_2(\text{thf})_2]$, respectively [17]. When the reactant was used stoichiometrically, the coupling pattern suggested the formation of mixed complexes $[\text{Cp}^*\text{Yb}(\text{thf})_2\{\text{Sn}(\text{CH}_2t\text{Bu})_3\}]$ and $[(\text{ArO})\text{Yb}(\text{thf})_2\{\text{Sn}(\text{CH}_2t\text{Bu})_3\}]$. In all cases, $\text{HSn}(\text{CH}_2t\text{Bu})_3$ was released.

3.3.2

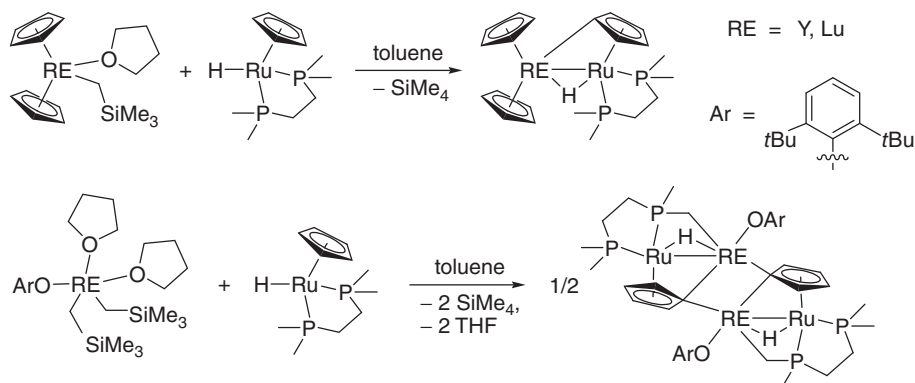
Intramolecular Deprotonation and C–H Activation

While the deprotonations described in the last section could be expected from the usual reactivity of the reactants, the reactions discussed here were not as clearly foreseen. During the experiments toward complexes of the type $[\text{RE}(\text{ReCp}_2)_3]$, poor yields were observed due to the formation of insoluble by-products. The nature of such side reactions remained unclear until $[\text{La}(\text{ReCp}_2)_3]$ was treated with THF, resulting in the formation of a La–Re cluster compound with C–H activated Cp ligands (Scheme 3.22, top) [25]. While this reaction is most likely mediated by the coordinating solvent, a related reactivity was observed when heating the monoalkyl Lu–Re complex $[(\text{Ar}^{t\text{Bu}2}\text{O})\text{Lu}(\text{CH}_2\text{SiMe}_3)\text{ReCp}_2]$ in toluene solution (Scheme 3.22, bottom) [26]. The resulting Lu–Re cluster features doubly C–H activated Cp ligands; in both cases, $[\text{Cp}_2\text{ReH}]$ is formed as side product, which emphasizes the delicate balance between co-ligand acidity and metal hydride acidity.

Recent studies also showed ligand deprotonation to be an alternative reaction path when attempting to form metal–metal bonds via alkane elimination. As depicted in Scheme 3.23, the reaction of $[\text{CpRu}(\text{dmpe})\text{H}]$ ($\text{dmpe} = 1,2\text{-bis}(\text{dimethylphosphino})\text{ethane}$) with RE alkyl precursors that gave access to RE–RE bonds (*cf.* Scheme 3.9) yielded C–H activated products in this case [50]. The hydride is incorporated into the resulting bimetallic complexes as a bridging ligand; deuteration experiments showed that the hydride ligand is not exchanged during the reaction. In a related study, $[\text{Cp}_2\text{MH}_2]$ ($\text{M} = \text{Mo}, \text{W}$) was used as the metal hydride component. Again, activation of the Cp ligands was observed, leading to polyhydride cluster compounds without newly formed unbridged metal–metal bonds (Scheme 3.24) [51].



Scheme 3.22 Cluster formation from RE-Re complexes via C–H activation.



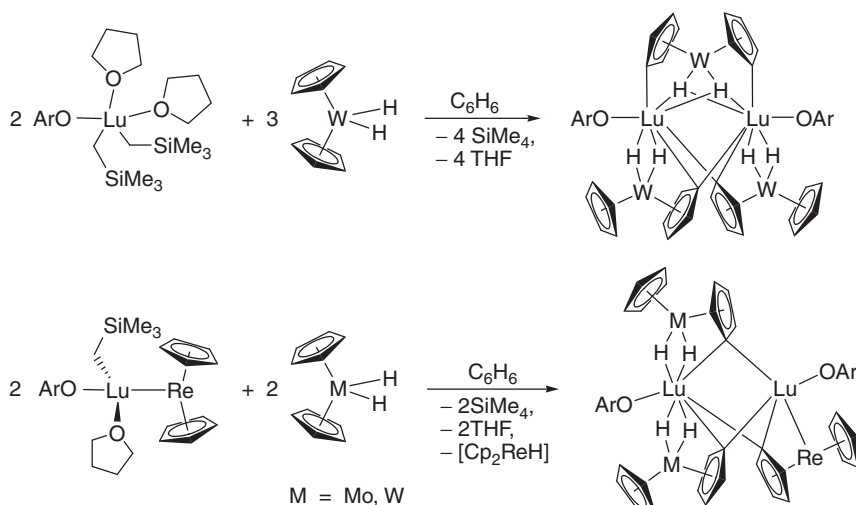
Scheme 3.23 Formation of hydride-bridged RE–Ru complexes via C–H activation.

3.3.3

Oxidation of the Metal–Metal Bond

f-Element–metal bonds can only be stabilized with rather nucleophilic MM or TM fragments, preferably with metalates. Because of this, it has to be expected that oxidation of the MM/TM part is a readily available reaction pathway. While the generation of metal hydrides discussed earlier formally already constitutes an example of this reaction type, only a few experiments using more common oxidants have otherwise been reported.

Upon treatment of (structurally not authenticated) $[\text{I}_2\text{La}(\text{thf})_3\text{RuCp}(\text{CO})_2]$ with methyl iodide, formation of $[\text{MeRuCp}(\text{CO})_2]$ and $[\text{LaI}_3(\text{thf})_3]$ as main products was observed [9]. The reaction of $[(\text{thf})_3\text{Yb}(\mu\text{-Ph})_3\text{Yb}(\text{thf})_2\text{SnPh}_3]$ with bromine was reported to yield a mixture mainly consisting of bromobenzene, Ph_3SnBr , and YbBr_3 [34]. In this example, the oxidation of all anionic ligands is accompanied by the oxidation of the divalent lanthanide. An elegant use of a metal–metal bond oxidation was shown in the calorimetric titration of $[\text{Cp}_3\text{UMPh}_3]$ ($\text{M} = \text{Si, Ge, Sn}$) and $[\text{Cp}_3\text{UMCp}(\text{CO})_2]$ ($\text{M} = \text{Fe, Ru}$) with iodine [52]. These reactions only yield $[\text{Cp}_3\text{UI}]$ and the respective iodo complex of the MM/TM fragment, thus allowing for the determination of bond disruption enthalpies (Table 3.1).



Scheme 3.24 Formation of polyhydride Lu-TM clusters via C-H activation.

Table 3.1 Bond disruption enthalpies of uranium complexes [52].

Complex	$D(U-M)$ (kJ mol ⁻¹)	Complex	$D(U-M)$ (kJ mol ⁻¹)
[Cp ₃ USiPh ₃]	156.2(17.6)	[Cp ₃ UFeCp(CO) ₂]	129.4(12.6)
[Cp ₃ UGePh ₃]	162.9(18.8)	[Cp ₃ URuCp(CO) ₂]	169.1(16.7)
[Cp ₃ USnPh ₃]	155.7(16.7)	—	—

3.4

Solid-State Structures

3.4.1

Typical Structures

The most interesting feature of the crystal structures of the heterometallic compounds is certainly the f-element–metal bond length, which is important to infer or evaluate bond strengths and steric strain, often in comparison to theoretical calculations (*vide infra*). However, regarding the overall complex geometry, it can be stated that the nucleophilic metal fragments behave just as more common ligands of comparable bulkiness. The coordination sphere around the f-element is governed by steric forces to a large extent, which is to be expected for metal cations with empty, and thus spherically symmetrical, valence electron shells. In the following, some aspects of typical examples are considered shortly.

Complexes [RE(ReCp₂)₃] (RE = Sm, Lu, La) show coordination number 3, which is fairly uncommon for lanthanoids, in a trigonal planar coordination sphere. The same (formal) coordination number is also found in the bulky amides [RE{N(SiMe₃)₂}] [53] and alkyls [RE{CH(SiMe₃)₂}] [54], suggesting a roughly similar steric bulk of these ligands. This is in contrast to the popular, slightly less bulky alkyl ligand CH₂SiMe₃⁻, which forms solvent adducts [RE(CH₂SiMe₃)₃(thf)_n] (*n* = 2, 3) [55]. It should be noted that the formation of agostic interactions is a common feature in these compounds, limiting the usefulness of comparisons solely based on formal coordination numbers.

A structural similarity can be found in most Ln–MM/TM complexes with divalent lanthanides and 2 equiv. metalloligands in that they tend to adopt an octahedral coordination sphere saturated by four solvent donors (usually THF). The three metal atoms lie on a roughly straight line in these compounds, that is, the metal fragments are situated *trans* to each other. This structural motif is found for $[(\text{thf})_4\text{Yb}(\text{SnPh}_3)_2]$ [30], $[(\text{thf})_4\text{Ln}(\text{Sn}(\text{SnMe}_3)_3)_2]$ (Ln = Yb, Sm) [34], $[(\text{tmeda})_2\text{Ln}\{\text{Ga}(\text{dad})\}_2]$ (Ln = Sm, Eu, Yb) [19], and $[(\text{thf})_4\text{Ln}\{\text{Ga}(\text{bian})\}_2]$ (Ln = Sm, Eu, Yb) [22]. When the steric requirements of the metalloligand are increased, however, coordination number 4 and a tetrahedral environment are observed, like in $[(\text{thf})_2\text{Yb}\{\text{Sn}(\text{CH}_2\text{tBu})_3\}_2]$ [17] and $[(\text{thf})_2\text{Yb}(\text{ReCp}_2)_2]$ [13].

The stabilization of U^{IV} –metal bonds was very successful when applying trianionic tripod ligands tris(aminoethyl)amine (tren) or tris(aminodimethylsilyl)methane (ts). This concept was adapted from earlier studies on related group IV–TM bimetallic complexes and nicely illustrates that steric protection is a most important factor governing the accessibility of such d^0 complexes. Despite the differing ionic radii of Ti^{4+} (75 pm), Zr^{4+} (86 pm), Hf^{4+} (85 pm), and U^{4+} (103 pm) [56], the formation of analogous complexes is observed with usually striking structural resemblance in many cases.

3.4.2

Metal–Metal Bond Lengths

In Tables 3.2 and 3.3, the known f-element–metal bond lengths as determined by XRD studies are presented together with information on coordination number and synthesis.

One of the main factors in determining the metal–metal bond lengths is the size of the two constituting metals. As the bonds are generally quite polar in nature (*vide infra*), it seems appropriate to use the (effective) ionic radii of the lanthanides as a guideline [56]. For example, the complexes $[(\text{tmeda})_2\text{Ln}\{\text{Ga}(\text{dad})\}_2]$ (Ln = Sm, Eu, Yb) nicely reflect the expected trend $\text{Sm}^{\text{II}} \approx \text{Eu}^{\text{II}} > \text{Yb}^{\text{II}}$ in their Ln–Ga distances (Sm–Ga, 331.24(9) pm; Eu–Ga, 331.24(11) pm; Yb–Ga, 320.50(7) and 324.73(7) pm) [19]. In a similar manner, complexes $[\text{RE}(\text{ReCp}_2)_3]$ (RE = La, Sm, Lu) show the expected behavior $\text{La}^{\text{III}} > \text{Sm}^{\text{III}} > \text{Lu}^{\text{III}}$ in their mean RE–Re distances (La–Re, 304.78(9) pm; Sm–Re, 297.34(10) pm; Lu–Re, 288.62(8) pm) [25].

It is interesting to note that the metal–metal bond lengths also seem to be governed by steric strain to a considerable extent. This can be seen, for example, by comparing the reported Yb–Sn bond lengths: the trend observed for compounds of the type $[(\text{thf})_x\text{Yb}(\text{SnR}_3)_2]$ is $[(\text{thf})_2\text{Yb}\{\text{Sn}(\text{CH}_2\text{tBu})_3\}_2] < [(\text{thf})_4\text{Yb}\{\text{Sn}(\text{SnMe}_3)_3\}_2] \approx [(\text{thf})_4\text{Yb}(\text{SnPh}_3)_2]$ (*cf.* Table 3.2), which reflects the prediction that smaller coordination numbers should lead to shorter metal–metal distances if sterics are most important. However, subtle changes in ligand bulkiness are not always reflected in metal–metal distances. Comparison of the reported U–Re and U–Ru bond lengths shows that in case of the tripod ligands tren and ts changes in the ligand substitution pattern have little impact on the metal–metal distance. It is likely that these changes do not have a larger effect because they happen rather far away from the metal–metal bond.

Sometimes even packing forces can have a substantial effect on f-element–metal bonding, as illustrated by $[(\text{tren}^{\text{TMS}})\text{U}(\text{thf})\{\text{Ga}(\text{dad})\}]$. The reported crystal structure shows two inequivalent molecules with substantially different U–Ga bond lengths (321.15(8) pm and 329.83(9) pm, respectively) [21]. In another example, complexes $[(\text{thf})_4\text{Ln}\{\text{Ga}(\text{bian})\}_2]$ were found to have Ln–Ga distances of 323.58(2) and 334.67(3) pm (Ln = Sm), 332.39(6) pm (Ln = Eu) and 312.95(5) pm (Ln = Yb) [23]. The two different values for the Sm–Ga complex reflect two polymorphs with different crystal solvent content. Obviously, this change in the molecular packing is sufficient to impose a change in the Sm–Ga bond length of about 11 pm. It is, therefore, of similar importance, at least in this case, as the influence of the ionic radii, which would suggest the trend $\text{Sm–Ga} \approx \text{Eu–Ga} > \text{Yb–Ga}$ (*vide supra*).

Table 3.2 f-element–main group metal bond lengths determined by XRD.

Compound	Metal combination	Bond length(s) (pm)	Coordination number of f-element ^{a)}	References
[(BIPM)Y(thf) ₂ {Ga(dad)}]	Y–Ga	317.57(4)	6	[20]
[(C ₅ Me ₄ Et) ₂ La(thf){Ga(bian)}]	La–Ga	301.34(8)	12 (8)	[22]
[Cp ₃ La{Sn(C ₅ H ₃ NMe) ₃ Li(thf)}]	La–Sn	331.75(4)	16 (10)	[45]
[(Cp ₃ La{Sn(C ₅ H ₃ NMe) ₃ }) ₂ Yb]	—	333.03(4), 334.04(4)	16 (10)	[47]
[(NHC ^{NtBu})Nd{N(SiMe ₃) ₂ }{Ga(dad)}(thf)]	Nd–Ga	321.99(3)	5	[18]
[(Cp ^{TMS}) ₃ NdGaCp*]	—	315.26(6)	16 (10)	[44b]
[(tmeda) ₂ Sm{Ga(dad)} ₂]	Sm–Ga	331.24(9)	6	[19]
[(thf) ₄ Sm{Ga(bian)} ₂]	—	323.58(2) ^{b)} , 334.67(3) ^{c)}	6	[23]
[(thf) ₄ Sm{Sn(SnMe ₃) ₃ } ₂]	Sm–Sn	340.2(4), 338.6(4)	6	[34]
[Cp* ₂ Sm(μ-η ² :η ² -Bi ₂)SmCp* ₂]	Sm–Bi	326.5(1), 328.3(1), 329.1(1), 331.1(1)	12 (8)	[38]
[Cp* ₂ EuAlCp*]	Eu–Al	336.52(10)	11 (7)	[42]
[Cp* ₂ Eu{GaCp*} ₂]	Eu–Ga	324.99(6), 339.07(6)	12 (8)	[43]
[(tmeda) ₂ Eu{Ga(dad)} ₂]	—	331.24(11)	6	[19]
[(thf) ₄ Eu{Ga(bian)} ₂]	—	332.39(6)	6	[23]
[(tmeda)Tm{Ga(dad)}(dad)]	Tm–Ga	297.42(16) ^{d)} , 297.69(16) ^{d)}	7 (6)	[19]
[Cp* ₂ YbAlCp*]	Yb–Al	319.81(11)	11 (7)	[42]
[Cp* ₂ Yb(thf)GaCp*]	Yb–Ga	328.72(4)	12 (8)	[43]
[(tmeda) ₂ Yb{Ga(dad)} ₂]	—	320.50(7), 324.73(7)	6	[19]
[(thf) ₄ Yb{Ga(bian)} ₂]	—	312.95(5)	6	[23]
[(thf) ₄ Yb{SnPh ₃ } ₂]	Yb–Sn	330.5(1)	6	[30, 32]
[(thf) ₃ Yb(μ-Ph) ₃ Yb(thf) ₂ SnPh ₃]	—	337.9(1)	6	[33]
[(thf) ₄ Yb{Sn(SnMe ₃) ₃ } ₂]	—	328.9(5) ^{b)} , 329.9(4) ^{b)} , 330.0(4) ^{c)}	6	[34]
[(thf) ₂ Yb{Sn(CH ₂ tBu) ₃ } ₂]	—	321.6(1)	4	[17]
[Cp ₃ Yb{Sn(C ₅ H ₃ NMe) ₃ Li(thf)}]	—	307.40(9)	16 (10)	[45]
[(Cp ^{TMS}) ₃ UAlCp*]	U–Al	311.7(3) ^{d)} , 312.4(4) ^{d)}	16 (10)	[44a]

(continued overleaf)

Table 3.2 (Continued)

Compound	Metal combination	Bond length(s) (pm)	Coordination number of f-element ^{a)}	References
$[(\text{Cp}^{\text{TMS}})_3\text{UGaCp}^*]$	U–Ga	306.48(12) ^{d)} , 308.00(13) ^{d)}	16 (10)	[44b]
$[(\text{tren}^{\text{TMS}})\text{U}(\text{thf})\{\text{Ga}(\text{dad})\}]$	—	321.15(8) ^{d)} , 329.83(9) ^{d)}	6	[21]
$[\text{Cp}_3\text{USnPh}_3]$	U–Sn	316.6(1)	16 (10)	[24]

a) Values in parentheses denote the formal number of donated electron pairs, if differing from the number of coordinated atoms.

b) First modification.

c) Second modification.

d) Two inequivalent molecules in the crystal structure.

3.5

Theoretical Calculations and Bonding

Possibly the most interesting aspect about metal–metal bonds is the insight into chemical bonding itself. It is therefore not surprising that many of the studies on new f-element–metal bonded compounds also report a theoretical discussion of some sort on this topic. Most of this material is connected with recent studies, which can likely be attributed to the fact that the complexes to be discussed are electron-heavy, often also open-shell molecules and as such challenging targets for computational chemistry.

3.5.1

Complexes with Rare Earth Metals

The complexes $[\text{Cp}^*_2\text{LnAlCp}^*]$ (Ln = Eu, Yb) [42] can be described as adducts of the respective divalent lanthanide cyclopentadienide with the Al^{I} fragment AlCp^* . This description was supported by density functional theory (DFT) calculations that show a molecular orbital resembling the unperturbed lone pair of AlCp^* . Thus, in this case, the bonding is predominantly electrostatic in nature. The bond-dissociation energy (BDE) of the two complexes amounts to only about 30 kJ mol^{-1} each (estimated using BP86) and explains their easy dissociation (*vide supra*). In two related studies, weakly bonded complexes $[(\text{Cp}^{\text{TMS}})_3\text{LnMCp}^*]$ (Ln = Ce, Nd; M = Al, Ga) were prepared in equilibria with their respective starting materials [44b, 57]. Their BDEs (determined by NMR titration; Ce–Ga, $17.6(4) \text{ kJ mol}^{-1}$; Nd–Ga, $12.6(4) \text{ kJ mol}^{-1}$) show even weaker metal–metal bonds. However, it is suggested by extensive theoretical calculations on the model compounds $[\text{Cp}_3\text{LnMCp}]$ (Ln = La to Lu, M = Al, Ga) that a considerable covalent character is present in the bond between the lanthanide and the group 13 fragment, which acts as a good σ -donor. The third type of complexes that are formally assembled from two neutral fragments, $[\text{Cp}_3\text{RE}\{\text{Sn}(\text{C}_5\text{H}_3\text{NMe})_3\text{Li}(\text{thf})\}]$ (RE = La, Yb) [45], feature an electron-rich tin donor. The higher stability of the resulting complexes is consistent with higher calculated BDEs (using BP86; La–Sn, $121.1 \text{ kJ mol}^{-1}$; Yb–Sn, 96.6 kJ mol^{-1}). Charge transfer from Sn to RE is found to occur to a limited degree, leading to a mainly electrostatic bond with some covalent character.

Table 3.3 f-Element–transition metal bond lengths determined by XRD.

Compound	Metal combination	Bond length(s) (pm)	Coordination number of f-element ^{a)}	References
[Cp ₂ YReCp ₂]	Y–Re	296.17(19)	11 (7)	[12]
[La(ReCp ₂) ₃]	La–Re	303.15(9), 305.42(9), 305.77(8)	3	[25]
[La ₂ (ReCp ₂) ₂ {ReCp(C ₅ H ₄) ₂ (thf) ₂ }]	—	310.89(8) ^{b)} , 310.17(9) ^{b)} , 309.02(8) ^{c)} , 307.21(8) ^{c)}	5	[25]
[(NHC ^{NtBu})Nd{N(SiMe ₃) ₂ }FeCp(CO) ₂]	Nd–Fe	299.42(7)	4	[14]
[Sm(ReCp ₂) ₃]	Sm–Re	296.00(10), 297.92(9), 298.09(10)	3	[25]
[Cp ₂ YbReCp ₂]	Yb–Re	289.71(17)	11 (7)	[12]
[(thf) ₂ Yb(ReCp ₂) ₂]	—	302.08(7), 303.66(7)	4	[13]
[{(MeCN) ₃ YbFe(CO) ₄] ₂ · MeCN] _∞	Yb–Fe	300.9(1) ^{d)} , 301.0(1) ^{d)}	6	[35a]
[(MeCN) ₃ YbFe(CO) ₄] _∞	—	304.6(1)	7	[35b]
[{(thf) ₃ Yb{Fe{CO} ₂ Cp ₂ }} ₂]	—	298.92(4)	6	[36]
[{Yb(NacNac)(thf) ₂ }{Yb{FeCp{CO} ₂ }} ₄ }]	—	299.61(5), 297.58(5), 314.98(5), 317.02(5)	4	[48]
[(thf) ₂ Yb{(μ-OC)RuCp(CO)} ₂] _∞	Yb–Ru	313.91(8), 318.08(7)	6	[13]
[(py ^{tBu}) ₃ Yb{RuCp(CO) ₂ }]	—	301.29(4), 306.26(4)	5	[13]
[Lu(ReCp ₂) ₃]	Lu–Re	287.73(8), 288.99(7), 289.13(8)	3	[25]
[(Ar ^{tBu2} O)Lu(CH ₂ SiMe ₃)ReCp ₂]	—	284.98(6)	4	[26]
[Lu ₃ Re ₂ Cp ₂ (C ₅ H ₃) ₂ (OAr ^{tBu2}) ₃ (thf) ₂]	—	298.42(4) ^{e)} , 299.81(4) ^{e)} , 291.20(4) ^{f)} , 291.97(4) ^{f)}	6 ^{e)} , 5 ^{f)}	[26]

(continued overleaf)

Table 3.3 (Continued)

Compound	Metal combination	Bond length(s) (pm)	Coordination number of f-element ^{a)}	References
[Cp ₂ Lu(thf)RuCp(CO) ₂]	Lu–Ru	299.5(2)	12 (8)	[9]
[Cp ₃ ThFeCp(CO) ₂]	Th–Fe	294.0(5)	16 (10)	[11]
[Cp* ₂ Th(1)RuCp(CO) ₂]	Th–Ru	302.77(6)	12 (8)	[10]
[(tren ^{TMS})UReCp ₂]	U–Re	304.75(4)	5	[15a]
[(tren ^{TBDMs})UReCp ₂]	—	304.79(6)	5	[28]
[(ts ^{Xy})UReCp ₂]	—	293.07(8)	4	[29]
[(ts ^{Xy})U(thf)ReCp ₂]	—	295.41(8) ^{b)} , 300.21(8) ^{b)}	5	[29]
[(tren ^{TMS})URuCp(CO) ₂]	U–Ru	309.25(3)	5	[15b]
[(tren ^{TBDMs})URuCp(CO) ₂]	—	307.39(2)	5	[15b]
[(ts ^{Tol})U(thf)RuCp(CO) ₂]	—	298.85(3)	5	[15b]
[(ts ^{Xy})U(thf)RuCp(CO) ₂]	—	300.62(5)	5	[15b]
[(ts ^{Xy})UCo(CO) ₃ (PPh ₃)]	U–Co	294.50(9)	4	[37]

a) Values in parentheses denote the formal number of donated electron pairs, if differing from the number of coordinated atoms.

b) Direct metal–metal bonds.

c) Metal–metal bonds with accompanying ($\eta^5:\eta^1$ -Cp) bridge.

d) Two inequivalent molecules in the crystal structure.

e) Bonds involving “outer” Lu atoms.

f) Bonds involving “central” Lu atom.

Regarding formally anionic gallyl ligands, the report on an NHC-stabilized neodymium–gallium complex (*cf.* Scheme 3.6) was supported by DFT calculations on a simplified model [18]. The charged nature of the fragments leads to a polarized covalent bond with 87% Ga and 13% Nd in character; the BDE amounts to 386 kJ mol^{−1} (using B3PW91). Using the same gallyl ligand [Ga(dad)][−] and a tridentate carbene ligand (*cf.* Scheme 3.6), a Ga–Y bonded complex was stabilized and subsequently treated with computational methods [20]. It shows a highly polarized covalent bond with only 2% Y contribution. With the above-mentioned NHC–Nd fragment, it was possible to study a Nd–Fe bonded complex (*cf.* Scheme 3.3), which showed on the DFT level a BDE of 384 kJ mol^{−1} (B3PW91) [14]. Here, the contribution of covalent bonding was found to be minimal, resulting in a predominantly ionic Nd–Fe interaction. For the bismetallocene [Cp₂YReCp₂], DFT calculations were used to study the electron localizability indicator (ELI-D) [12]. Its topological analysis shows an attractor (local maximum of ELI-D) roughly between both metal atoms, indicative of a covalent Y–Re bond. Partitioning of the electronic charge within the bonding basin between the atoms leads to relative contributions of 84% for Re and 14% for Y, respectively, which indicates a high bond polarity. A similar bond polarity was also found for [La(ReCp₂)₃] with 87% of the basin population belonging to Re and 11% belonging to La [25]. The BDE was estimated to be 527(5) kJ mol^{−1} (using BLYP), while the relative contributions were found to be 68% electrostatic and 32% due to orbital interactions. In the complexes [(thf)₂Yb(ReCp₂)₂] and [(py^{tBu})₃Yb{RuCp(CO)₂}₂], a comparable situation was found with 80–90% of the bonding population belonging to the respective transition metal [13]. The bonding situation in [(thf)₃Yb(Fe{CO}₂Cp)₂]₂] was studied by DFT, showing a BDE of 143.3 kJ mol^{−1} (using PBE) and again a dominating electrostatic term in the energy decomposition [36]. A predominantly ionic bond was concluded to be present in f-element–metal bonds, following perhaps the most in-depth theoretical study on this topic so far: in a purely computational paper, 11 f-element–metal

bimetallic complexes were studied using DFT as well as multiconfigurational complete active space self-consistent field method (CASSCF), corrected by second-order perturbation theory (CASPT2) [58]. The results suggest that no clear difference can be found between 4f and 5f elements in these compounds, that the metal–metal bonds are primarily ionic in nature (the electrostatic contribution to the attractive interaction is about 65–75%), and that only σ -donation is likely to have any significant influence, regardless of the ligand (*vide infra*). It may also be worthwhile to note at this point that the classifications “predominantly ionic” and “highly polarized covalent” cannot be exactly defined and are thus fluent to some degree.

3.5.2

Complexes with Actinide Metals

Regarding actinide compounds, the possible extent of f-electron involvement in chemical bonding is a very interesting aspect that is widely addressed [59]. In an early study, the metal–metal bond in $[\text{Cp}^*_2\text{Th}(\text{I})\text{RuCp}(\text{CO})_2]$ was probed using quasirelativistic $X\alpha$ -SW calculations on the model complex $[\text{Cp}_2\text{Th}(\text{I})\text{RuCp}(\text{CO})_2]$ [60]. The orbital contributions to metal–metal bonding were found to be 16% Th and 69% Ru, rendering the Ru fragment similar to other more common anionic ligands such as halides or alkyls. It was thus proposed to regard $[\text{RuCp}(\text{CO})_2]^-$ as an “organometallic pseudohalide,” a notion that has proved to be quite useful.

In addition to the adducts discussed, the uranium complexes $[(\text{Cp}^{\text{TMS}})_3\text{UMCp}^*]$ ($M = \text{Al}, \text{Ga}$) were also studied [44], yielding a BDE for U–Ga of $24.3(8) \text{ kJ mol}^{-1}$. This higher stability of the uranium complexes compared to the neodymium complexes was explained by a better overlap of U orbitals with the diffuse group 13 donors. The degree of covalency was thus stated to be even higher than in the corresponding Nd and Ce complexes.

All of the recent syntheses of U–metal bonded complexes stabilized by tripodal ligands have been supplemented with theoretical studies, sometimes on slightly simplified model compounds. The metal–metal bonds were found to be mainly ionic with some covalent contribution. Bond interaction energies (BIEs) were calculated to be $408.5 \text{ kJ mol}^{-1}$ for $[(\text{tren}^{\text{TMS}})\text{U}(\text{thf})\{\text{Ga}(\text{dad})\}]$ [21], $561.3 \text{ kJ mol}^{-1}$ for $[(\text{tren}^{\text{TMS}})\text{UReCp}_2]$ [15a], $557.2 \text{ kJ mol}^{-1}$ for $[(\text{tren}^{\text{TBDMS}})\text{UReCp}_2]$ [28], 657.5 and $599.5 \text{ kJ mol}^{-1}$ for $[(\text{ts}^{\text{Xy}})\text{U}(\text{thf})_n\text{ReCp}_2]$ ($n = 0, 1$) [29], 466.6 to $528.4 \text{ kJ mol}^{-1}$ for $[\text{LURuCp}(\text{CO})_2]$ ($L = \text{tren}^{\text{TMS}}, \text{tren}^{\text{TBDMS}}, \text{ts}^{\text{Xy}}, \text{ts}^{\text{Tol}}$) [15b], and $400.8 \text{ kJ mol}^{-1}$ for $[(\text{ts}^{\text{Xy}})\text{UCo}(\text{CO})_3(\text{PPh}_3)]$ [37]. It should be noted that actual BDEs, which were impracticable to calculate due to the size of the computational models, are likely to be smaller than these values, which may also be the case for some of the values mentioned in Chapter 3.5.1 [15b]. In some cases, small π -donations were discussed in addition to σ -donation; however, a detailed study has shown these contributions to be relatively minor [58]. Overall, the differences between lanthanide–metal and actinide–metal bonding seem to be rather subtle and only of great importance under special circumstances.

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4

Group 4 Metal–Metal Bonds*Lutz H. Gade*

4.1

Introduction

The chemistry of di- and polynuclear complexes of group 4 metals is characterized by an almost complete absence of significant metal–metal bonding interaction for homonuclear species. This is contrasted by a limited, but nevertheless steadily growing, number of compounds in which group 4 metal atoms are directly bonded to late transition metals or p-block metals. The latter are not reviewed in this chapter because the role of the p-block metal fragment as either a ligand or a ligating complex fragment is ambiguous. The main focus is thus on heteronuclear complexes of the “early-late” type [1].

This linkage by direct metal–metal bonds of metal centers having very different oxidation states has been a challenge to synthetic chemists. The chemical characteristics of such species are not only influenced by the nature of the metals involved but equally so by the set of ligands coordinated to the metals. The latter reflects the formal oxidation states of the metal centers and thus – to some extent – the charge distribution between them.

The suppression of degradative reaction channels caused by the intramolecular single electron transfer and the protection of highly Lewis-acidic early transition metal centers by an appropriately designed ligand shell have opened up the systematic investigation of such systems. Concomitant with this development, advances in the conceptual framework for the quantitative description of bond polarity have led to a refined understanding of the nature of this type of metal–metal bonding. The greatest stimulus for the development of this field of research is the investigation of the cooperative reactivity of two or more coordination centers in their interaction with and transformation of organic substrates. This cooperativity, which is characterized by the different functions adopted by the metal centers in these conversions, offers attractive perspectives in stoichiometric or even catalytic transformations.

4.2

Homodinuclear Group 4 Complexes: Metal–Metal Bonding or Not?

Homodinuclear group 4 metal complexes containing unsupported metal–metal bonds remain elusive despite many attempts to synthesize such species. In this sense, direct evidence for the M–M bonds as structurally determining features is still missing.

All known compounds for which some degree of metal–metal bonding has been invoked contain bridging ligands, and several examples are given in Figure 4.1 [2–6]. The presence of bridging ligands and the way they force the neighboring metal atoms into proximity renders the assignment of a metal–metal bond ambiguous. This is further accentuated by the fact that the observed diamagnetism in most of these compounds may be explained by antiferromagnetic coupling of the metal atoms through superexchange mediated by the bridging ligands.

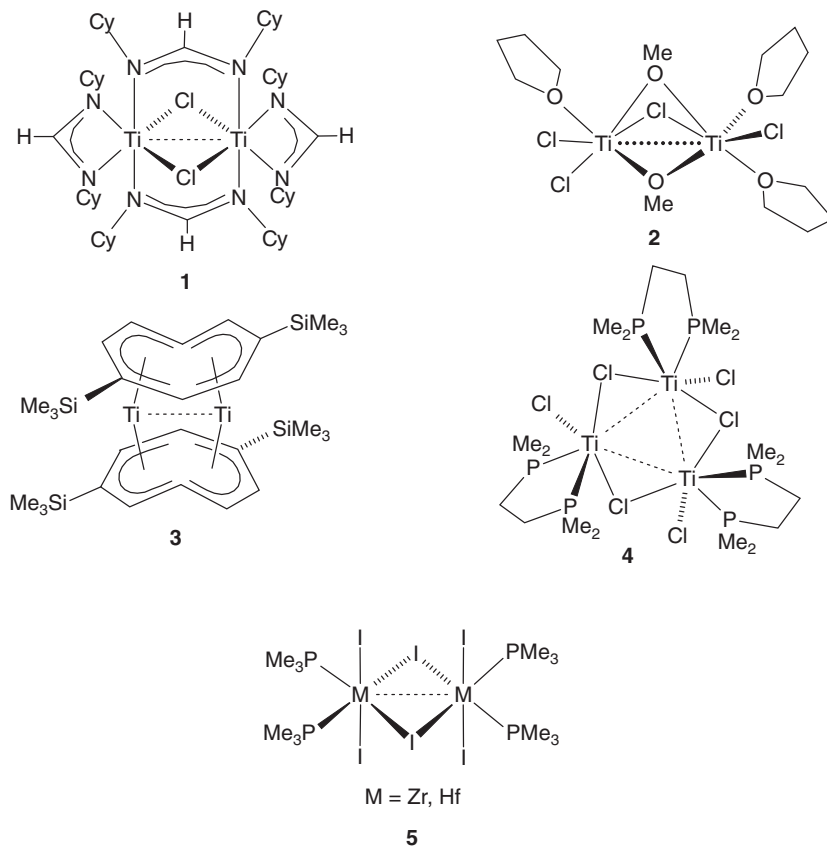


Figure 4.1 Di- and trinuclear group 4 metal complexes for which various degrees of metal–metal bonding interaction have been proposed.

Based on computational modeling, there has been some support for the notion of direct metal–metal bonding for compounds **1**, **2**, and **5** [2–4]. An analysis of the electron pair distribution in complex **2** using the electron localization function (ELF) analytical tool revealed weak local ELF maxima between the Ti atoms, which were interpreted as an indication of direct Ti–Ti bonding [2]. However, in the case at hand, further analysis of the data would have been helpful since the observed feature is weak, which is in part due to the involvement of high angular momentum frontier (d-) orbitals. This approach had been used earlier on for the analysis of metal–metal bond polarity in Ti–Co heterodinuclear complexes containing unsupported (and thus unambiguous) metal–metal bonds. This particular case is described in what follows.

A particularly notable homodinuclear complex is the dititanium compound **3** displayed in Figure 4.1. For this complex, a remarkably short Ti–Ti distance of 2.362 Å was found, which is undoubtedly in part enforced by the bridging cyclooctatetraene ligand.

4.3

Heterobimetallic Complexes Containing Metal–Metal Bonds Involving Group 4 Metals

The stabilization and unambiguous identification of complexes containing metal–metal bonds between the transition metal atoms from the two ends of the d-block in the periodic table had only been achieved since the late 1970s [1]. The first structural characterization of such an unsupported

metal–metal bond was achieved by Schmid and coworkers for a rather complicated system $[\text{Cp}\{\text{Co}_3(\text{CO})_9(\mu\text{-CO})\}_2\text{Ti-Co}(\text{CO})_4]$ (**6**), which was isolated from the reaction of $[\text{CpTiCl}_3]$ with $\text{Na}[\text{Co}(\text{CO})_4]$ [7]. However, a systematic investigation of these “early-late” heteronuclear complexes was initially hampered by the apparent instability of most compounds synthesized at that stage.

4.3.1

Metal–Metal Bond Polarity in Early-Late Heterobimetallic Complexes Involving Group 4 Metals

A high degree of metal–metal bond polarity is to be expected if the metal atoms in two complex fragments have significantly different partial atomic charges. This is to be expected upon combination of complex fragments from the extreme ends of the d-block in the periodic table, as shown in Figure 4.2 for Ti–M and Zr–M complexes **7–10** [8–12]. The d-electron-rich metal atoms in these “early-late” heterodimetallic complexes are directly bound to d-electron poor metal centers without the support of a bridging ligand. The frequencies of the $\nu(\text{CO})$ infrared vibrations indicate that the negative charge at the late (low-valent) transition metal lies somewhere in the middle between those of the homonuclear dimers and the carbonyl metalate anion.

Complexes **7–10** are formally derived from tetravalent group 4 compounds in which one anionic ligand has been replaced by a carbonyl metalate derivative. The late transition metal fragment, therefore, plays the role of a pseudohalide, a notion that was put forward by Bursten and coworkers in their analysis of this type of metal–metal bonding [13]. The metal–metal bond in **7–10** may therefore be interpreted as polar single bonds although the actual covalent bond order may be well below unity, as is discussed later. However, the high-valence state of the early transition metal and the metal–metal bond polarity render these bonds remarkably short (2.4–2.7 Å for the Ti–M complexes) in comparison to homometallic single bonds, which normally range between 2.7 and 3.0 Å.

The concept of bond polarity, which is used in main group chemistry with reference to electronegativities of the atoms involved, is less readily applied in a quantitative way to bonds between transition metals. Their nature may be more significantly influenced by the coordination spheres of the metal centers involved rather than intrinsic properties of the metal itself. This increased level of sophistication required in a meaningful discussion of bond polarity in M–M' bonds necessitates elaborate quantum chemical methods to be used. However, this may render it difficult to extract information from the results of such calculations, which are interpretable within the established paradigms of structure and bonding familiar to the chemist.

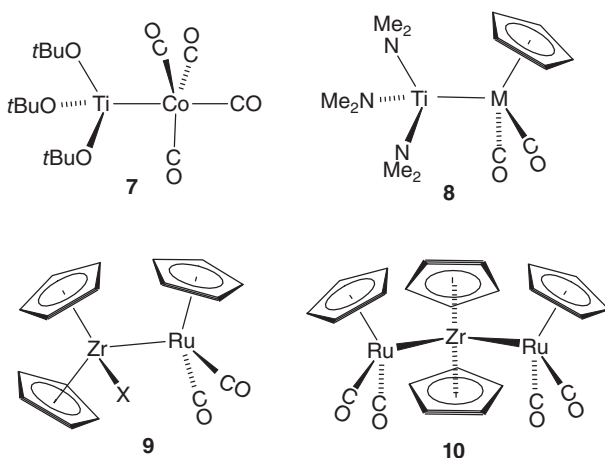


Figure 4.2 Early-late heterobimetallic complexes containing unsupported metal–metal bonds (M = Fe or Ru).

First attempts to tackle the problem of metal–metal bond polarity in early-late heterodinuclear complexes were reported by Bursten and Novo-Gradac who applied $X\alpha$ –SW molecular orbital methods, *inter alia*, to Casey's system $[\text{Cp}_2(\text{X})\text{Zr}–\text{Ru}(\text{CO})_2\text{Cp}]$ (**9**) [13, 14]. According to this early study, the Zr–Ru bonding may be described as the donation from the filled $4d_{z^2}$ orbital of ruthenium into the empty d_{z^2} orbital of Zr, resulting in a slightly bent M–Ru σ -bonding orbital to which the frontier orbitals of the two metal centers contribute highly unequally [Zr: 15%; Ru: 72%], which may be interpreted as qualitatively representing a highly polar bond.

This and subsequent extended Hückel MO calculations on various early-late heterobimetallic complexes [15] offered a qualitative analysis of the principal bonding interactions between the early and late metal centers. However, although providing some valuable insights into the nature of this class of compounds, they were unsuitable for addressing issues such as metal–metal bond polarity even in a semiquantitative way.

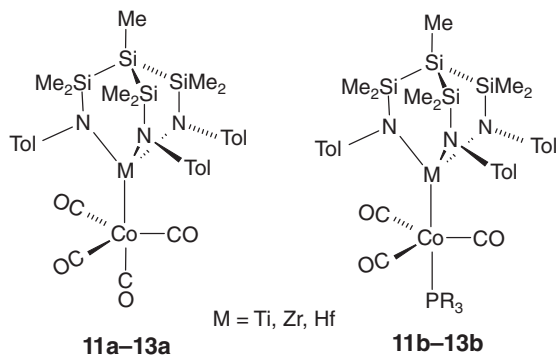


Figure 4.3 Ti–Co, Zr–Co, and Hf–Co complexes, which served as reference systems for the theoretical modeling of metal–metal bond polarity in Ref. [16].

In the model system chosen in an early comprehensive study, two complex fragments, joined through a direct metal–metal (M–M') bond, were required to have the same symmetry with respect to this bonding axis in order to facilitate the interpretation of the results. The experimental point of reference was provided by $[\text{MeSi}\{\text{SiMe}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\}_3\text{M}–\text{Co}(\text{CO})_3(\text{L})]$ [M = Ti: **11**, Zr: **12**, Hf: **13**; L = CO (**a**), PR_3 (**b**)] in which the *trans*-axial position at the Co atom is occupied either by a CO or a triarylphosphine ligand (Figure 4.3) [16]. The theoretically optimized structural parameters obtained by DFT methods of the simplified model systems, the heterobimetallic complexes $[(\text{H}_2\text{N})_3\text{Ti}–\text{Co}(\text{CO})_4]$ and $[(\text{H}_2\text{N})_3\text{Ti}–\text{Co}(\text{CO})_3(\text{PH}_3)]$, were found to be in good general agreement with those obtained experimentally.

To establish the degree of metal–metal bond polarity, several independent theoretical approaches were used. In particular, the combination of Bader's partitioning of molecules into atomic domains and the localization of electron pairs using the ELF formalism gave a consistent picture of the nature of the Ti–Co bonds in dinuclear complexes: while the covalent metal–metal bond order was found to be less than 0.5, high partial charges assigned to the complex fragments of greater than 0.5e were established, which emphasized the highly polar character of the Ti–Co bonds [16].

Visualization of the nature of these Ti–Co bonds was most persuasively achieved by the representation of the ELF isosurface in relation to the AIM-boundary (AIM = atoms in molecules) surface between the two complex fragments bound to each other (Figure 4.4). The metal–metal bond electron pair localization domain – being disk-shaped – and very close to the separating surface between the metal atoms is essentially concentrated on the side of the Co atom and, thus, is mainly in the atomic domain of that metal atom toward which the bond is polarized.

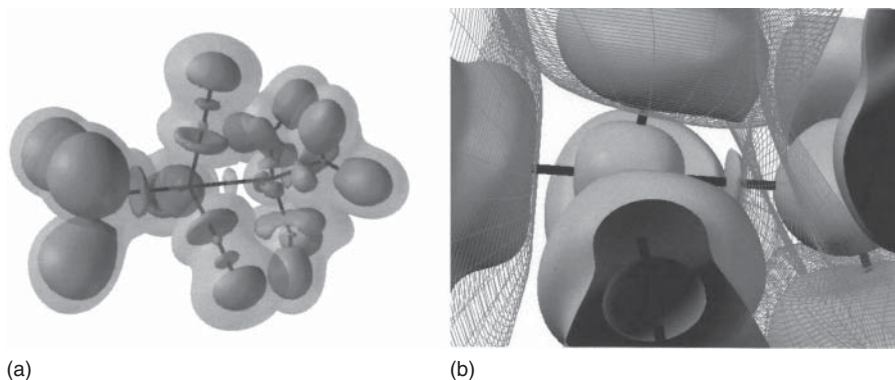


Figure 4.4 (a) The ELF = 0.42 (translucent) and ELF = 0.83 (solid) isosurfaces of $[(\text{H}_2\text{N})_3\text{Ti-Co}(\text{CO})_3(\text{PH}_3)]$ superimposed. (b) A zoom into the Co–Ti bond region for ELF = 0.43,

along with some of the Bader surfaces. This very clearly illustrates the localization of the bond electron pair close to the Co–Ti separating surface.

The heterobimetallic complexes **11–13** as well as related systems (the as-yet-unknown Ti/Zr/Hf–Rh/Ir analogs) have been the subject of two recent theoretical studies by Frenking *et al.*, who applied energy decomposition analyses to the metal–metal bonding [17]. Their conclusions concerning the polarity issue are entirely consistent with the study discussed above.

4.3.2

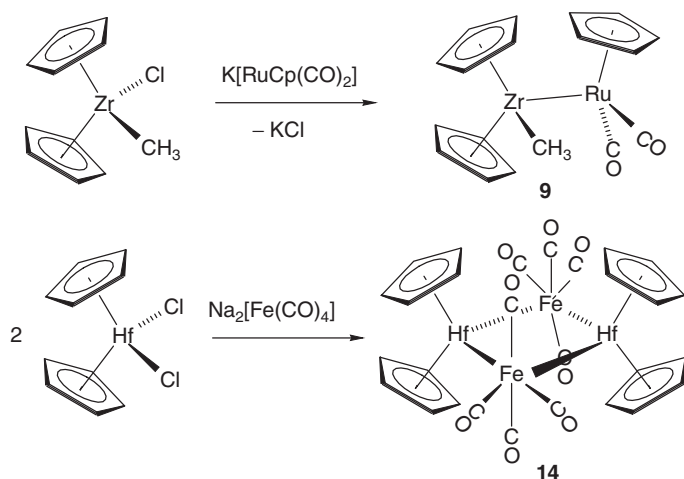
Synthetic Strategies for the Generation of Highly Polar Metal–Metal Bonds

The linking of two electronically different transition metal centers to give a dinuclear complex containing a highly polar metal–metal bond may be achieved by several basic synthetic strategies. The most widely used method is the simple salt metathesis, which for early-late heterodinuclear complexes involves the reaction of an early (high-valent) transition metal halide with an alkali metal salt of an anionic late (low-valent) transition metal complex (mostly carbonyl metalates). Two examples of this method, including the reaction of a dihalide with a dianionic metal carbonylate, are summarized in Scheme 4.1.

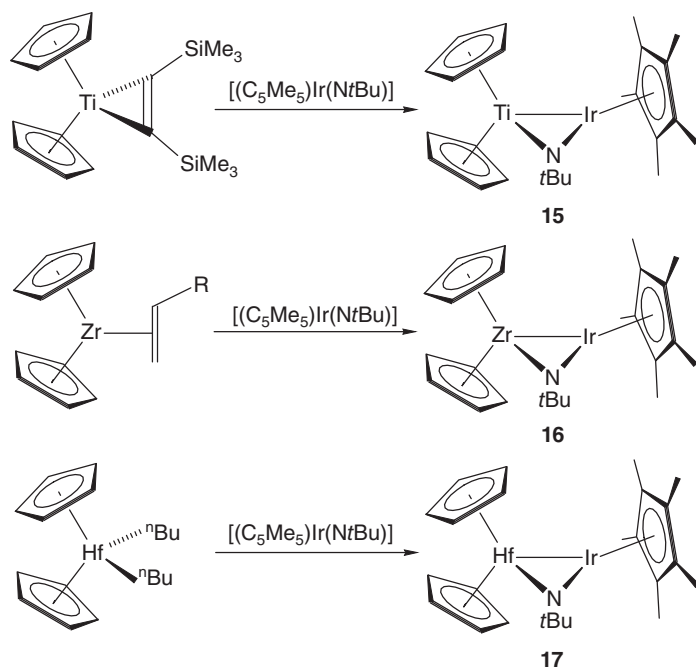
A severe limitation of this approach is the possibility of a single-electron transfer competing with the salt elimination and formation of a metal–metal bond. The high-valent, early transition metal complex fragments are almost always potential oxidizing agents, and the carbonyl metalates can be reducing agents. Thus, an alternative M–M' coupling strategy involves the reaction of neutral complexes and the elimination of a less polar molecule upon formation of a dinuclear complex. A prominent example of the latter strategy is provided by the synthesis of the imido-bridged Ti–Ir, Zr–Ir, and Hf–Ir complexes **15–17** (Scheme 4.2) [18, 19].

Dimetallic elimination reactions leading to metal–metal bond formation are the amine or alkane eliminations that result from the “condensation” of a late transition metal hydrido complex with an early transition metal amido or alkyl complex, respectively. Examples of this method are Selegue’s synthesis of the first Ti–Fe and Ti–Ru complexes **8a,b** [8, 9] and the reaction of $[\text{Zr}(\text{CH}_2\text{Ph})_4]$ with $[\text{CoH}(\text{CO})_4]$, although only spectroscopic evidence was provided for compound **18** (Scheme 4.3) [20].

A method frequently used in the synthesis of homodinuclear complexes is the elimination of halide ligands by reduction. This strategy is applicable in the synthesis of heterodinuclear complexes if bridging ligands effect the prearrangement of the two metal centers, as is exemplified by the synthesis of the Ti–Rh complex **19**, which was obtained by Slaughter and Wolczanski upon Na/Hg reduction of a halide precursor (Scheme 4.4) [21]. Its most characteristic structural element is the extremely short

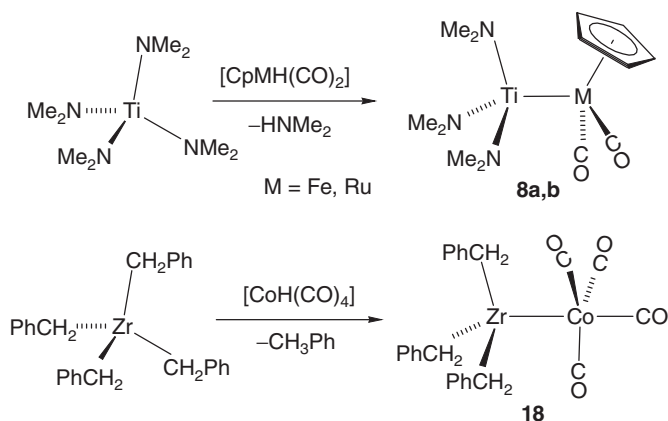


Scheme 4.1 Synthesis of heterodinuclear complexes by salt metathesis using alkali metal salts of the carbonyl metalates.

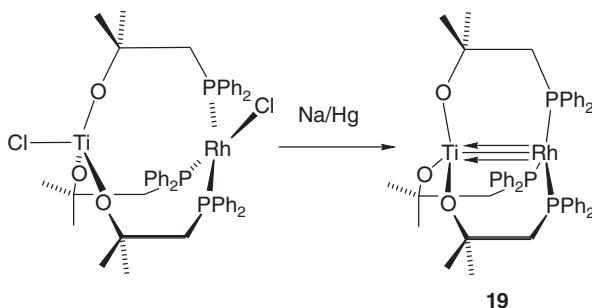


Scheme 4.2 Synthesis of heterodinuclear Ti/Zr/Hf–Ir complexes by combination of neutral complex fragments.

Ti–Rh distance of 2.2142(11) Å, which is 0.362 Å less than the sum of the covalent metal radii. Since the bridging ligands are fairly flexible and undistorted in complex **19**, this short metal–metal distance was interpreted as arising from the additional Ti–Rh donor–acceptor interaction and thus increased metal–metal bond order.



Scheme 4.3 Metal–metal bond formation by bimolecular amine or alkane elimination.



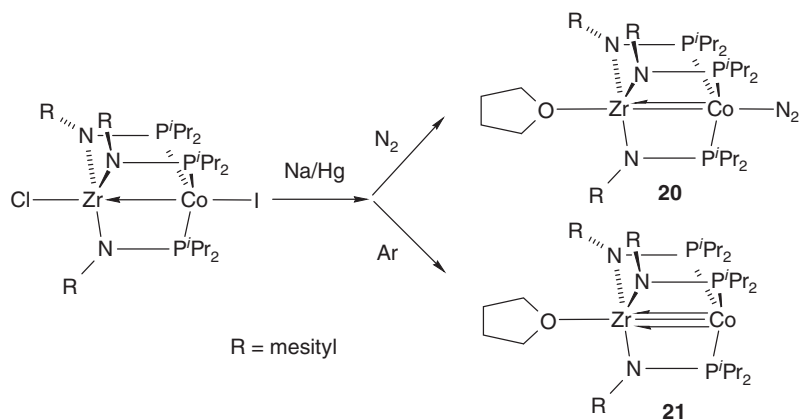
Scheme 4.4 Reductive formation of a Ti–Rh heterodinuclear complex with significant metal–metal multiple bond character.

Recently, the same strategy had been applied by Thomas and coworkers (Scheme 4.5) [22]. The phosphinoamide bridging ligands are the key structural feature that orientates the metal complex fragments in such a way that selective transformation to the Zr–Co heterodinuclear complexes **20** and **21** took place. On the basis of the structural data and a computational study, partial multiple Zr–Co bond character was established, the actual bonding situation being determined by coordination or noncoordination of an axial N_2 ligand. This system has given rise to some interesting heterobimetallic reactivity, which is discussed in what follows.

4.3.3

Factors Influencing the Stability of “Unsupported” Metal–Metal Bonds in Ti/Zr/Hf–M Heterodinuclear Complexes

The stabilization of unsupported metal–metal bonds in early–late heterodinuclear complexes may be achieved by the appropriate choice of ancillary ligands, in particular, for the early transition metal fragment, which is generally highly Lewis acidic and chemically hard and, thus, requires an appropriate set of hard σ - and π -donors. Consequently, most early–late heterodinuclear complexes relevant to this chapter have sets of ligands coordinated to the high-valent transition metal center, which comprise alkoxy or amido groups. Amido functions (R_2N^-), which possess two substituents at the donor atom, may be readily incorporated into polydentate ligand systems, which are designed to shield most



Scheme 4.5 Reductive formation of Zr–Co heterodinuclear complexes **20** and **21** with variable metal–metal multiple bond character depending on the axial ligands.

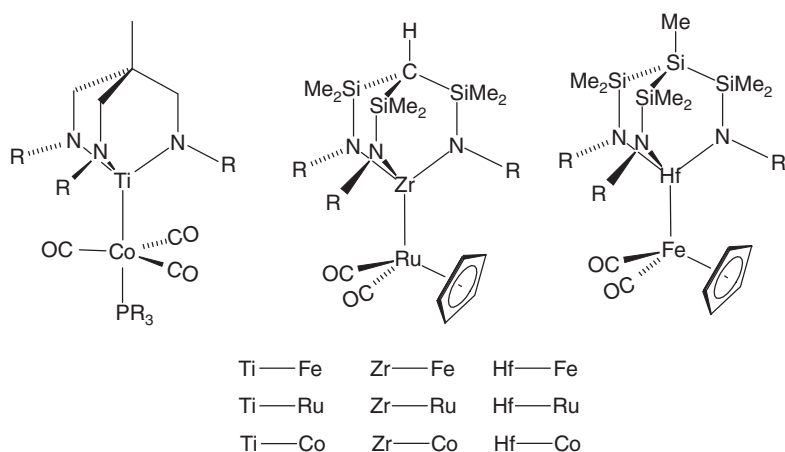


Figure 4.5 Unsupported group 4 metal early-late heterodinuclear complexes stabilized by tripodal amido ligands.

of the coordination spheres of the metal centers and, additionally, enforce a given coordination geometry. The tripodal amido ligands displayed in Figure 4.5 provided the key to a systematic program of complex synthesis [16, 23]. The ligand framework effectively shields the part of the coordination sphere opposite to the metal–metal bond, whereas the latter is kinetically protected by the peripheral (silyl or aryl) substituents at the nitrogen donor functions.

At least as important as this kinetic stabilization of the dinuclear complexes is a significant thermodynamic contribution to their stability, which is the result of the incorporation of the early transition metal into the rigid [2,2,2]-bicyclooctane cage structure of the tripod-amide unit. This geometric fixation destabilizes the potential fragmentation product, the triamidometal fragment. In the analogous systems containing monodentate anionic ligands at the early transition metal center, the $\{ML_3\}$ -fragment undergoes planarization upon cleavage of the metal–metal bond, a process that stabilizes the fragment. This planarization is suppressed in the tripod cage.

In order to have an estimate of the energetic contribution of this geometric relaxation of the early transition metal complex fragment, a theoretical study was carried out on the Ti–Co model complex

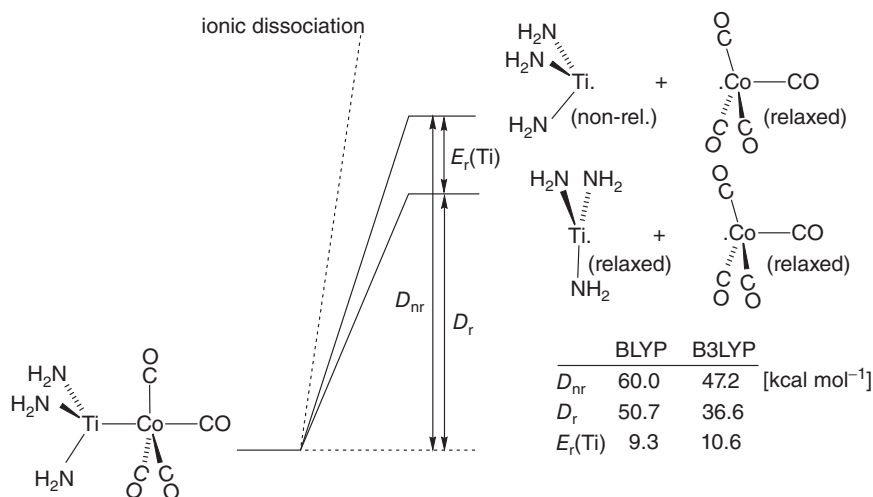


Figure 4.6 Schematic representation of the energetics associated with the homolytic dissociation of the metal-metal bond in $[(\text{H}_2\text{N})_3\text{Ti}-\text{Co}(\text{CO})_4]$ [16].

$[(\text{H}_2\text{N})_3\text{Ti}-\text{Co}(\text{CO})_4]$, which was already discussed in the previous section [16]. Figure 4.6 schematically represents the overall energetics for the dissociation into two neutral fragments. D_r and D_{nr} are the dissociation energies for the dissociation into, respectively, completely relaxed and partially nonrelaxed complex fragments. In the nonrelaxed case, the geometry of the Ti fragment was fixed to that of $[(\text{H}_2\text{N})_3\text{Ti}-\text{Co}(\text{CO})_4]$, while in both cases the Co fragment was energetically minimized [16].

As indicated in Figure 4.6, the planarization energy $E_r(\text{Ti})$ of the Ti fragment is about 10 kcal mol⁻¹. This represents an upper boundary of the hypothetical relaxation energy of the Ti fragment containing the tripod ligand, which is unable to achieve the planar geometry of the free $\text{Ti}(\text{NH}_2)_3$ fragment. Therefore, one can estimate that the tripod ligand thermodynamically stabilizes the Co-Ti complex by about 10 kcal mol⁻¹ with respect to fragmentation of the metal-metal bond. Since the early transition metal fragment is the same in the whole range of heterodinuclear complexes coordinated by tripodal amido ligands, this figure can be regarded as a general estimate of the thermodynamic stabilization of the complexes with respect to their mononuclear fragments.

The same strategy and ligand sets as described above for the synthesis of early-late heterodinuclear complexes involving group 4 metals have been recently successfully used for the preparation of stable U-Ru heterobimetallic compounds (see Chapter 3) [24].

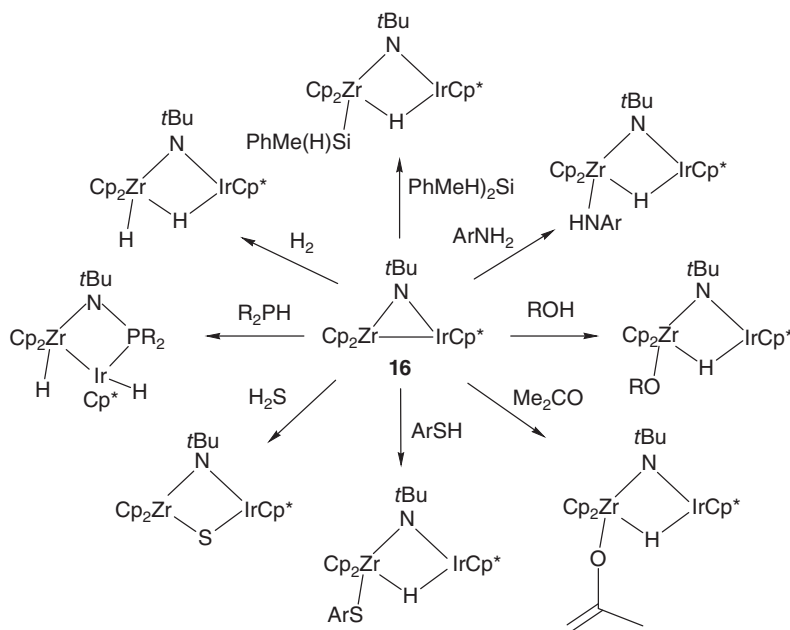
4.4

Basic Patterns of Reactivity Observed for Metal-Metal Bonded Early-Late Heterodinuclear Complexes

Early-late heterodimetallic complexes containing unsupported Zr-M bonds were found to undergo redistribution reactions of their metal fragments, such as the “conproportionation” of $[\text{Cp}_2\text{Zr}\{\text{RuCp}(\text{CO})_2\}_2]$ with $[\text{Cp}_2\text{ZrCl}_2]$ to give the dinuclear complex $[\text{Cp}_2(\text{Cl})\text{Zr}-\text{RuCp}(\text{CO})_2]$ or similar reactions involving the amido-stabilized complexes [10, 11, 25]. The scope of this complex fragment redistribution is limited. It was, for instance, not possible to obtain the heterotrimetallic complex $[\{\text{CH}_2(\text{CH}_2\text{NSiMe}_3)_2\text{Zr}\{\text{FeCp}(\text{CO})_2\}\{\text{RuCp}(\text{CO})_2\}]$ by the reaction of the ZrFe_2 with the ZrRu_2 complex [25].

The reactivity of polar metal-metal bonds toward organic substrates is of more general interest. As for many other types of heterodinuclear complexes, extensive reactivity studies were carried out with

the aim of establishing cooperative reactivity between the electronically very different reactive sites that may interact with the substrate. Essentially, two types of reactions are possible. The first involves the interaction of the metal–metal bond with substrates of no or low polarity, which are fragmented and transformed to a “polarized” form at the two metal centers. For example, this is the general pattern of the addition of H_2 or a silane to the Zr–Ir bond in Bergman’s heterodinuclear complex **16** (Scheme 4.6) [26]. Reactivity toward substrates that match the polarity of the metal–metal bonds is far more common. Examples in Scheme 4.6 are the reactions of alcohols, amines, thiols, ketones, and H_2S with the Zr–Ir complex.



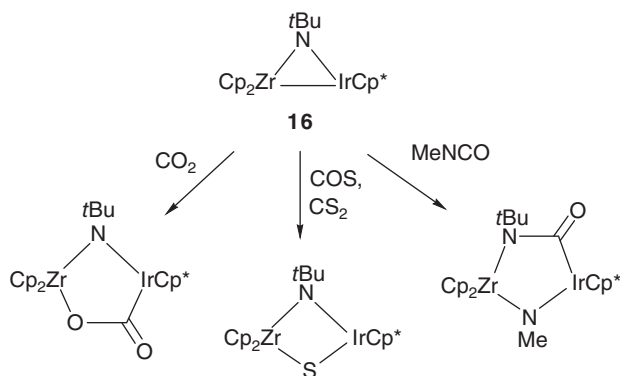
Scheme 4.6 Cooperative reactivity of the heterodinuclear complex **16** with nonpolar and polar substrates.

In the simplest case, heterodinuclear complexes will react as pairs of metal electrophiles and nucleophiles. Cooperative reactivity is particularly likely with polar substrates. In this case, the electropositive early transition metal center may react with the more Lewis-basic part of the substrate, while the nucleophilic late transition metal complex fragment will attack the more Lewis-acidic part of the substrate molecule. For metal–metal single bonds between the two metal centers, this interaction will go along with the cleavage of the metal–metal bond. In many cases, it is difficult to establish whether the scission of the metal–metal bond precedes the transformation of the substrate or whether it occurs at a later stage.

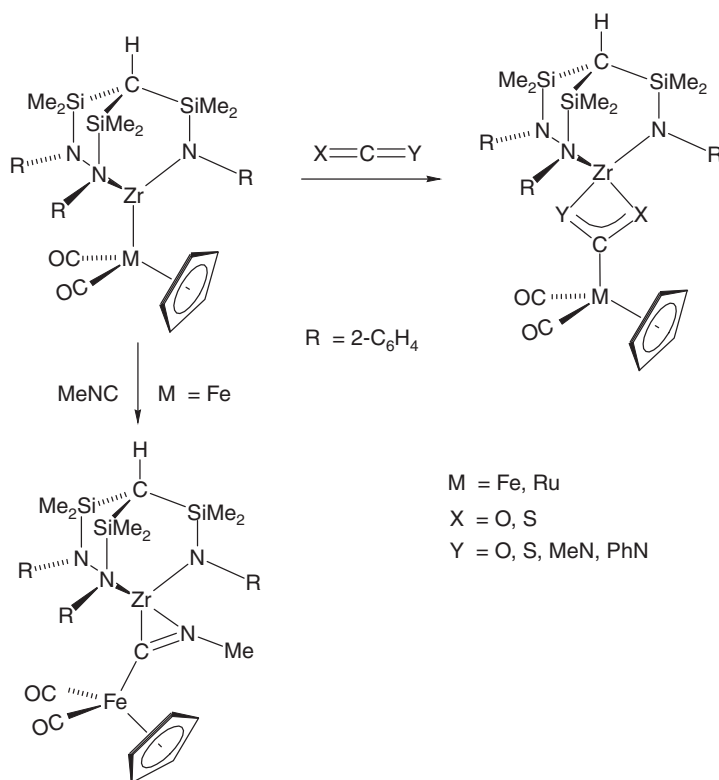
4.4.1

Insertions into Polar Metal–Metal Bonds and Subsequent Transformations

The simplest pattern of reactivity observed for early-late heterodimetallic compounds is the insertion of an unsaturated polar organic substrate into the metal–metal bond. The first such a reaction was reported by Culter and coworkers who showed that Casey’s Zr–M complexes insert CO_2 into their metal–metal bond [27], while Bergman *et al.* studied the reactions of the imido-bridged Ir–Zr complex **16** with CO_2 , COS, CS_2 , and MeNCS (Scheme 4.7) [28]. Whereas the insertion of CO_2 occurs



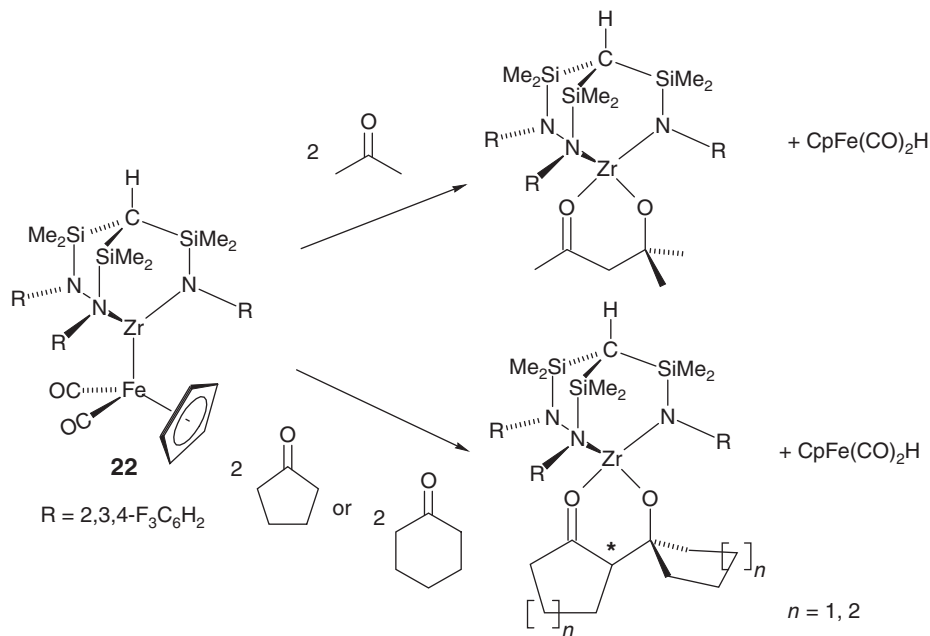
Scheme 4.7 Insertion and fragmentation of heteroallenes upon reaction with the Zr–Ir complex **16**.



Scheme 4.8 Insertion of isocyanides and heteroallenes into the unsupported metal–metal bond of Zr–M heterodinuclear complexes.

in the expected manner with the CO-unit bridging the two metal centers remain still linked by the imido ligand, the other heteroallenes undergo fragmentation.

The insertion of isocyanides provides another example of this reactive behavior. Insertion reactions of isocyanides and heteroallenes carried out with the tripod-stabilized early-late heterodinuclear complexes (represented in Figure 4.5) that led to stable products are summarized in Scheme 4.8.

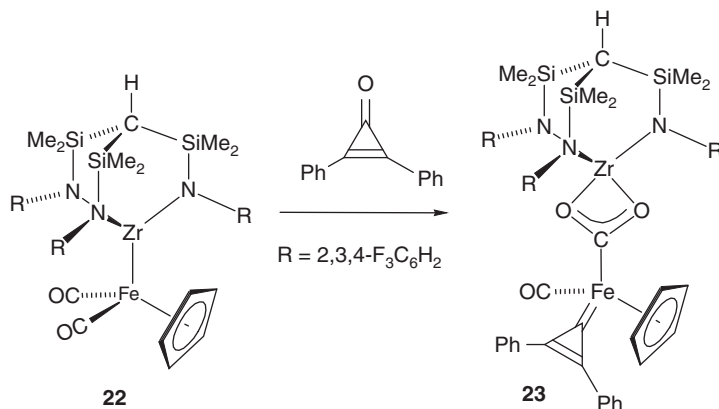


Scheme 4.9 Aldol coupling products obtained from the reaction of $[\text{HC}(\text{SiMe}_2\text{N}(2,3,4\text{-F}_3\text{C}_6\text{H}_2))_3\text{Zr-FeCp}(\text{CO})_2]$ with ketones.

The products of the simple insertion of an organic molecule (or a functional group in it) into the polar metal–metal bond are rarely isolable and, most often, further transformations follow this initial step. In the simplest case, these subsequent transformations closely mimic those which the organic molecules undergo with “classical” nucleophiles and electrophiles [29]. Aryl aldehydes react with Zr–M heterodinuclear complexes according to the pattern of a Cannizzaro or Tishchenkov reaction, yielding the aroyl–M complex and the benzoxyzirconium derivative [30a]. Finally, the reaction of $[\text{HC}(\text{SiMe}_2\text{N}(2,3,4\text{-F}_3\text{C}_6\text{H}_2))_3\text{Zr-FeCp}(\text{CO})_2]$ with ketones gave the aldol coupling products ligated to the Zr center and equivalent amounts of the hydridoiron complex $[\text{CpFeH}(\text{CO})_2]$ (Scheme 4.9). The hydrido complex is believed to be formed in the first reaction step following the insertion of the carbonyl group into the metal–metal bond, yielding an extremely reactive enolate, which in turn rapidly undergoes aldol coupling with a second molecule of ketone [30a].

Most transformations leave the ligand already present in the starting materials unchanged; however, the carbonyls coordinated to the late transition metal may participate directly in the conversion of a substrate. This type of cooperativity has been found in a series of oxygen transfer reactions. The most remarkable of these is the reaction of the Zr–Fe complex **22** with 1,2-diphenylcyclopropenone giving the carbene–iron complex **23** in which the oxidized carbonyl ligand links the two metal centers as a $\mu\text{-CO}_2$ unit (Scheme 4.10) [30]. The result is thus formally a reduction of a ketone by CO, yielding a carbene and CO_2 , a reaction that is thermodynamically driven by the formation of two Zr–O bonds and the stable CO_2 unit in the product.

Similar oxygen transfer reactions have been observed with sulfoxides and other element oxides, yielding the late transition metal-bound thioethers or the corresponding reduced ligands [31]. The pattern of the oxygen transfer has been established by ^{17}O and ^{13}C labeling studies in all these cases [23d]. That both metal centers participate in the conversion of the element oxide is evident from the inability of either of the metal complex fragments linked by the Zr–M bond to affect these transformations on their own.



Scheme 4.10 Deoxygenation of 1,2-diphenylcyclopropanone giving the carbene-iron complex **23**.

Rapid transfer of oxygen has also been observed in reactions of $[\text{Cp}_2\text{Zr}(\mu\text{-NtBu})\text{Ir}(\text{C}_5\text{Me}_5)]$ with pyridine N-oxide, nitrous oxide, and styrene oxide [28]. However, the result of these reactions is the formation of oxo-bridged heterobimetallic complexes.

4.4.2

Reactivity of Phosphinoamide-Bridged Zr–Co Heterobimetallic Complexes

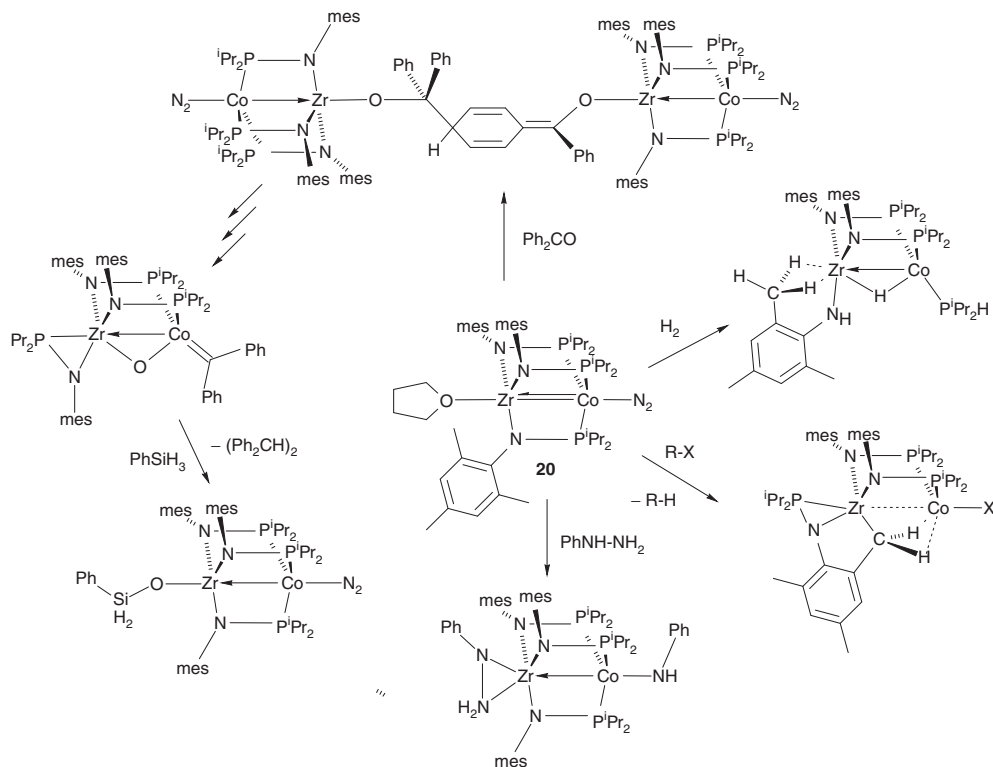
An interesting reactive behavior involving both the metal–metal bond and transformations of the bridging phosphinoamide ligands has been recently reported by Thomas *et al.* for Zr–Co complexes $[(\text{N}_2)\text{Co}(\text{Pr}_2\text{PNMe}_3)_3\text{Zr}(\text{thf})]$ (**20**) and $[\text{Co}(\text{Pr}_2\text{PNMe}_3)_3\text{Zr}(\text{thf})]$ (**21**) [22]. Selected examples for these transformations are summarized in Scheme 4.11 [32]. Notable reactions include the C–O bond cleavage of benzophenone, which is subsequently transformed to a Co-bonded carbene ligand [33]. Of particular interest has been also the cleavage and subsequent (reductive) conversion of CO_2 as represented in Scheme 4.12 [34]. In general, both the bridging ligands and the metal atoms interact with the substrates, and it is, therefore, difficult to differentiate between the role of the metal–metal bond and the coordination sphere.

The Zr–Co complex $[(\text{N}_2)\text{Co}(\text{Pr}_2\text{PNMe}_3)_3\text{Zr}(\text{thf})]$ (**20**) has been found to catalyze the hydrosilylation of ketones. Since the direct interaction of the complex with benzophenone gave rise to a metal-bonded ketyl radical, a reaction mechanism involving such a radical species has been postulated by Thomas and coworkers [35]. The same complex was also found to be a precatalyst for Kumada–Corriu–Tamao coupling reactions [36].

4.5

Early-Late Heterobimetallic Complexes of Group 4 Metals as Potential Catalysts

The role that a direct bonding interaction between the late transition metal component in a heterogeneous catalyst and the early transition metal support material may play for TiO_2 -supported contacts (“strong metal-support interaction”) inspired the first systematic study on the reactivity of directly metal–metal bonded early-late heterobimetallic compounds. This was carried out by Casey and coworkers in connection with the renewed interest in the chemistry of the Fischer–Tropsch process that emerged in the wake of the oil crisis in the 1970s [37]. A concept for a potential catalytic system was formulated in Casey’s group and based on the accessibility of a heterometallic dihydrido complex containing one “hydridic” M–H bond to a high oxidation state early transition metal along with an acidic hydride at the late transition metal center.

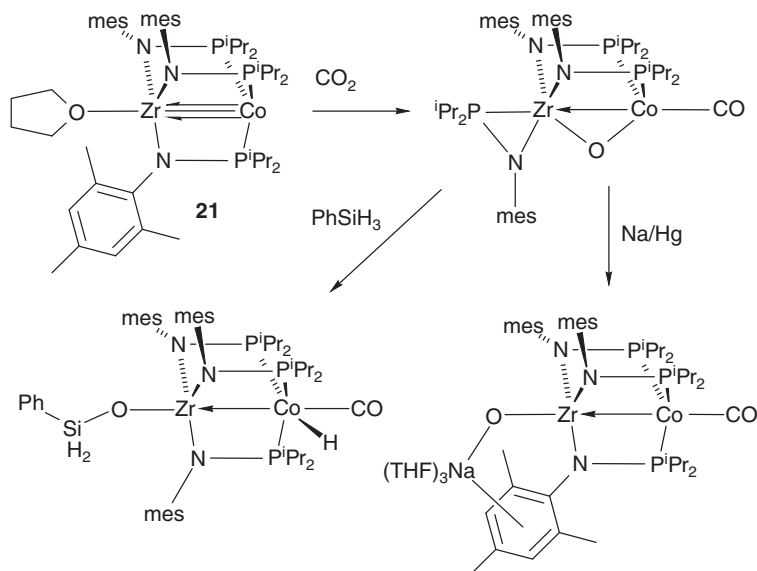


Scheme 4.11 Reactivity of the Zr–Co complex **20** involving the metal–metal bond as well as transformations of the bridging phosphinoamide ligands mes=mesityl.

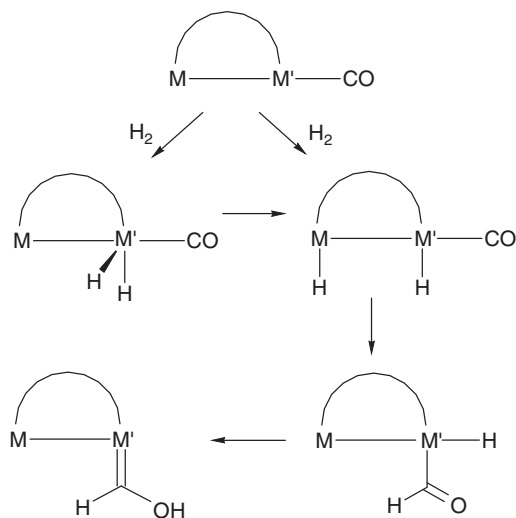
Ideally, the two metal centers were to be linked by a bridging ligand that would ensure their proximity even after the metal–metal bond was cleaved. The combination of two differently polarized metal hydrides, generated by activation of H_2 , would then provide the appropriate “reagent” for hydrogenation of a metal-bound CO molecule, possibly along the route proposed by Casey, which is outlined in Scheme 4.13. The experimental study carried out throughout the 1980s mainly focused on the unsupported Zr–Ru heterodimetallic complexes **9** and **10**.

While the original objective of H_2 splitting, generating a pair of hydridic and acidic hydrides and the subsequent reduction of CO, was not achieved with these complexes, this work led to the discovery of some fascinating organometallic chemistry [37]. One example of a reaction sequence involving the conversion of CO in compound **10** is given in Scheme 4.14 [38].

There are a considerable number of reports of catalytic activity of early-late heterobimetallic complexes, which is believed to differ substantially from that of the mononuclear and/or homometallic reference systems. The hydrosilylation of ketones and the Kumada couplings catalyzed by the Zr–Co complex **20** have already been mentioned earlier. Previously, Fandos *et al.* reported the Ti/Rh heterometallic complex $[(C_5Me_5)Ti(\mu-O)_3\{Rh(COD)\}_3]$, which they regarded as a molecular model for SMSI in TiO_2 -supported Fischer–Tropsch catalysts. In the presence of this material, CO was indeed reduced at 250 °C and 20 bar (H_2 :CO 3:1) to give, *inter alia*, methane and short-chain alcohols. However, neither the catalytically active species nor the importance of a possible bonding interaction between the metal centers has been established [39].

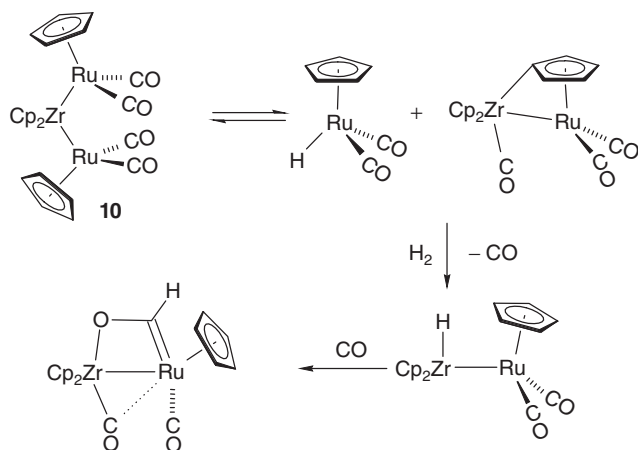


Scheme 4.12 Reactivity of the Zr-Co heterobimetallic complex **21** toward CO_2 : C–O cleavage and subsequent reductive transformation.



Scheme 4.13 Mechanistic scheme of a nonsymmetrical activation of H_2 across a polar metal–metal bond in an early-late heterodinuclear complex (containing a bridging ligand) and the subsequent hydrogenation of coordinated CO.

The area of early-late transition metal complex catalysis has been reviewed recently [40]. While there is an ever-growing number of studies in this field, a conclusive and unambiguous example for cooperativity of the two $\text{M}-\text{M}'$ -bonded metal centers is still lacking.



Scheme 4.14 Reaction of a trinuclear complex **10** with H₂ and CO resulting in the transfer of a hydride to a carbonyl ligand.

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5

Group 5 Metal–Metal Bonds

Sundargopal Ghosh and Dipak Kumar Roy

5.1

General Remarks

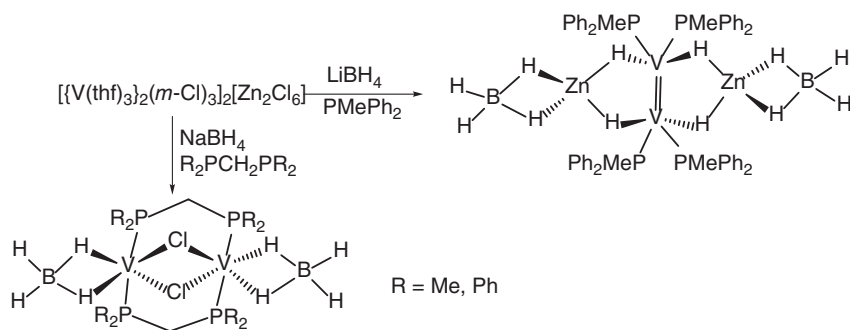
Discrete single and multiple transition metal–metal bonds constitute some of the most novel structural groups in current inorganic and organometallic chemistry with metal–metal quadruple bonds having no analog in non-transition-metal chemistry. Metal–metal bonds are found in wide varieties of dinuclear and polynuclear species with or without bridging ligands. An extensive study of multiply bonded dinuclear complexes [1–5] has widened the research field from synthetic to theoretical chemistry. Compared to extensive chemistry of analogous group 6 metals [1], metal–metal complexes involving group 5 metals were relatively rare. The relative scarcity of dinuclear chemistry for the early transition metals is partly due to the presence of limited appropriate starting materials in lower oxidation states [6, 7] and the technical difficulties in handling the high-valent metal halide precursors.

Nevertheless, since late 1970s, there has been a continuous growth in this area of early transition metal organodimetallic chemistry led mostly by the pioneering work of McCarley [8–14], Brown [15, 16], Cotton [1–5], Allen and Naito [17], Sattelberger *et al.* [18–23], Schrock [24–32], and Hubert-Pfalzgraf *et al.* [33–38] and their coworkers. This includes some remarkable and exceptional reactivity in organometallic and metal–metal multiple bond chemistry [1, 8, 9, 11] comprising the first examples of direct hydrogenation of a metal–metal double bond [18, 20, 21, 23], migratory insertion of carbon monoxide into a metal–hydride bond to yield a formyl species [31, 32], reductive coupling of carbon monoxide and intermolecular C–H bond activation by a metal–metal multiple bond [36, 38]. It is also worth noting that a large number of binuclear group 5 metal complexes have been isolated and structurally characterized in the last few decades, which include chalcogenide, triple-decker, paddlewheel, metallaborane, metallaheteroborane complexes, and more. This chapter reviews the synthesis, structure, and reactivity of distinct group 5 metal–metal bonded dinuclear and coordinatively unsaturated organodimetallic complexes.

5.2

Vanadium Complexes

In spite of a large amount of work in the area of divanadium compounds' preparation, nonorganometallic metal–metal bonded divanadium complexes are limited due to the absence of suitable metal–metal bonded divanadium precursors. However, a series of synthetically useful divanadium precursors of general formula $[(VL_3)_2(\mu-X)_3]^+$ ($L = \text{thf}$, 3-methyltetrahydrofuran, and PMe_3) have been prepared and structurally characterized [39–42]. The divanadium(I) species $[\{V(\text{PMePh}_2)_2\}_2(\mu-\text{H}_2\text{ZnH}_2\text{BH}_2)]$ has been prepared by borohydride reduction of the cation $[(V(\text{thf})_3)_2(\mu-\text{Cl})_3]^+$ in the presence of $[\text{PMePh}_2]$ (Scheme 5.1) [43]. Interestingly, Cotton and coworkers prepared the methylenebis(phosphine) analogs by nonreducing method with the same



Scheme 5.1

vanadium precursor [44, 45]. Henkel [46], Holm [47], Christoua [48], and coworkers reported the preparation of divanadium 1,2-ethanedithiolate complexes by the reaction of $[\text{VCl}_3]$, either with the dithiol or the disodium salt, followed by cation (Et_4N^+ or Ph_4P^+) exchange reaction.

5.2.1

Carbonyl Complexes

Transition metal carbonyl compounds constitute one of the most prominent classes of complex in inorganic and organometallic chemistry [49–53]. The reaction of vanadium hexacarbonyl with aromatic solvents has been reported by Calderazzo [54] to produce complexes of the type $[(\text{arene})\text{V}(\text{CO})_4]^+[\text{V}(\text{CO})_6]^-$. Churchill and coworkers found that treatment of $[\text{V}(\text{CO})_6]$ with benzene produced a crystalline material of formula $[(\text{C}_6\text{H}_6\text{V})(\text{CO})_2]_2$ with a poor quality of X-ray data. The toluene analog has been prepared as $[(\text{C}_6\text{H}_5\text{CH}_3\text{V})(\text{CO})_4]_2$ from $[\text{V}(\text{CO})_6]$, which has been hypothesized to possess a V–V triple bond [55]. Compound $[\text{Cp}(\text{OC})\text{V}(\mu, \eta^2\text{-CO})_2\text{V}(\text{CO})_2\text{Cp}]$ [56–61] was first reported by Fischer and Schneider [56] in 1970 via protonation of vanadium carbonyl dianion. The same compound was also prepared by photolysis of $[\text{CpV}(\text{CO})_4]$ [59]. Cotton and coworkers revealed the X-ray structure of $[(\text{CpV})_2(\text{CO})_5]$, which has been synthesized from $[\text{CpV}(\text{CO})_4]$. As shown in Figure 5.1, in $[(\text{CpV})_2(\text{CO})_5]$ one of V atoms (V(1)) contains a total of 16 electrons, while the other one (V(2)) has a total of 14 electrons. From this, it is clear that there is a metal–metal bond; however, its order is uncertain. It appears that V(1)–V(2) distance is shorter than the expected single bond distance, but it is too long to be called a triple bond [57]. Another divanadium complex, $[\{\text{V}(\text{CO})_4\}_2(\mu\text{-PMe}_2)_2]$ with a V–V bond has been reported by Vahrenkamp [62]. Although the X-ray structure of the molecule showed a long V–V separation, according to electron counting, it was interpreted as a double bond and the calculation by Hoffmann and coworkers reinforced an approximate double-bond character [63]. Ligand substitution reactions with tertiary phosphines and arsines afforded new organodivanadium derivatives with the replacement of either one or two carbonyl ligands [64]. Diphosphine and distibine organodivanadium complexes with bridging $[\text{E}_2\text{R}_4]$ ($\text{E} = \text{P, Sb}$) ligands have been reported by Rehder and coworkers [65].

5.2.2

Amido, Imido and Nitride Complexes

Bradley and Lappert pioneered the use of anionic organic amides as supporting ligands in transition metal chemistry [66, 67]. However, early transition metal amides remained relatively young field until a renewal of interest encouraged the development of this field [68–80]. Several features make these anions attractive particularly as an alternative to other ligand systems. As described

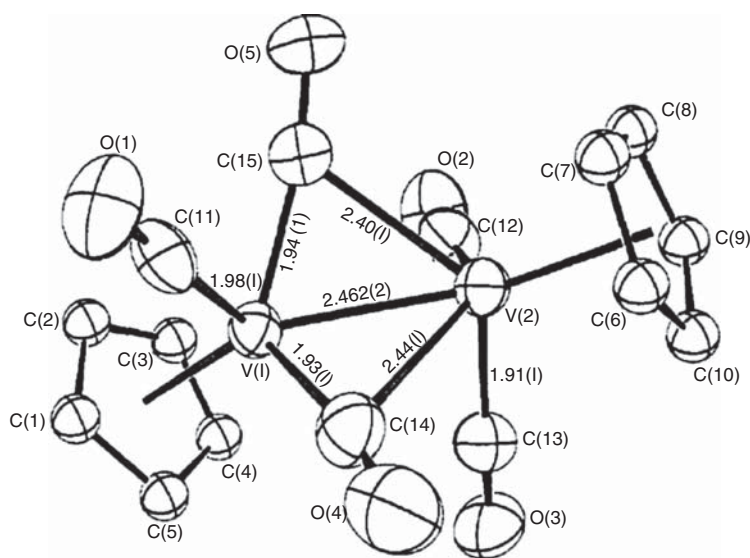
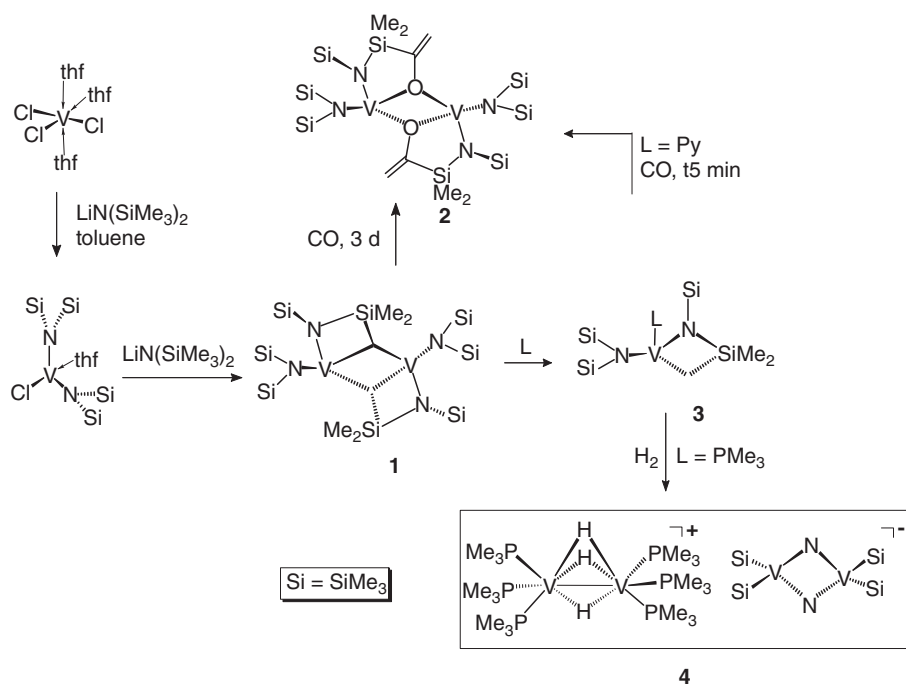


Figure 5.1 ORTEP drawing of the $(\text{C}_5\text{H}_5)_2\text{V}_2(\text{CO})_5$. (Reprinted with permission of American Chemical Society from Ref. [57].)

in Scheme 5.2, the reaction of $[\text{VCl}_3(\text{thf})_3]$ with 3 equiv. of $[\text{LiN}(\text{SiMe}_3)_2]$ does not produce the expected homoleptictris(amido) complex [81], as observed when $[\text{VCl}_3(\text{NMe}_3)_2]$ was used as starting material. Instead, the reaction afforded green monomeric $[\text{V}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Cl}(\text{thf})]$, which on further reaction with $[\text{LiN}(\text{SiMe}_3)_2]$ produced dimeric $\{[(\text{Me}_3\text{Si})_2\text{N}]\text{V}(\mu\text{-CH}_2\text{SiMe}_2\text{N}(\text{SiMe}_3))\}_2$ **1** [82]. The structure of the divanadium complex **1** consists of two $[(\text{Me}_3\text{Si})_2\text{N}]\text{V}$ moieties bridged by two $\{\mu\text{-CH}_2\text{Si}(\text{Me})_2\text{N}(\text{SiMe}_2)\}$ units with a fairly short V–V distance (2.736(2) Å). The room temperature reaction of **1** with CO at atmospheric pressure generates blue crystals of $\{[(\text{Me}_3\text{Si})_2\text{N}]\text{V}(\mu\text{-O}(\text{C}=\text{CH}_2)\text{SiMe}_2\text{N}(\text{SiMe}_3))\}_2$, **2**, in 55% yield (Scheme 5.2) [83]. The crystal structure of complex **2** revealed an unprecedented V(III) dinuclear enolate complex. The two enolate moieties form puckered five-membered rings with two vanadium atoms and two shared oxygen atoms. The V–V distance of 3.126 Å in **2** is significantly longer than in complex **1**, and this lengthening of bond length also reflects magnetic moment values. The reaction of **1** with phosphine led to the formation of a monomeric phosphine adduct $\{[(\text{Me}_3\text{Si})_2\text{N}]\text{V}(\mu\text{-CH}_2\text{SiMe}_2\text{N}(\text{SiMe}_3))\}(\text{py})$, **3**, which on hydrogenolysis yielded complex **4** containing discrete $\{[(\text{Me}_3\text{P})_3\text{V}]_2(\mu\text{-H})_3\}^+$ and $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{V}_2(\mu\text{-N})_2\}^-$ ions [84]. The V–V distance (2.399(1) Å) suggests a direct metal–metal interaction in the cation part. The mixed-valent anion is also dinuclear and contains two bridging nitrido moieties. The hydrogenation of an amido complex $[\text{V}\{\eta^2\text{-C}(\text{Mes})=\text{NBU}^t\}_3]$ ($\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) led to the isolation of an amide complex $[\eta^2\text{-C}(\text{Mes})=\text{NBU}^t]\text{V}\{(\text{MesCH}_2\text{NBU}^t)\}_2$, which on thermal rearrangement resulted in a divanadium complex having a very short V–V distance (2.460(1) Å) that supports the $d^1\text{--}d^1$ metal–metal bond [85].

Reaction of $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{VCl}(\text{thf})\}$ with S_8 led to the formation of dinuclear diamagnetic complex $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{V}_2(\mu\text{-S})_2\}$, which has a V–V bond length of 2.857(1) Å [86]. The oxidation of $[\text{CpV}(=\text{NBU}^t)(\text{PMe}_3)_2]$ with S_8 , Se, Te, or I_2 produces imido-vanadium complexes $[\text{VCp}(\mu\text{-E})(\mu\text{-NBU}^t)]_2$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$), $[\text{VCp}(\mu, \eta^1\text{-E})(\mu\text{-NBU}^t)]_2$ ($\text{E} = \text{Se}, \text{Te}$), and $[\text{VCp}(\mu\text{-NBU}^t)\text{I}]$ [87, 88]. In $[\text{VCp}(\mu, \eta^1\text{-Te})(\mu\text{-NBU}^t)]_2$, two Te atoms are bridged to the V–V axis, in which the vanadium atoms are 2.4665(8) Å apart [87] (Figure 5.2). Both reduction and aryl/alkylation are involved in the reactions of aryl and alkyl Grignard reagents, with the less bulky terminal (imido) vanadium complex to form vanadium dimer species. These species are diamagnetic with a V–V bond length of 2.45–2.49 Å.



Scheme 5.2 Synthesis and reactivities of amide complexes.

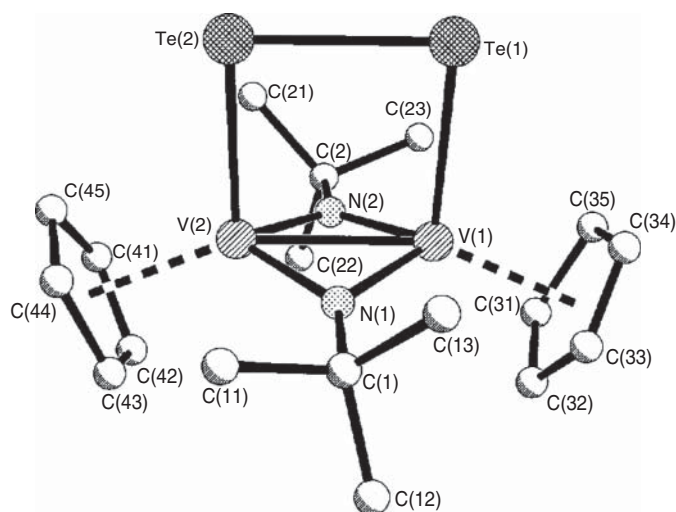


Figure 5.2 ORTEP drawing of the $[(\text{CpV})_2(\mu\text{-}\eta^1\text{-Te}_2)(\mu\text{-N}^i\text{Bu})_2]$. (Reprinted with permission of Wiley-VCH from Ref. [87].)

Reductive oligomerization of $[(C_5Me_4R) VX_3]$ or addition of $[(C_5Me_4R) SnBu_3]$ to $[VX_3L_3]$ ($L = thf, tht; X = Cl, Br$) yielded (peralkylcyclopentadienyl)vanadium(III) halides $[(\eta^5-C_5Me_4RV)_2(\mu-Br)_4]$, **5** and $[(\eta^5-C_5Me_4R)_3V_3(\mu-Cl)_6]$ ($R = Me, Et$), **6** [89]. In both structures, the vanadium atoms adopt four-legged piano-stool geometries. The solid-state structure of **5** exhibits a V–V bond (2.565(1) Å), while the spin-frustrated, antiferromagnetic **6** is a cyclotrimer with nonbonded V–V edge (3.3732 Å). Alternatively, complex **6** has been prepared by slight variations in the reaction conditions [90–92]. Treatment of **6** with $[Me_3SnF]$ afforded a tetrameric complex $[Cp^*V(\mu-F)_2]_4$, **7**, which has been confirmed by X-ray analysis. Four vanadium atoms in **7** are arranged at the vertices of a distorted tetrahedron with four long bridged edges of one F atom each with a V–F–V obtuse angle (mean 129.8°) and the other two short edges bridged by two F atoms with a right angle V–F–V arrangement (mean 90.5°). The mean length of the short edges is 2.84 Å, whereas that of the long edges is 3.63 Å [93].

Reduction of $[(thf)V(salophen)Cl]$ (salophen = *N,N'*-*o*-phenylenebis(salicylideneiminato)) with Na led to the dimerization of metallic species through two C–C bonds, which resulted in dimeric vanadium(III) complex joined by a V–V double bond (2.406(3) Å) [94]. Nitrido-bridged transition metal compounds have been the target of many researchers to develop synthetic routes to new transition-metal-containing materials. The reactive N–Si bonds of silylimido complexes have been engaged to prepare both the linear chain and bimetallic nitrido-bridged complexes. The stepwise reaction of $[Cp^*VCl_3]$ with excess $[Me_3SiN_3]$ in refluxing benzene or $[NaN_3]$ led to the formation of azido-bridged complexes, $[Cp^*VCl_2(\mu-N_3)]_2$, $[Cp^*VCl(N_3)(\mu-N_3)]_2$, and $[Cp^*V(N_3)_2(\mu-N_3)]_2$ (Table 5.1). The azide-rich binuclear complex $[Cp^*V(N_3)_2(\mu-N_3)]_2$ is also formed from pentane solution of $[Cp^*V(CO)_4]$ in the presence of excess $[Me_3SiN_3]$ in an open vessel. According to the X-ray analysis, molecules are centrosymmetric with a planar $[V(N_2)V]$ four-membered ring and a very long V–V distance (3.427 and 3.440 Å) [95, 96]. The oxidation of $[Cp^*V(\mu-Cl)_2]_3$ with $[Me_3SiN_3]$ generates the symmetric dimeric vanadium nitride complex $[Cp^*V(\mu-N)Cl]_2$ **8** in high yield [97, 90]. Compound **8** on reduction with alkali metals yielded $[Cp^*V(N_3)_2(\mu-N_3)]_2$, **9** (Scheme 5.3) having all three connected vanadium and nitrogen atoms [98, 99]. Cluster **9** has a short V–V and V–N distance (2.674(8) and 1.87(2) Å, respectively), indicative of a strong V–N bond, and it is very much similar to those of $[Cp^*Ti(N_3)_2(\mu-N_3)]_2$ (Ti–Ti = 2.788 Å, Ti–N = 1.939 Å) [100]. Complex **9** can reversibly be reduced to $[Cp^*V(N_3)_2(\mu-N_3)]_2^-$ by electrochemical methods.

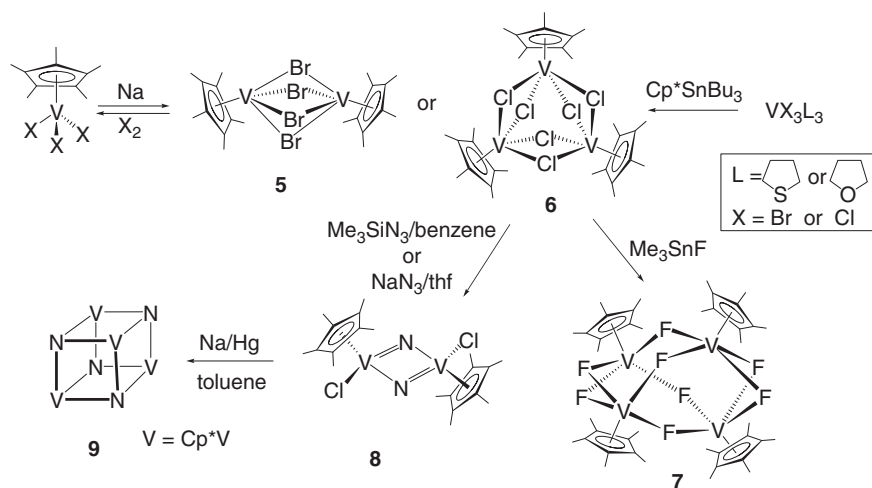
5.2.3

Hydride, Alkyl and Aryl Complexes

Hydrogenolysis of dimethyl pincer $[((Me_3Si)N=PPh_2)_2CH]VMe_2$ [101] derivative yielded a extremely air-sensitive, dinuclear hydride complex $[((Me_3Si)N=P(Ph)_2C(H)P(Ph)_2=N(SiMe_3))V]_2(\mu-H)_2$, which on oxidative addition to the styrene β -C–H bond afforded novel dinuclear trivalent vanadium complex $[((Me_3Si)N=P(Ph)_2C(H)P(Ph)_2=N(SiMe_3))V]_2-(H)(\mu-H)_2(\mu, \eta^1: \eta^2-CHCHPh)$, **11** [102]. The composition of **11** was elucidated by a solid-state structure determination study that shows two vanadium atoms bonded differently to a phosphinimide $[(Me_3Si)N=P(Ph)_2C(H)P(Ph)_2=N(SiMe_3)]^-$ anion. Consistent with the solid-state structure, the ^{51}V NMR spectrum showed two magnetically distinct vanadium environments (2003.7 and –290.3 ppm). The V–V distance is rather short (2.5074(16) Å) and possibly falls in the

Table 5.1 Spectroscopic and structural parameters of vanadium-nitrido complexes.

Complexes	δ^1H (ppm)	$\delta^{51}V$ (ppm)	$d[V-V]$ (Å)	References
$[Cp^*V(\mu-N)Cl]_2$, 8	2.05	–144	2.561(2)	[97, 90]
$[Cp^*V(\mu_3-N)]_4$, 9	1.75	19.2	2.674(8)	[98, 99]
$[Cp^*V(\mu-N)(N_3)]_2$, 10	1.80	–377	2.5633(14)	[90]



Scheme 5.3 Synthesis of vanadium-halide derivatives and their reactivities.

V–V bonding range. Complex **11** on reaction with ethylene under atmospheric pressure at room temperature generated dinuclear mixed-valence V(II)/V(III) trihydride derivative $[(\text{Me}_3\text{Si})\text{N}=\text{P}(\text{Ph})_2\text{C}(\text{H})\text{P}(\text{Ph})_2=\text{N}(\text{SiMe}_3)\text{V}]_2(\text{H})(\mu\text{-H})_3(\mu, \eta^1:\eta^2\text{-CHCHPh})$, **12**. The molecular connectivity was elucidated by an X-ray crystal structure [102].

Addition of $[\text{VCl}_2(\text{tmeda})_2]$ ($\text{tmeda} = N,N,N',N'$ -tetramethylenediamine) to *in situ* generated $[\text{Cy}_2\text{NLi}]$ gave a mixture of products from which a dinuclear ethylidyne complex $[(\text{Cy}_2\text{NV})_2(\mu_3, \eta^1\text{-O})(\mu_2, \eta^1:\eta^1\text{-CMe})]$, **13** was isolated [103]. This complex probably results from the unexpected fragmentation of tetrahydrofuran promoted by a vanadium(II) amide intermediate. The crystal structure shows that the complex consists of a *nido*-trigonalbipyramidal $[\text{V}_2\text{LiO}(\text{CMe})]$ core. Figure 5.3 depicts that the basal plane of the distorted square pyramid is bound by two vanadium atoms, the oxygen, and a bridging carbon atom of the ethylidyne unit. The rather short V–V distance ($\text{V}-\text{V} = 2.640(2) \text{ \AA}$) probably indicates a degree of metal–metal interaction [104]. A recent review on oxido vanadium complexes has explained the development of the synthetic protocols of μ -oxidodivanadium(V) compounds $[\text{LOV}^{\text{V}}-(\mu\text{-O})\text{-V}^{\text{V}}\text{O}(\text{Salen})]$ ($\text{L} = \text{L}^1\text{-L}^5$). The $[\text{V}_2\text{O}_3]$ core in these compounds has a rare type of twist-angular structure. The V–V separations ($3.7921(7) \text{--} 3.3084(6) \text{ \AA}$) are by far the largest in these compounds compared to their peers containing a $\{\text{V}_2\text{O}_3\}$ core [105]. Another interesting oxo-vanadium complex has been isolated with two mixed-valence metal centers of (V) and (IV). The V–V distance ($2.9875(10) \text{ \AA}$) is also similar to other related complexes [106].

Direct alkylation of arylimido complex $[\text{CpV}(\text{NAr})\text{Cl}_2]$ ($\text{Ar} = \text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$) with alkylating reagents generated different set of products through reduction/decomposition of the $[(\text{ArN}=\text{V})\text{Cp}]$ fragment (Scheme 5.4) [107]. For example, using Grignard reagent $[\text{MeMgBr}]$ affords the tetravalent complex **14** with two methyl groups bridging between the vanadium atom of the $[(\text{ArN}=\text{V})\text{Cp}]$ fragment and the core Mg atom [108]. In the presence of Et_2O and thf, $[\text{CpV}(\text{NAr})\text{Cl}_2]$ reacts with an excess of $[\text{MeMgCl}]$ to afford the paramagnetic mono μ -methyl complex $[\text{CpV}(\mu\text{-NAr})_2(\mu\text{-Me})]$, **15**. The crystal structure of **15** consists of a single methyl and two arylimido groups bridging between two $[\text{CpV}]$ units. The V–V distance of $2.324(1) \text{ \AA}$ is within the range of a bonding interaction. Another similar imido complex $[\text{CpV}(\mu\text{-N-}p\text{-tolyl})\text{Me}]_2$, **16**, having a V–V distance of $2.5095(6) \text{ \AA}$ has been reported [108]. The complex $[(\text{CpV})_2(\mu, \eta^2\text{-C}_4\text{H}_8)_2]$, which has been synthesized by the reaction of cyclopentadienyl(η^6 -naphthalene)vanadium with excess of ethylene, exhibits a very interesting bonding with four- to fivefold coordinated bridging C atoms and a small V–V distance ($2.315(1) \text{ \AA}$) [109].

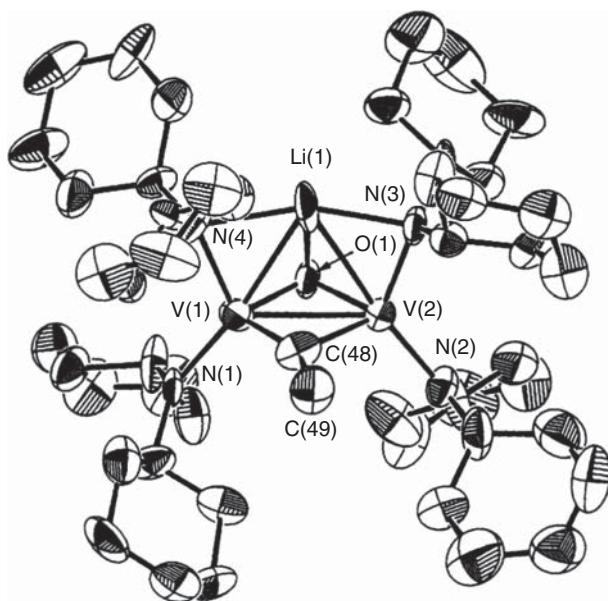
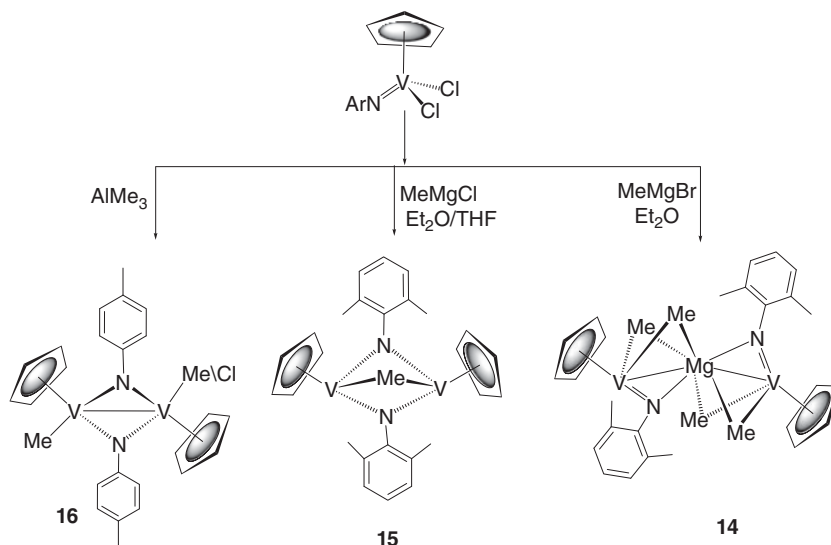


Figure 5.3 ORTEP drawing of the $[(C_2NV)_2(\mu_3,\eta^1-O)(\mu_2,\eta^1:\eta^1-CMe)]$. (Reprinted with permission of Royal Society of Chemistry from Ref. [104].)



Scheme 5.4 Alkyl and arylation of imido complexes.

5.2.4

Chalcogenide Complexes

Chalcogenide clusters have opened many avenues for their exploration [110, 111]. Starting from the 1960s, both solid-state and coordination chemists have worked extensively to enrich this field to mature enough to summarize pertinent work in this chapter [112]. In $[PV_2S_{10}]$, the cluster has

Table 5.2 Characteristic structural data of vanadium chalcogenide complexes.

Complexes	$d[M-M]$ (Å)	$d[E-E]$ (Å) ^{a)}	References
$[Cp^*V(CO)_2(\mu-SPh)]_2$	3.07	2.78	[130]
$\{[CpV(\mu-SePh)]_2(\mu-Se)\}$, 18	2.74	3.22	[131]
$[Cp^*V(CO)_2(\mu-TePh)]_2$	3.29	3.19	[130]
$[(^iPrCp)_2V_2S_4]$	2.610	2.027	[125]
$[(MeCp)_2V_2S_4(C_2(CF_3)_2)]$	2.574	2.040	[125]
$[(CH_3CS)_4V_2S_4]$	2.800	1.997	[117]
$[(MeCp)_2V_2S_3Fe(CO)_3]$	2.510	na ^{b)}	[132]
$[(MeCp)_4V_4S_4]$	2.873	na ^{b)}	[133]
$[(MeCp)_4V_4S_4][BF_4]$	2.854	na ^{b)}	[133]
$[(^iBu_2NCS)_4V_2(S_2)_2]$	2.851	1.998	[115]
$[(MeCp)_5V_5S_6][(TCNQ)_2]_3$ ^{c)}	3.110	2.77	[134]

a) E = S, Se, Te.

b) na = no E–E bond.

c) TCNQ = tetracyanoquinodimethane.

a 1D array in which the $[V_2S_4]^{4+}$ moiety ($V-V=2.852$ Å) is connected through extra $[S_2]^{2-}$ and $[P_2S_8]^{4-}$ groups [113]. The vanadium chalcogen cluster of general formula $[V_2(E_2)_2X_4]$ can be synthesized through various synthetic routes [114–119]. The selenium analog $[V_2(Se_2)_2]^{4+}$ can be obtained from anionic $[V_2Se_{13}]^{2-}$, produced from $[NH_4VO_3]$, $[Et_4NCl]$, and $[(Me_2OctSi)_2Se]$. In this unique cluster core, two vanadium atoms are coordinated by two terminal Se_2^{2-} ligands and bridged by a Se_5^{2-} chain with a $V-V$ distance of $2.779(5)$ Å, which is shorter than that of $[V_2(S_2)_2]^{4+}$ analogs [120].

Two vanadium atoms, bridged by $\mu-E$ units, are found in $[V_2(\mu-E)_2(NSiMe_3)_2]$ derivatives. These complexes can be made from $[V(N(SiMe_3)_2)_2Cl(thf)]$ and S_8 or from $[V(N(SiMe_3)_2)_2Cl(thf)]$ and $[LiSeC(SiMe_3)_3]$ [86, 121]. The affinity of V for oxygen is very well known and accordingly complexes $[V_2O_2(\mu-S)_2(Et_2NCS_2)_2]^{2-}$ ($V-V=2.78-2.81$ Å) [122], $[V_2O_2(Se)_2(Se_4)_2]^{2-}$ ($V-V=2.90-2.96$ Å), and $[V_2O_2(\mu-Se)_2(Se_2)(Se_4)_2]^{2-}$ ($V-V=2.958(7)$ Å) [123] are prepared, where two monochalcogenide ligands are bridged between two $[VO]^{2+}$ ions and the bidentate moieties such as $[Et_2NCS_2]^{2-}$, $[Se_4]^{2-}$, or $[Se_2]^{2-}$ are coordinated to $[VO]^{2+}$. In complex $[V_2(O)(S)_4(edt)]^{3-}$ (edt = ethanedithiol; $V-V=2.977(1)$ Å), the $[VO]^{2+}$ ion linked to edt^{2-} and VS_4^{3-} ligands in the coordination sphere [124].

A chalcogen complex $[(RCp)_2V_2S_4]$ ($R = ^iPr$, $V-V=2.610(1)$ Å, Table 5.2) has been identified [125] by sulfur abstraction from $[(RCp)_2V_2S_5]$ [125], **17**, or by reacting $[(RCp)V(CO)_4]$ with elemental sulfur [126]. The corresponding selenide analog having Cp^* as ancillary ligand has been prepared in a similar way [125]. One of the bridging chalcogens (E) can be replaced by oxygen, giving $[(RCpV)_2(E_2)(E)(O)]$ ($E = S, Se, Te$). These oxo-chalcogenido clusters are formed as side products from reactions between vanadium carbonyls and a chalcogen [127]. The chalcogen-rich cluster $[(MeCp)_2V_2S_5]$ ($V-V=2.658(1)$ Å), synthesized from $[(MeCp)_2VS_5]$ in refluxing thf, has a $\mu-E$ bridge, a $\mu-\eta^2-E_2$ bridge, and $\mu-\eta^1-E_2$ bridge (Figure 5.4) [128, 129]. The reactivity of $[(^iPrCp)_2V_2S_4]$ with an alkyne has been reported (Scheme 5.5) [125].

The dichalcogenide ligands of the type $[E_2R_2]$ or $[REH]$, ($E = S, Se, Te$; $R = Me, Ph$), are known to react with group 5 carbonyls such as $[Cp^*V(CO)_4]$, $[CpV(CO)_4]$, or $[Cp^*Ta(CO)_4]$ to yield dinuclear carbonyl complexes $[CpM(CO)_2(\mu-ER)]_2$ and noncarbonyl complexes $[CpM(\mu-ER)_2]_2$ ($M = V, Ta$; $E = S, Se, Te$) under drastic reaction conditions [130, 135]. In contrast, reaction of $[Cp_2VCl_2]$ with $[Ph_2Se_2]$ yielded $\{[CpV(\mu-SePh)]_2(\mu_3-Se)\}$, **18** [131]. The X-ray analysis of the structure reveals two $\{SePh\}$ moieties and one selenium ($Se3$) are bridged to two vanadium atoms (Figure 5.5). Each vanadium atom is in an elongated tetrahedral coordination environment with the Cp ligand occupying

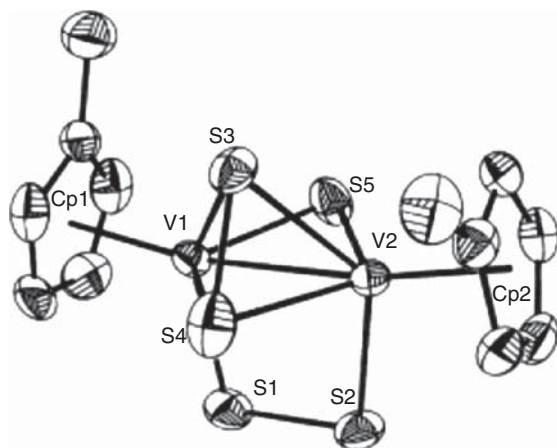
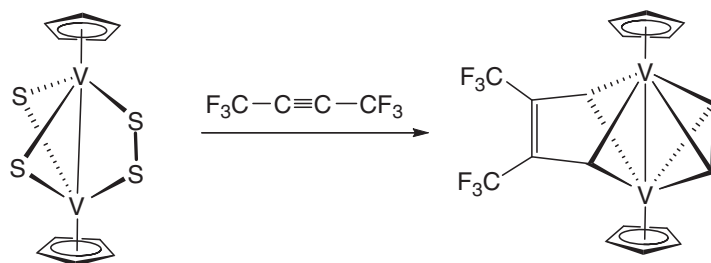


Figure 5.4 ORTEP drawing of the $[(\text{MeCp})_2\text{V}_2\text{S}_5]$. (Reprinted with permission of American Chemical Society from Ref. [128].)



Scheme 5.5

the apical position and the two coordination polyhedra sharing a common basal plane comprising three bridging Se atoms. The vanadium atoms are joined by a V–V single bond (2.7435(6) Å).

5.2.5

Vanadaboranes

There has been a significant growth in metallaborane chemistry [136–141] in which three areas stand out: (i) the chemistry of monoboranemetallaborane especially the metal borides explored by Housecroft [138], (ii) the rational and high yield routes to metallaboranes by sequential cluster build up reaction from monoboranes and cyclopentadienyl metal halides, developed by Fehlner *et al.* [142], and (iii) the development of macropolyhedral chemistry investigated mostly by Kennedy [143, 144]. Our discussions of this area, which is a hybrid of polyhedral metal compounds and boron hydrides [136, 141, 142, 145–150], will be limited to metallaborane clusters of group 5 metals. Despite the availability of metallaboranes of group 6–9 metals [151–161], examples of group 5 dimetallaboranes are limited [162, 163]. Vanadaborane clusters are even scarcer, and only a few crystallographically characterized clusters are known; [162, 164] the first divanadaborane cluster $[(\text{CpV})_2(\text{B}_2\text{H}_6)_2]$, **19**, was isolated and structurally characterized only in 2009 by Ghosh and coworkers from the fast metathesis of $[\text{Cp}_2\text{VCl}_2]$ with borane reagents [165]. Compound $[(\text{CpV})_2(\text{B}_2\text{H}_6)_2]$ is described as an edge-fused $\{\text{V}_2\text{B}_2\}$ tetrahedra (Figure 5.6) or as a bis- $[\text{B}_2\text{H}_6]^{2-}$ complex of $[\text{CpV}]_2^{4+}$, with 6 skeleton electron pairs or 44-cluster valence electrons, giving each V center a formal +3 oxidation state. The V–V distance is 2.787(2) Å and the V–H distances for the V–H–B bridges average 1.779 Å. It displays a

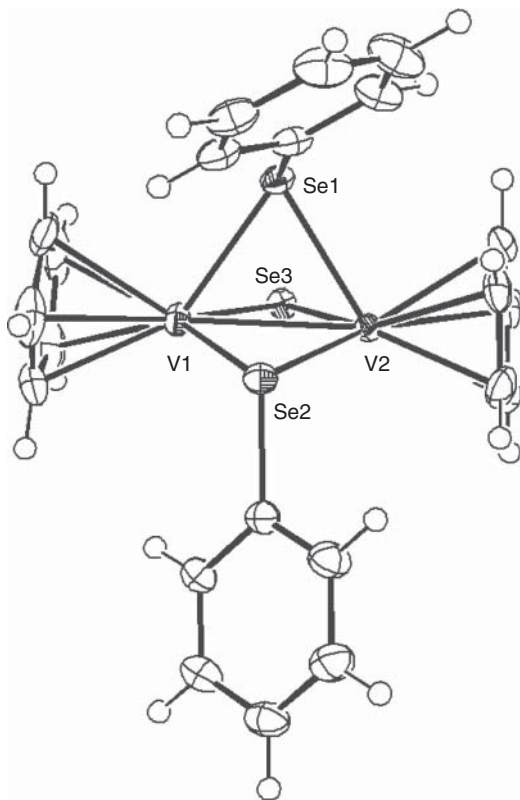


Figure 5.5 ORTEP drawing of the $[\{\text{CpV}(\mu\text{-SePh})\}_2(\mu_3\text{-Se})]$. (Reprinted with permission of Elsevier from Ref. [131].)

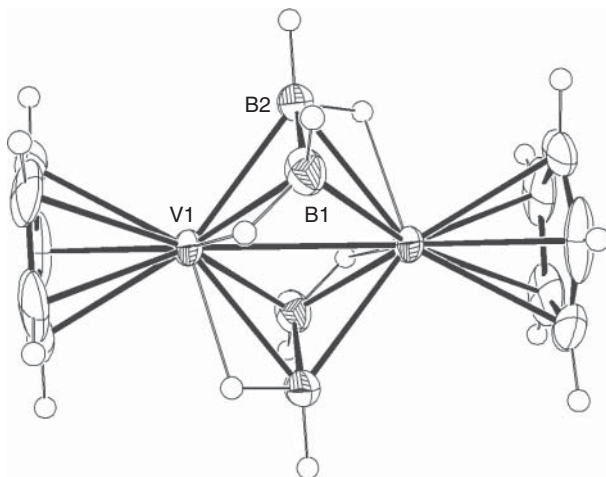


Figure 5.6 ORTEP drawing of the $[(\text{CpV})_2(\text{B}_2\text{H}_6)_2]$. (Reprinted with permission of Wiley-VCH from Ref. [165].)

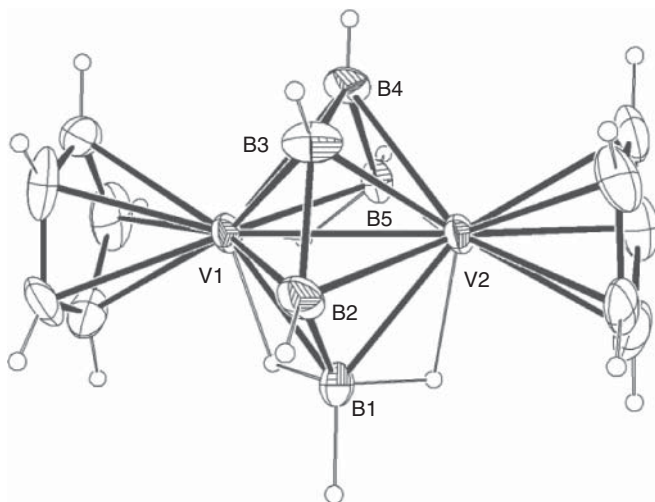


Figure 5.7 ORTEP drawing of the $[(\text{CpV})_2\text{B}_5\text{H}_{11}]$. (Reprinted with permission of Wiley-VCH from Ref. [166].)

single resonance in the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum ($\delta = 1.7$ ppm), which broadens on coupling with ^1H , indicating a highly symmetrical structure in solution.

After the isolation of the first divanadaborane, $[(\text{CpV})_2\text{B}_5\text{H}_{11}]$ **20** was synthesized from the same vanadium precursor with modifications to reaction procedure [166]. The ^{11}B NMR spectrum of **20** displays three resonances in the ratio of 1 : 2 : 2, indicating the presence of two pairs of equivalent boron atoms and a unique boron atom. The solid-state structure of **20**, shown in Figure 5.7, confirms the geometry that resembles a hexagonal bipyramid with a missing equatorial vertex or it can be described as the trigonal-bipyramidal $\{\text{M}_2\text{B}_3\}$ unit capped by two BH_3 fragments over the M_2B faces. This interpretation implies the presence of a V–V single bond, and the bond distance of $2.7604(10)$ Å is also consistent with this. Several $[\text{M}_2\text{B}_5]$ ($\text{M} = \text{V}, \text{Ta}, \text{Cr}, \text{Mo}, \text{W}, \text{Re}$) cores have been synthesized, which are discussed in Section 5.4.5.

5.2.6

Vanadaheteroboranes

With modified reaction conditions, $[(\text{CpV})_2\text{B}_3\text{H}_8(\mu_3\text{-OEt})]$ **21** has been isolated [166]. The molecular structure clearly shows that one ethoxy group is bound to two V metal atoms and one B atom (Figure 5.8). The V1–V2 bond length ($2.7589(10)$ Å) is slightly shorter than that in $[(\text{CpV})_2(\text{B}_2\text{H}_6)_2]$. The sharp ^{11}B NMR resonance at $\delta = -25.8$ ppm has been assigned to the boron atom that is attached to the oxygen atom. Few structurally characterized single-cluster oxametallaboranes are known to have their oxygen atom in an open-face position and a cluster connectivity of three. Likewise, it exhibits an oxygen atom that has an oxygen-to-cluster connectivity number of three and is bound contiguously to the B3, V1, and V2 atoms. This compound can be viewed as an edge-fused cluster in which two tetrahedral units, $\{\text{V}_2\text{BO}\}$ and $\{\text{V}_2\text{B}_2\}$, have been fused by a common V_2 edge. The incorporation of oxygen may be due to the cleavage of thf in the presence of butyllithium, which has already been described by Bates *et al.* [167]. A detailed structural description is given in Section 5.4.8.

The reaction of $[\text{Cp}_2\text{VCl}_2]$ with excess of $[\text{LiBH}_4 \cdot \text{thf}]$, followed by thermolysis with diphenylditeluride (Ph_2Te_2) or 2-mercaptobenzothiazole ($\text{C}_7\text{H}_5\text{NS}_2$), yielded $[(\text{CpV}(\mu\text{-TePh}))_2(\mu_3\text{-Te})\text{BH} \cdot \text{thf}]$, **22** [166], and $[(\text{CpV})_2(\text{BH}_3\text{S}_2)]$, **23**, respectively [166]. The ^{11}B NMR spectrum of compound **22** shows a single resonance at $\delta = 21.7$ ppm, which is consistent with a tri- or tetra-coordinated boron

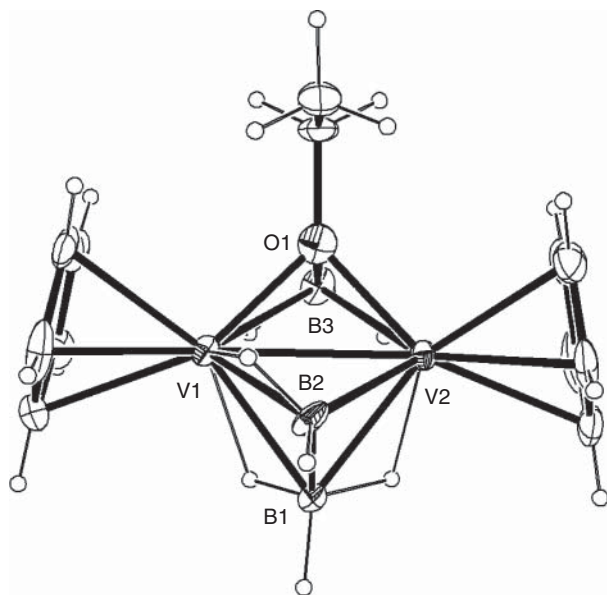


Figure 5.8 ORTEP drawing of the $[(\text{CpV})_2\text{B}_3\text{H}_8(\mu_3\text{-OEt})]$. (Reprinted with permission of Wiley-VCH from Ref. [166].)

environment. The molecular structure of **22** represents an edge-fused divanadatelluraboranes, in which two $\{\text{CpV}\}$ units are linked by a pair of bridging $\{\text{TePh}\}$ ligands and a $\{\text{TeBH}\cdot\text{thf}\}$ unit in a side-on manner. The interesting feature of this molecule is almost square-planar arrangement of one boron atom and three Te atoms. The molecule contains two μ_2 and one μ_3 type of Te atoms. The V–V distance of $2.8587(9) \text{ \AA}$ in **22** is significantly longer than that found in vanadaborane $[(\text{CpV})_2(\text{B}_2\text{H}_6)_2]$ (V–V = $2.787(2) \text{ \AA}$). The sulfur atoms in **23** are triply bridged, and in the $[\text{V}_2\text{S}_2\text{B}_2]$ core, they are four skeletal electrons donor that is isoelectronic with the BH_3 unit (Figure 5.9). Thus, replacement of the boron hydride (BH_3) in $[(\text{CpV})_2(\text{B}_2\text{H}_6)_2]$ by two sulfur atoms necessitates the formation of an edge-fused tetrahedral $[\text{V}_2\text{S}_2\text{B}_2]$ framework. A V–V distance of $2.777(2) \text{ \AA}$ is consistent with a single bond in **23**.

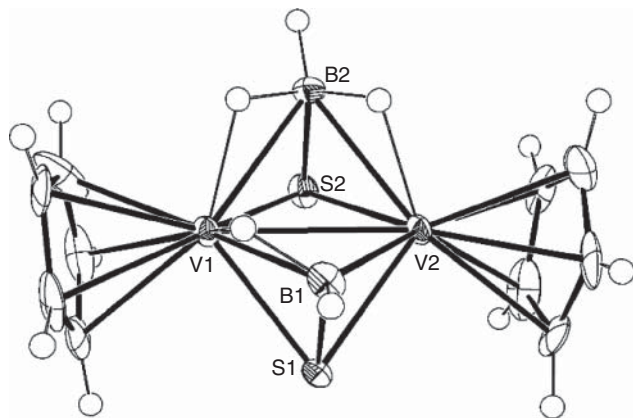


Figure 5.9 ORTEP drawing of the $[(\text{CpV})_2(\text{BH}_3\text{S})_2]$. (Reprinted with permission of Wiley-VCH from Ref. [166].)

Metallaborane and metallaheteroborane chemistry is extensive by assimilating one, two, or three atoms other than boron into the borane cluster. To access products not found with chalcogen powders (S, Se), the reactivity of diaryl disulfide and diselenide in the cluster building process has been explored. Klumpp and coworkers first reported the reactivity of dialkyl and diaryl disulfides with metal carbonyl fragments, in which they observed that RS–SR ligands (R = alkyl or aryl) act as a source of both “S” or “SR” and the product distribution mainly depends on the nature of the R group [130, 135]. The binuclear halfsandwich-type complexes with organochalcogenolato bridges can have various structural arrangements of the folded inner $[M(\mu\text{-ER})_2 M]$ core and have also been synthesized by the groups of Herberhold and Wei [130, 168]. Until now, much of work has been dedicated to metal complexes with chalcogenide ligands. The extreme interest in this area stems from the richness of their structural, bonding, and reactivity patterns and their relevance to materials science. In contrast to the larger number of sulfur-containing clusters, those containing selenium and tellurium have little success [169, 170].

In the same line, the reaction of the vanadaborane complex $[(\text{CpV})_2(\text{B}_2\text{H}_6)_2]$ with diphenyl disulfide and dibenzyl diselenide has been investigated [171]. In this process, synthesis of metallaheteroboranes was not achieved; however, cage-substituted products were isolated. Thermolysis of $[(\text{CpV})_2(\text{B}_2\text{H}_6)_2]$ with bis-chalcogenide ligands (Ph_2S_2 or Bz_2Se_2) in *p*-xylene yielded B–H substituted metallaborane products, **24–26** (**24**: $[(\text{CpV})_2\text{B}_4\text{H}_9(\text{PhS})_3]$, **25**: $[(\text{CpV})_2\text{B}_4\text{H}_{10}(\text{PhS})_2]$, and **26**: $[(\text{CpV})_2\text{B}_4\text{H}_{11}(\text{BzSe})]$). All the compounds possess the same core geometry with a V–V single bond.

While the dichalcogenide ligands produce the B–H substituted product, the reaction of elemental sulfur with $[(\text{CpV})_2(\text{B}_2\text{H}_6)_2]$ in *p*-xylene produced an interesting cluster $[(\text{CpV})_2\text{S}_4(\mu\text{-}\eta^1\text{-S}_2)]$, **27**, in 64% yield [171]. The solid-state structure of **27**, shown in Figure 5.10, reveals that two vanadium ions are linked by a disulfide ligand, which displays η^1 -coordination to each metal atom in an end-on manner. The V–V distance of 2.665 Å is at the appropriate range assigned to the V–V single bond. The V–S–V angles are quite acute ($\text{V1–S3–V2} = 68.98(11)^\circ$; $\text{V1–S6–V2} = 67.50(9)^\circ$) and are indicative of a metal–metal interaction.

5.2.7

Triple-Decker Complexes

Triple-decker sandwich complexes, in which the heteroarene rings are simultaneously and equivalently bonded to two transition metal atoms lying opposite to each other, are rare. Jonas has reported

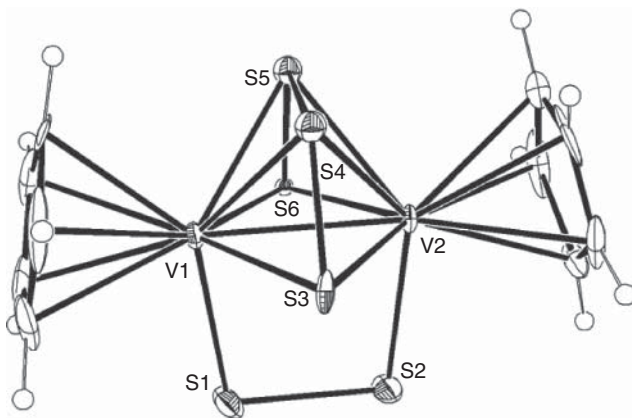


Figure 5.10 ORTEP drawing of the $[(\text{CpV})_2\text{S}_6]$. (Reprinted with permission of American Chemical Society from Ref. [171].)

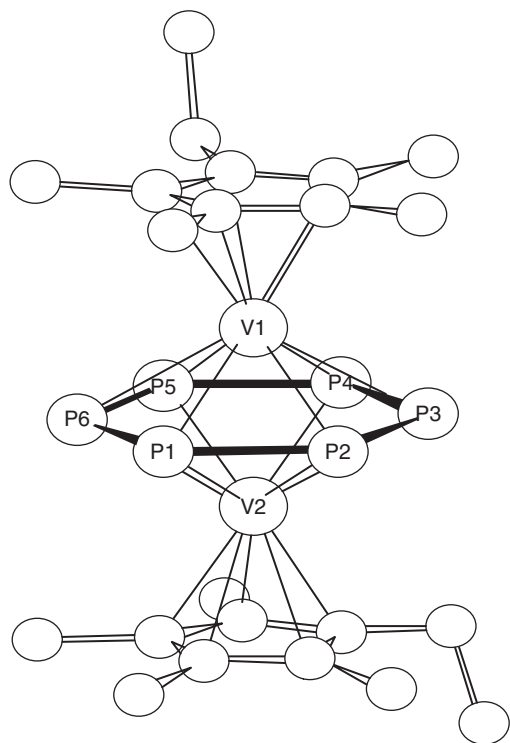


Figure 5.11 ORTEP drawing of the $[(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{V}]_2(\mu,\eta^6:\eta^6\text{-P}_6)$. (Reprinted with permission of Wiley-VCH from Ref. [173].)

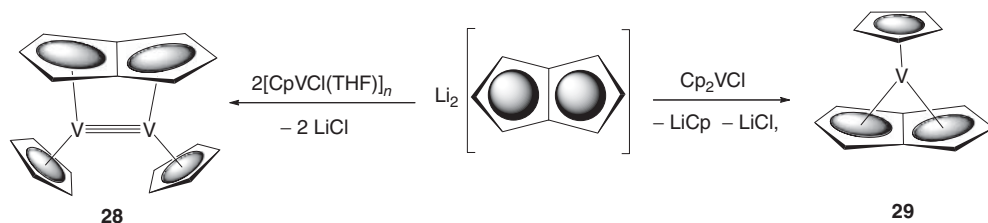
the synthesis of first binuclear metal complex that has two metal centers bonded to one face of a η^6 -bonded C_6H_6 with vanadium–vanadium distance of $2.425(1) \text{ \AA}$ [172]. Co-thermolysis of white phosphorous (P_4) and $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_n\text{W}_2]$ ($n = 4, 6$), as well as $[(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{V}(\text{CO})_4]$, affords the triple-decker sandwich complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{W}]_2(\mu\text{-}\eta^6:\eta^6\text{-P}_6)$ and $[(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{V}]_2(\mu,\eta^6:\eta^6\text{-P}_6)$ ($\text{R} = \text{C}_2\text{H}_5$) [173]. The solid-state structure shows that two vanadium moieties are linked through P_6 -plane, and the interatomic distance ($2.627(2) \text{ \AA}$) shows the presence of intermetallic interaction (Figure 5.11).

5.2.8

Paddlewheel Complexes

Since the inception of the first dimetal species containing a quadruple bond in $[\text{Re}_2\text{Cl}_8]^{2-}$ [174], the chemistry of metal–metal bonded species has grown rapidly. These compounds have many important applications such as in catalysis [175], medicine [176, 177], and supramolecular chemistry [178, 179]. Perhaps the most interesting structural motif is the “paddlewheel” complex, in which two metal atoms are held by four bridging ligands, such as carboxylates, amidates, amidinates, and others. Computational studies for the model system $[\text{V}_2(\text{O}_2\text{CH})_4]$ signify that vanadium–vanadium multiple bonds should be stable [180]. However, all efforts in synthesizing $[\text{V}_2(\text{carboxylato})_4]$ from the reaction of carboxylates and the known starting materials (e.g., $[\text{V}(\text{H}_2\text{O})_6(\text{CF}_3\text{SO}_3)_2]$, $[\text{V}_2\text{Cl}_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$, or $[\text{VCl}_2(\text{py})_4]$) went in vain [181]. The first organodivanadium complex with a vanadium–carbon σ -bond, $[\text{V}_2(2,6\text{-dimethoxyphenyl})_4]$

was reported by Seidel and coworkers and was completely characterized by Cotton and Millar in 1977 [182, 183]. As shown in Scheme 5.6, bimetallic pentalene-bridge complex $[(\text{CpV})_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_8\text{H}_6)]$, **28**, is generated by the reaction of $[\text{Li}_2(\text{C}_8\text{H}_6 \cdot x\text{L})]$ (L = dimethylether) with 2 equiv. of divalent $[\text{CpVCl}(\text{thf})]_n$ [184]. In this complex, two metal centers are coordinated in *syn*-manner to the same face of the pentalene, which moves the pentalene from planarity. It presents an unusually short V–V bond (2.5380(5) Å), and according to the DFT study, it has been suggested to be a rare example of V–V triple bond. In solution, it disproportionates into **29** over time.



Scheme 5.6 Synthesis of pentalene-bridge vanadium complex.

Quadruply bonded Re_2^{6+} unit was recognized in 1964 in $[\text{Re}_2\text{Cl}_8]^{2-}$ [174], and the existence of Tc_2^{5+} (in $\text{Tc}_2\text{Cl}_8^{3-}$) and Mo_2^{4+} (in $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$) was established in 1965 [185, 186]. However, the emergence of first compound of triply bonded V_2^{4+} occurred only in 1992 through the isolation of $[\text{V}_2(\text{DTolF})_4]$ (DTolF = *N,N'*-di-*p*-tolylformamidine). The key step for the synthesis of $[\text{V}_2(\text{DTolF})_4]$ is the use of a thf solution of $[\text{VCl}_3(\text{thf})_3]$, which is reduced with 1 equiv. of $[\text{NaEt}_3\text{BH}]$. The resulting solution of $[\text{VCl}_2(\text{thf})_n]$ reacts with $[\text{LiDTolF}]$ to produce the air-sensitive, diamagnetic compound $[\text{V}_2(\text{DTolF})_4]$ in very high yield. The X-ray analysis shows a short V–V distance (1.978(2) Å). An alternative method for the synthesis of V–V bonded compounds begins with the reaction of *trans*- $[\text{VCl}_2(\text{tmeda})_2]$ and LiDCyF (DCyF = *N,N'*-dicyclohexylformamidinate) in toluene at room temperature. This produces the mononuclear compound $[\text{V}(\text{tmeda})(\text{DCyF})_2]$, which upon heating gives dinuclear $[\text{V}_2(\text{DCyF})_4]$ with a V–V distance of 1.968(2) Å. The structurally characterized dimeric paddlewheel complexes are listed in Table 5.3. A formal triple bond between the bridged vanadium atoms has been assigned for $[\text{V}_2(2,6\text{-(MeO)}_2\text{Ph})_4 \cdot \text{thf}]$ (2.200(2) Å).

Table 5.3 Structural data for vanadium paddlewheel complexes.

Compounds	$d[\text{V}–\text{V}]$ (Å)	Core	References
$[\text{V}_2(\text{hpp})_4]$	1.932(1)	V_2^{4+}	[187]
$[\text{V}_2(\text{ap})_4 \cdot 2\text{C}_6\text{H}_6]$	1.942(1)	V_2^{4+}	[188]
$[\text{V}_2(\text{TPG})_4 \cdot 4\text{C}_6\text{H}_6]$	1.952(1)	V_2^{4+}	[188]
$[\text{V}_2(\text{DCyF})_4]$	1.968(2)	V_2^{4+}	[189, 190]
$[\text{V}_2(\text{DTolF})_4 \cdot \text{C}_7\text{H}_8]$	1.978(2)	V_2^{4+}	[191, 192]
$[\text{V}_2(\text{DTolF})_4 \cdot \text{C}_7\text{H}_8]$	1.974(4)	V_2^{4+}	[192]
$[\text{V}_2(\text{D}^{\text{Cl}}\text{PhF})_4]$	1.974(1)	V_2^{4+}	[188]
$[\text{V}_2(\text{DPhF})_4]$	1.978(1)	V_2^{4+}	[188]
$[\text{V}_2(\text{DAniF})_4]$	1.988(1)	V_2^{4+}	[188]
$\text{K}_3(\text{thf})_3[\text{V}_2(\text{DPhF})_4]$	1.929(1)	V_2^{3+}	[188]
$[\text{K}(18\text{-crown-6})(\text{thf})_2][\text{V}_2(\text{DPhF})_4]$	1.924(2)	V_2^{3+}	[188]

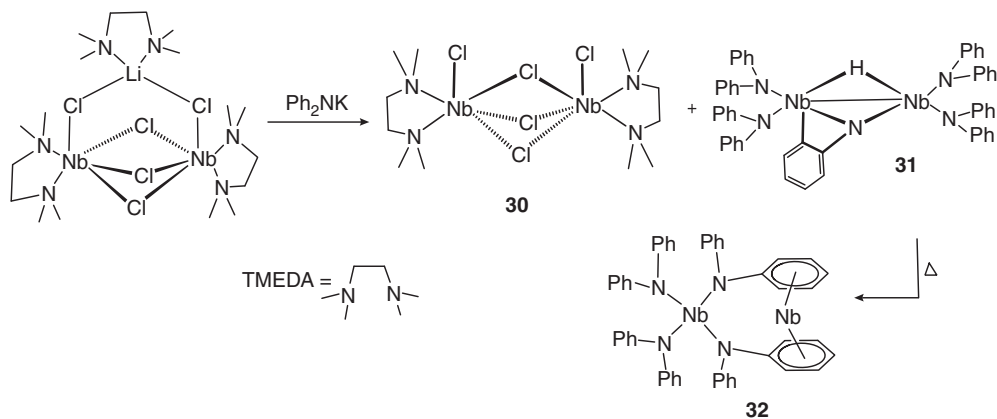
5.3

Niobium Complexes

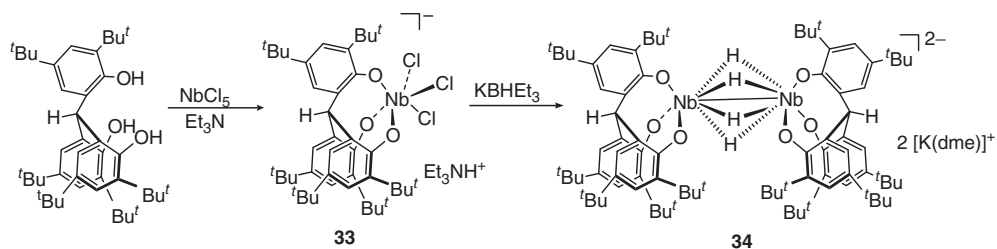
5.3.1

Hydride, Alkyl, and Aryl Complexes

The area of niobium hydride chemistry continues to be an extremely important area. It has been observed that hydrides, supported by bulky aryloxo ligands, catalyze homogenous hydrogenation of arenes. Reaction of the dinuclear and divalent $[(\text{tmeda})_2\text{Nb}_2\text{Cl}_5\text{Li}(\text{tmeda})]$ with $[\text{Ph}_2\text{NK}]$ led to the formation of three different dinuclear compounds (Scheme 5.7). The first complex is a mixed-valence dinuclear and paramagnetic species with a typical face-sharing bioctahedral structure $[\text{Cl}_2\text{Nb}_2(\mu\text{-Cl})_3(\text{tmeda})_2]$, **30**. The second complex can be formulated as $\{[(\text{Ph}_2\text{N})_2\text{Nb}]_2[\mu\text{-NPh}(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}_6\text{H}_4)](\mu\text{-H})\}\{\text{Li}(\text{tmeda})_2\}\cdot\text{toluene}$, **31**, with one hydride and one cyclometallated aromatic ring (Scheme 5.8) [193]. The third complex **32** is also a dinuclear mixed-valence complex containing +4 and 0 oxidation states. The complex **31** is a diamagnetic species; therefore, it requires one hydrogen, which has not been located through X-ray study. However, its presence has been confirmed by ^1H NMR study. The Nb–Nb bond lengths of these complexes are 2.545(1), 2.569(12), and 3.025(2) Å, respectively. The Nb–Nb distance of 3.025(2) Å for the third compound is rather long and perhaps not in agreement with the formation of significant Nb–Nb bonding interaction. Reaction of $[\text{Nb}_2\text{Cl}_5\text{Li}(\text{tmeda})_3]$ with 4 equiv. of 7-azaindolyllithium in thf afforded a deep blue solution, from which dark blue crystals of $[(7\text{-azaindoly})_4\text{Nb}_2\{(\mu\text{-Cl})\text{Li}(\text{thf})_3\}_2]\cdot 2\text{thf}$ were isolated in good yield [194].



Scheme 5.7



Scheme 5.8

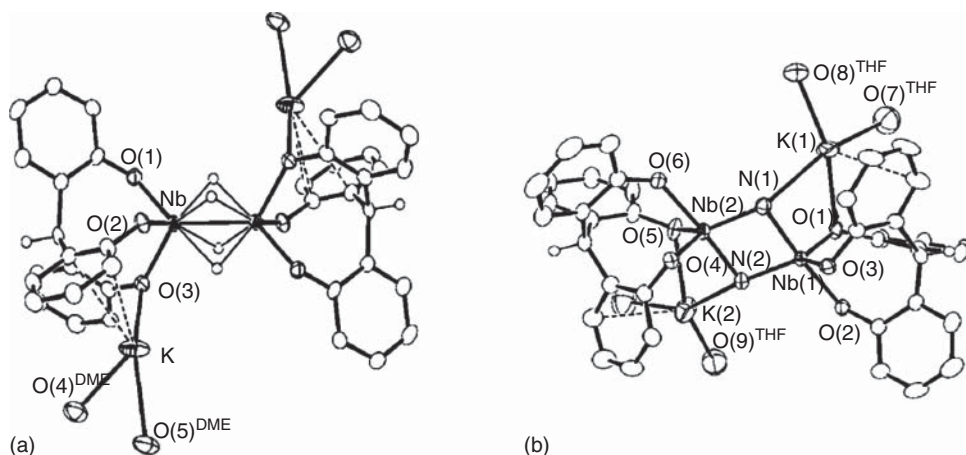
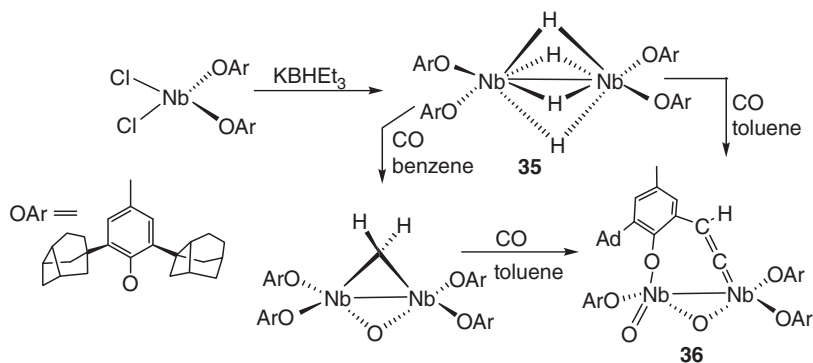


Figure 5.12 ORTEP drawing of the $[K(dme)]_2\{[(anti-O_3)Nb]_2(\mu-H)_4\}$ (a) and $[K(thf)_2]_2\{[(anti-O_3)Nb]_2(\mu-N)_2\}$ (b). (Reprinted with permission of Wiley-VCH from Ref. [195].)

As shown in Scheme 5.8, reaction of $[NbCl_5]$ with $H_3(O_3)$ ligand ($H_3(O_3)$ is a triaryloxide ligand) in CH_3CN followed by deprotonation with $[NEt_3]$ yielded red $[NEt_3H][{(anti-O_3)NbCl_3}]$, **33**. The solid-state structure shows that the tridentate O_3 ligand linked to Nb facially and the methine proton is slanting away from the metal center. Slow addition of $[KBHET_3]$ in thf to a cooled toluene solution of $[NEt_3H][{(anti-O_3)NbCl_3}]$ generated a niobium hydride complex $[K(dme)]_2\{[(anti-O_3)Nb]_2(\mu-H)_4\}$, **34** (dme = dimethoxyethane) as yellow crystals. The short Nb–Nb distance of 2.5690(5) Å indicates metal–metal bonding, which has also been accounted for the observed diamagnetism (Figure 5.12) [195].

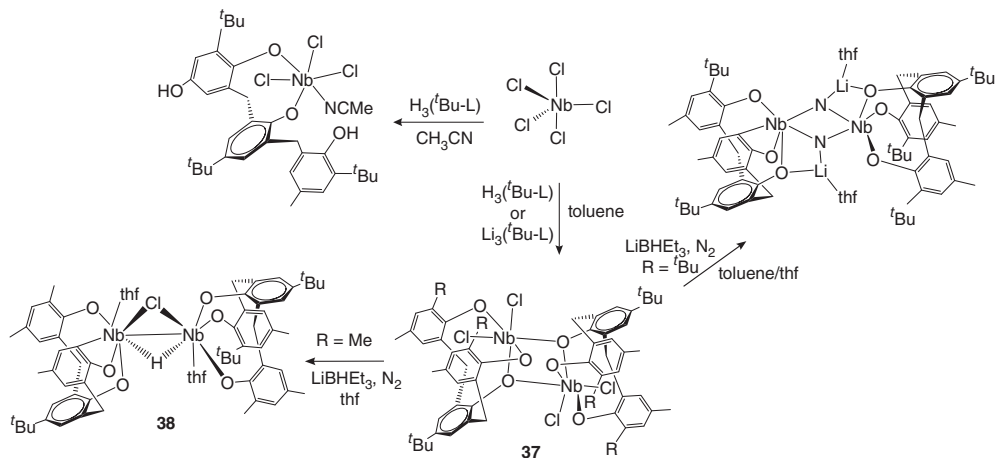
The reaction of the aryloxide–chloride complex $[(ArO)_2NbCl_2]$ with 2 equiv. of $[KBHET_3]$ in thf solution resulted in diamagnetic hydride complex $\{[(ArO)_2Nb]_2(\mu-H)_4\}$, **35** [196]. The Nb–Nb single bond (2.6674(5) Å) is stretched, which may be due to the presence of bulky adamantane groups. The reaction of **37** with CO yielded a dinuclear oxo-complex **36** with concomitant release of hydrogen [196] (Scheme 5.9). Compound $[(\eta^5:\eta^1-C_5H_4)(\eta^5-C_5H_5)Nb_2H_2]$ is a notable complex that possesses two bridging C_5H_4 ligands and terminal hydrides with a Nb–Nb bond length of 3.105(6) Å. The reaction of $[(\eta^5:\eta^1-C_5H_4)(\eta^5-C_5H_5)Nb_2H_2]$ with azo-aromatics provides a novel route to the Nb_2 complexes $[(\eta^5:\eta^5-C_5H_4C_5H_4)(\eta^5-C_5H_5)_2Nb_2(\mu-NC_6H_4R)_2]$ (R = H or OCH_3). Further, oxidation of these complexes either with $[AgBF_4]$ or $[HgX_2]$ leads



Scheme 5.9

to the formation of paramagnetic salts, $[(\eta^5:\eta^5\text{-C}_5\text{H}_4\text{C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}_2(\mu\text{-NC}_6\text{H}_4\text{R})_2]\text{BF}_4$ and $[(\eta^5:\eta^5\text{-C}_5\text{H}_4\text{C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}_2(\mu\text{-NC}_6\text{H}_4\text{R})_2](\text{HgX}_4)$ ($\text{X} = \text{Cl}$ or Br). Upon oxidation of $[(\eta^5:\eta^5\text{-C}_5\text{H}_4\text{C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}_2(\mu\text{-NC}_6\text{H}_4\text{OCH}_3)_2]$, the Nb–Nb bond length increases slightly from 2.834(5) to 2.921(1) Å [197, 198].

Scheme 5.10 describes the synthesis of niobium alkyl complex $[\text{Nb}(\text{R-L})\text{Me}_2]_2$, **38**, obtained from the reaction of niobium chloride complex $[\text{Nb}(\text{Me-L})\text{Cl}_2]_2$, **37**, and borate reagent [199]. Compound **37** can be prepared from the reaction of $[\text{NbCl}_5]$ and 2,6-bis(4,6-dimethylsalicyl)-4-*tert*-butylphenol $[\text{H}_3(\text{Me-L})]$ or 2,6-bis(4-methyl-6-*tert*-butylsalicyl)-4-*tert*-butylphenol $[\text{H}_3(\text{Bu}^t\text{-L})]$ in toluene. The Nb–Nb bond distances in these two chloro complexes are 3.554(1) and 3.649(1) Å, respectively.



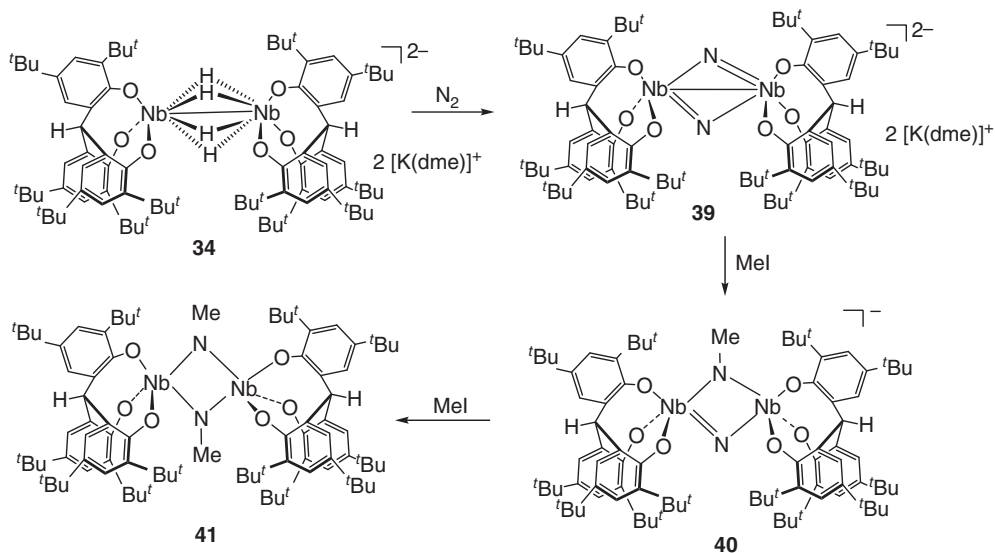
Scheme 5.10 Preparation of niobium alkyl complexes.

5.3.2

Nitride Complexes

As shown in Scheme 5.11, the reaction of $[\text{K}(\text{dme})]_2[\{(\text{anti-O}_3)\text{Nb}\}_2(\mu\text{-H})_4]$, **34**, with nitrogen led to the isolation of nitride complex $[\text{K}(\text{thf})_2]_2[\{(\text{anti-O}_3)\text{Nb}\}_2(\mu\text{-N})_2]$, **39**, through the reduction of N_2 by **34**. The X-ray crystal structure, shown in Figure 5.12, reveals a dimeric structure, constructed around a $\{\text{Nb}_2\text{N}_2\}$ four-membered ring that resides on a pseudo-twofold axis. This complex occurs as an ion pair in which the potassium cations are tightly bound with the nitride ligands. This compound readily reacts with MeI to give imide complex **40**, which is later converted into bis-imide complex **41** on further reaction with 1 equiv. of MeI [195].

Floriani and coworkers have shown that the calixarene skeleton can impose a quasi-planar O_4 donor set to the metal center to provide $(\sigma, 2\pi)$ frontier orbitals for M–X multiple bonding. Four-electron reduction of dinitrogen by $[\{p\text{-Bu}^t\text{-calix-[4]}-(\text{O})_4\}_2\text{Nb}_2(\mu\text{-M})_2]$, (**42**, $\text{M} = \text{Li}$; **43**, $\text{M} = \text{Na}$; **44**, $\text{M} = \text{K}$), generates the dinuclear nitrogen complexes $[\{p\text{-Bu}^t\text{-calix[4]}-(\text{O})_4\}_2(\text{Nb} = \text{N} - \text{N} = \text{Nb})]^{2-} \cdot [\text{M}_2]^{2+}$ (**45**, $\text{M} = \text{Li}$; **46**, $\text{M} = \text{Na}$; **47**, $\text{M} = \text{K}$) [for **46**, $\text{Nb} = \text{N} = 1.747(12)$ Å, $\text{N} - \text{N} = 1.390(17)$ Å]. Two-electron reduction of **46** using sodium metal leads to bis(μ -nitrido) species $[\{p\text{-Bu}^t\text{-calix[4]}-(\text{O})_4\}_2\text{Nb}_2(\mu\text{-N})_2(\mu\text{-Na})_2\text{Na}_2]$, **48**, which maintains an equilibrium with the monomeric form $[\{p\text{-Bu}^t\text{-calix[4]}-(\text{O})_4\}\text{Nb} = \text{N} - \text{NaS}_n]$, **49**, in solution. The X-ray structure of **48** shows the complete cleavage of N–N bonds and formation of a nitride species. The Nb–Nb and N–N separations are 2.800(1) and 2.597(8) Å, respectively, and coordination around each niobium atom is octahedral. Instead of thf, when dme was used as solvent during the reduction of **46** to **48**, another



Scheme 5.11 Cleavage of dinitrogen in the synthesis of niobium nitride complex.

dimeric compound $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}_2\text{Nb}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)(\mu\text{-Na})_3\text{-Na}]$, **50** ($\text{Nb}\text{--Nb} = 2.635(1) \text{ \AA}$) was isolated. Due to the formation of the metal–metal bond, an overall distortion of the dimeric unit occurred, which forced the dinitrogen to rearrange its bonding arrangement from a terminal $\eta^1\text{:}\eta^1$ mode to a bridging $\mu\text{-}\eta^2\text{:}\eta^2$ mode. The reaction of **50** with oxygen or pyridine oxide led to the insertion of an oxygen atom between the two Nb ions, while dinitrogen remains $\mu\text{-}\eta^2\text{:}\eta^2$ bonded across the two niobium ions. The N–N bond is orthogonal to the Nb–Nb bond ($2.876(9) \text{ \AA}$). The change of solvent from thf or dme to toluene in the reaction of **42** with N_2 resulted in a nitrido complex, $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}_3\text{Nb}_3(\mu\text{-N})_2\text{Na}_3(\text{thf})_2]$, **51**. This fact suggests that the presence of alkali metal ions in the active bifunctional species magnifies the role of the solvent in dinitrogen reduction assisted by transition metal complexes [200–203]. Upon addition of tmeda to complex **51** in CHCl_3 or toluene breaks the complex into $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}_2\text{Nb}_2(\mu\text{-N})_2\{\mu\text{-Na}_2\text{-(tmeda)}_2\}\text{Na}_2]$, **52**, and $[\{p\text{-Bu}^t\text{-calix[4]-(O)}_4\}_2\text{Nb}_2(\mu\text{-N})][\text{Na}(\text{tmeda})_2]$, **53**.

5.3.3

Triple-Decker Complexes

During the last few years, many novel triple-decker sandwich complexes with *cyclo*- P_n - or *cyclo*- As_n units as middle deck have been synthesized [204, 205]. Several theoretical studies also shed insights into the bonding and electronic structure of these compounds [206, 207]. Co-thermolysis of $[\text{LNb}(\text{CO})_4]$ ($\text{L} = \eta^5\text{-C}_5\text{Me}_4\text{Et}$) and P_4 in decalin afforded the triple-decker sandwich complex $[\text{LNb}]_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-P}_6)$ with a Nb–Nb length of $2.828(1) \text{ \AA}$. A similar compound $[(\text{L}'\text{Nb})_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-P}_6)]$ has also been reported ($\text{L}' = \eta^5\text{-C}_5\text{H}_3(\text{Bu}^t)_2\text{-1,3}$) [208]. Both complexes have 26 cluster valence electrons, which is two electrons less than that of undistorted, symmetric, and planar middle rings. By reducing the valence electron count from 28 to 26 in group 5 metals ($\text{M} = \text{V}, \text{Nb}$), a severe bis-allylic in-plane distortion of P_6 ligand is observed (Figure 5.13). A similar type of bis-allylic distortion is observed in the triple-decker complex $[(\text{CpV})_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_6)]$ with the same electron count. In $[(\text{L}'\text{Nb})_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-P}_6)]$, four short and two long P–P bonds are found, whereas in the case of V the opposite situation is observed.

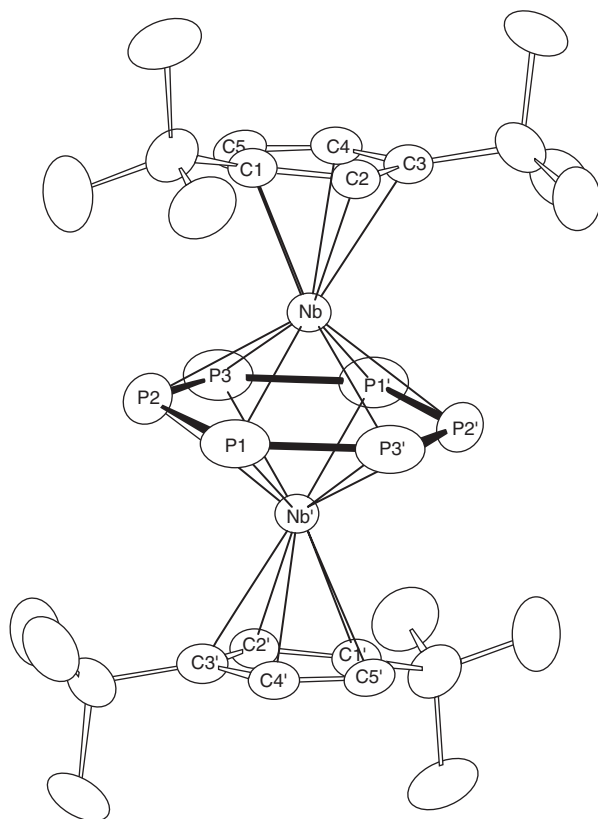


Figure 5.13 ORTEP drawing of the $[(\eta^5\text{-C}_5\text{H}_3(\text{Bu}^t)_2\text{Nb})_2(\mu_2\text{-}\eta^6:\eta^6\text{-P}_6)]$. (Reprinted with permission of American Chemical Society from Ref. [208].)

5.3.4

Paddlewheel Complexes

Low oxidation state Nb–Nb triply bonded complexes fall primarily into two categories, anionic face-sharing biotetrahedral or paddlewheel complexes (Table 5.4). In 1997, the niobium paddlewheel complex $[\text{Nb}_2(\text{hpp})_4]$ was isolated from the reaction of $[\text{NbCl}_3(\text{dme})]$ and $[\text{Li}(\text{hpp})]$ using $[\text{KC}_8]$ as

Table 5.4 Structural matrices of niobium paddlewheel complexes.

Compounds	$d[\text{Nb-Nb}]$ (Å)	Core	References
$[\text{Nb}_2(\text{hpp})_4]$	2.204(1)	Nb_2^{4+}	[209, 210]
$[\text{Nb}_2(\text{hpp})_4 \cdot \text{Na}(\text{C}_2\text{H}_5)_3\text{BH}]$	2.219(1)	Nb_2^{4+}	[210]
$[\text{Nb}_2(\text{hpp})_4 \cdot 2\text{Na}(\text{C}_2\text{H}_5)_3\text{BH}]$	2.206(1)	Nb_2^{4+}	[210]
$[\text{Nb}_2(\text{azin})_4 \cdot 2\text{LiCl} \cdot 4\text{thf}]$	2.278(2)	Nb_2^{4+}	[210]
$[\text{Nb}_2(\text{azin})_4 \cdot 4\text{thf}]$	2.263(1)	Nb_2^{4+}	[211]
$[\text{Nb}_2(\text{azin})_4 \cdot 2\text{LiCl} \cdot 6\text{thf}]$	2.268(1)	Nb_2^{4+}	[194]
$[\text{Na}_4\text{Nb}_2(\text{calix})_2 \cdot 10\text{C}_4\text{H}_8\text{O}_2]$	2.385(2)	Nb_2^{4+}	[212]

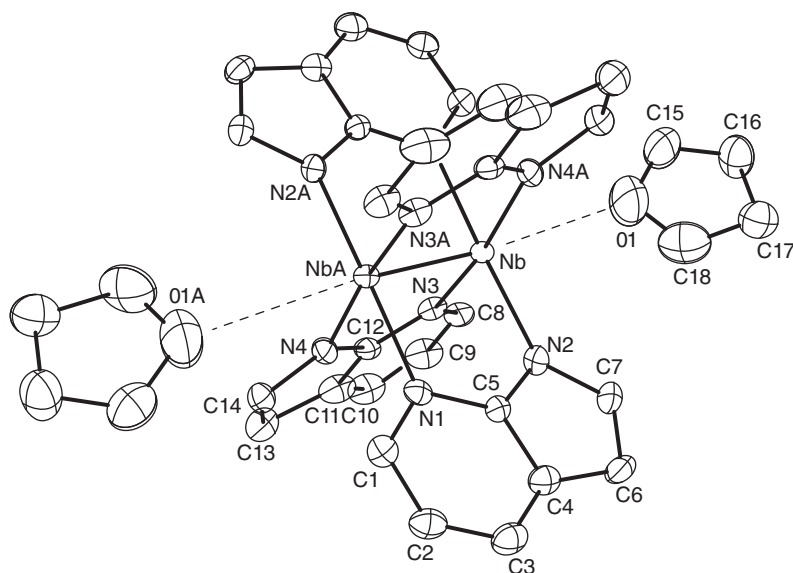


Figure 5.14 ORTEP drawing of paddlewheel complex. (Reprinted with permission of American Chemical Society from Ref. [211].)

reducing agent. The green paddlewheel complex $[\text{Nb}_2(\text{hpp})_4]$ [209] has a Nb–Nb bond length of 2.2035(9) Å, which can be compared to the metal–metal bond distance of isostructural vanadium triple-decker complexes. Other reducing agents have also been investigated, such as lithium naphthalenide and sodium triethylborohydride, $[\text{NaB}(\text{CH}_3\text{CH}_2)_3\text{H}]$ [210].

Paddlewheel compounds of second- and third-row metals provide a substantially different scenario compared to first-row transition metals. The preparation and characterization of a diamagnetic $[(7\text{-azaindolyl})\text{Nb}]_2$ offers the ground for an interesting comparison with two axially ligated dimeric $[(7\text{-azaindolyl})_2\text{Nb}]_2\{(\mu\text{-Cl})[\text{Li}(\text{thf})_3]\}_2$ and polymeric $\{[(7\text{-azaindolyl})_2\text{Nb}]_2\{(\mu\text{-Cl})[\mu\text{-Li}(\text{thf})_2]\}_2\}_n$ compounds. Complex $[(7\text{-azaindolyl})\text{Nb}]_2$ has been synthesized from the reaction of $[\text{Nb}_2\text{Cl}_5\text{Li}(\text{tmeda})_3]$ and potassium salt of 7-azaindolyl, whereas the similar reaction with lithium salt afforded $[(7\text{-azaindolyl})_2\text{Nb}]_2\{(\mu\text{-Cl})[\text{Li}(\text{thf})_3]\}_2$.

The crystal structure displays the characteristic of the paddlewheel geometry with four ligands organized in the usual manner around the Nb–Nb bond (Figure 5.14). The Nb–Nb distance (2.263(1) Å) is close to the distance observed in LiCl adducts $[(7\text{-azaindolyl})_2\text{Nb}]_2\{(\mu\text{-Cl})[\text{Li}(\text{thf})_3]\}_2$ (2.268(1) Å) and $\{[(7\text{-azaindolyl})_2\text{Nb}]_2\{(\mu\text{-Cl})[\mu\text{-Li}(\text{thf})_2]\}_2\}_n$ (2.278(2) Å), respectively. Depending on the solvation of the alkali metal ion, either linear polymeric or dimeric structure has been observed.

5.3.5

Niobaborane and Niobaheteroboranes

The early report of $[(\text{Cp}^+\text{Nb})_2(\text{B}_2\text{H}_6)_2]$ [213] ($\text{Cp}^+ = \text{EtMe}_4\text{C}_5$) as a minor product in complex reactions shaped the synthetic goal for Watcher and coworkers. As a result, $[\text{Cp}^+_2\text{Nb}_2\text{Cl}_2(\text{B}_2\text{H}_6)]$, **54**, $[\text{Cp}^+_2\text{NbBH}_4]$, **55**, and $[\text{Cp}^+_2\text{Nb}_2(\text{B}_2\text{H}_6)_2]$, **56**, have been generated from the reaction of NbCl_5 , NaBH_4 , and LiCp^+ [214]. Subsequently, Ghosh and coworkers have developed a route for the synthesis of the Cp analog of **56** considerably in high yield (**57**) [165]. The single resonance at $\delta = 1.7$ ppm in the ^{11}B NMR spectrum indicates a highly symmetrical structure in solution. The

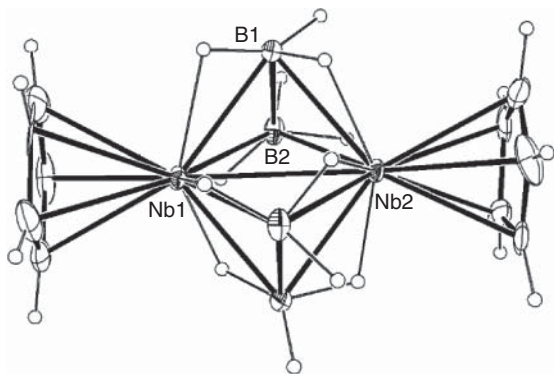
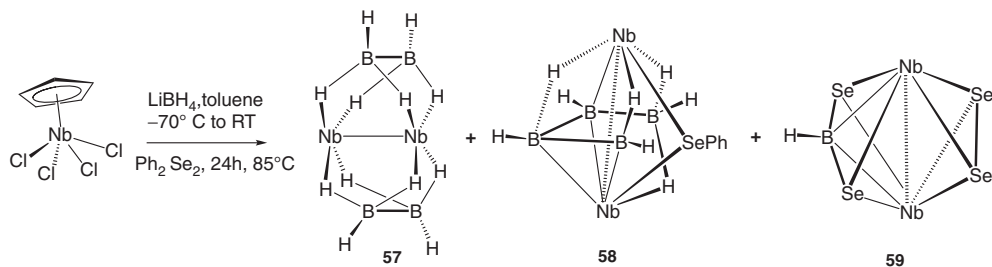


Figure 5.15 ORTEP drawing of $[(\text{CpNb})_2(\text{B}_2\text{H}_6)_2]$. (Reprinted with permission of Wiley-VCH from Ref. [165].)

molecular structure of **57** (Figure 5.15) is similar to that of **56**, and the square-pyramidal niobium centers are $2.9477(16)$ Å away from each other; this is substantially longer than expected for the formally determined Nb=Nb bond.

The fast metathesis of $[\text{CpNbCl}_4]$ followed by the addition of dichalcogenide ligands $[\text{Ph}_2\text{Se}_2]$ led to the formation of $[(\text{CpNb})_2\text{B}_4\text{H}_9(\text{SePh})]$, **58**. The molecular structure contains central $\{\text{Nb}_2\text{B}_2\}$ tetrahedral geometry with two other boron atoms are in the capping position and the $\mu\text{-SePh}$ group is bridged between two Nb atoms of the central tetrahedron (Scheme 5.12) [131]. On the basis of the capping principle, the skeletal electron count is decided by the central polyhedron, that is, the $\{\text{M}_2\text{B}_2\}$ tetrahedron in **58**, which is consistent with six skeletal electron pairs (sep). Formally, the $\mu\text{-SePh}$ group contributes three electrons; hence, six seps are available and the observed structure obeys the counting rules. The Nb–Nb distance of $2.8618(5)$ Å in **68** is comparable with Nb–Nb distances in niobium metal (2.858 Å); however, it is shorter than those of dinuclear niobium complexes $[\text{Nb}_2\text{Se}_4][\text{Te}_2\text{I}_6]_2$ ($2.926(2)$ Å), $[\text{Nb}_2(\mu\text{-S}_2)_2(\text{H}_2\text{O})_8](\text{pts})_4 \cdot 4\text{H}_2\text{O}$ ($2.8984(7)$ Å; Hpts = *p*-toluenesulfonic acid) and $[\text{Nb}_2(\mu\text{-Se}_2)_2(\text{dtc})_4]$ ($2.974(2)$ Å; dtc = diethyldithiocarbamate) [215]. Upon lowering the temperature to -60°C , the $^1\text{H}\{^{11}\text{B}\}$ resonance at $\delta = -8.55$ ppm of compound **58** splits into three distinct peaks in a 2:2:1 ratio. Based on the pattern of assembly of peaks for the bridging protons in ^1H NMR spectra, the resonances at $\delta = -8.58$ and -8.60 ppm have been assigned to those, which bridge the open face of boron atoms, and the resonance at $\delta = -16.75$ ppm has been assigned to the tetrahedral core proton. In the same reaction, another niobaselenaborane $[(\text{CpNb})_2\text{BH}(\text{Se})_4]$, **59** [216], was isolated in good yield. The ^{77}Se NMR of **59** shows two chemical shifts, each at $\delta = 330$ and 282 ppm, comparable with other dimetallaselenaborane clusters.



Scheme 5.12 Synthesis of niobaheteroborane complexes.

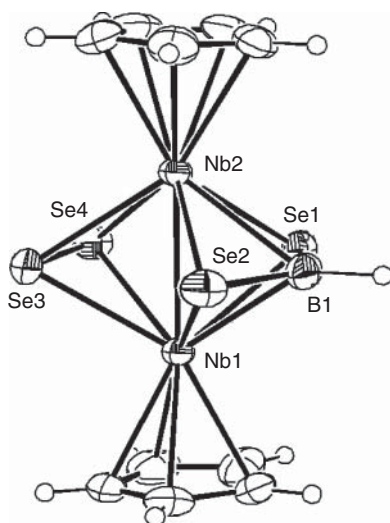


Figure 5.16 ORTEP drawing of $[(\text{CpNb})_2\text{BH}(\text{Se})_4]$. (Reprinted with permission of Elsevier from Ref. [216])

The X-ray analysis of **59** shows that the asymmetric unit contains an unknown molecule that was proposed to be $[(\text{CpNb})_2\text{B}_5\text{H}_{13}]$. The crystal was a cocrystal of two components, namely, $[(\text{CpNb})_2\text{BH}(\text{Se})_4]$ and $[(\text{CpNb})_2\text{B}_5\text{H}_{13}]$ with 50% occupancy. Physically, it denotes that 50% of the molecular site in the crystal is occupied by $[(\text{CpNb})_2\text{BH}(\text{Se})_4]$ and other 50% by $[(\text{CpNb})_2\text{B}_5\text{H}_{13}]$. As shown in Figure 5.16, the solid-state structure of **59** can be described as an edge-fused cluster, generated from the fusion of trigonal-bipyramidal unit $\{\text{Nb}_2\text{Se}_2\text{B}\}$ and tetrahedral unit $\{\text{Nb}_2\text{Se}_2\}$, with two Nb atoms held common between the subclusters. The Nb1–Nb2 bond length of 2.811 Å is comparatively shorter than that observed in **57** (2.9477(16) Å).

The reaction of previously reported compound $[(\text{Cp}^+\text{Nb})_2(\text{B}_2\text{H}_6)_2]$ with elemental sulfur in decane afforded a trimetallic sulfido cluster $[(\text{Cp}^+\text{Nb})_3\text{S}_6\text{B}(\text{SH})]$ [217]. In the solid-state structure, it reveals that three Nb atoms form an equilateral triangle, with edges spanned by the corners of a BS_4 tetrahedron. The occupation of the two electrons of the three niobium core leads to the formation of equal M–M bonds of the formal bond order 2/3. This fact reflects through the Nb–Nb distances of 3.157(3) Å, which are between bonding and nonbonding interactions.

The reaction of $[\text{CpNbCl}_4]$ with $\text{LiBH}_4 \cdot \text{thf}$ followed by the thermolysis with $[\text{Ar}_2\text{S}_2]$ ($\text{Ar} = 2,6\text{-}(\text{t}\text{-Bu})_2\text{-C}_6\text{H}_2\text{OH}$) yielded an edge-fused cluster $[(\text{CpNb})_2\text{B}_4\text{H}_{10}\text{S}]$, **60**. The molecular structure of **60** is considered to be a fused structure of trigonal-bipyramidal unit $[\text{Nb}_2\text{B}_2\text{S}]$ and tetrahedral core $[\text{Nb}_2\text{B}_2]$ through a common Nb_2 edge [166]. The ^{11}B NMR of compound **60** shows four distinct boron environments at $\delta = 24.0, -1.4, -17.5$, and -31.3 ppm. This edge-fused cluster alternatively can be viewed as a pentagonal bipyramid with two missing equatorial connections (Figure 5.17). The Nb1–Nb2 bond length (2.8044(5) Å) is shorter than that observed in **57** (2.9477(16) Å). The shortening of the Nb–Nb bond might have arisen from the effect of the sulfur atom, which withdraws electron density from the cluster.

Dinuclear niobium complexes of general formula $[\{\text{NbCl}_2\text{L}\}_2(\mu\text{-Cl})_2(\mu\text{-L})]$ ($\text{L} = \text{C}_4\text{H}_8\text{S}$) have been prepared from the reaction of dinioibium(V)decachloride $[\text{Nb}_2\text{Cl}_{10}]$ with magnesium in tetrahydrothiophene [218]. This complex was successfully used in the catalytic cyclotrimerization of alkynes. In the solid-state structure, the Nb–Nb bond distance found to be 2.6956(9) Å that coincides within the range of atomic distances of $\text{Nb}^{\text{III}}\text{--Nb}^{\text{III}}$ double bonds, 2.60–2.86 Å [218].

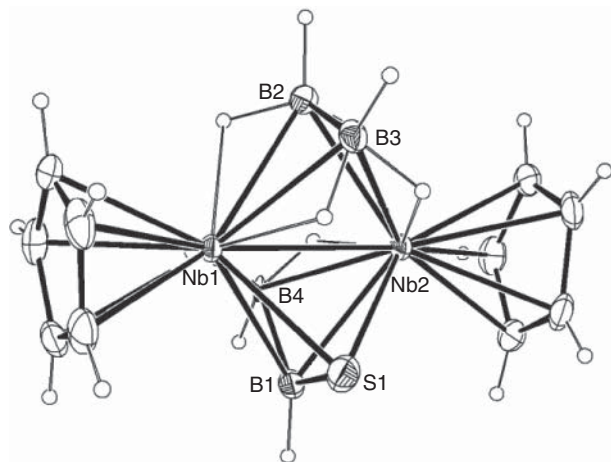


Figure 5.17 ORTEP drawing of $[(\text{CpNb})_2\text{B}_4\text{H}_{10}\text{S}]$. (Reprinted with permission of Wiley-VCH from Ref. [166].)

5.4

Tantalum Complexes

5.4.1

Carbonyl Complexes

The anionic homoleptic complex $[\text{Ta}(\text{CO})_6]^-$ having oxidation state -1 is a resourceful starting material for the synthesis of tantalum-carbonyl derivatives. Reductive carbonylation of $[\text{TaCl}_5]$ by alkali metal naphthalenides, pioneered by Ellis and groups, was an effective synthetic method for $[\text{Ta}(\text{CO})_6]^-$ under mild conditions [219]. Later, using a different reducing agent based on Mg–Zn in pyridine, Calderazzo *et al.* synthesized $[\text{Ta}(\text{CO})_6]^-$ [220]. The photochemically generated unsaturated species derived from $[\text{Cp}^*\text{Ta}(\text{CO})_4]$ is reactive toward oxidants, such as RE–ER, that yielded $[\text{Cp}^*\text{Ta}(\text{CO})_2]_2(\mu\text{-ER})_2$ (**61**, E = Sph) (ER = TeMe, SPh, SePh, TePH, SFc, SeFc, TeFc, *S''*Bu, *S'*Bu). Although the complexes are diamagnetic, as indicated by NMR spectra, the presence of direct metal–metal interactions is a matter of debate. Among them, the $\mu\text{-Sph}$ complex **61** has the X-ray structure, in which the Ta–Ta distance is 3.120(1) Å (Figure 5.18) [130]. The reaction of $[\text{Cp}^*\text{Ta}(\text{CO})_4]$ with chlorine leads to $[\text{Cp}^*\text{TaCl}_4]$, whereas the corresponding reactions with bromine or iodine yielded the oxo-bridged dinuclear complexes $[(\text{Cp}^*\text{TaX}_3)_2(\mu\text{-O})]$ (X = Br, I), which in air are converted into mononuclear complexes $[\text{Cp}^*\text{Ta}(\text{O})\text{X}_2]$ [221].

5.4.2

Hydride, Alkyl, and Aryl Complexes

The field of hydride complexes of Ta is a prosperous area in organometallic chemistry. Recent progress has shown that electrophilic mono- and binuclear tantalum hydride complexes are capable of reducing CO and N_2 , whereas the alkyl/aryl complexes are important in organic and organometallic chemistry. $[\text{TaCp}^*\text{Cl}_2(\text{propylene})]$ and $[\text{TaCp}^*\text{Cl}_2(\text{styrene})]$ react cleanly with molecular hydrogen to give insoluble green $[\text{TaCp}^*\text{Cl}_2\text{H}]_2$, **62**, and a mixture of olefin and alkane in 2:1 ratio (Scheme 5.13) [222]. In a similar manner, $[\text{TaCp}^*\text{Cl}_2\text{H}]_2$ has also been prepared by reacting $[\text{TaCp}^*\text{Cl}_2\text{Np}_2]$ ($\text{Np} = \text{CH}_2\text{CMe}_3$) with hydrogen. The mono-alkyl derivative of **62** has been synthesized from the reaction of $[\text{Ta}(\text{C}_5\text{Me}_4\text{R})\text{Cl}_2\text{H}]$ and $[\text{Mg}(\text{CH}_2\text{CMe}_3)]$ or $[\text{ZnMe}_2]$ in moderate yields. A single-crystal X-ray diffraction study shows that the asymmetric unit contains

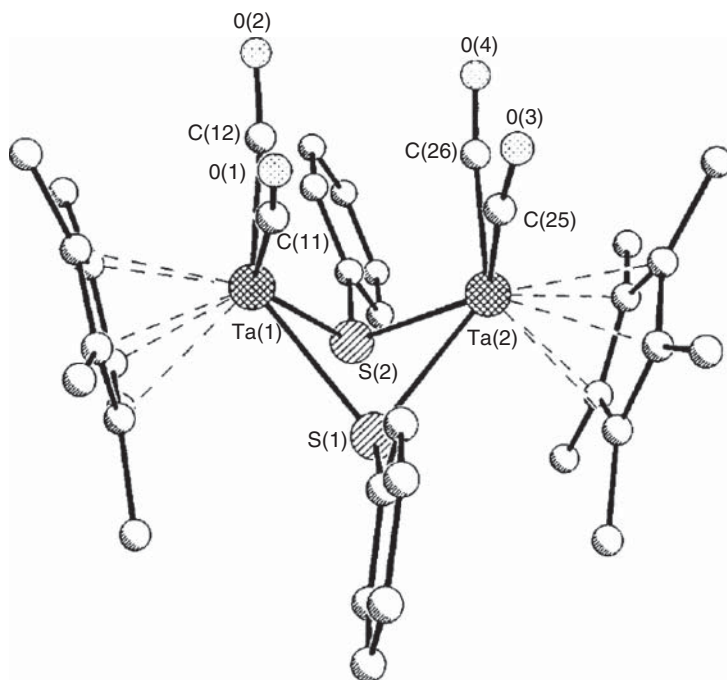
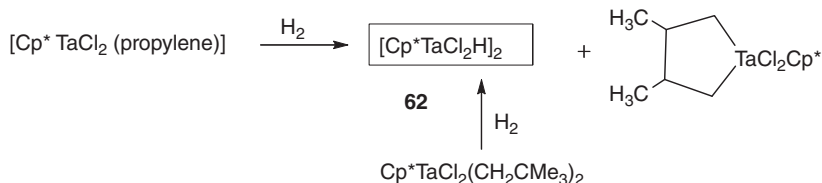


Figure 5.18 ORTEP drawing of $[\text{Cp}^*\text{Ta}(\text{CO})_2]_2(\mu\text{-SPh})_2$. (Reprinted with permission of Wiley-VCH from Ref. [130].)

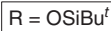
two independent molecules. The Ta–Ta bond lengths in these two molecules are 2.854(1) and 2.815(1) Å, respectively [223].



Scheme 5.13

Reduction of $[(\text{silox})_2\text{TaCl}_3]$, **63**, with Na/Hg under 1 atm of hydrogen yielded an unbridged dimer $[(\text{silox})_2\text{TaH}_2]_2$, **64**, in which the Ta–Ta bond length is 2.720(4) Å [224]. When the reduction of **63** was carried out in the presence of hydrogen and deuterium, the ^1H NMR data proves the exchange of H with D. The complex **64** has been used as a successful precursor for many ditantalum compounds. Photolysis of **65** in the presence of hydrogen produced $\{[(\text{silox})_2\text{TaCl}]_2(\mu\text{-H})_2\}$, **66**, C_7H_8 , and a trace of bibenzyl. Exposure of **64** to 2 equiv. of HCl, 1.0 equiv. of oxygen, and 1.0 equiv. of Me_3NO provided **66–68**, respectively. Derivatization of **68** with C_2H_4 gave $\{[(\text{silox})_2\text{TaCH}_2\text{CH}_3]_2(\mu\text{-O})_2\}$, **69**. Exposure of **64** to 1.0 equiv. of CO afforded $\{[(\text{silox})_2\text{TaH}]_2(\mu\text{-CH}_2)(\mu\text{-O})\}$, **70** (Scheme 5.14) [224].

The mononuclear trimethyl complexes $\text{R}[\text{NPN}]\text{TaMe}_3$ ($\text{R} = \text{Ph}, \text{Cy}$), **71**, have been used for the synthesis of dinuclear tetrahydride complexes $\{[\text{R}(\text{NPN})\text{Ta}]_2(\mu\text{-H})_4\}$, **72** [225–227]. The tetrahydride complexes exclude dihydrogen to generate coordinatively unsaturated dinuclear dihydride (Ta = Ta) species, **73**, that activates *ortho*-C–H bond of phenyl group of the NPN ligand to generate **74** [228]. Addition of 1 equiv. of hydrazine to **72** results in the clean formation of

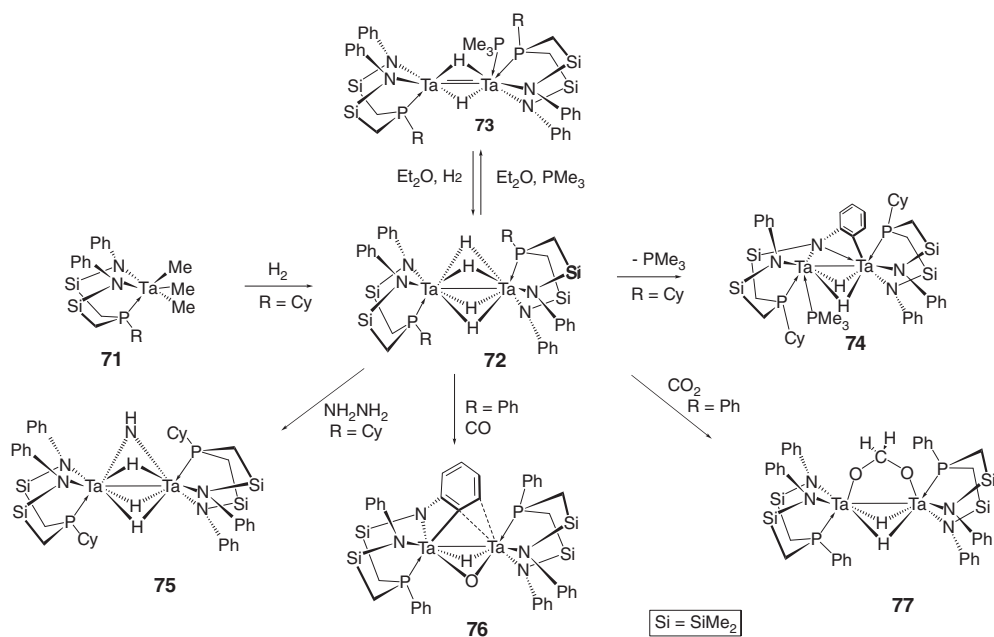


Scheme 5.14 Synthesis of tantalum hydride complexes and their reactivities.

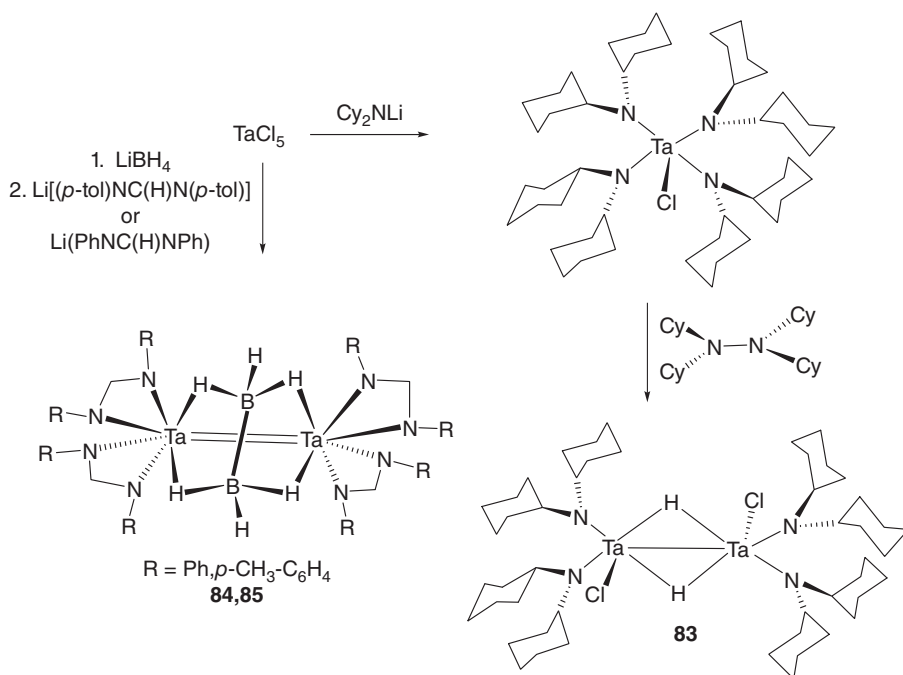
[Cy[NPN]Ta)₂(μ-NH)₂(μ-H)₂], **75** [229]. The reaction of 1 equiv. of carbon monoxide with **72** results in the cleavage of the CO triple bond that yielded ([NPN]Ta)(μ-O)(μ-H)(Ta[NPN']), **76** (where NPN' = PhP(CH₂SiMe₂NPh)(CH₂SiMe₂NC₆H₄)) via elimination of CH₄. The X-ray structure of **76** shows a dinuclear complex, with a Ta-Ta bond length of 2.7240(6) Å, having both a bridging hydride and oxo unit [230]. On the other hand, the reaction with CO₂ led to the formation of [[NPN]Ta)₂(μ-OCH₂O)(μ-H)₂], **77**, via both migratory insertion and reductive elimination. X-ray studies of **77** describe the presence of a methylene diolate fragment bridged between two Ta units, which is 2.7688(7) Å apart from each other (Scheme 5.15) [231].

Fryzuk and coworkers synthesized the ditantalum hydride compound $[(\text{P}_2\text{N}_2)\text{Ta}_2(\mu\text{-H})_4]$, **78** [232], having tridentate $[\text{P}_2\text{N}_2]$ ligand ($[\text{P}_2\text{N}_2] = \text{PhP}(\text{CH}_2\text{SiMe}_2\text{NSiMe}_2)_2\text{PPh}$). The generation of a trihydride complex from hydrogenolysis of trimethyl Ta-compound has been tracked through the addition of PMe_3 to produce $[\text{P}_2\text{N}_2]\text{TaH}_3(\text{PMe}_3)$, **79** [233]. Reaction of $[(\text{P}_2\text{N}_2)\text{Ta}_2(\mu\text{-H})_4]$ with MeI produces a cationic tetrahydride $\{[(\text{P}_2\text{N}_2)\text{Ta}_2(\mu\text{-H})_4]^+\text{I}^-\}$, **80**. The Ta-Ta bond distance in **78** is 2.6165(5) Å, while in the reduced product **80**, it is 2.7721(5) Å. This enhanced bond length is due to one electron reduction of the Ta-Ta bond [232]. The carborane derivative of Ta-hydride $[\text{Cp}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{Ta}(\text{H})](\mu\text{-Cl})_2$, **81**, has been prepared by the reduction of $[\text{Cp}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{TaCl}_2]$ with $[\text{LiAlH}_4]$. The reaction of **78** with internal alkynes, such as diphenylacetylene and phenylmethylacetylene, resulted in alkyne hydride compounds, while *p*-tolylacetylene and styrene got inserted into a Ta-H bond [234].

The first claim of a ditantalum compound without bridging hydrogen was by Gambarotta [70], obtained from the reaction of $[\text{TaCl}_5]$ and $[\text{C}_2\text{N}_2\text{Li}]$ (Scheme 5.16). An X-ray crystal structure determination suggested that complex **82** is dimeric and composed of two pyramidal $[(\text{C}_2\text{N}_2)_2\text{TaCl}]$ moieties linked together by a direct Ta–Ta bond (2.8484(7) Å) [70]. Subsequently, Cotton and coworkers reformulated the same compound as $[(\text{C}_2\text{N}_2)_2\text{ClTa}(\mu\text{-H})_2]_2$, **83**, which was earlier proposed to be $[(\text{C}_2\text{N}_2)_2\text{ClTa}]_2$. Reevaluation of the structure and ^1H NMR spectroscopy indicated the presence of two bridging hydride ligands in **83** [235].



Scheme 5.15

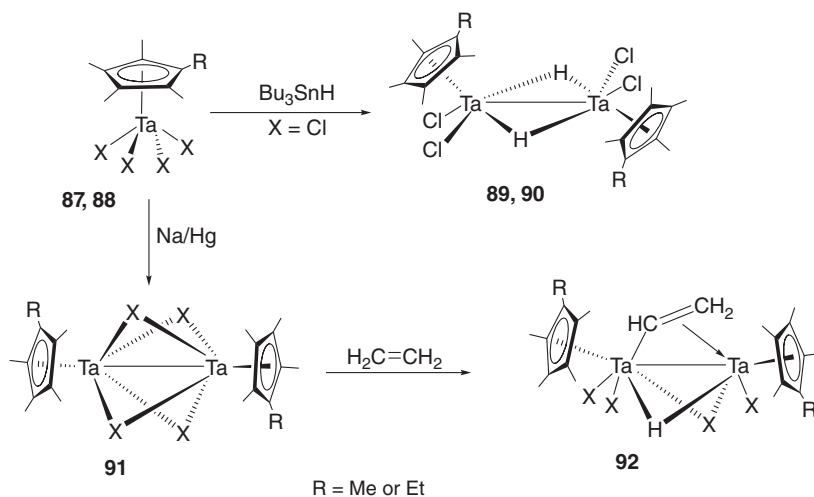


Scheme 5.16

The reduction of tantalum pentachloride with an excess of $[\text{LiBH}_4]$ in toluene at reflux temperature in the presence of $\text{Li}[(p\text{-tol})\text{NC}(\text{H})\text{N}(p\text{-tol})]$ or $[\text{Li}(\text{PhNC}(\text{H})\text{NPh})]$ led to the formation of *nido*-metallaborane complexes $[\text{Ta}_2(\mu_2, \eta^4\text{-B}_2\text{H}_6)(\text{DTolF})_4 \cdot 2\text{Et}_2\text{O}]$, **84**, or $[\text{Ta}_2(\mu_2, \eta^4\text{-B}_2\text{H}_6)(\text{DPhF})_4 \cdot \text{Et}_2\text{O}]$, **85**, respectively (Scheme 5.16) [236]. Compounds **84** and **85** are homologous and differ only in the presence of R-groups on the nitrogen atom of the amidinato ligands. They possess a C_2 axis that passes through the centers of the B–B and Ta–Ta bonds. The Ta–Ta bond lengths of **84** and **85** are 2.7251(11) and 2.7359(9) Å, respectively. The molecules have an ethane-like B_2H_6 unit that bridges the Ta center by four B–H bonds, similar to the structure of $[\text{B}_4\text{H}_{10}]$.

The synthetic precursor for $\text{Ta}_2^{\text{IV,IV}}$ complexes with bridging hydrides is $[\text{Ta}_2\text{Cl}_6(\text{P}(\text{CH}_3)_3)_4]$ [237]. The addition of hydrogen to $[\text{Ta}_2\text{Cl}_6(\text{PMe}_3)_4]$ generated the diamagnetic compound $[\text{Ta}_2\text{Cl}_6(\text{PMe}_3)_4\text{H}_2]$, **86** (Ta–Ta = 2.721(1) Å) having two bridging chlorides and two bridging hydrides. The oxidative addition of Cl_2 to $[\text{Ta}_2\text{Cl}_4(\text{PMe}_3)_4\text{H}_2]$ is considered to be an alternative synthetic route for **86** [238]. The related hydride complex $[\text{Ta}_2\text{Cl}_8(\text{PMe}_3)_3\text{H}_4]$ (2.830(1) Å) has been prepared as a side product [239] and in another synthetic method by the Na/Hg reduction of a toluene slurry of $[\text{TaCl}_5]$ and trimethylphosphine [240].

Tributyltin hydride has been utilized both as reducing agent and hydride transfer to synthesize tantalum hydride complexes [241]. The reaction between $[(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{TaCl}_4]$ (**87**: R = Me, **88**: R = Et) and 2 equiv. of $[\text{Bu}_3\text{SnH}]$ yielded a hydride-bridging ditantalum(IV) compound $[(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{TaCl}_2]_2(\mu\text{-H})_2$, (**89**: R = Me, **90**: R = Et) [241] shown in Scheme 5.17. To find the source of μ -hydride, the reaction of $[(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{TaCl}_4]$ with 2 equiv. of $[\text{Bu}_3\text{SnD}]$ was carried out, which yielded $[(\eta^5\text{-C}_5\text{Me}_5)\text{TaCl}_2]_2(\mu\text{-D})_2$. This result proves the hydride transfer from $[\text{Bu}_3\text{SnH}]$ to $(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{TaCl}_4$. The diamagnetic doubly bonded complex $[\text{C}_5\text{Me}_4\text{RTa}]_2(\mu\text{-X})_2$ (R = Me, Et; X = Cl, Br) has been prepared in good yield by reductive dimerization of $\text{C}_5\text{Me}_4\text{RTaX}_4$. A single-crystal X-ray diffraction study of $[\text{Cp}^*\text{Ta}]_2(\mu\text{-Br})_2$, **91**, shows that the Ta–Ta double bond (2.748 (2) Å) is bridged symmetrically by four bromide ligands (Figure 5.19) [242]. The reaction of the tantalum–tantalum doubly bonded complex $[\text{Cp}^*\text{TaX}_2]_2(\mu\text{-H})_2$ with ethylene in ether leads to the formation of ditantalum vinyl hydride complex, **92**, on the basis of analytical and spectroscopic data (Scheme 5.17) [124].



Scheme 5.17

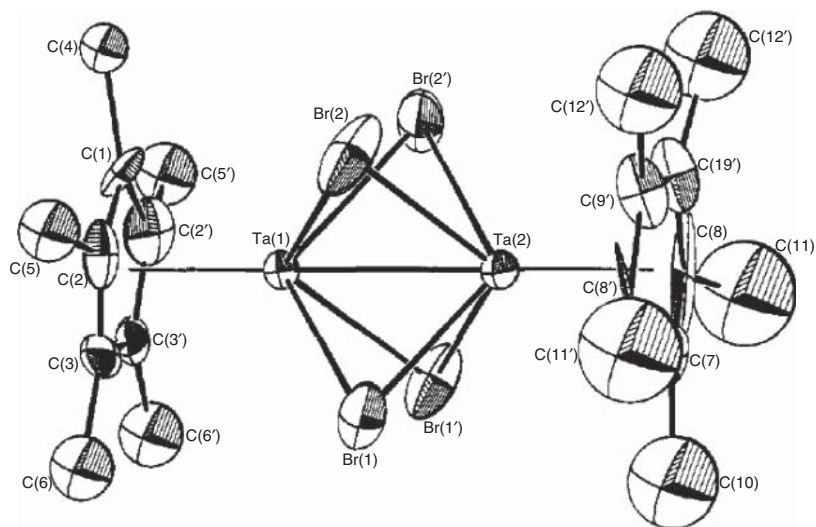


Figure 5.19 ORTEP drawing of $[\text{Cp}^*\text{Ta}]_2(\mu\text{-Br})_2$. (Reprinted with permission of Royal Society of Chemistry from Ref. [242].)

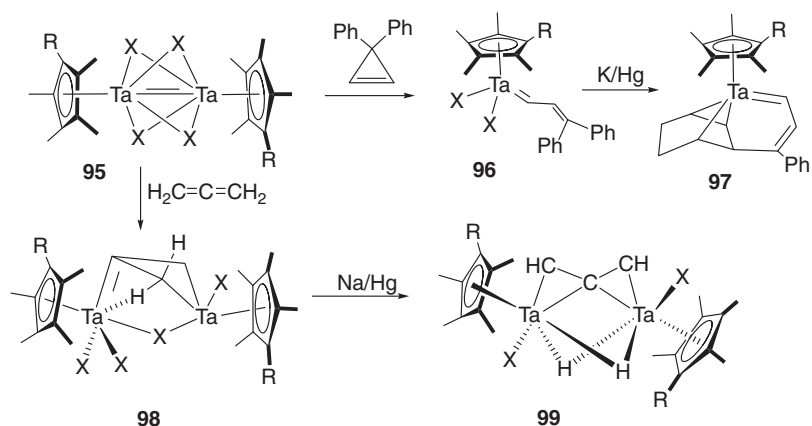
5.4.3

Akylidene and Alkylidene Complexes

The intramolecular α -hydrogen abstraction reaction has been used for the generation of $[\text{Ta}(\text{=CHSiMe}_3)(\text{CH}_2\text{SiMe}_3)_3]$ from $[\text{Ta}(\text{CH}_2\text{SiMe}_3)_5]$ [243]. This complex gradually converted into the dimeric alkylidyne complex $[(\text{Me}_3\text{SiCH}_2)_2\text{Ta}(\mu\text{-CSiMe}_3)_2\text{Ta}(\text{CH}_2\text{SiMe}_3)_2]$ [244]. Reaction of $[(\text{Me}_3\text{SiCH}_2)_3\text{TaCl}_3]$ with $[\text{LiSi}(\text{SiMe}_3)_3]$ resulted in unstable $[(\text{Me}_3\text{SiCH}_2)_3\text{TaCl}(\text{Si}(\text{SiMe}_3)_3)]$, **93**, which subsequently leads to a dimeric alkylidene-bridged complex **94** [245–247]. $[(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Ta}]_2(\mu\text{-X})_4$ ($\text{R} = \text{Me}, \text{Et}$; $\text{X} = \text{Cl}, \text{Br}$), **95**, reacts with 3,3-diphenylcyclopropene to give the corresponding mononuclear compounds $[(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Ta}(\text{=CHCH=CHPh}_2)]$, **96**, which can be reduced by K/Hg to give tantalano-*bornadiene* complexes, **97** [248]. As shown in Scheme 5.18, reaction of $[\text{Cp}^*\text{Ta}]_2(\mu\text{-X})_4$ ($\text{X} = \text{Cl}, \text{Br}$) with allene resulted in the alkylidene compound, which on reduction with Na/Hg caused double C–H bond activation of allene ligand to give the propynylidene [249] compound, **98** (Scheme 5.18).

A single-crystal diffraction study of **99** revealed the presence of a μ -propynylidene moiety, which is coplanar with two Ta atoms (Figure 5.20). The Ta–Ta distance of 2.8817(7) Å is in the single bond range, suggesting a $\text{d}^1\text{--d}^1$ Ta(IV)–Ta(IV) complex. However, the Ta–C(2) distance is consistent with a Ta=C double bond representing an allenediylidene(4-)/Ta(V)₂ description with no Ta–Ta bonding. To get insights into the structure and bonding of these complexes, theoretical calculation has been done, which demonstrates that there is no net Ta–Ta bonding molecular orbital and the total electron density shows no evidence of a Ta–Ta bond. This picture suggests the formal bonding representation is a three-center two-electron bridging bond [249].

Compound $[\text{Ta}_2(\mu\text{-CSiMe}_3)_2(\text{CH}_2\text{SiMe}_3)_4]$, **100**, was first isolated by Wilkinson and coworkers, which represents a thermally stable organometallic derivative of tantalum having a 1,3-dimetallacyclobutadiene core [250]. The terminal alkyl groups have shown to undergo a stepwise substitution with protic reagents [251]. Scheme 5.19 describes that the carbazole-substituted product $[\text{Ta}_2(\mu\text{-CSi}(\text{CH}_3)_2)_2(\text{cb})_4]$, **101**, on hydrogenation in the presence of $[\text{PMe}_2\text{Ph}]$ leads to the formation of a ditantalum compound $[(\text{cb})(\text{PMe}_2\text{Ph})(\text{H})\text{Ta}(\mu\text{-H})_2\text{Ta}(\text{H})(\text{PMe}_2\text{Ph})(\text{cb})]$, **102**, with a Ta–Ta bond length of 2.184(4) Å.



Scheme 5.18 Preparation of Ta-alkylidene complexes.

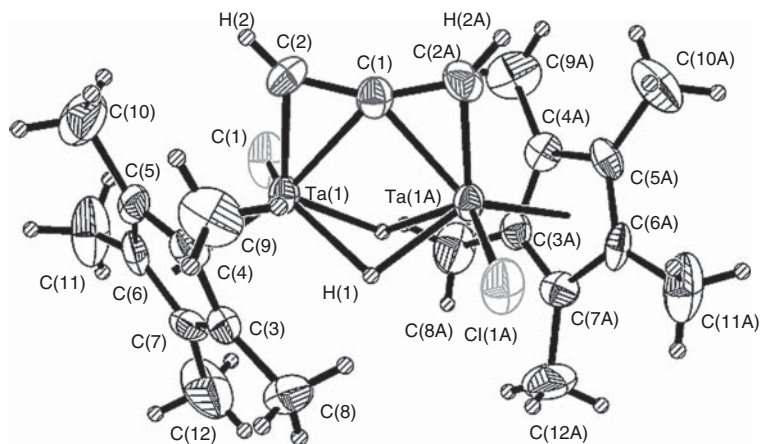
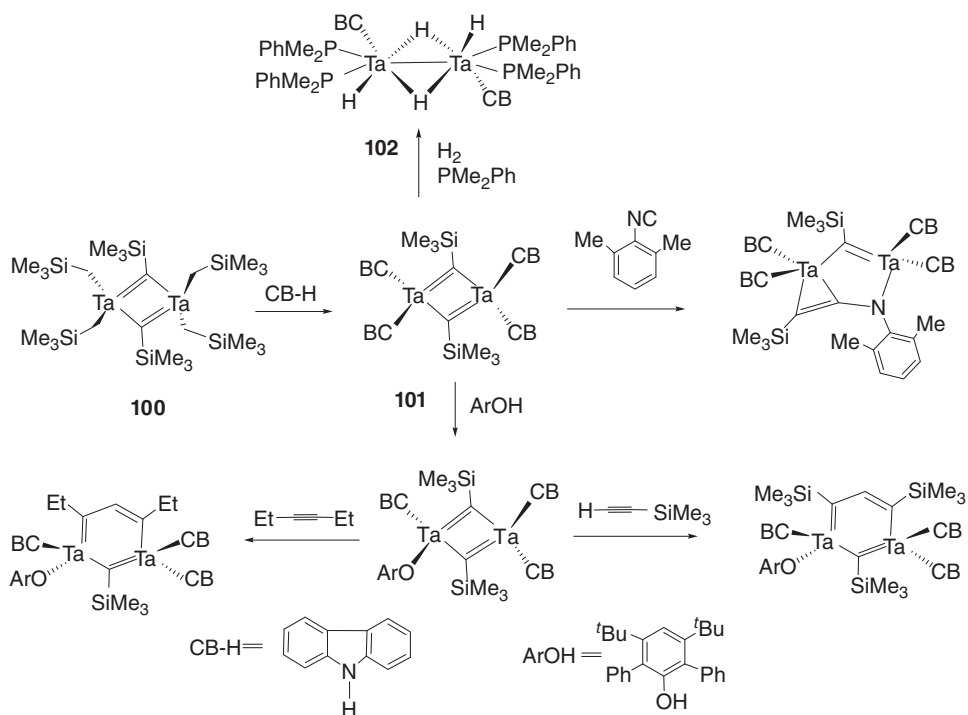


Figure 5.20 ORTEP drawing of tantalum μ -propynylidene complex **99**. (Reprinted with permission of American Chemical Society from Ref. [249].)

5.4.4

Nitride and Phosphine Complexes

On introduction of nitrogen gas to $[\{\text{R}[\text{NPN}]\text{Ta}\}_2(\mu\text{-H})_4]$, **72** ($\text{R}[\text{NPN}]=\text{RP}(\text{CH}_2\text{SiMe}_2\text{NPh})_2$), a side-on end-on dinitrogen complex $[\{(\text{NPN})\text{Ta}\}_2(\mu\text{-H})_2(\mu\text{-}\eta^1, \eta^2\text{-N}_2)]$, **103**, is formed, having a Ta–Ta bond length of 2.830(4) Å (Scheme 5.20) [225]. The complex exhibits diverse reactivity with various substrates. For example, the reaction of this nitride complex **103** with 2 equiv. of butylsilane and 9-BBN yielded disilylimide, **104**, and a borylimide nitride complex, **105**, through cleavage of the N–N bond, respectively [252–257], whereas the reaction with the Lewis acids MR_3 resulted in adducts $[\{(\text{NPN})\text{Ta}\}_2(\mu\text{-H})_2(\mu\text{-}\eta^1, \eta^2\text{-NNMR}_3)]$, $\text{MR}_3 = \text{GaMe}_3$, AlMe_3 , $\text{B}(\text{C}_6\text{F}_5)_3$ **106** [258]. Reaction of $\text{PhN}=\text{C}=\text{NPh}$ with **103** led to the formation of the ditantalum carbodiimide complex, **107**, through the coordination on side-on nitrogen. Compared to the nitride species **103**, only a slight increase in the nitrogen–nitrogen bond length and the Ta–Ta distance was observed in **107** ($\text{Ta1}–\text{Ta2} = 2.8418(4)$ Å) [259]. With phenyl acetylene and simple alkenes such as propene, displacement of the N_2 unit or migratory insertion into the tantalum hydrides occurs, which gives **108** [260].



Scheme 5.19 Synthesis of alkylidene complexes preparation.

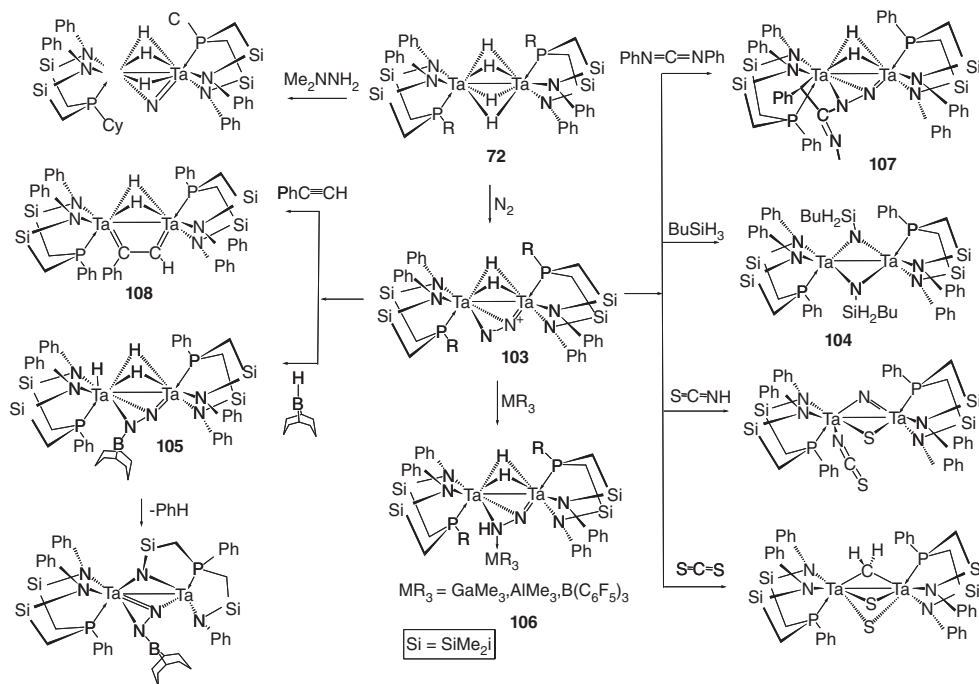
The addition of bis-phosphino ligand $[\text{Me}_2\text{PCH}_2\text{PMe}_2]$ to $[\text{Ta}_2\text{X}_6(\text{thf})_3]_2$ resulted in complexes of the general formula $[\text{TaX}_2]_2(\mu\text{-X})_2(\text{R}_2\text{PCH}_2\text{PR}_2)_2$ ($\text{X} = \text{Cl}$), whose structures are halogen dependent. The X-ray analysis shows an edge-sharing bioctahedral structure and two of the metal centers are 2.692 (2) Å apart from each other. As shown in Figure 5.21, the solid-state structure revealed a doubly bonded ditantalum moiety with two bridging chlorine atoms and two bridging diphosphine ligands [261].

5.4.5

Tantalaboranes

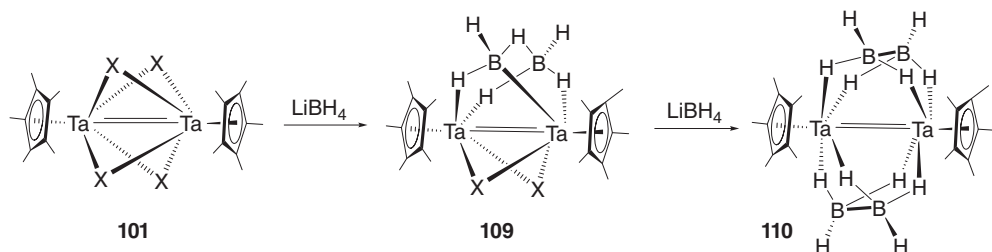
Continuous studies on doubly bonded organo-ditantalum(III) complexes $[(\text{C}_5\text{Me}_4\text{R})\text{Ta}]_2(\mu\text{-X})_4$ ($\text{R} = \text{Me, Et}$; $\text{X} = \text{Cl, Br}$) by Ting and Messerle have provided ample information on the varied nature of reactivity of these novel compounds [230, 262]. The doubly bonded $[(\text{C}_5\text{Me}_4\text{R})\text{Ta}]_2(\mu\text{-X})_4$, **95**, has been found to react with LiBH_4 in a unique mode to the formation of diamagnetic hexahydridoborate (diborane(2-)) complexes $[(\text{C}_5\text{Me}_4\text{RTa})_2(\mu\text{-X})_2(\mu\text{-H}_4\text{B}_2\text{H}_2)]$, **109**, and $[(\text{C}_5\text{Me}_4\text{RTa})_2(\mu\text{-H}_4\text{B}_2\text{H}_2)_2]$, **110**. The molecular structure of **109** as determined by single-crystal X-ray diffraction consists of a long tantalum–tantalum double bond, 2.839(1) Å in length, bridged by two bromine atoms and an unsymmetrical B_2H_6 group [165]. The other complex **110** can also be formed from the addition of 2 equiv. of LiBH_4 to **109** and postulated to have a highly symmetric structure with two bridging $[\text{B}_2\text{H}_6]^{2-}$ groups.

Although compound **110** has been isolated and characterized by Messerle, the solid-state structure was confirmed when Ghosh and coworkers made an extensive development on tantalaborane chemistry using the $[\text{Cp}^*\text{TaCl}_4]$ as a starting material [165, 263]. As shown in Scheme 5.21, an air- and moisture-sensitive intermediate generated from the reaction of $[\text{Cp}^*\text{TaCl}_4]$ with $[\text{LiBH}_4 \cdot \text{thf}]$, which



Scheme 5.20

on thermolysis by $[\text{BH}_3 \cdot \text{thf}]$, yielded a series of tantalaborane compounds $[(\text{Cp}^*\text{Ta})_2(\text{B}_2\text{H}_6)_2]$, **110** $[(\text{Cp}^*\text{Ta})_2\text{B}_4\text{H}_{10}]$, **111** $[(\text{Cp}^*\text{Ta})_2\text{B}_5\text{H}_{11}]$, **112**, and $[(\text{Cp}^*\text{TaCl})_2\text{B}_5\text{H}_{11}]$, **113**. The solid-state structure of **110** reveals that a pair of $[\text{B}_2\text{H}_6]$ moieties linked symmetrically to two $\{\text{Cp}^*\text{Ta}\}$ units. The B–B distance of 1.75(3) Å is in the range expected for the directly bonded ethane-like $(\text{H}_3\text{B}-\text{BH}_3)^{2-}$ ligand, but markedly shorter than that observed for the hydrogen-bridged $[(\text{H}_2\text{BHBH}_3)]^{2-}$ ligand in $[(\text{Cp}^*\text{TaBr})_2\text{B}_2\text{H}_6]$ (1.88(3) Å). The Ta–Ta bond length is amounted to be 2.9325(4) Å, and according to the electron counting rule, it is believed to possess a double-bond character. The spectral data are consistent with an ethane-like $[\text{B}_2\text{H}_6]^{2-}$ unit symmetrically bridging a ditantalum framework. Some structural and spectroscopic parameters of the compounds having same ligand sets (two B_2H_6 moieties) are listed in Table 5.5.



Scheme 5.21 Synthesis of tantalaborane complexes.

The solid-state X-ray structure of compound **111** can be viewed as a dimetallatetrahedron in which a BH_3 moiety is capped on each $\{\text{Ta}_2\text{B}\}$ face. The extra four hydrogen atoms are located on the butterfly-shaped face generated by the $\{\text{Ta}_2\text{B}_2\}$ tetrahedron (Figure 5.22). The selective decoupling ^1H

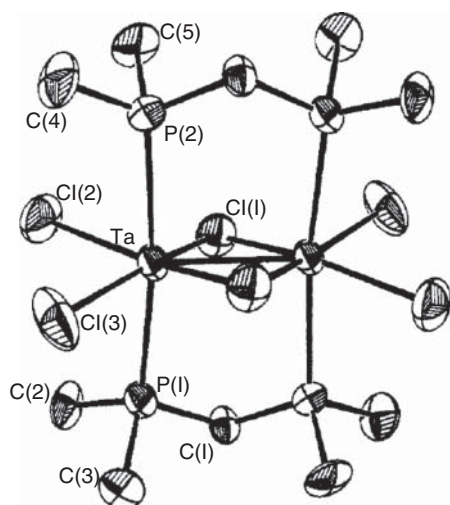


Figure 5.21 ORTEP drawing of $[\text{Ta}_2\text{Cl}_6(\text{dmpp})]$. (Reprinted with permission of American Chemical Society from Ref. [261].)

Table 5.5 Structural parameters and chemical shift values of various metallaboranes having $\{\text{M}_2\text{B}_2\}$ fragment.

Metallaboranes	$d[\text{M}-\text{M}]$ (Å)	^1H NMR $[\text{M}-\text{H}-\text{B}]$ (ppm)	^{11}B NMR (ppm)	References
$[(\text{CpV})(\text{B}_2\text{H}_6)]_2$	2.78	−9.7	1.7	[165]
$[(\text{CpNb})(\text{B}_2\text{H}_6)]_2$	2.94	−10.0	1.7	[165]
$[(\text{Cp}^+\text{Nb})(\text{B}_2\text{H}_6)]_2$	2.94	−10.0	−1.4	[214]
$[(\text{Cp}^*\text{Ta})(\text{B}_2\text{H}_6)]_2$	2.93	−10.5	−4.6	[165]
<i>cis</i> - $[(\text{Cp}^*\text{ReH}_2)\text{ML}]^{\text{a}}$	2.82	na ^b	13.6, −1.9	[264]
<i>trans</i> - $[(\text{Cp}^*\text{ReH}_2)\text{ML}]^{\text{a}}$	2.77	na ^b	−7.7, −20.1	[264]
$[(\text{Cp}^*\text{MoCl})_2(\text{B}_2\text{H}_6)]$	2.69	−13.4	−44.1	[156]
$[(\text{Cp}^*\text{WCl})_2(\text{B}_2\text{H}_6)]$	na ^c	−13.8	−47.8	[157]
$[(\text{Cp}^*\text{TaBr})_2(\text{B}_2\text{H}_6)]$	2.83	−7.6, −7.1	18.8, 10.5	[265]
$[\text{Ta}_2(\text{B}_2\text{H}_6)(\text{DtolF})_4 \cdot \text{Et}_2\text{O}]^{\text{d}}$	2.72	na ^c	na ^c	[266]
$[(\text{Cp}^*\text{M})(\text{B}_2\text{H}_6)]_2$ (M = Mo, W)	na ^c	−10.24 (W) −12.4 (Mo)	−53.9 (W) −58.6 (Mo)	[156, 157]

a) $\text{ML} = \text{Cp}^*\text{Re}(\text{CO})(\text{B}_4\text{H}_4)$.

b) No $\text{M}-\text{H}-\text{B}$.

c) na = not available.

d) $\text{DtolF} = N,N'$ -di(4-methylphenyl)formamidinium anion.

NMR experiment of **111** shows four of the six Ta–H–B protons bridge the open four-membered face, while the other two are located on the boron atoms of the tetrahedral $\{\text{Ta}_2\text{B}_2\}$ core. Two $\{\text{Ta}_2\text{B}_2\}$ units are fused through the Ta–Ta edge with a distance of 2.8909(4) Å, which is in the single bond range. The structural parameters of $\{\text{Ta}_2\text{B}_4\}$ can be compared with a similar core geometry metallaborane clusters $[(\text{Cp}^*\text{Cr})_2\text{B}_4\text{H}_8]$, and $[(\text{Cp}^*\text{ReH}_2)_2\text{B}_4\text{H}_4]$ having five and six seps, respectively (Table 5.6). The increased dihedral angle (167°) of the hydrogen-bridged butterfly may reflect the larger metal radius of Ta.

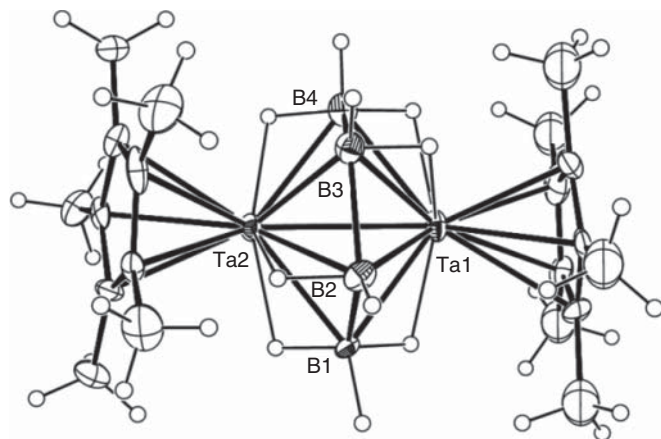


Figure 5.22 ORTEP drawing of $[(\text{Cp}^*\text{Ta})_2\text{B}_4\text{H}_{10}]$. (Reprinted with permission of Wiley VCH from Ref. [263].)

Table 5.6 Chemical shift, sep count, and structural parameters of M_2B_4 core.

Compounds	$d[\text{M}–\text{M}]$ (Å)	sep ^{a)}	Dihedral angle [°] [M_2B_2], Td	^1H NMR [M–H–B] (ppm)	^{11}B NMR	References
$[(\text{Cp}^*\text{Cr})_2\text{B}_4\text{H}_8]$	2.87	5	147.6	–3.90	34.3, 126.5	[154]
$[(\text{Cp}^*\text{ReH}_2)_2\text{B}_4\text{H}_4]$	2.81	6	163.4	–11.52	1.30, 68.7	[158, 159]
$[(\text{Cp}^*\text{Ta})_2\text{B}_4\text{H}_{10}]$	2.89	5	167.7	–7.23, –3.88	0.3, 16.6	[263]

a) sep = skeletal electron pair.

A fascinating hydrogen-rich tantalaborane $[(\text{Cp}^*\text{Ta})_2\text{B}_5\text{H}_{11}]$, **112**, has been isolated from the reaction of $[\text{Cp}^*\text{TaCl}_4]$ and borane reagents. As shown in Figure 5.23, the molecular geometry of **112** resembles a hexagonal bipyramid with a single missing equatorial vertex. The skeletal electron count for **112** is six seps, which is more accurately agreed with a structure of a bicapped trigonal bipyramid. A similar structural interpretation has been suggested for $[(\text{CpV})_2\text{B}_5\text{H}_{11}]$, $[(\text{Cp}^*\text{M})_2\text{B}_5\text{H}_9]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), and $[(\text{Cp}^*\text{ReH})_2\text{B}_5\text{Cl}_5]$. In each case, the trigonal-bipyramidal $[\text{M}_2\text{B}_3\text{H}_3]$ unit is capped by two BH_3 fragments over the M_2B faces. Such interpretation implies the presence of a Ta–Ta single bond and the bond length of 2.9261(4) Å is consistent with this. The structural parameters and spectral data of $\{\text{Ta}_2\text{B}_5\}$ and other $\{\text{M}_2\text{B}_5\}$ analogs have been listed in Table 5.7. The M–M bonds and the M–B and B–B bonds are significantly longer in $\{\text{Ta}_2\text{B}_5\}$, which can be accounted for the larger size of the Ta center and two extra bridging hydrogen atoms compared to the case of Cr. Although the M–H–B proton chemical shifts are not much significant, there is a large difference in ^{11}B chemical shifts of three types of boron atoms in the M_2B_3 core on moving from first- to third-row transition metals.

The above-described tantalaborane clusters $[\text{Cp}^*_2\text{Ta}_2\text{B}_n\text{H}_{n+6}]$ ($n = 4, 5$) are isoelectronic with previously reported group 6 dimetallaboranes of general formula $[\text{Cp}_2\text{M}_2\text{B}_n\text{H}_{n+4}]$. They have *oblatonido* polyhedral structures, which can be derived from the *oblatocloso* dirhenaboranes $[\text{Cp}_2\text{Re}_2\text{B}_{n+1}\text{H}_{n+1}]$ by the removal of an equatorial BH vertex with the adjustment of the skeletal electron count by adding hydrogen atoms. During the synthesis of $[\text{Cp}^*_2\text{Ta}_2\text{B}_n\text{H}_{n+6}]$ ($n = 4, 5$) from $[\text{Cp}^*\text{TaCl}_4]$ and $\text{LiBH}_4/\text{BH}_3$, a less reduced product $[(\text{Cp}^*\text{TaCl})_2\text{B}_5\text{H}_{11}]$, **113**, has also been isolated. The ^{11}B NMR spectrum (temperature-independent down to -55°C) exhibits four doublets in the intensity ratio of

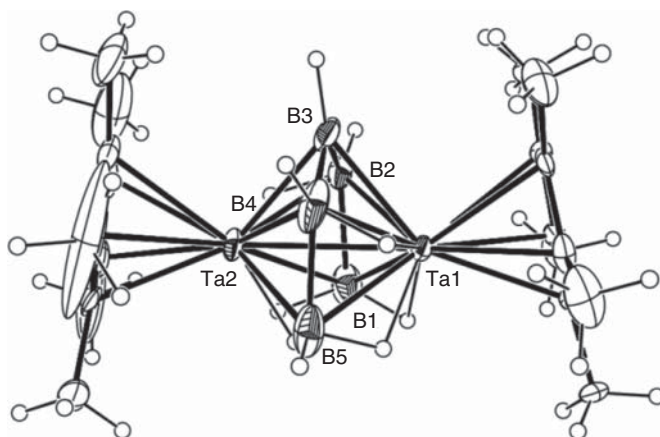


Figure 5.23 ORTEP drawing of $[(\text{Cp}^*\text{Ta})_2\text{B}_5\text{H}_{11}]$. (Reprinted with permission of Wiley VCH from Ref. [263].)

Table 5.7 Structural matrices and chemical shifts of metallaboranes having M_2B_5 core.

Metallaboranes	$d[\text{M}-\text{M}]$ (Å)	^1H NMR $[\text{M}-\text{H}-\text{B}]$ (ppm)	^{11}B NMR (ppm) ^{a)}	References
$[(\text{CpV})_2\text{B}_5\text{H}_{11}]$	2.76	−9.01 and −8.2	−1.8, 3.4, and 21.9	[166]
$[(\text{Cp}^*\text{Ta})_2\text{B}_5\text{H}_{11}]$	2.92	−6.6 and −3.8	3.7, 23.9, and 44.7	[263]
$[(\text{Cp}^*\text{Ta})_2\text{B}_5\text{H}_{10}\text{L}]^{\text{b)}}$	2.90	na ^{c)}	na ^{c)}	[263]
$[(\text{Cp}^*\text{Cr})_2\text{B}_5\text{H}_9]$	2.62	−6.20	25.0, 91.5, and 86.2	[152]
$[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9]$	2.80	−6.99	62.9 ^{d)} (3B) and 25.8	[153]
$[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9]^{\text{e)}}$	2.81	−7.01	61.6, 27.8, 59.7	[267]
$[(\text{Cp}^*\text{W})_2\text{B}_5\text{H}_9]$	2.81	−8.20	26.8, 46.9, and 49.2	[154]
$[(\text{Cp}^*\text{ReH})_2\text{B}_5\text{Cl}_5]$	2.76	−9.30	48.3, 88.3, and 28.1 ^{f)}	[155]

a) Three ^{11}B resonances: capped, apical, and the unique equatorial boron in M_2B_5 bicapped *thp* core.

b) $\text{L} = \text{C}_6\text{H}_4\text{CH}_3$.

c) na = not available.

d) Accidental overlap of the capping and equatorial ^{11}B resonances.

e) $\text{Cp}^* = \eta^5\text{-C}_5\text{H}_4\text{Me}$.

f) All five terminal hydrogens are substituted by chlorine atoms.

1 : 1 : 1 : 2, consistent with a symmetric structure or a fluxional system. The ^1H NMR shows resonances beside the BH protons (1 : 1 : 1 : 2), one Ta–H–Ta, one B–H–B, and four Ta–H–B protons. A $^1\text{H}/^{11}\text{B}$ HETCOR experiment showed two of the four Ta–H–B protons to be coupled exclusively to a pair of equivalent boron atoms and the other two to the unique boron atom (open face). The solid state structure unravels that $\{\text{Ta}_2\text{B}_5\text{Cl}_2\}$ is a *nido* structure based on a *closo* dodecahedron (Figure 5.24). The Ta–Ta distance is too long for a Ta–Ta single bond (cf. $[\{\text{TaCp}^*\text{Cl}_2\text{H}\}_2]$); however, it is too short to propose that there is no significant interaction at all between the two metal centers. Another interesting feature of **113** is the presence of a bridging hydride ligand between the two Ta centers. Usually, a bridging hydride ligand pulls the metal atoms together to form a three-center two-electron bond, but this is in marked contrast to **112**, in which the M–M distance is too large for a significant bonding interaction (Ta–Ta = 3.2219(3) Å). If we compare both $[\text{Cp}^*_2\text{Ta}_2\text{B}_5\text{H}_{11}]$ and $[\text{Cp}^*_2\text{Ta}_2\text{Cl}_2\text{B}_5\text{H}_{11}]$, the latter one contains two extra chlorine atoms, and it can formally be generated from the addition of chlorine atoms across the Ta–Ta double bond of $[\text{Cp}^*_2\text{Ta}_2\text{B}_5\text{H}_{11}]$ [268].

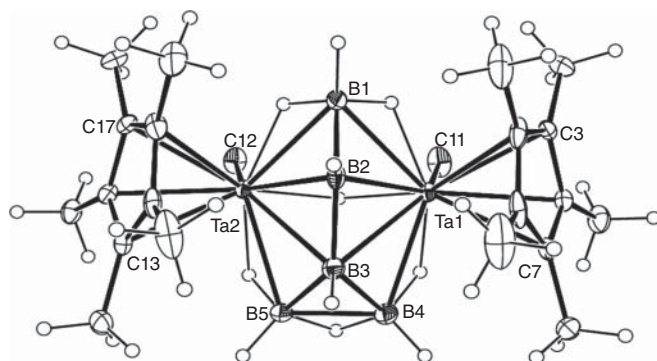


Figure 5.24 ORTEP drawing of $[(\text{Cp}^*\text{Ta})_2\text{B}_5\text{Cl}_2]$. (Reprinted with permission of Wiley VCH from Ref. [263].)

5.4.6

Cluster Growth Reaction of Ditanalaboranes

Cluster expansion reaction is very well known in metallaborane chemistry, and several approaches to the construction of clusters have been reported. For example, (i) condensation involving monoborane reagents, (ii) insertion or fragmentation involving borane or metal carbonyl fragments, and (iii) intercluster fusion with two or more atoms held in common between the constituent subclusters. In this way, thermolysis of **110** with $[\text{BH}_3 \cdot \text{thf}]$ yielded tanatallaborane $[(\text{Cp}^*\text{Ta})_2\text{B}_4\text{H}_9(\mu\text{-BH}_4)]$, **114**. The ^{11}B NMR resonances correspond closely to those of the comparable atoms of **111** along with another upfield resonance at $\delta = -20.8$ ppm. The variable-temperature ^1H NMR data (Figure 5.25) revealed that the resonance at $\delta = -10.9$ ppm collapses into four resonances. Among the four resonances, two Ta–H–B protons are appeared at $\delta = -10.7$ and -11.4 ppm, whereas the signals at $\delta = 4.15$ and -15.9 are assigned to two B–H_t (t = terminal) protons, and Ta–H_t hydride proton respectively. While the peak at $\delta = -10.9$ ppm started sharpening, resonance at $\delta = -7.4$ ppm (four Ta–H–B protons) splits into two distinct peaks at $\delta = -6.7$ and -7.8 ppm in a 1 : 1 ratio. The Cp* resonance became two separate signals in low-temperature study because the presence of one Ta–H_t made two different Ta centers inequivalent. As shown in Figure 5.26, the X-ray structure reveals that coordination of tetrahydroborate ligand through two Ta–H–B bridges in an end-on manner to a bicapped tetrahedral cage made by $\{\text{Ta}_2\text{B}_4\}$ units. The Ta–Ta bond length of $2.8946(2)$ Å clearly indicates the presence of a metal–metal interaction. The “BH₄” moiety is distorted from a tetrahedral geometry as the angles

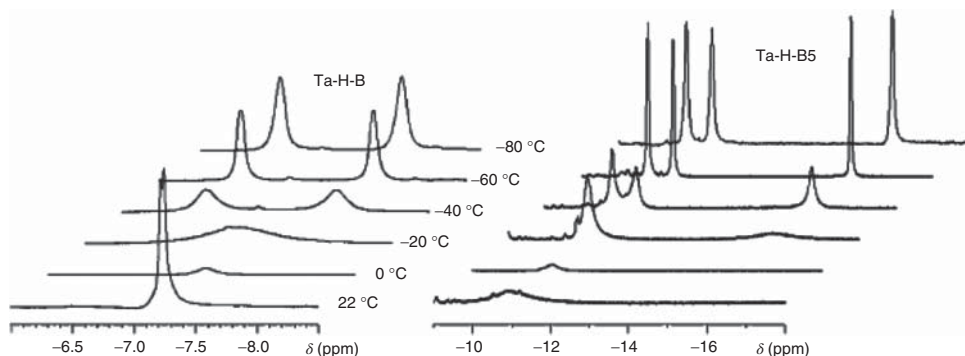


Figure 5.25 Variable temperature $^1\text{H}(^{11}\text{B})$ NMR of $[(\text{Cp}^*\text{Ta})_2\text{B}_4\text{H}_9(\mu\text{-BH}_4)]$.

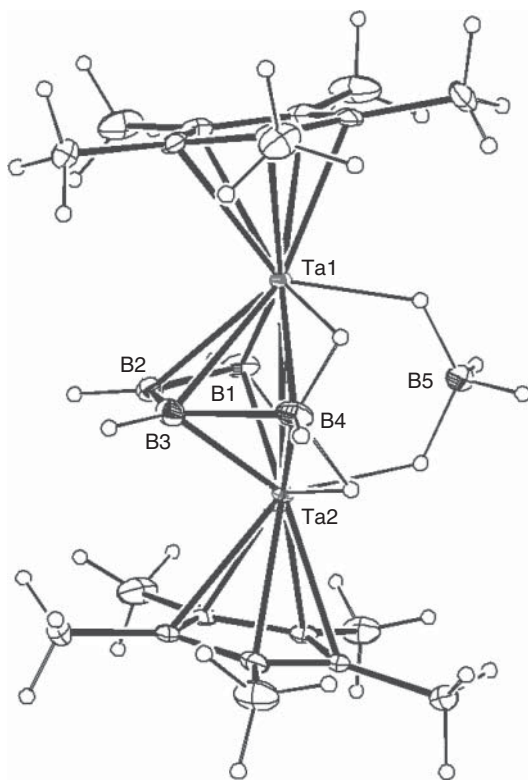


Figure 5.26 ORTEP drawing of $[(\text{Cp}^*\text{Ta})_2\text{B}_4\text{H}_9(\mu\text{-BH}_4)]$. (Reprinted with permission of Wiley VCH from Ref. [165].)

around the borohydride boron atom range from 97.97° to 126.20° , which are quite different from the expected value of 109.58° for a regular tetrahedral geometry.

5.4.7

μ -Acyl Complexes

Metal acyl derivatives are significant intermediates in many catalytic processes, and in general, these complexes (η^1 - or η^2 -acyl) can be synthesized by the migratory insertion of the CO molecule into the transition metal alkyl bond. There are three different classes of metal acyl derivatives, which have been shown in Chart 5.1: (a) C-bonded σ -acyl; (b) η -acyls, C- and O-bonded to the same metal; and (c) C- and O-bonded μ -acyls, bridging two metal centers. Using freshly prepared $[\text{BH}_3 \cdot \text{thf}]$ permits the isolation of the μ - η^2 -acyl complex $[(\text{Cp}^*\text{Ta})_2\text{B}_4\text{H}_8(\mu\text{-}\eta^2\text{-COCH}_3)]$, **115** [269]. All attempts to increase the yield through changes in the solvent, temperature, and time did not meet with success. The single-crystal X-ray diffraction studies not only established the location of all atoms but also revealed the nature of the acyl moiety attached to tantalum atoms (Figure 5.27).

The observed Ta–Ta bond length of $2.8738(6) \text{ \AA}$, comparable to that of $[(\text{Cp}^*\text{Ta})_2\text{B}_4\text{H}_{10}]$, indicates a weak bridging property of the acyl group. Although the Ta2–O1 bond length of $2.003(11) \text{ \AA}$ is in the range for Ta–O single bonds, the Ta1–O1 distance of $2.314(12) \text{ \AA}$ is much longer than for a single bond. This notable difference in the bond length may be due to two different bonding modes of the acyl group to Ta atoms. The bond angles

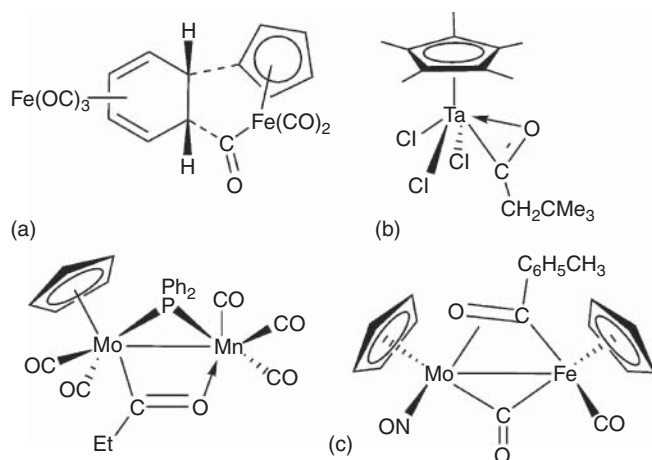


Chart 5.1 Different metal acyl derivatives: (a) C-bonded σ -acyl, (b) η -acyls, C- and O-bonded to same metal, and (c) C- and O-bonded μ -acyls, bridging two metal centers.

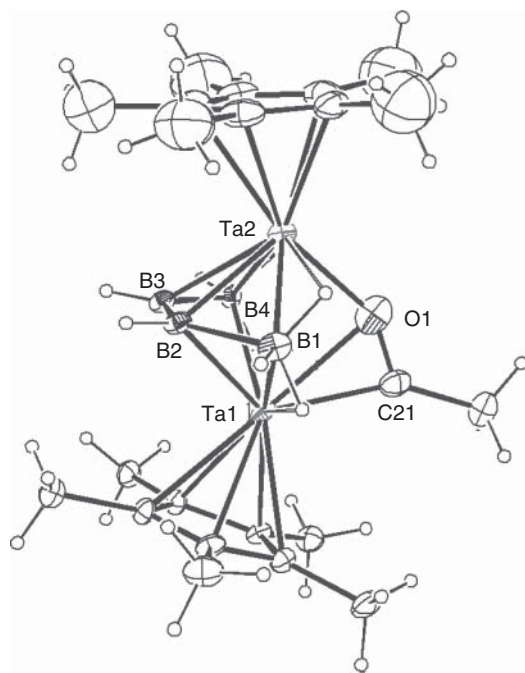


Figure 5.27 ORTEP drawing of $[(\text{Cp}^*\text{Ta})_2\text{B}_4\text{H}_8(\mu\text{-}\eta^2\text{-COCH}_3)]$. (Reprinted with permission of American Chemical Society from Ref. [269].)

and lengths associated with the μ -acyl moiety are in line with other μ -acyl compounds. Mechanistic study with $\text{BH}_3 \cdot \text{thf-d}_8$ and the intermediate, generated from the reaction of $[\text{Cp}^*\text{TaCl}_4]$ and $[\text{LiBH}_4 \cdot \text{thf}]$, revealed that formation of the acyl bridging occurs from the fragmentation of thf ligand, which is coordinated to the metal center to form the acyl complex **115**.

5.4.8

Oxametallaboranes

Polyhedral heteroborane chemistry is dominated by carboranes and metallacarboranes [270–272]. By contrast, structurally characterized polyhedral oxametallaborane clusters that contain oxygen as a cluster constituent with a cluster connectivity of three are very rare. Until now, few of these types are known (Chart 5.2); these are *nido*- $[(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{FeOB}_8\text{H}_{10}]$ [273], *arachno*- $[(\text{PMe}_2\text{Ph})_2\text{PtOB}_8\text{H}_{10}]$ [274], *nido*- $[\text{Cp}^*\text{RhOB}_{10}\text{H}_{10}(\text{NEt}_3)]$ [275, 276], *nido*- $[\text{Cp}^*\text{RhOB}_{10}\text{H}_9\text{Cl}(\text{PMe}_2\text{Ph})]$ [277, 278], $[(\text{Cp}^*\text{Mo})_2\text{B}_5(\mu_3\text{-OEt})\text{H}_6\text{R}]$ ($\text{R} = \text{H}, n\text{-BuO}$) [278], $[(\text{Cp}^*\text{Ta})_2\text{B}_4\text{H}_{10}\text{O}]$ [279], and $[(\text{CpV})_2\text{B}_3\text{H}_8(\mu_3\text{-OEt})]$ [166]. Reaction of $[\text{Cp}^*\text{TaCl}_4]$ with $[\text{LiBH}_4]$ followed by thermolysis with $[\text{BH}_3 \cdot \text{thf}]$ led to the isolation of a rare class of oxametallaborane compound, **116**. The X-ray structure shows that one oxygen atom is bound to two Ta metals and one boron atom, and it can be considered an edge-fused cluster, in which a trigonal-bipyramidal unit $[\text{Ta}_2\text{B}_2\text{O}]$ has been fused with a tetrahedral core $[\text{Ta}_2\text{B}_2]$ by a common $[\text{Ta}_2]$ edge (Figure 5.28). The source of the oxygen atom is probably the presence of trace amounts of water/air bound to the silica gel. The Ta–Ta bond length of 2.7554(2) Å is significantly shorter compared to other tantalaborane clusters. The significant shortening of the Ta–Ta bond might arise from the effect of the oxygen atom, which withdraws electron density from the cluster. The short Ta–Ta bond has been exemplified as a double bond through DFT calculation. A σ -bond involving the d_{z^2} orbital and a π -bond involving the d_{yz} orbital of the metals are responsible for the double-bond character.

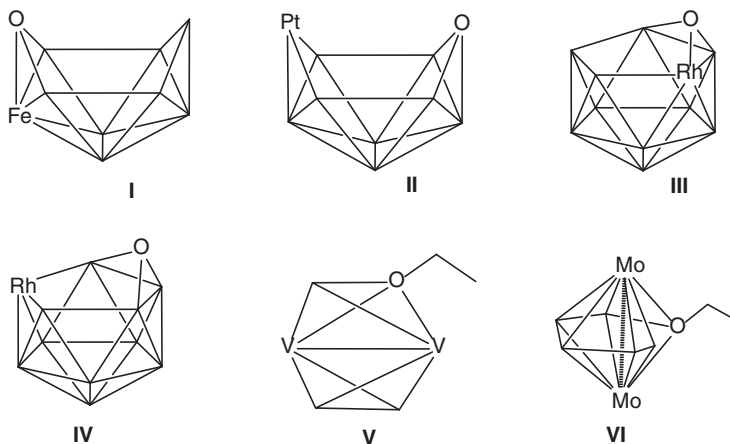


Chart 5.2 Various oxametallaborane clusters.

5.4.9

Triply Bridged Borylene Complexes

Metallaborane and borylene complexes are related to some extent because both types possess direct metal–boron bonds; however, the nature of these interactions is varied. In metallaborane clusters, the framework is made up by nonclassical, electron-deficient, multicenter two-electron bonds, while the borylene ligand (BR) is related to one or more transition metal centers by classical, electron-precise, two-center two-electron (2c–2e) bonds [280–283]. Since the discovery of various bridged and terminal borylene complexes by Braunschweig and Aldrige, the chemistry of this subarea of transition metal complexes of boron has received significant attention from both structure/bonding and

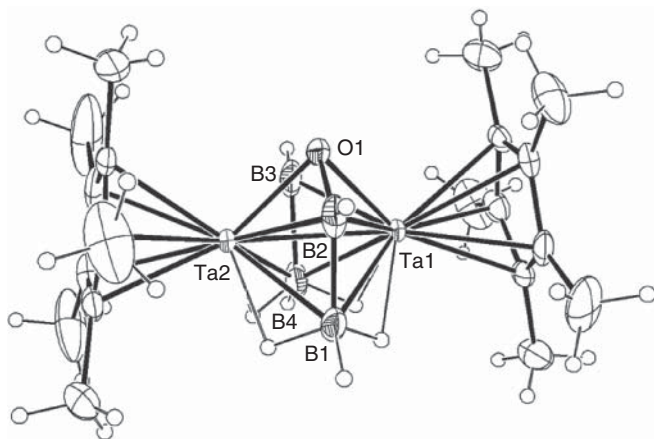


Figure 5.28 ORTEP drawing of $[(\text{Cp}^*\text{Ta})_2\text{B}_4\text{H}_{10}\text{O}]$. (Reprinted with permission of American Chemical Society from Ref. [279].)

reactivity perspectives [284–286]. Owing to the coordination of boron to stabilizing the metal centers and additional steric protection, bridging borylene complexes (Chart 5.3) are in general more stable than their terminal analogs [287–291].

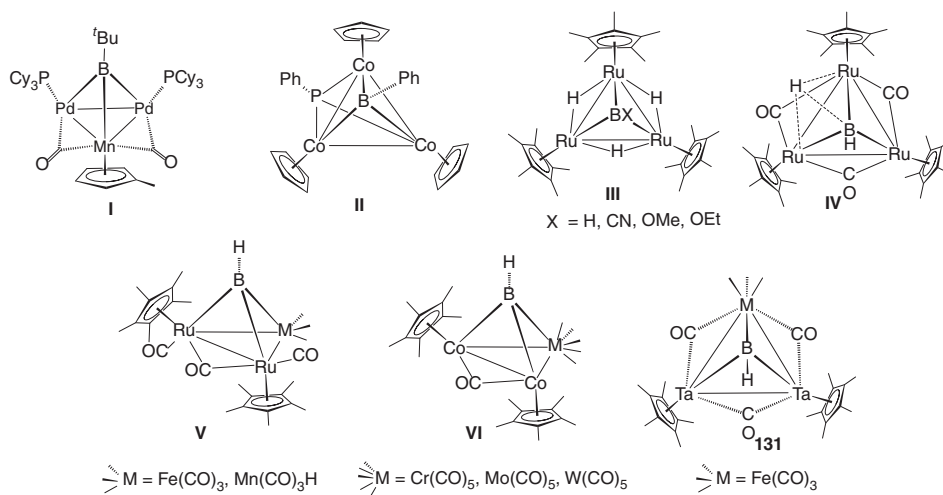


Chart 5.3 Different types of triply bridged borylene molecules.

Mild pyrolysis of **114** with $[\text{Fe}_2(\text{CO})_9]$ yielded triply bridged borylene compound $[(\mu_3\text{-BH})(\text{Cp}^*\text{TaCO})_2(\mu\text{-CO})\{\text{Fe}(\text{CO})_3\}]$, **117**, along with $[(\text{Cp}^*\text{Ta})_2\text{B}_5\text{H}_9\{\text{Fe}(\text{CO})_3\}_4]$, **118**, and $[(\text{Cp}^*\text{Ta})_2\text{B}_5\text{H}_7\{\text{Fe}(\text{CO})_3\}_2]$, **119** [292]. The composition of triply bridged borylene complex, **117**, has been determined by comparing the spectroscopic data with the known triply bridged borylene complexes. The ^{11}B NMR of **117** shows a broad resonance at $\delta = 119.5$ ppm, which is consistent with a bridging borylene ligand. Various triply bridged (homo- or heterometallic) complexes are known and they are listed in Table 5.8. A closer examination reveals the relationship between the electron count and the structural matrices present in these compounds.

Table 5.8 Structural parameters and chemical shift values of triply bridged borylene complexes.

Compounds	sep	$d_{\text{avg.}}$ [M–M] (Å)	$d_{\text{avg.}}$ [M–B] (Å)	^{11}B NMR (ppm)	^1H NMR [M–H–M] (ppm)	References
$[(\mu_3\text{-B}'\text{Bu})\{[(\eta^5\text{-Cp}')\text{Mn}(\text{CO})_2][\text{Pd}(\text{PCy}_3)_2]\}]^{\text{a}}$	3	2.644	2.086	150	na ^{b)}	[293]
$[(\text{CpCo})_3(\mu_3\text{-BPh})\text{PPh}]$	6	2.529	2.038	143.7	na ^{b)}	[287]
$[(\mu\text{-H})\text{Fe}_3(\text{CO})_9\text{BH}_3\text{R}]$	6	2.622	2.167	1.8	–24.4	[294]
$[(\text{Cp}^*\text{Ru})_3(\mu\text{-H})_3(\mu_3\text{-BOEt})]$	4	2.677	2.154	87.7	–2.23	[288]
$[(\text{Cp}^*\text{Ru})_3(\mu\text{-H})_3(\mu_3\text{-BH})]$	4	2.757	2.137	131.3	–1.93	[288]
$[(\text{Cp}^*\text{RuCO})_3(\text{H})(\mu_3\text{-BH})]$	6	2.757	2.137	91.3	–7.53	[290]
$[(\mu_3\text{-BH})(\text{Cp}^*\text{RuCO})_2(\mu\text{-CO})\{\text{Fe}(\text{CO})_3\}]$	6	2.725	2.092	119.3	na ^{b)}	[289]
$[(\text{Cp}^*\text{Ta})_2(\mu\text{-CO})_3(\mu_3\text{-BH})\{\text{Fe}(\text{CO})_3\}]$	3	na ^{b)}	na ^{b)}	na ^{b)}	na ^{b)}	[289]
$[(\mu_3\text{-BH})(\text{Cp}^*\text{RuCO})_2(\mu\text{-H})(\mu\text{-CO})\{\text{Mn}(\text{CO})_3\}]$	6	2.784	2.155	89.0	–6.37	[289]
$[(\mu_3\text{-BH})(\text{Cp}^*\text{Co})_2(\mu\text{-CO})\text{Cr}(\text{CO})_5]$	6	na ^{b)}	na ^{b)}	138.3	na ^{b)}	[291]
$[(\mu_3\text{-BH})(\text{Cp}^*\text{Co})_2(\mu\text{-CO})\text{Mo}(\text{CO})_5]$	6	2.696	1.766	139.3	na ^{b)}	[291]
$[(\mu_3\text{-BH})(\text{Cp}^*\text{Co})_2(\mu\text{-CO})\text{W}(\text{CO})_5]$	6	2.688	2.098	141.3	na ^{b)}	[291]

a) $\text{Cp}' = \text{C}_5\text{H}_4\text{Me}$.

b) na = not available.

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6

Group 6 Metal–Metal Bonds

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6.1

Metal–Metal Quadruple Bonds

The majority of dimetal quadruply bonded group 6 compounds are either the square parallelepiped type $[M_2X_{8-n}L_n]^{(4-n)-}$ ($n = 0-4$; L = neutral donor ligand) compounds or paddlewheel compounds of form $M_2(EE'CR)_4$ (E, E' = O, N{R}, S; R = alkyl or aryl group), shown in Chart 6.1. The dimetal core in these compounds has a $\sigma^2\pi^4\delta^2$ electronic configuration that results in a formal quadruple bond between the metal centers, and these compounds often have interesting redox and optoelectronic properties. The eclipsed arrangement of the ligands in square parallelepiped compounds maximizes the δ -bonding overlap. The paddlewheel compounds are particularly versatile as a range of bridging ligands, such as amidinates, 2-oxy- or 2-amino-pyridinates and carboxylates, can be used (Chart 6.1). There are now literally hundreds of examples of these compounds in the literature, which reflects both the maturity of the field and the continued strong interest in these compounds, as they have applications that range from chemical reducing agents to models for electronic transfer processes. In the following section, we focus on the more recent advances in the field since 2005 and in particular on structures and properties since the synthetic methodologies are now well developed. Readers can find a comprehensive and authoritative review of the field in the most recent edition of the book *Multiple Bonds Between Metal Atoms*. [1]

6.1.1

Synthesis and Characterization

6.1.1.1 Chromium

The structures of $Cr(II)_2$ compounds show a surprisingly large range of Cr–Cr bond lengths (1.77–2.60 Å). The record for the shortest metal–metal bond length was held for nearly 30 years by the quadruply bonded compounds $Cr_2(2-MeO-5-MeC_6H_5)_4$ and $Li_6Cr_2(2-O-C_6H_4)_4Br_2(Et_2O)_6$, which were structurally characterized by Cotton and coworkers in 1978, and these compounds have “supershort” Cr–Cr bond lengths of 1.828(2) and 1.830(4) Å [2]. This record was not beaten until the recent discovery of dichromium compounds with formal metal–metal quintuple bonds. Another $Cr(II)_2$ compound with an even shorter Cr–Cr bond length than Cotton’s oxyphenyl compounds was reported in 2008. The reaction of bis(guanidinate) $Cr(CyNC\{N(SiMe_3)_2\}NCy)_2$ with $AlMe_3$ afforded the quadruply bonded compound $Cr_2(CyNC\{N(SiMe_3)_2\}NCy)_2(Me)_2$ [3]. The structure of this compound is shown in Figure 6.1, and the Cr–Cr bond length of 1.773(1) Å is the shortest reported to date for a Cr_2^{4+} compound. Interestingly, the bridging methyl groups in this compound are each oriented toward a chromium atom, which suggests the presence of four-center agostic interactions.

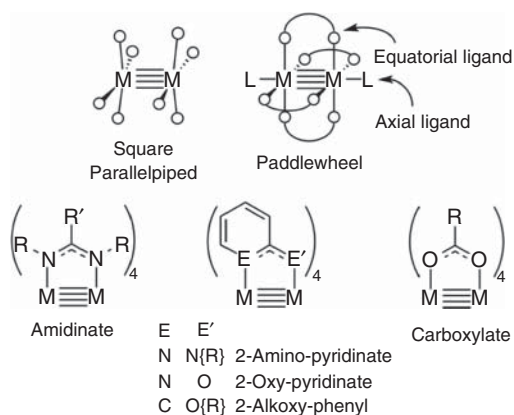


Chart 6.1 Different types of dimetal quadruply bonded compounds.

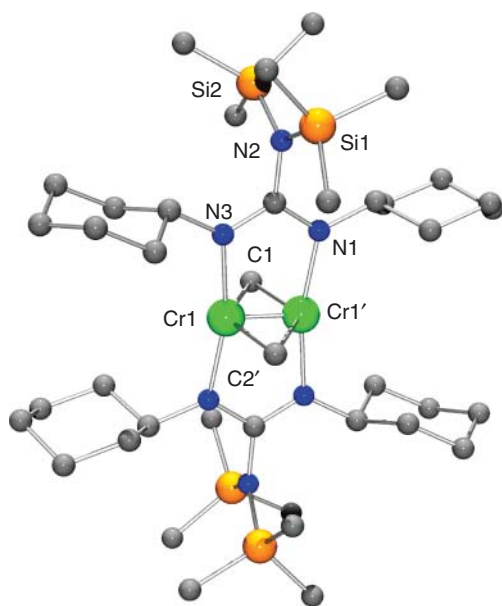


Figure 6.1 Crystal structure of $\text{Cr}_2(\text{CyNC}\{\text{N}(\text{SiMe}_3)_2\}\text{NCy})_2(\text{Me})_2$.

While the electronic structure of Mo_2^{4+} and W_2^{4+} compounds can be relatively well described as $\sigma^2\pi^4\delta^2$ whatever class of bridging ligand is used, the nature of the quadruple bond in Cr_2^{4+} compounds is more complicated. For example, dichromium tetracarboxylates often exhibit weak paramagnetism at room temperature that can be attributed to thermal population of paramagnetic excited states. This often means that DFT calculations on dichromium compounds can struggle to model their structural and spectroscopic properties, and multiconfigurational calculations are required to more accurately predict these properties and calculate effective bond orders (EBOs) [4]. Complications in understanding the nature of the Cr–Cr bond have also been highlighted in a joint resonance Raman spectroscopy and DFT study on $\text{M}_2(\text{dmp})_4$ ($\text{M} = \text{Cr}$ or Mo ; $\text{dmp} = 2,6\text{-dimethoxyphenyl}$) [5]. The experimental data for $\text{Mo}_2(\text{dmp})_4$ matched the theoretical and empirical predictions, whereas the vibrational data for $\text{Cr}_2(\text{dmp})_4$ differed radically from theory. The Cr–Cr stretch was predicted

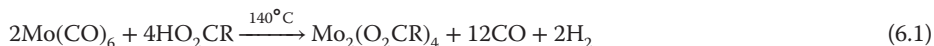
both empirically and theoretically to be in the region $650\text{--}700\text{ cm}^{-1}$; this stretch was not observed, but rather three bands were found at a much lower frequency ($\sim 350\text{ cm}^{-1}$), with ^{50}Cr and ^{54}Cr isotope labeling showing that these modes have both Cr–Cr and Cr–ligand characters.

The presence of solvent ligands or intermolecular contacts in the axial position of Cr(II)_2 compounds is known to strongly influence the Cr–Cr bond length in the solid state because of back-bonding into antibonding orbitals such as the $\text{Cr}_2\text{--}\sigma^*$. For dichromium carboxylates, solid-state structural characterization without axial ligands proved problematic until the report of a $\text{Cr}_2(\text{T}^i\text{PB})_4$ ($\text{T}^i\text{PB} = 2,4,6\text{-triisopropylbenzoic acid}$) by Cotton and Murillo [6]. The bulky T^iPB ligand protected the axial positions, and a short Cr–Cr bond length of $1.9662(5)\text{ \AA}$ was found. By contrast, the acetonitrile adduct $\text{Cr}_2(\text{T}^i\text{PB})_4(\text{MeCN})_2$ had a significantly longer Cr–Cr bond length ($2.389(2)\text{ \AA}$).

More recent efforts have targeted using the metal complexes coordinated to the axial site to modulate the electronic structure and properties of the Cr–Cr quadruple bond. A range of heterotrimetallic $\text{CrCr}\cdots\text{M}$ chains with the general form $(\text{Y})\text{Cr}_2\text{M}(\text{dpa})_4(\text{Cl})$ ($\text{M} = \text{Fe, Mn, Co, Zn}$; $\text{dpa} = 2,2'\text{-dipyridylamide}$; $\text{Y} = \text{Cl, OTf, NCS}$; see Figure 6.2) have been synthesized by Nippe and Berry. When $\text{M} = \text{Fe}$ and $\text{Y} = \text{Cl}$, the redox potential of the $\text{Fe}^{2+/3+}$ couple is remarkably low by comparison to related compounds that have been used as models for peroxidase enzymes [7]. Given that the axial ligand Y is remote from the N_4FeCl complex, it was surprising to observe that as Y is changed from Cl to NCS to OTf, the iron oxidation potential shifts to significantly higher potential [8]. Structural studies showed that more weakly bound axial anions such as OTf cause a tilting of the dpa ligand toward the Cr(II)_2 core, weakening the binding to Fe, and significantly altering the ligand field strength. Other first row transition metals from Mn to Zn were also incorporated into the heterotrimetallic chains, and the Cr–Cr bond distances in these compounds span a narrow range of $2.00\text{--}2.07\text{ \AA}$. This invariance of the Cr–Cr bond length to the nature of the axial metal “ligand” indicates that there is little or no $\text{Cr}_2\cdots\text{M}$ heterometallic bonding, in agreement with other experimental and theoretical studies [9].

6.1.1.2 Molybdenum and Tungsten

Dimolybdenum tetracarboxylates are readily prepared from the reaction of Mo(CO)_6 and the relevant carboxylic acid under anaerobic conditions in refluxing organic solvents, such as 1,2-dichlorobenzene or diglyme, which have high boiling points (Eq. (6.1)) [10]. Small amounts of other solvents, such as THF or hexane, are often added to the reaction vessel in order to wash the unreacted metal hexacarbonyl from the top of the flask. Dimolybdenum compounds with amidate or amidinate ligands are often prepared either by the reaction of $\text{M}_2(\text{O}_2\text{CCH}_3)_4$ with the alkali metal salt of the ligand, or again by a thermolysis reaction between M(CO)_6 and the ligand [11].



The chemistry of ditungsten paddlewheel compounds is substantially less developed than the periodically related dichromium and dimolybdenum analogs. This is in part due to the increased susceptibility of the W_2^{4+} core to reaction with O_2 and in part to the increased difficulty in synthesizing the tetracarboxylate analogs. One of the most commonly used methods is the reaction of WCl_4 and the sodium carboxylate with Na/Hg in THF (Eq. (6.2)) [12]. While this route works for a number of carboxylates, $\text{W}_2(\text{O}_2\text{CCH}_3)_4$ has to be prepared by metathesis of

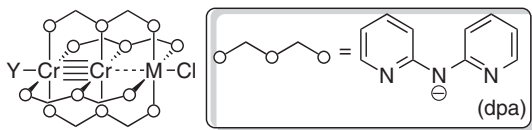


Figure 6.2 Structure of $(\text{Y})\text{Cr}_2\text{M}(\text{dpa})_4(\text{Cl})$ compounds.

$W_2(O_2CCF_3)_4$ [13] with $[NBu_4][O_2CCH_3]$ instead. Recent attempts have been made to generate ditungsten tetracarboxylates by carboxylate exchange with the readily accessible $W_2(mhp)_4$ ($Hmhp$ = 2-hydroxy-6-methylpyridine) starting material [14]. The reactions generated a mixture of $W_2(mhp)_{4-n}(O_2CR)_n$ products, which exist in a dynamic equilibrium in solution. However, an exception was found when 9-anthracene carboxylate was used; the $W_2(O_2CR)_4$ product precipitated from the reaction mixture driving the reaction to the desired product.



In addition to homoleptic compounds, species with more than one ligand type can be prepared. For example, the reaction of $M_2(T^iPB)_4$ ($M = Mo, W$; T^iPB = 2,4,6-triisopropylbenzoate) with 2 equiv. of 2-thienylcarboxylic acid (O_2C-Th) yields *trans*- $M_2(T^iPB)_2(O_2C-Th)_2$ [15]. Mixed carboxylate/amidinate compounds of form *trans*- $M_2(O_2CR)_2(R'NC\{R''\}NR')_2$ can also be prepared by the reaction of dimetal tetracarboxylate with the alkali metal salt of the ligand [16].

A number of quadruply bonded dimolybdenum compounds with unusual geometries have also been reported recently. The quadruply bonded compound $Mo_2(\mu-\eta^2-Me_2Si(NDipp)_2)_2$ ($Dipp$ = 2,6-*i*-Pr₂C₆H₃; Figure 6.3) was prepared by reduction of the triply bonded precursor $Mo_2(\mu-\eta^2-Me_2Si(NDipp)_2)_2Cl_2$ with Na/Hg [17]. The Mo–Mo bond length in this compound is 2.1784(12) Å, which is relatively long for a Mo–Mo quadruple bond. DFT calculations indicate that the δ -bonding in the Mo_2^{4+} core of this compound, which has *pseudo*- D_{2h} symmetry, results from overlap of the $d_{x^2-y^2}$ orbitals with the d_{xy} orbitals involved in forming metal–ligand bonds; this is the opposite of paddlewheel compounds with D_{4h} symmetry in which the d_{xy} orbitals are involved in M_2 δ -bonding and the $d_{x^2-y^2}$ in metal–ligand bonding. Also shown in Figure 6.3 is the crystal structure of $Mo_2(O_2CH)_2(Ar^{Xyl2})_2$ (Ar^{Xyl2} = C₆H₃-2,6-(C₆H₃-2,6-Me₂)₂), which displays a Mo–Mo bond length (2.095(1) Å) typical of a quadruple bond [18]. It appears as though there is a possible bonding between one of the flanking aryl rings and a Mo atom ($Mo1 \cdots C15$ = 2.78 Å) in this compound and its monosubstituted analog, $Mo_2(O_2CCH_3)_3(Ar^{Xyl2})$, although DFT calculations showed that these are very weak interactions that are primarily ionic in nature. The benzene–dimolybdenum complex $Mo_2(HL^{iPr})_2(\mu-C_6H_6)$ (HL^{iPr} = *N,N'*-bis(2,6-diisopropylphenyl)-1,4-diazadiene) was synthesized by the reaction of $MoCl_4(THF)_2$, HL^{iPr} , and magnesium powder in benzene. The structure is displayed in Figure 6.3 and shows that the aryl ligand bridges the dimolybdenum core with a Mo–Mo bond length of 2.1968(4) Å [19]. This compound employs the same ligand set as $Cr_2(HL^{iPr})_2$ (5) and is analogous to the arene complex $Mo_2(\mu-RC\{N-2,6-iPr_2-C_6H_3\}_2)(\mu-C_6H_6)$ (15-C₆H₆), both of which are discussed in Section 6.2. It is difficult to assign a formal Mo–Mo bond order in this compound as it is likely to be reduced by mixing of the Mo_2 - δ and HL^{iPr} - π orbitals (cf. 5), as well as a possible further reduction due to mixing of the Mo_2 - δ^* orbitals with the benzene- π^* orbitals (cf. 15-C₆H₆), but the Mo–Mo bond length suggests a long quadruple bond.

One of the most useful features of the quadruple bond is its redox chemistry. The dimetal core readily loses one electron to generate a radical cation with a $\sigma^2\pi^4\delta^1$ electronic configuration and a formal MM bond order of 3.5. The radical cations are typically unstable in solution for more than a few minutes at room temperature unless the M_2^{5+} core is protected by a bulky ligand [20]. The $M_2^{4+/5+}$ redox couple is often reversible in electrochemical experiments; the M_2^{4+}/M_2^{3+} redox couple is also sometimes observed, although it is typically irreversible. The potential richness of the chemistry associated with the redox behavior of these compounds is perhaps best exemplified by the reversible four-electron oxidation of $W_2(dpa)_4$ [21]. This compound can be oxidized by four electrons to generate the W(IV)-oxo species $[W_2O(dpa)_4]^{2+}$. This process is reversible, and the oxo species undergoes a four-electron reduction upon reaction with P^tBu_3 to regenerate $W_2(dpa)_4$, but surprisingly no phosphine oxide is formed. Instead, phosphonium ions and acetamide, the hydrolysis product of the acetonitrile solvent, are the oxidation products.

The potential of the $M_2^{4+/5+}$ redox couple can be tuned by over 1 V by changing the metal and axial or equatorial ligands. For example, the oxidation potential of a series of compounds of form $Mo_2(EE'C\equiv CPh)_4$ ($EE' = \{NPh\}_2, \{NPh\}O, \{NPh\}S$, and OO) can be tuned by 0.9 V with simple N for

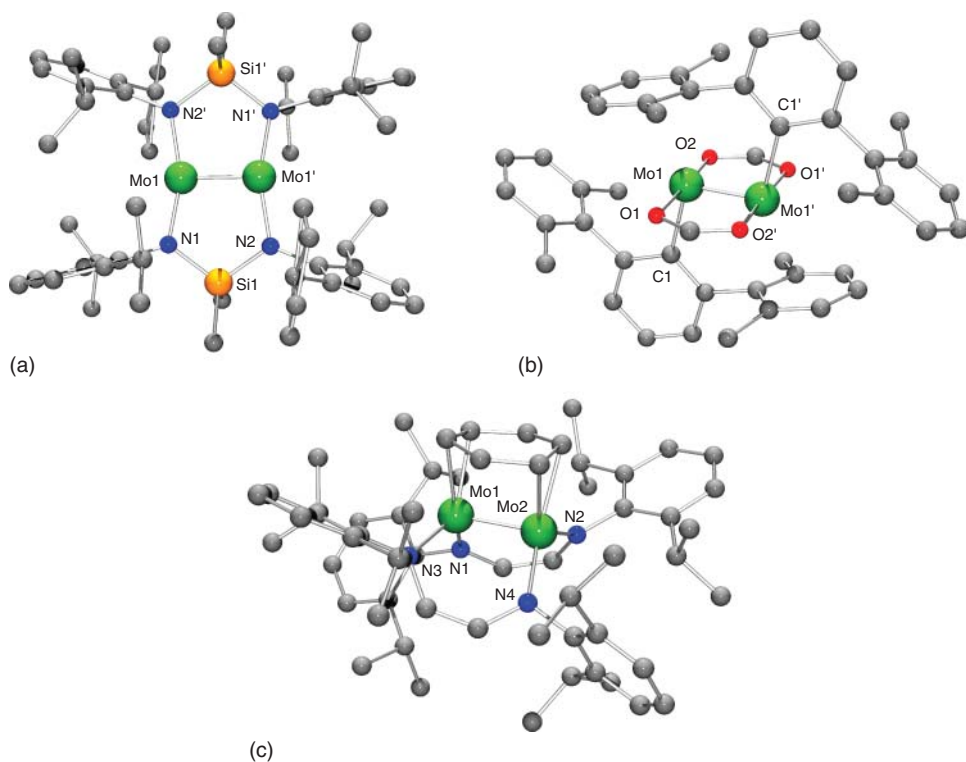


Figure 6.3 Crystal structures of $\text{Mo}_2(\mu\text{-}\eta^2\text{-Me}_2\text{Si(NDipp)}_2)_2$ (a) [17], $\text{Mo}_2(\text{O}_2\text{CH})_2(\text{Ar}^{\text{Xyl}2})_2$ (b) [18], and $\text{Mo}_2(\text{H}^{\text{iPr}})_2(\mu\text{-C}_6\text{H}_6)$ (c) [19].

O for S substitution [22]. This large change in redox potential can alter the reactivity of the Mo_2 core; the dimolybdenum tetracarboxylate $\text{Mo}_2(\text{T}^{\text{iPB}})_4$ can act as a catalyst for radical addition reactions of polyhaloalkanes to 1-alkenes, whereas amidinate and guanidinate analogs are catalysts for the radical polymerization of methyl methacrylate [23].

The axial sites of dimolybdenum and ditungsten compounds are weak Lewis acids that can coordinate to a variety of neutral or anionic ligands. It has been found that the Lewis acidity of one axial site can be enhanced by axial coordination of a lithium ion to the opposite axial site; an increase in the affinity of Mo_2 for Cl^- was found in $\text{LiMo}_2(\text{monothiosuccinimide})_4\text{Cl}$ [24]. The Lewis acid activation results from a polarization of the Mo–Mo bond, induced by the lithium cation coordinated to the other axial site.

6.1.2

Molecular Assemblies

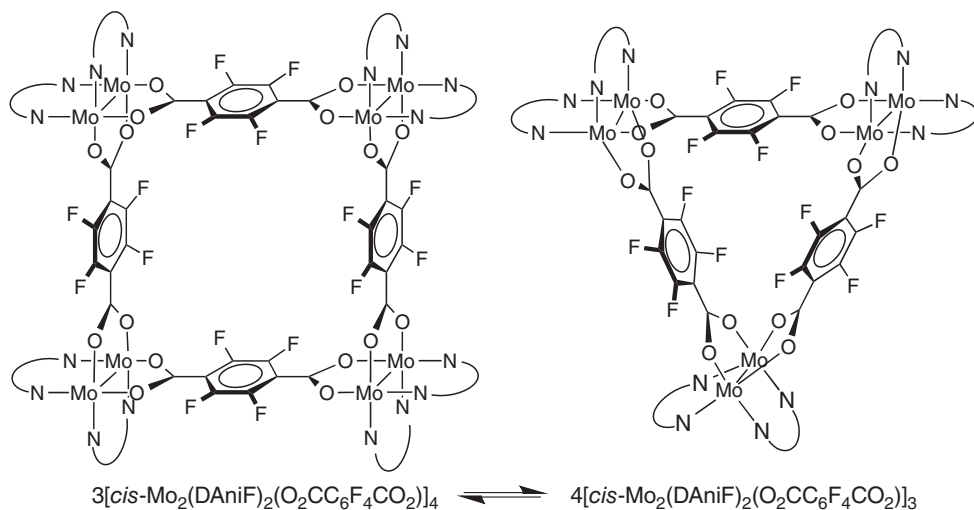
The redox activity properties of the MM quadruple bond, combined with its electron transport (Section 6.1.3) and photophysical (Section 6.1.4) properties, make it an attractive target as a building block for incorporation into functional materials. The first reports of oligomeric or polymeric materials incorporating three or more M_2^{4+} fragment were from Cotton and Murillo, who employed the *cis*- $\text{Mo}_2(\text{DAniF})_2^{2+}$ ($\text{DAniF} = N,N'$ -di-*p*-anisylformamidinate) molecular fragment in combination with dicarboxylate linkers in order to generate molecular triangles and squares [25]. This section discusses some of the more recent efforts in this area, although small clusters and higher ordered

assemblies incorporating quadruply and triply bonded metal atoms were extensively reviewed by Chisholm and Macintosh in 2005 [26], and cages and metal–organic frameworks (MOFs) incorporating dimetal paddlewheel compounds were reviewed by Kühn and coworkers [27].

The reaction of the $cis\text{-Mo}_2(\text{DAniF})_2^{2+}$ fragment with a dicarboxylic acid [28] or a diamidate anion [29] often leads to a mixture of squares and triangles as the products. It is possible that the square and triangle both exist in equilibrium in solution (Scheme 6.1). The triangle might appear to be less favorable than the square as there is significant strain about the M_2^{4+} paddlewheel core. However, as three molecules of the square are in equilibrium with four molecules of the triangle, the triangle is entropically favored and can often be more stable than the enthalpically favored square, particularly if flexible linking ligands are used. The triangle-square dynamic equilibrium was studied for $[cis\text{-Mo}_2(\text{DAniF})_2(\text{O}_2\text{CC}_6\text{F}_4\text{CO}_2)]_n$ ($n = 3$ and 4 , Scheme 6.1), for which both the triangle and square had been structurally characterized, by examining the concentration and temperature dependence of the equilibrium using ^1H and ^{19}F NMR spectroscopy in CDCl_3 [30]. The thermodynamic parameters for the conversion of four moles of square into three moles of triangle in this system were found to be $\Delta G^\circ = 21.0 \text{ kJ mol}^{-1}$, $\Delta H^\circ = 23.5 \text{ kJ mol}^{-1}$, and $\Delta S^\circ = 8.2 \text{ J mol}^{-1} \text{ K}^{-1}$. By contrast, the oxalate-bridged triangles $[cis\text{-Mo}_2(\text{NN})_2(\text{O}_2\text{CCO}_2)]_3$ ($\text{NN} = \text{DAniF}$, PhNC(H)NPh) did not show any variance in their ratio with the corresponding squares at various temperatures, which indicates that in this instance the squares and triangles are formed in competition with one another and are not in equilibrium [31].

More recently, the $cis\text{-}\{(\text{MeCN})_4\text{Mo}_2\}^{4+}$ fragment has been incorporated into oligomeric species. Reaction of $[\text{Mo}_2(\text{NCMe})_{10}][\text{BF}_4]_4$ with a dicarboxylic acid leads to the formation of molecular triangles and squares of form $[cis\text{-}(\text{MeCN})_4\text{Mo}_2(\text{O}_2\text{CRCO}_2)]_n^{2n+}$ ($n = 4$, $\text{R} = \text{C}_6\text{F}_4$ or ferrocene; $n = 3$, $\text{R} = 1,3\text{-C}_6\text{H}_3\text{-5-OH}$ or $1,3\text{-C}_6\text{H}_3\text{-5-F}$) [32]. The advantage of the weakly bound acetonitrile ligands in these molecules is that further substitution reactions to give MOFs should be relatively facile and not require the solvothermal conditions usually needed to generate MOFs.

Dimolybdenum compounds have also been incorporated into a variety of supramolecular polyhedral clusters by using nonlinear bridging dicarboxylate ligands. For example, the reaction of $\text{M}_2(\text{O}_2\text{C}^t\text{Bu})_4$ ($\text{M} = \text{Mo}$, W) with 3,4-thienyldicarboxylic acid results in the formation of a $[\text{M}_2]_4\text{L}_6$ polyhedron, which has a bisphenoidal (S_4) arrangement of the M_2^{4+} units [33]. A detailed study of the effect of bridging ligand angle on molecular assembly has been undertaken by Zhou and coworkers [34]. A range of dicarboxylate linkers with bridging angles of 0° , 60° , 90° , and 120° were reacted with $\text{Mo}_2(\text{O}_2\text{CCX}_3)_4$ ($\text{X} = \text{H}$ or F) to generate a remarkable range of polyhedra, as illustrated in Figure 6.4. The size of the polyhedral cage was found to be dependent on the linker bridging angle,



Scheme 6.1

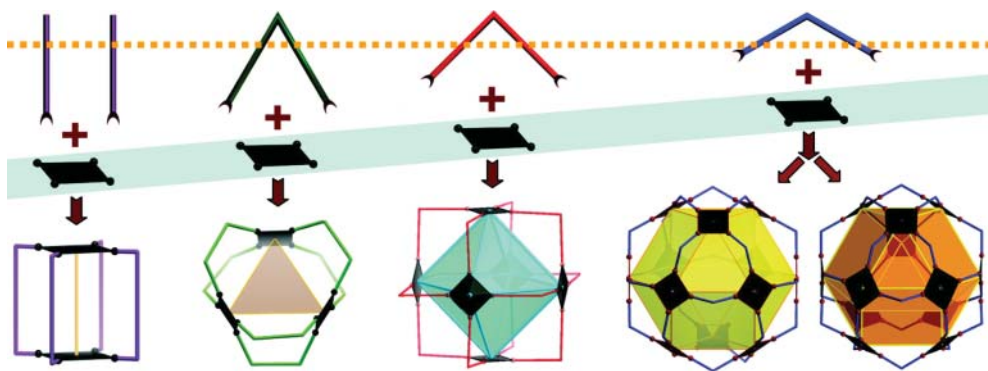


Figure 6.4 Schematic representation of the polyhedral obtained by reaction of various angular linkers with the square $\text{Mo}_2(\text{O}_2\text{C})_4$ node. (Reprinted with permission from Ref. [34]. Copyright 2010 American Chemical Society.)

with the largest clusters, incorporating 12 Mo_2^{4+} units into a cuboctahedral or anticuboctahedral arrangement, found for the 120° linkers.

6.1.3

Electronic Coupling

As noted in the previous section, the quadruply bonded units may be linked together to form larger molecular assemblies, molecular triangles, squares, and polygons. The majority of such assemblies involve Mo_2^{4+} units, and when the linking group couples these units via a bridge that spans the $\text{M}-\text{M}$ bond with a conjugated π -system, the M_2^{4+} units become electronically coupled via $\text{M}_2\delta$ -to-bridge π -to- $\text{M}_2\delta$ conjugation. This is seen in the simplest linker of this type, namely, oxalate. Of the six π -molecular orbitals of the oxalate dianion, only two, namely, the LUMO, which is $\text{C}-\text{C}$ π -bonding and $\text{C}-\text{O}$ antibonding, and the filled CO_2 π combinations can interact with the $\text{M}_2-\delta$ combinations. A frontier MO diagram depicting these interactions is shown in Figure 6.5. On the basis of simple

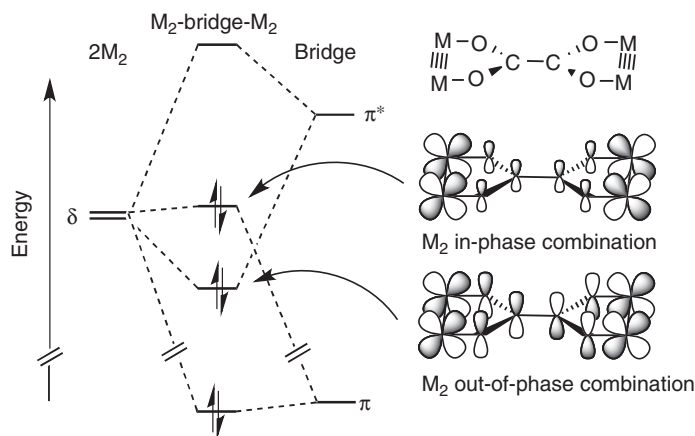


Figure 6.5 Frontier molecular orbital energy diagram showing the interactions of the oxalate anion and the two $\text{M}_2-\delta$ combinations that have the correct symmetry to electronically couple the two M_2 centers via $\text{M}_2-\delta$ to bridge- π conjugation.

considerations of orbital energies and metal–ligand overlap, the interaction involving the filled M_2 - δ combination and the oxalate LUMO is the most important. Also, since in otherwise related M_2^{4+} centers the W_2 - δ orbitals lie approximately 0.5 eV higher in energy than their Mo_2 - δ counterparts, the electronically coupling is notably greater in linked W_2^{4+} centers.

Replacing the oxygen of a carboxylate by NR or S raises the energy of the filled π -orbital combinations and notably for molybdenum increases the magnitude of the electronic coupling [35]. Increasing the length of the bridge decreases the electronic coupling [36].

A simple estimate of electronic coupling can be obtained from studies employing cyclic voltammetry [37]. If two M_2^{4+} centers are strongly coupled, then oxidation of the electronically coupled centers will lead to two successive waves that are well separated. If the two M_2^{4+} centers were connected by a perfect insulator, that is, no electronic coupling, then each M_2^{4+} center would undergo oxidation at the same potential and the single cyclic voltammetric wave on oxidation would correspond to a two-electron process.

The separation of two oxidation waves, $\Delta E_{1/2}$ in millivolts, can be related to the relative stability of the mixed-valence ion and the comproportionation constant, K_c , as shown by Eq. (6.3).

$$[M_2 \sim M_2] + [M_2 \sim M_2]^{2+} \xrightleftharpoons{K_c} 2[M_2 \sim M_2]^+ \\ K_c = \exp\left(\frac{\Delta E_{1/2}}{25.69}\right) \quad \text{at } 298 \text{ K} \quad (6.3)$$

Values of $\Delta E_{1/2}$ typically range from a few millivolts to 1000 mV and K_c values 10^{-10} – 10^{12} . The determination of K_c is typically solvent dependent and is only a rough guide concerning the magnitude of electronic coupling of the metal centers. A K_c value of 4 represents a statistical situation where $\Delta G^* = 0$ and K_c values that fall in the range 10^{-10} – 10^2 may merely reflect electrostatic effects. Values from 10^2 to 10^4 are suggestive of electronic coupling that might be classified as Class II on the Robin–Day scheme [37], while K_c values of 10^5 and greater are *indicative* of strong electronic coupling that is likely *but not certain* to be Class III on this scheme, that is, a situation where the positive charge is fully delocalized over both dinuclear centers.

Cotton and Murillo and coworkers have made extensive use of electrochemical measurements in their studies of linked Mo_2^{4+} units supported by formamidinate ligands [38], while the Chisholm group have employed pivalate attendant ligands for both Mo_2^{4+} and W_2^{4+} linked centers. Within the recent years, this topic has been extensively reviewed [39], and in this chapter we concentrate more on the principles that have arisen from this work.

Table 6.1 gives electrochemical data for representative linked Mo_2^{4+} and W_2^{4+} systems. The main virtue of examining related Mo_2^{4+} and W_2^{4+} systems is that the size of ions and their solvation are essentially identical due to the lanthanide contraction, and so the differences in electrochemical data reflect electronic differences due to the 4d versus 5d orbitals and the relative energies of the respective M_2 - δ orbitals.

The salient points to note are that $\Delta E_{1/2}$ and K_c values are always greater for tungsten than for molybdenum. With increasing the length of the bridge, the magnitude of both rapidly decreases, and replacing O by S in the bridging group greatly enhances the coupling as determined by $\Delta E_{1/2}$ values.

It must also be emphasized that the electronic coupling arises entirely as a result of the mixing of the M_2 - δ and the bridge π -orbitals. This is nicely seen in a comparison of the electrochemical data for the pair of bridging ligands anthracene-1,8-dicarboxylate and 2,7-dioxynaphthyridine, which are shown in I and II (Figure 6.6). These link the M_2 centers in a parallel manner where the short M_2 to M_2 contact distance is only a little over 3 Å yet the electronic coupling as measured by $\Delta E_{1/2}$ values is very small for the anthracenyl bridge.

The singly oxidized linked dinuclear complexes contain an unpaired electron and are EPR active. Since both molybdenum and tungsten have some nuclei that have $I \neq 0$ (^{95}Mo and ^{97}Mo have $I = 5/2$ with a combined natural abundance of $\sim 25\%$ and ^{183}W has $I = 1/2$ and is $\sim 15\%$ abundant) their EPR spectra can be most informative with regard to the location of the odd electron. Typically, $g_{\text{iso}} \sim 1.9$

Table 6.1 Summary of electrochemical data for $[(^t\text{BuCO}_2)_3\text{M}_2]_2(\mu\text{-bridge})$ ($\text{M} = \text{Mo}, \text{W}$) compounds.^{a)}

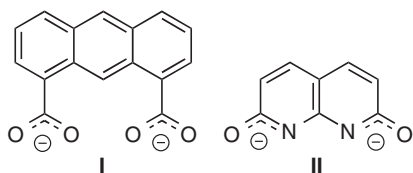
Bridge	$E_{1/2}(1)$ (V)	$E_{1/2}(2)$ (V)	$\Delta E_{1/2}$ (mV)	Kc	References
<i>M = Mo</i>					
Oxalate	−0.03	0.25	280	5.4×10^4	[40]
Terephthalate ^{b)}	−0.10	—	—	~ 4	[41]
Perfluoroterephthalate ^{c)}	0.10	—	65	1.3×10^1	[40]
2,5-Dihydroxyterephthalate	0.00	0.08	79	2.1×10^1	[42]
2,6-Azulenedicarboxylate	−0.09	0.02	112	7.8×10^1	[43]
Dithioterephthalate	0.00	0.18	184	1.3×10^3	[35a]
Anthracene-1,8-dicarboxylate ^{d)}	0.06	—	—	—	[44]
3,6-Dioxypyridazine	−0.15	0.28	280	5.4×10^4	[45]
2,7-Dioxynaphthyridine	−0.07	0.32	389	3.8×10^6	[40]
<i>M = W</i>					
Oxalate	−1.26	−0.54	717	1.3×10^{12}	[40]
Terephthalate	−0.34	−0.18	160	5.1×10^2	[42]
Perfluoroterephthalate	−0.66	−0.37	285	6.6×10^4	[40]
2,5-Dihydroxyterephthalate	−0.72	−0.52	202	2.6×10^3	[42]
2,6-Azulenedicarboxylate	−0.91	−0.44	468	8.2×10^7	[43]
Dithioterephthalate	−0.78	−0.26	518	5.7×10^8	[35a]
Anthracene-1,8-dicarboxylate	−0.66	−0.51	156	4.3×10^2	[44]
3,6-Dioxypyridazine	−0.91	−0.28	630	4.5×10^{10}	[46]

a) Voltammograms were recorded in $^n\text{Bu}_4\text{NPF}_6/\text{THF}$ solutions and referenced to the $\text{FeCp}_2^{0/+}$ couple.

b) Single redox process observed corresponding to two overlapping one-electron oxidation processes.

c) The potential represents the average $E_{1/2}$ value for both redox couples involving the removal of two electrons.

d) Second oxidation potential obscured by anthracene oxidation processes.

**Figure 6.6** Structures of anthracene-1,8-dicarboxylate (I) and 2,7-dioxynaphthyridine (II).

for Mo_2^{5+} and $A_{\text{iso}} = 28$ G and for W_2^{5+} , $g_{\text{iso}} \sim 1.8$ and $A_{\text{iso}} = 50$ G. In linked compounds where the electron is equally shared over both dinuclear centers, the A_{iso} value is reduced to roughly one half the value of that for the isolated M_2^{5+} center. The room temperature spectra for the oxalate- and perfluoroterephthalate-bridged Mo_2 linked complexes $[(^t\text{Bu}^t\text{CO}_2)_3\text{Mo}_2]_2(\mu\text{-bridge})^+$ are shown in Figure 6.7, where it can be seen that in the oxalate-bridged complex ion the single electron is delocalized over both Mo_2 centers, whereas in terephthalate it is localized on just one Mo_2^{5+} center [47].

In the case of tungsten, the terephthalate-bridged cationic complex shows EPR spectra consistent with delocalization over all four W atoms [48].

Undoubtedly, the best way to examine the degree of electronic coupling involves the use of UV–vis–NIR spectroscopy on the singly oxidized ions. Robin and Day Class III fully delocalized mixed-valence ions show low-energy electronic transitions corresponding to the promotion of an electron from the HOMO-1 to the singly occupied HOMO, an $\text{M}_2\text{-}\delta$ to $\text{M}_2\text{-}\delta$ transition as can be envisioned from Figure 6.5 upon the removal of a single electron from the HOMO. The magnitude

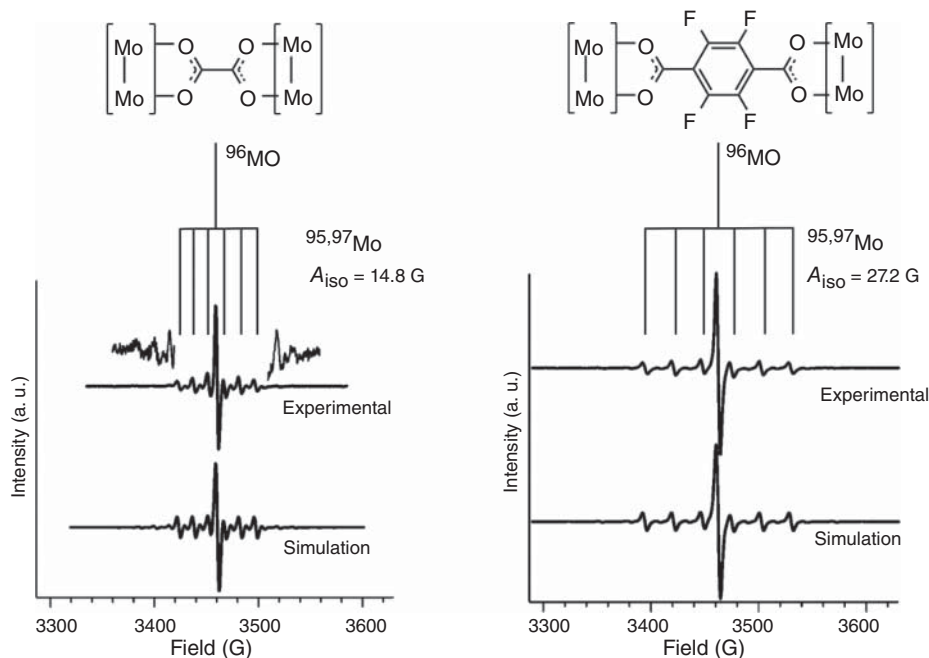


Figure 6.7 X-band EPR spectra recorded in a THF/CH₂Cl₂ (2:1) solution at 210 K of the complexes [(Bu^tCO₂)₃ M₂]₂(μ-bridge)⁺PF₆[−], where the bridge is oxalate (a), $g_{\text{iso}} = 1.937$, $A_{\text{iso}} = 14.8$ G, and

1,4-perfluoroterephthalate (b), $g_{\text{iso}} = 1.942$, $A_{\text{iso}} = 27.2$ G together with their simulated spectra. (Adapted from Ref. [47] by permission of The Royal Society of Chemistry.)

of the electronic coupling, H_{AB} , is just one half the energy of this electronic transition in cm^{−1}. As the electronic coupling gets weaker, the energy of this transition moves to lower energy and the shape of the absorption becomes notably asymmetric with a sharp rise at low energy and a long tail toward higher energy. This is nicely seen in the spectra of the oxalate-bridged cations of the MM' centers, where MM' = Mo₂, MoW, and W₂ [49]. These low-energy absorptions are shown in Figure 6.8. The asymmetry of these electronic transitions near the Class II/III border has been the subject of considerable interest [50].

As the electronic coupling gets weaker, this low-energy absorption feature is replaced by a higher energy broad transition, the so-called intervalence charge transfer (IVCT) transition, which was predicted and accounted for by Hush [51]. Here, the degree of electronic coupling is calculated according to Eq. (6.1), where d is the electron transfer distance (Å), typically estimated as the distance between the redox centers; $\bar{\nu}_{\text{max}}$ is the energy of the IVCT band in cm^{−1} at the maximum extinction coefficient; $\Delta\bar{\nu}_{1/2}$ is the peak width at half height (cm^{−1}); and ϵ_{max} is the peak intensity (M^{−1} cm^{−1}).

$$H_{\text{AB}} = \left(\frac{0.0206}{d} \right) (\bar{\nu}_{\text{max}} \cdot \Delta\bar{\nu}_{1/2} \cdot \epsilon_{\text{max}})^{1/2} \quad (6.4)$$

The shapes of the absorptions arising from Class II and Class III mixed-valence ions are very different as is seen in the section of the terephthalate-bridged cations of the Mo₂ and W₂ linked complexes shown in Figure 6.9 [42]. The singly oxidized linked W₂ ion shows a very low energy relatively sharp but asymmetric absorption typical of a Class III ion close to the Class II/III border, while the related molybdenum cation has a much higher energy broad absorption typical of a Class II ion.

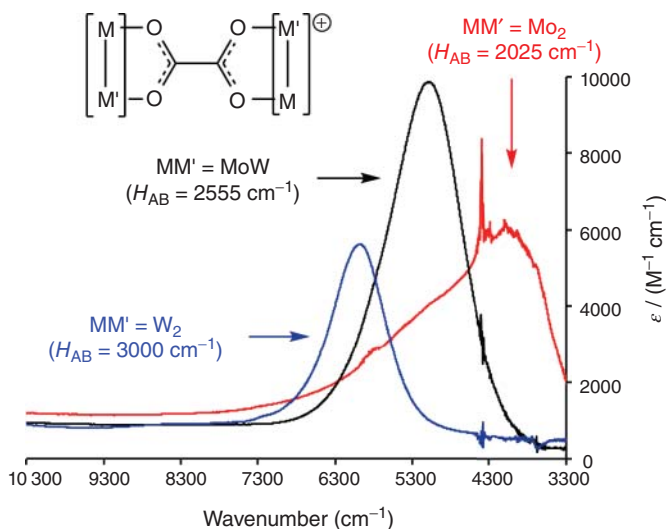


Figure 6.8 The low-energy charge resonance electronic transitions for the cations $[(\text{Bu}^t\text{CO}_2)_3\text{MM}']_2(\text{O}_2\text{CCO}_2)^+$, where $\text{MM}' = \text{Mo}_2$, MoW , and W_2 recorded in THF at room temperature.

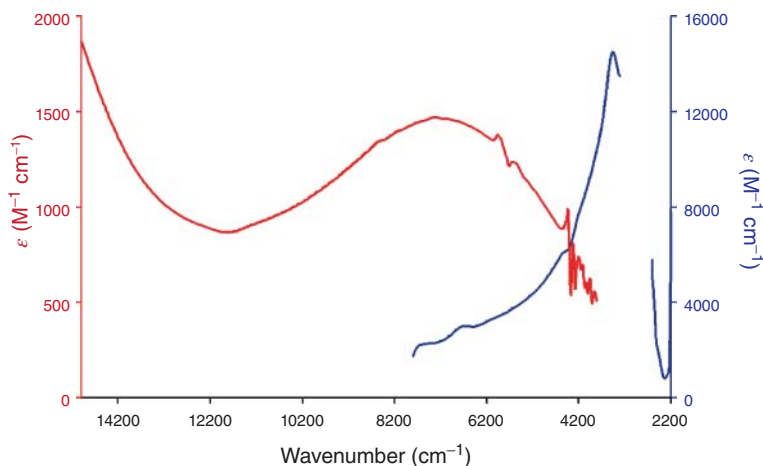


Figure 6.9 NIR electronic absorption spectra of $[(\text{Bu}^t\text{CO}_2)_3\text{M}_2]_2(\mu\text{-2,5-dihydroxyterephthalate})^+\text{PF}_6^-$ [$\text{M} = \text{Mo}$ (red) and W (blue)] recorded in THF at room temperature. The gap between 2610

and 3280 cm^{-1} for the tungsten cation corresponds to a THF solvent absorption. (Reprinted with permission from Ref. [42]. Copyright 2005 American Chemical Society.)

Table 6.2 lists various H_{AB} values for some related molybdenum and tungsten complexes, and, as seen from the electrochemical data, the coupling for tungsten is always greater than that for molybdenum.

Mixed-valence systems are not limited to metal centers but may also be found in organic compounds that have active redox centers linked by a conjugated bridge, and the single-electron reduction of the compounds $\text{trans-M}_2(\text{T}^i\text{PB})_2[\text{O}_2\text{C}-\text{C}_6\text{H}_4\text{N}-\text{B}(\text{C}_6\text{F}_5)_3]_2$, where $\text{T}^i\text{PB} = 2,4,6$ -triisopropylbenzoate and $\text{O}_2\text{CC}_6\text{H}_4\text{N}(\text{B}(\text{C}_6\text{F}_5)_3)$ is the Lewis acid adduct of the 4-isonicotinate ligand, gives rise to spectra for a Class III fully delocalized mixed-valence ligand system [52]. The

Table 6.2 Summary of the NIR absorptions observed for selected $[(^t\text{BuCO}_2)_3\text{M}_2](\mu\text{-bridge})^+\text{PF}_6^-$ ($\text{M} = \text{Mo}, \text{W}$) compounds.

Bridge	$\bar{\nu}_{\text{max}}$ (cm^{-1})	$\Delta\bar{\nu}_{1/2}$ (obs.) ^{a)} (cm^{-1})	$\Delta\bar{\nu}_{1/2}$ (calc.) ^{b)} (cm^{-1})	ϵ_{max} ($\text{M}^{-1} \text{cm}^{-1}$)	H_{AB} (cm^{-1})	Class ^{c)}	References
<i>M = Mo</i>							
Oxalate	4000	2800	3040	6000	2025	III	[47]
2,5-Dihydroxyterephthalate ^{d)}	7200	5720	4078	1470	446	II	[42]
2,6-Azulenedicarboxylate ^{d)}	6250	4800	3800	2070	380	II	[43]
<i>M = W</i>							
Oxalate	5960	940	3710	5620	3000	III	[47]
Terephthalate	3220	2220	2727	18000	1610	III	[42]
Perfluoroterephthalate	3570	582	2872	9600	1785	III	[42]
2,5-Dihydroxyterephthalate	3430	1270	2815	14400	1715	III	[42]
2,6-Azulenedicarboxylate	3080	750	2660	4550	1540	III	[43]
Dithioterephthalate	4325	668	3161	8170	2163	III	[35a]
3,6-Dioxypyridazine	3775	1320	2950	5000	1888	III	[46]

Spectra were acquired in THF solutions at room temperature.

- Bandwidth determined from the high-energy side of the band for nonsymmetrical absorptions to avoid low-energy cutoff effects.
- Calculated using $\Delta\bar{\nu}_{1/2} = (2310 \bar{\nu}_{\text{max}})^{1/2}$.
- Based on the observations that for a Class III system $\Delta\bar{\nu}_{1/2}(\text{calc.}) > \Delta\bar{\nu}_{1/2}(\text{obs.})$ and the absorption intensity is typically $> 5000 \text{ M}^{-1} \text{ cm}^{-1}$.
- Class II system hence H_{AB} calculated using Eq. (6.1), with d approximated using the calculated $\text{M}_2 \cdots \text{M}_2$ separation in the optimized geometry obtained from gas-phase DFT calculations.

single electron is delocalized over both isonicotinate ligands, giving rise to an EPR spectrum with $g = 2.0$ and low-energy sharp electronic transitions in the region $4500 - 3500 \text{ cm}^{-1}$ of the UV-vis-NIR spectra. Once again, the electronic coupling, this time of the two π -acceptor ligands, is greater in the W_2 coupler due to the better $\text{W}_2\delta$ -ligand π^* interactions.

The MM quadruply bonded systems lend themselves to detailed studies of mixed valence and have been the topic of several recent reviews that provide many more examples [39a, 53]. In many ways, they are spectroscopically much simpler than the d^5 - d^6 systems, such as Creutz–Taube ion [54], that were initially explored.

In addition to covalently linked M_2^{4+} units, it is also possible to generate “dimers of dimers” using hydrogen bond interactions. The compounds $\text{Mo}_2(\text{T}^i\text{PB})_3(\text{HDON})$ (**Mo₂HDON**) ($\text{H}_2\text{DON} = 2,7$ -dihydroxynaphthyridine) and $\text{Mo}_2(\text{T}^i\text{PB})_3(\text{HDOP})$ ($\text{H}_2\text{DOP} = 3,6$ -dihydroxypyridazine) (**Mo₂HDOP**) were synthesized by the reaction of $\text{Mo}_2(\text{T}^i\text{PB})_4$ with 1 equiv. of the relevant acid [55]. These compounds have a pendant 2-pyridone functional group and dimerize to form $[\text{Mo}_2\text{HDON}]_2$ and $[\text{Mo}_2\text{HDOP}]_2$ (Figure 6.10) through self-complementary hydrogen bond interactions in nondonor solvents and the solid state. Two one-electron oxidation processes are observed for both compounds in CH_2Cl_2 , with K_c values of 233 ($[\text{Mo}_2\text{HDON}]_2^+$) and 487 ($[\text{Mo}_2\text{HDOP}]_2^+$), but no intervalence charge-transfer bands are observed in the NIR region for these radical cations. This indicates that the stabilization of the mixed-valence state is not due to overlap of the donor–bridge–acceptor

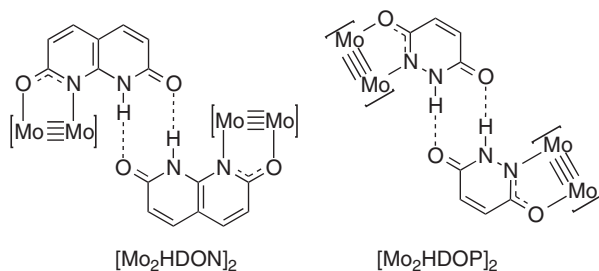


Figure 6.10 Drawings highlighting the hydrogen bonding in $[\text{Mo}_2(\text{T}^i\text{PB})_3(\text{HDON})]_2$ ($[\text{Mo}_2\text{HDON}]_2$) and $[\text{Mo}_2(\text{T}^i\text{PB})_3(\text{HDOP})]_2$ ($[\text{Mo}_2\text{HDOP}]_2$).

wavefunctions (superexchange mechanism), but is rather a rare example of proton-coupled mixed valency, in which the electron transfer is dependent on the proton coordinate. In an effort to further probe the mechanism of this process, the compounds $[\text{W}_2(\text{T}^i\text{PB})_3(\text{HDON})]_2$ ($K_c = 111$) and $[\text{Mo}_2(\text{T}^i\text{PB})_2(\text{O}_2\text{CCH}_2\text{Cl})(\text{HDON})]_2$ ($K_c = 164$) have been prepared [56]. Changing Mo for W results in many orders of magnitude increase in K_c for covalently linked systems, *vide supra*, so the modest decrease in the K_c value for these compounds by comparison to $[\text{Mo}_2\text{HDON}]_2^+$ is consistent with a mechanism other than the superexchange. The modest changes in the K_c value associated with changing the metal or ancillary ligand means that further studies involving bridging ligand modification will be required in order to elucidate the mechanism by which the proton coordinate and electron transfer affect the stability of the mixed-valence state.

There has also been interest in incorporating group 6 metal atoms into molecular wires [57], which use ligands to constrain less than three metal atoms in a linear chain that can have interesting electron transport properties [58]. These compounds are known as “extended metal atom chains” or “molecular string complexes.” [59] A full review of this area is outside the scope of this chapter, but the majority of the compounds use oligo- α -pyridylamino ligands such as dpa (Figure 6.2) [60]. High-nuclearity penta- [61] and nona-chromium [62] metal string complexes incorporating two or four CrCr quadruple bonds have been isolated. Single molecule conductance experiments on the pentanuclear string complexes $[\text{M}_5(\mu_5\text{-tpda})_4(\text{NCS})_2]$ ($\text{M} = \text{Ni}, \text{Co}, \text{Cr}$; H_2tpda = tripyridyldiamine) show that the chromium wires have the highest conductance [63], with computational studies suggesting that electron transport through chromium chains utilizes unoccupied σ -orbitals [64]. These studies highlight the potential versatility of MM quadruple bonds as a construct for incorporation into molecular electronic devices, as electron transfer is facile through both the axial and equatorial positions.

6.1.4

Photophysical Studies

6.1.4.1 Absorption and Steady State Emission; Homoleptic Compounds

The majority of the earlier studies focused on the assignment of the $\delta \rightarrow \delta^*$ transition, its intensity, its relevance to the strength of the δ component of the quadruple bond and variance with the removal of fourfold symmetry and twist angle [1, 65]. For the dimetal carboxylates that have the paddlewheel structure with virtual D_{4h} symmetry, the $\delta \rightarrow \delta^*$ transition is commonly masked by the presence of a fully allowed metal-to-ligand charge transfer MLCT that falls close in energy to the $\delta \rightarrow \delta^*$ transition [66]. This $^1\text{MLCT}$ transition corresponds to a $\text{M}_2\text{-}\delta \rightarrow \text{CO}_2\text{-}\pi^*$ transition that can be significantly lowered in energy by changing the metal from molybdenum to tungsten or by introducing an organic π -system that conjugates with the CO_2 π -orbitals [67]. For otherwise related compounds of molybdenum and tungsten, the $\text{M}_2\text{-}\delta$ orbital lies ~ 0.5 eV higher in energy for tungsten [1]. This is readily seen in the photoelectron ionization spectra of related compounds and also can be seen in the electrochemical potentials for the oxidation of the quadruply bonded complexes as determined

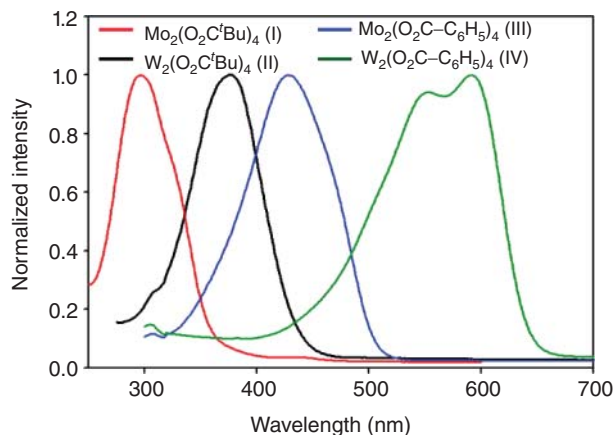


Figure 6.11 Room temperature electronic absorption spectra of the homoleptic compounds $\text{M}_2(\text{O}_2\text{C}^t\text{Bu})_4$ and $\text{M}_2(\text{O}_2\text{CPh})_4$, where $\text{M} = \text{Mo}$ or W , recorded in THF solution. (Reprinted with permission from Ref. [66]. Copyright 2012 American Chemical Society.)

by cyclic voltammetric studies. The UV–visible absorption spectra of the compounds $\text{M}_2(\text{O}_2\text{C}^t\text{Bu})_4$ and $\text{M}_2(\text{O}_2\text{CPh})_4$ are shown in Figure 6.11 for $\text{M} = \text{Mo}$ and W and nicely reveal these trends. Only for $\text{Mo}_2(\text{O}_2\text{C}^t\text{Bu})_4$ is the weak $\delta \rightarrow \delta^*$ absorption detectable at ~ 440 nm. For $\text{W}_2(\text{O}_2\text{C}^t\text{Bu})_4$, this is completely masked by $\text{M}_2\text{-}\delta \rightarrow \text{CO}_2\text{-}\pi^*$ transition, which is moved to lower energy by the relative higher energy of the $\text{W}_2\text{-}\delta$ orbital. The replacement of the Bu^t group by phenyl allows for extended π -conjugation and thus further lowers the energy of the $\text{M}_2\text{-}\delta \rightarrow$ ligand π^* transition. Indeed, this $\text{M}_2\text{-}\delta$ to ligand π^* transition can be tuned to span the entire visible region of the electronic absorption spectrum and even further into the near IR, 400–1200 nm, by the judicious choice of metal and ligand [67].

Many of these compounds show weak luminescence from both the $\delta\delta^*$ singlet and triplet states. Singlet emission had been seen previously [68] in compounds such as $\text{Mo}_2\text{Cl}_4(\text{PR}_3)_4$, but triplet emission had not. As the energy of the $\text{MM}\delta$ orbital is raised in energy, the $^1\text{MLCT}$ transition is lowered in energy while the $^3(\delta\delta^*)$ energy level is raised and the phosphorescence energy is thus inversely related to the singlet absorption energy. This is nicely seen in the absorption and phosphorescence spectra of the compounds $\text{MM}(\text{T}^i\text{PB})_4$, where $\text{T}^i\text{PB} = 2,4,6\text{-triisopropylbenzoate}$ and $\text{MM} = \text{Mo}_2, \text{MoW}, \text{and W}_2$ [69]. The spectra recorded in toluene are shown in Figure 6.12.

For nearly all Mo_2 carboxylates, the emission from the $^3\delta\delta^*$ state occurs at ~ 1100 nm and at 77 K is typically more intense and shows vibronic features associated with $\nu(\text{MoMo}) \sim 400\text{ cm}^{-1}$ as the potential energy curve of the $^3\delta\delta^*$ state, which has a MM triple bond, is offset from that of the ground state.

Formamidinate bridging ligands, $\text{RNC}(\text{H})\text{NR}$, also contain NCN π -orbitals, and the homoleptic compounds $\text{M}_2(\text{RNC}(\text{H})\text{NR})_4$ are typically yellow, orange, or red as a result of the MLCT absorptions corresponding to $\text{M}_2\text{-}\delta$ to $\text{NCN } \pi^*$ transitions. Since nitrogen is less electronegative than oxygen, the $\text{M}_2\text{-}\delta$ orbitals lie higher in energy than in their related carboxylates [1]. This is readily seen from electrochemical studies. The higher energy of the $\text{M}_2\text{-}\delta$ orbital similarly raises the energy of the $\text{M}_2\text{-}\delta^*$ and emission from the $^3(\delta\delta)$ state likewise moves to higher energy, typically in the region 800–900 nm [70].

6.1.4.2 Heteroleptic Compounds

trans- $\text{M}_2(\text{T}^i\text{PB})_2(\text{O}_2\text{CR})_2$ compounds, where $\text{R} = \text{a } \pi\text{-conjugated organic variety}$, have been extensively studied. Here, the bulky 2,4,6-triisopropylbenzoate groups are twisted nearly 90° from their respective CO_2 groups, whereas the R groups enjoy extensive $\text{M}_2\text{-}\delta$ to $\text{-O}_2\text{CR } \pi$ conjugation.

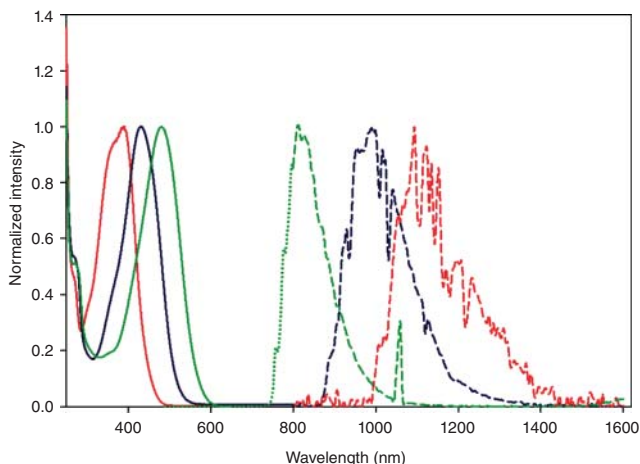


Figure 6.12 Electronic absorption spectra and triplet emission for the compounds $\text{MM}(\text{T}^i\text{PB})_4$, where $\text{MM} = \text{Mo}_2$ (red), MoW (blue), or W_2 (green) and $\text{T}^i\text{PB} = 2,4,6$ -triisopropylbenzoate recorded in THF at room temperature.

This is nicely seen in the molecular structure of the azulene carboxylate ester derivative shown in Figure 6.13 [71]. Similar structures are found in the solid state for $\text{R} = \text{phenyl}$, aryl , thienyl , bithienyl , and cyanoacrylate [72].

In these types of compounds, the $\text{M}_2\text{-}\delta$ orbital can mix with only the out-of-phase combination of the O_2CR ligands, as shown in the schematic frontier MO energy level diagram in Figure 6.14. This causes a splitting of the two carboxylate π -systems, and the magnitude of the splitting is a rough indication of the magnitude of the coupling of the two O_2CR ligands via the $\text{M}_2\text{-}\delta$ orbital. Indeed, reduction of these complexes places an electron into the in-phase LUMO and may lead to mixed-valence ligands that can be fully delocalized Class III on the Robin and Day classification for mixed-valence ions.

Although this carboxylate– $\text{M}_2\text{-}\delta$ –carboxylate conjugation favors the planar arrangement of the two *trans*-ligands, as seen in Figure 6.13, thermal energy in solution leads to a Boltzmann distribution of rotamers [72]. Thus, the solution absorption spectra for these complexes show thermochromism. By using a solvent such as 2-methyltetrahydrofuran, which can be cooled and forms a glass, the

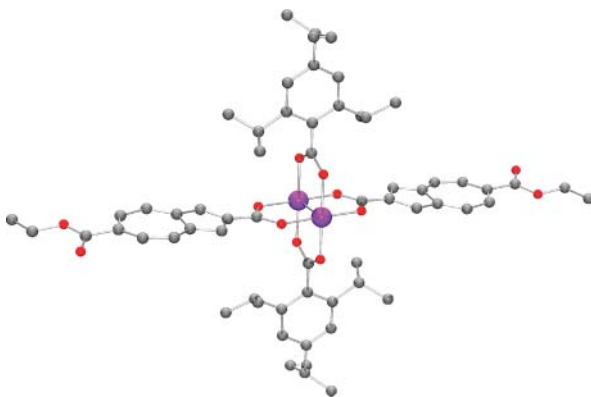


Figure 6.13 Molecular structure of $\text{Mo}_2(\text{T}^i\text{PB})_2(\text{O}_2\text{C-Azu})_2$ seen in the solid state. Azu is azuleneethylcarboxylate.

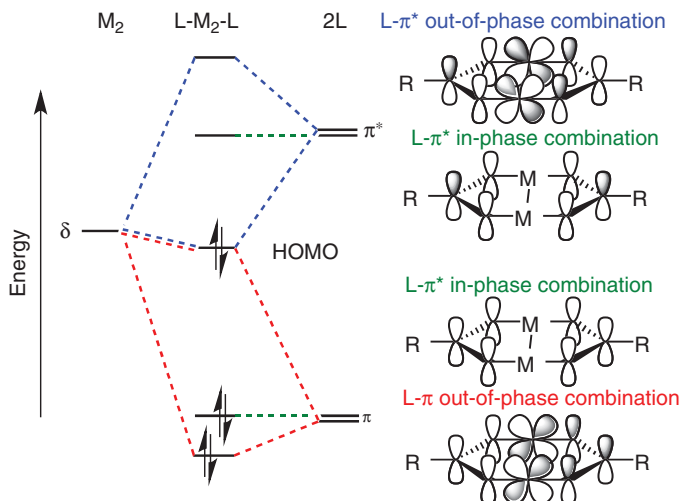


Figure 6.14 Frontier molecular orbital energy diagram showing the interaction of the M_2 - δ orbital with the *trans*-carboxylate π and π^* orbitals.

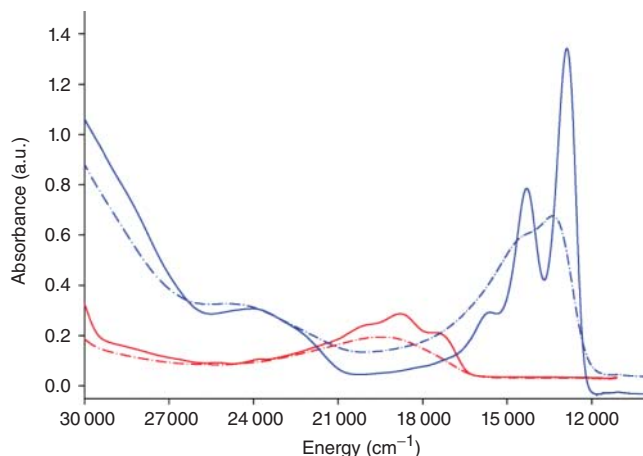


Figure 6.15 Absorption of $Mo_2(TiPB)_2(O_2C-CH=CH-2-C_4H_3S)_2$ in 2-MeTHF at room temperature (red dashed) and 99 K (red solid) and $W_2(TiPB)_2$

$(O_2C-CH=CH-2-C_4H_3S)_2$ in 2-MeTHF at room temperature (blue dashed) and 98 K (blue solid). (Reproduced from Ref. [72] with permission from The Royal Society of Chemistry.)

variable temperature spectra for a wide variety of these compounds have been recorded. The room temperature and 77 K spectra for the complex where $R = 2$ -vinyl-thiophene and $M_2 = Mo_2$ or W_2 are shown in Figure 6.15 and are typical of this class of compounds [72].

The broad absorption band assignable to the M_2 - δ to O_2CR - π^* transition sharpens, and its maximum intensity moves to lower energy upon cooling. Also, vibrational features sharpen and show a marked progression. Interestingly, in comparing W_2 with Mo_2 -containing compounds, the (0, 0) transition is the most intense for tungsten, whereas for molybdenum the (0, 1) transition is the most intense. This reflects the magnitude of the mixing of the two ligand π -systems, which is greater for tungsten due to the higher energy of the W_2 - δ orbital and its better overlap with the ligand π

system. This greater mixing enhances the nesting of the potential energy surfaces of the M_2 - δ and LUMO [53a].

Another point to note in the spectra of $M_2(T^iPB)_2(O_2CR)_2$ compounds is the appearance of the higher energy M_2 δ -to- CO_2 π^* transition associated with the T^iPB ligands. This is seen in the region of 400–450 nm. These compounds show weak fluorescence from the ^1MLCT S1 state. Phosphorescence is typically seen for Mo_2 -containing compounds from the $^3\delta\delta$ state at ~ 1100 nm, but for W_2 -containing compounds weak emission is seen from the ^3MLCT state in only a few compounds. As will be noted later, this state has a notably shorter lifetime than the $^3\delta\delta^*$ state [73].

As noted earlier, by extending the conjugation in the R groups and by introducing strongly π -accepting groups such as CN or NO_2 , the ^1MLCT absorption can be tuned to extend well into the near IR of the spectrum, 400 $\rightarrow$ 1200 nm [67].

Two other series of heteroleptic compounds have been studied, namely, *cis*- $Mo_2(ArNCHNAr)_2(O_2CR)_2$ and $Mo_2(ArNCHNAr)_3(O_2CR)$, where Ar = *p*-anisole. In these, the lowest energy ^1MLCT occurs to the carboxylate ligand R = thienyl, bithienyl, and terthienyl, $-C\equiv C-Ph$, *p*- C_6H_4CN , and $C_4H_2SC\equiv CH$ (2-carboxylate-5-ethynylthienyl) [70].

6.1.4.3 Transient Absorption Spectra

Several of the aforementioned compounds have now been examined by femtoseconds and nanoseconds, transient absorption spectroscopy in THF solutions. From the decay of the transients, the lifetimes of the photoexcited states S1 and T1 have been determined. Representative compounds that have been examined in this manner are given in Table 6.3.

From the data, we obtain a fairly consistent view that the ^1MLCT S1 lifetimes are in the range 1–20 ps. These are notably a great deal longer than those seen for d^6 -octahedral polypyridyl complexes of the later transition metals (Ru, Ir, Rh, Os) that have been so extensively studied. The latter show very rapid intersystem crossing, ISC to triplet MLCT states. Their S1 states have lifetimes in the region of 50–150 fs [77]. Also from the data shown in Table 6.3, we can see that the S1 lifetimes of the tungsten complexes are not significantly shorter than those of their molybdenum counterparts despite the notably larger spin–orbit coupling constant of the 5d elements. Indeed, in some instances, the S1 lifetime is longer for tungsten than that found in its molybdenum counterpart.

It is interesting to speculate why the lifetimes of the S1 states are so long. At this time, it has been proposed that the ^1MLCT has significant ligand character and that the charge on the ligand is notably further removed from the metal center compared to that in pyridyl-bound ligands. In the

Table 6.3 S1 and T1 lifetimes of various M_2 compounds.

Compound	Mo_2		W_2		References
	S1 (ps)	T1	S1	T1	
$M_2(O_2CC(CH_3)_3)_4$	50	—	<300 fs	—	[66]
$M_2(T^iPB)_4$	6	40 μ s	390 ps	2 μ s	[69]
$M_2(O_2CC_6H_5)_4$	2.5	—	400 fs	—	[66]
$M_2(T^iPB)_2(O_2C-2\text{-azulene-6-carboethoxy})_2$	7.6	260 ns	4.5 ps	3–10 ns	[71]
$M_2(T^iPB)_2(O_2C-Th)_2$	4.1	77 μ s	0.7 ps	3–10 ns	[74]
$M_2(T^iPB)_2(O_2C-TTh)_2$	12	72 μ s	21.6 ps	90 ns	[75]
$M_2(T^iPB)_2(O_2C-C(CN)=CH-Th-Ph-NPh_2)_2$	7.1	54 μ s	16.3 ps	1–3 ns	[67]
$M_2(T^iPB)_2(O_2C-Ph-p-CN)_2$	3.9	93 μ s	7.2 ps	4.6 μ s	[76]
$M_2(ArNCHNAr)_3(O_2C-CCPh)$	2	78 μ s	—	—	[70]
$M_2(ArNCHNAr)_3(O_2C-C_4H_2SC\equiv CH)$	4.5	59 μ s	—	—	[70]
$M_2(ArNCHNAr)_3(O_2C-Ph-p-CN)$	5	75 μ s	—	—	[70]

series $M_2(T^iPB)_2(O_2CR)_2$, where R = thienyl, bithienyl, and terthienyl, with increasing chain length the S1 lifetimes increase [73].

The T1 lifetimes that are in the range 1–100 μ s are assigned to the $^3\delta\delta^*$ states, and again there is not a great deal of difference between related molybdenum and tungsten complexes. The T1 lifetimes that fall in the 1–10 ns range are assigned to ^3MLCT states, notably those of tungsten complexes.

6.1.4.4 Time-Resolved Infrared Studies, TRIR

Because the carboxylates have relatively long-lived photoexcited states, femtoseconds TRIR studies allow one to probe the charge distribution in the S1 and T1 states as a function of time. Particularly helpful in this regard are ligands that have reporter IR groups that are located in a region of the infrared spectrum that is devoid of other vibrations. Thus, $C\equiv X$ bonds, where X = O, N, or C, that are IR active in the region 2000–2200 cm^{-1} are ideal.

For *trans*- $Mo_2(T^iPB)_2(O_2CR)_2$ compounds, where the O_2CR ligands are involved in the ^1MLCT S1 state, the question arises as to whether the electron is delocalized over both *trans*- O_2CR ligands or is localized on just one. These photoexcited states thus can represent excited state mixed-valence (MV) ions that may be classified as Class III (delocalized) or Class I (valence trapped) on the Robin and Day scheme [78]. For the valence-trapped situation, we would expect to see the values of $\nu(C\equiv X)$ in the excited state representative of two different O_2CR ligands, while for the fully delocalized situation both ligands are equally reduced. As a further estimation of the anticipated shift in the value of $\nu(C\equiv X)$, calculations using density functional theory on model compounds *trans*- $M_2(O_2CH)_2(O_2CR)_2$ and the anion *trans*- $M_2(O_2CH)_2(O_2CR)_2^-$ are useful. In the anion, the MO calculation places the negative charge in the LUMO (see Figure 6.5) and is delocalized over both O_2CR ligands. In general, it is known that ^1MLCT states have ligand vibrations that resemble those of the reduced ligand.

A number of compounds of the form *trans*- $M_2(T^iPB)_2(O_2CR)_2$ have been investigated by femtoseconds TRIR, where the R group contains π -acceptor $C\equiv X$ functionalities. Table 6.4 lists the $\Delta\nu(C\equiv X)$ values observed, that is, the shift of $\nu(C\equiv X)$ from the ground state and those calculated by DFT for the model anions $M_2(O_2CH)_2(O_2CR)_2^-$, both at short times corresponding to the S1 states and at longer times corresponding to T1 states. The substitution of formate for T^iPB saves on computational time and is a reasonable approximation given that the aryl groups are twisted out of conjugation with their CO_2 moiety as shown in Figure 6.11.

The TRIR spectra for the compounds *trans*- $M_2(T^iPB)_2(O_2CC_6H_4-p-CN)_2$ recorded in THF are shown in Figure 6.16 [76]. These are illustrative of the type of spectra seen for the majority of compounds of this class. There is a single relatively broad IR band in the $\nu(C\equiv X)$ region shifted to lower energy than that observed in the ground state. This is assignable to $\nu(C\equiv X)$ in the S1 photoexcited, where the ^1MLCT contains the photoexcited electron delocalized over both of the O_2CR ligands. The magnitude of the reduction in $\nu(C\equiv X)$, $\Delta\nu(C\equiv X)$ corresponds reasonably well to that predicted by

Table 6.4 Experimental and calculated $\Delta\nu(C\equiv X)$ values in cm^{-1} of compounds $M_2(T^iPB)_2(O_2C-R)_2$.

R=	Mo_2		W_2		References
	Anion (calc)	S1 (exp)	Anion (calc)	S1 (T1) (exp)	
–Ph– <i>p</i> -CN	–67	–73	–64	–61 (–63)	[76]
–CC– <i>p</i> -tolyl	—	—	–142	–80, –245 (–85, –222)	[79]
–CC-9-anthracenyl	–101	–91	–100	–59	[79]
– $C_4H_2SC\equiv CH$	–57	–66	–55	–52 (–68)	[80]
– $C(CN)=CH$ –Ph–NPh ₂	–50	–52	–50	–41 (–35)	[67]
– $C(CN)=CH$ –Th–Ph–NPh ₂	–25	–49	–25	–48 (–43)	[67]

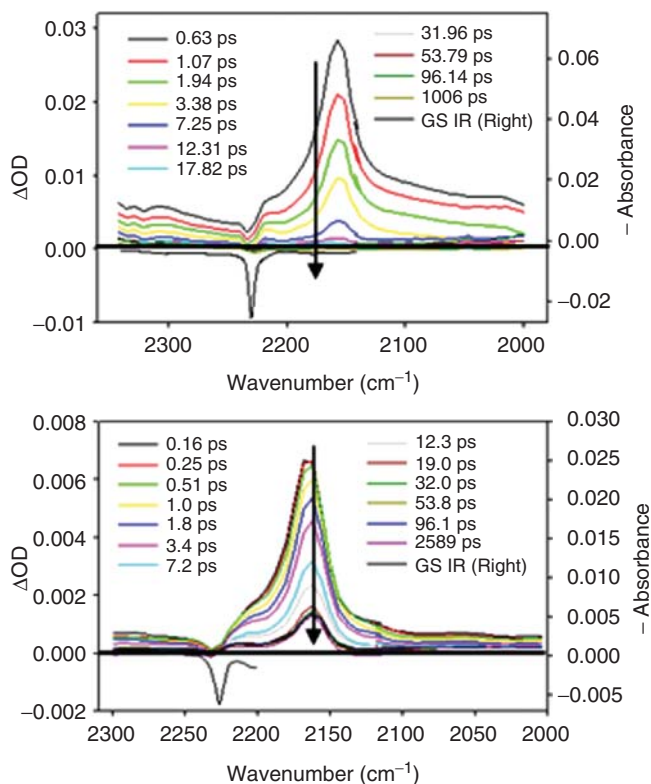


Figure 6.16 Time-resolved infrared spectra of the compounds $trans\text{-}M_2(T^iPB)_2(O_2CC_6H_4\text{-}p\text{-}CN)_2$ ($M = Mo$ (a) and W (b)) showing the $C\equiv N$ stretching vibration in the photoexcited state. (Taken from Ref. [76].)

DFT calculations for the anion $[M_2(O_2CH)_2(O_2CR)_2]^-$. In the case of molybdenum complexes, this signal is lost within a few picoseconds, typically 2–20 ps, as the T1 state is formed. This is $^3MoMo\delta\delta^*$, and this state has little effect on the ligand $C\equiv X$ vibration.

For tungsten, the situation is quite different in that the initial $C\equiv N$ stretch decays with time, but there is still a $\nu(C\equiv N)$ on the nanosecond time scale. The latter shifts to a slightly lower frequency and is indicative of the charge delocalization in the ^3MLCT state. The appearance of a single $\nu(C\equiv X)$ stretch with a shift to lower frequency is consistent with the electron in a molecular orbital that is ligand π^* in character and delocalized over both *trans*-ligands, O_2CR . This situation is typical for most $trans\text{-}M_2(T^iPB)_2(O_2CR)_2$ and the shift in $\nu(C\equiv X)$; the $\Delta\nu(C\equiv X)$ values observed are close to those predicted by the DFT calculations on the anions $trans\text{-}M_2(O_2CH)_2(O_2CR)_2^-$. For the tungsten complex with 9-anthracene ethynylcarboxylate, the lack of a $\nu(C\equiv C)$ stretching mode at long times, nanoseconds, is a notable exception in this trend. From transient absorption spectroscopy, it appears that the ^3MLCT state involves principally the anthracene and has little $C\equiv C$ character. This is also supported by the appearance of lower energy $C-C$ vibrations that are characteristic of the anthracene anion [79].

In contrast to the above, the fs TRIR spectra of the compounds $trans\text{-}M_2(OCMe)_2[(Pr^iN)_2CC\equiv C-Ph]_2$ are shown in Figure 6.17 [76]. Here, the amidinate ligands are the π -acceptor ligands, and the lowest energy $M_2\text{-}\delta$ -to-ligand charge transfer involves the amidinate and not the acetate group. With excitation into these MLCT bands, there appear two new $\nu(C\equiv C)$ modes both shifted to lower energy relative to the ground state. The most intense $\nu(C\equiv C)$ appears shifted $\sim 200\text{ cm}^{-1}$ to lower energy, while the higher energy vibration has a smaller shift of $\sim 40\text{ cm}^{-1}$. For molybdenum,

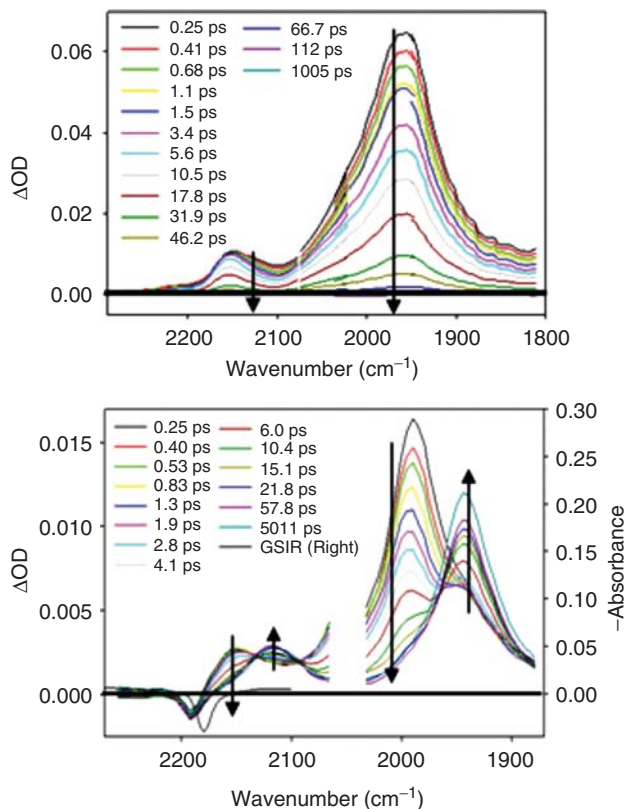


Figure 6.17 Time-resolved infrared spectra of the compounds $trans\text{-}M_2(O_2CMe)_2[NPr_2CC\equiv CPh]_2$ ($M = Mo$ (a) or W (b)) showing the $C\equiv C$ stretching vibrations in the photoexcited states. (Taken from Ref. [76].)

both of these vibrations decay within a few picoseconds, and at longer times there are no vibrations assignable to $\nu(C\equiv C)$. The former can be assigned to the ^1MLCT S1 state, while at longer times the T1 state is $^3MoMo\delta\delta^*$ as is apparent from the emission spectrum at 1100 nm. This state apparently has little influence on the $C\equiv C$ bond.

The spectra of the tungsten analog differ in that with time two new $\nu(C\equiv C)$ bands appear as the S1 to T1 state transition occurs. Both of the T1 $\nu(C\equiv C)$ bands are shifted to lower wavelength, indicating that the charge distribution is more localized on the $C\equiv C$ π^* orbital relative to the S1 state. The appearance of the two stretching $C\equiv C$ vibrations is consistent with the view that here the charge is unequally distributed over the two *trans*-amidinate ligands, that is, the MLCT states are not delocalized. Furthermore, the shift in $\nu(C\equiv C)$ to $\sim 200\text{--}240\text{ cm}^{-1}$ lower in energy is much greater than that predicted for the anions $trans\text{-}M_2(O_2CH)_2[(NPr^i)_2CC\equiv CPh]_2^-$.

A more limited series of compounds of formula $Mo_2(ArNCHNAr)_3(O_2CR)$ have also been examined by TRIR spectroscopy, where $Ar = p$ -anisole [70]. Here, the O_2CR ligands are the lowest energy π^* -acceptor ligands, and, thus, the ^1MLCT state involves the transfer of an $Mo_2\text{-}\delta$ electron to the single O_2CR ligand. The observed $\nu(C\equiv X)$ values and the shifts of this stretching mode are given in Table 6.5. As can be seen, the shift $\Delta\nu(C\equiv X)$ to lower energy is greater than that seen for the $trans\text{-}M_2(T^iPB)_2(O_2CR)_2$ compounds, which is consistent with the charge being localized on one ligand rather than delocalized over two as in $trans\text{-}M_2(T^iPB)_2(O_2CR)_2$ compounds.

The homoleptic compounds $Mo_2(O_2CR)_4$, where $R = C_6H_4\text{-}p\text{-}C\equiv CH$ and $C_6H_4\text{-}p\text{-}CN$, have also been examined by TRIR in the region of $\nu(C\equiv X)$ [81]. With D_{4h} symmetry, the O_2CR π^* orbitals

Table 6.5 Experimental and calculated $\nu(\text{C}\equiv\text{X})$ values in cm^{-1} comparing compounds $\text{Mo}_2(\text{T}^i\text{PB})_2(\text{O}_2\text{C}-\text{R})_2$ and $\text{Mo}_2(\text{ArNC}\{\text{H}\}\text{NAr})_3(\text{O}_2\text{C}-\text{R})$.

Compound	Experimental			Calculated	References
	Ground state $\nu(\text{C}\equiv\text{X})$	$^1\text{MLCT}$ state $\nu(\text{C}\equiv\text{X})$	Shift $\Delta\nu(\text{C}\equiv\text{X})$	Anion shift $\Delta\nu(\text{C}\equiv\text{X})$	
$\text{Mo}_2(\text{ArNCHNAr})_3(\text{O}_2\text{C}-\text{CCPh})$	2135	1975	−249	a)	[70]
$\text{Mo}_2(\text{T}^i\text{PB})_2(\text{O}_2\text{CC}\equiv\text{C}-9-\text{An})_2$	2204	2113	−91	−101	[79]
$\text{Mo}_2(\text{ArNCHNAr})_3(\text{O}_2\text{CC}_4\text{H}_2\text{SC}\equiv\text{CH})$	2100	1970	−130	−155	[70]
$\text{Mo}_2(\text{T}^i\text{PB})_2(\text{O}_2\text{CC}_4\text{H}_2\text{SC}\equiv\text{CH})_2$	2099	2033	−66	−57	[80]
$\text{Mo}_2(\text{ArNCHNAr})_3(\text{O}_2\text{C}-\text{Ph}-p-\text{CN})$	2230	2145	−85	−112	[70]
$\text{Mo}_2(\text{T}^i\text{PB})_2(\text{O}_2\text{C}-\text{Ph}-p-\text{CN})_2$	2230	2157	−73	−67	[76]

a) Frequency calculation returned with a negative frequency.

transform as e_u , a_{2g} , and b_{2g} . The HOMO, the $\text{M}_2-\delta$ orbital transforms as b_{2g} and the δ^* as b_{1u} . The $\text{M}_2-\delta$ and ligand π^* orbitals of b_{2g} can thus mix. This stabilizes the $\text{M}_2-\delta$ by back-bonding and raises the energy of the ligand π^* b_{2g} orbital. The frontier orbitals for the compound $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_4-p-\text{C}\equiv\text{CH})_4$ are shown in Figure 6.18. Those of the *p*-cyanobenzoate are similar though the π^* -orbitals are lowered in energy due to the greater electron-withdrawing properties of the cyano group. In all cases, the ligand-based π^* orbitals of e_u symmetry lie lowest and the $\text{Mo}_2-\delta$ to ligand π^* e_u represents

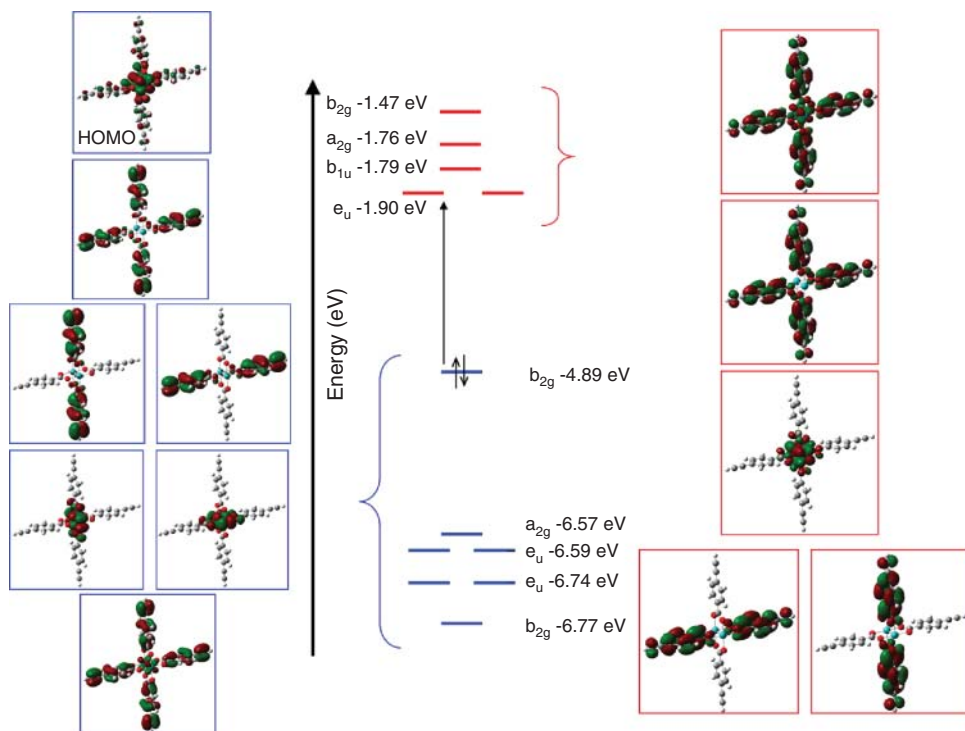


Figure 6.18 Frontier molecular orbital energy level diagram for the compound $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_4-p-\text{C}\equiv\text{CH})_4$ with Gauss view plots of the orbitals. (Reprinted with permission from Ref. [81]. Copyright 2013 American Chemical Society.)

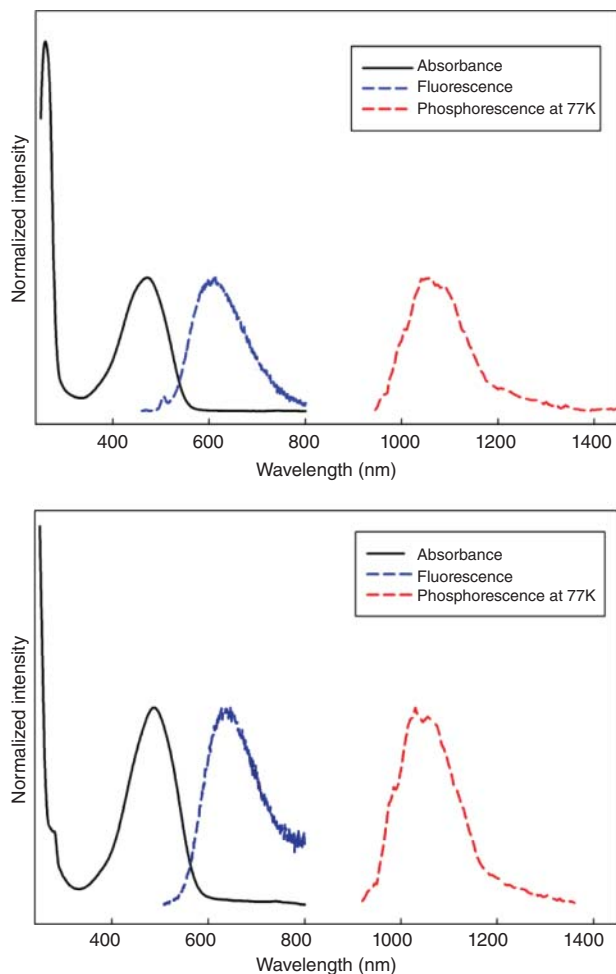


Figure 6.19 Electronic absorption and triplet emission spectra of the compounds $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-C}\equiv\text{X})_4$ where $\text{X}=\text{CH}$ or N recorded in THF at room temperature. (Reprinted with permission from Ref. [81]. Copyright 2013 American Chemical Society.)

the fully allowed $^1\text{MLCT}$. The absorption and emission spectra for the two compounds are shown in Figure 6.19. The phosphorescence is from the $^3\text{MoMo}\delta\delta^*$ states that have lifetimes $\sim 60\ \mu\text{s}$.

The fs TRIR spectra of the two compounds are shown in Figure 6.20. As expected, the $\nu(\text{C}\equiv\text{X})$ frequencies are shifted to lower energy consistent with an $^1\text{MLCT}$ state. However, it is quite clear for the *p*-cyanobenzoate that there are two $\nu(\text{C}\equiv\text{N})$ stretches. The situation for the *p*-ethynylbenzoate is less clear, but one might also propose that there is evidence of two $\nu(\text{C}\equiv\text{C})$ bands.

The photoexcited state places an electron in an e_u orbital, and this is subject to a Jahn–Teller distortion. Though the Jahn–Teller theorem does not predict the nature of the distortion, it is not unreasonable to suppose that this simply removes the degeneracy of the two e_u orbitals shown in Figure 6.18. This would lead to a situation similar to that for a *trans*- $\text{M}_2(\text{T}^i\text{PB})_2(\text{O}_2\text{CR})_2$ compound that could be either delocalized or localized. The appearance of two $\nu(\text{C}\equiv\text{N})$ modes suggests a localized or polarized electronic distribution of charge.

Listed in Table 6.6 are the observed values of $\nu(\text{C}\equiv\text{X})$ for these two compounds, where a comparison is also made with related *trans*-substituted compounds.

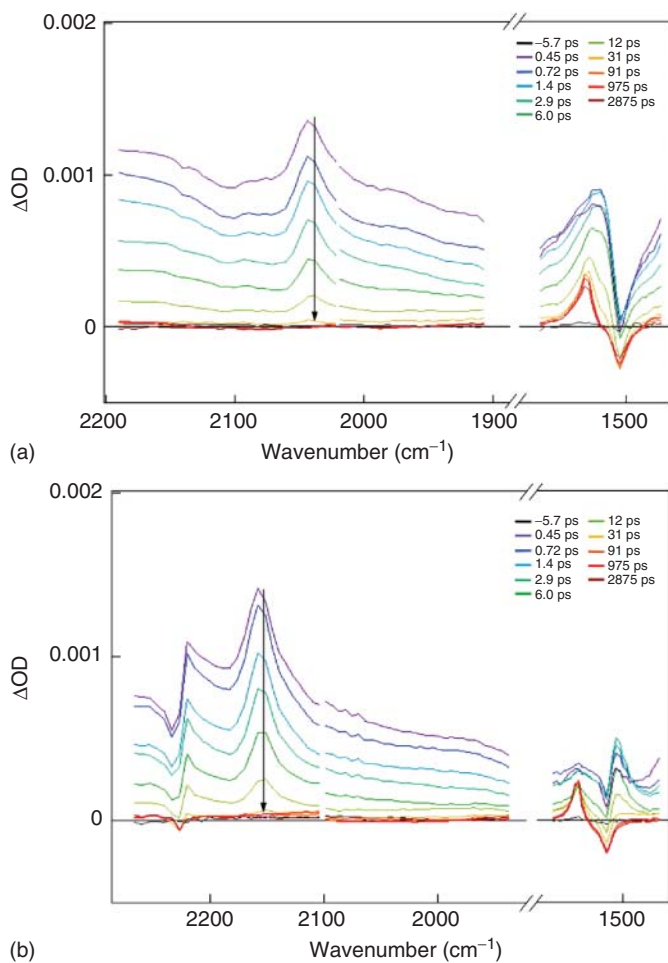


Figure 6.20 Time-resolved infrared spectra of the compounds $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-C}\equiv\text{X})_4$, where $X=\text{CH}$ (a) or N (b) recorded in THF at room temperature. (Reprinted with permission from Ref. [81]. Copyright 2013 American Chemical Society.)

Table 6.6 Experimental and calculated $\Delta\nu(\text{C}\equiv\text{X})$ values in cm^{-1} of compounds $\text{Mo}_2(\text{O}_2\text{C-R})_4$ and $\text{M}_2(\text{T}^i\text{PB})_2(\text{O}_2\text{C-R})_2$ compounds.

Compound	Experimental	Calculated	Assignment	References
$\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-C}\equiv\text{CH})_4$	-61	-34	Localized ^{a)}	[81]
$\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-C}\equiv\text{N})_4$	-10, -72	-41	Localized ^{a)}	[81]
$\text{Mo}_2(\text{T}^i\text{PB})_2(\text{O}_2\text{CC}_4\text{H}_2\text{SC}\equiv\text{CH})_2$	-65	-57	Delocalized	[80]
$\text{Mo}_2(\text{T}^i\text{PB})_2(\text{O}_2\text{C-Ph-}p\text{-CN})_2$	-73	-67	Delocalized	[76]
$\text{Mo}_2(\text{OAc})_2(\text{}^i\text{PrN}_2\text{CC}\equiv\text{CPh})_2$	-45, -241	-141	Localized	[76]

a) Localized principally over two of four *trans*-ligands.

Within ps, the spectra associated with the $\nu(\text{C}\equiv\text{X})$ modes are bleached as the T1, $^3\text{MoMo}\delta\delta^*$ state is formed. This shows $\nu_{\text{as}}(\text{CO}_2)$ of the carboxylate group at $\sim 1540\text{ cm}^{-1}$ shifted to higher energy relative to the ground state. This shift to higher energy is also seen in $\text{Mo}_2(\text{O}_2\text{CBu}^t)_4$ and seems to be a general feature of the T1 states of Mo_2 -carboxylates [66]. Because the M_2 - δ orbital is back-bonding to the CO_2 - π^* orbital, it is not unreasonable that removal of an electron from the δ -orbital reduces the degree of back-bonding and so the $\nu_{\text{asym}}(\text{CO}_2)$ stretching frequency is at higher energy.

6.2

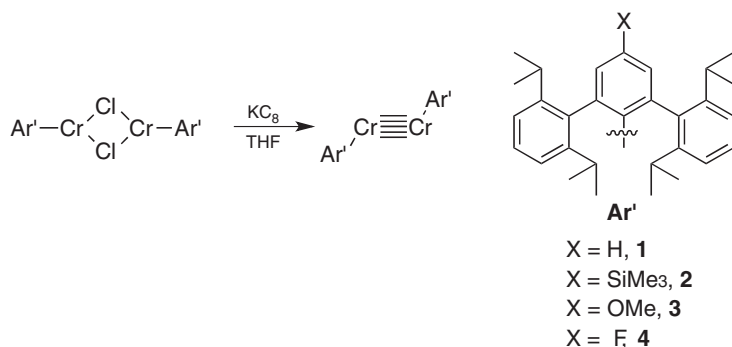
Quintuple Bonds

While compounds with a formal MM quadruple bond have been isolated and studied since the mid-1960s, the first report of a compound with a formal MM quintuple bond was as recent as 2005. Bond order is a concept that is difficult to distinguish experimentally. For example, there are dichromium compounds with formal quadruple bonds that have shorter Cr–Cr bond lengths than those with quintuple bonds. Mixing of the metal and ligand molecular orbitals complicates trying to assign a definitive electronic structure in theoretical studies and also reduces the calculated bond order between the metals. Therefore, we use the term “quintuple bond” in this section to simply illustrate that five electron pairs are involved in the metal–metal interaction [82].

6.2.1

Discovery

In a milestone for the field of MM multiple bonds, Power and coworkers reported the synthesis of the quintuply bonded dichromium species $\text{Ar}'\text{CrCrAr}'$ (**1**; $\text{Ar}' = \text{C}_6\text{H}_3$ -2,6- $\{\text{C}_6\text{H}_3$ -2,6-*i*Pr $_2\}_2$; see Scheme 6.2), by the reaction of $[\text{Cr}(\mu\text{-Cl})\text{Ar}']_2$ with KC_8 [82]. The bulky ancillary ligand serves to prevent intermolecular interactions that could generate chromium oligomers or polymers and helps protect the dimetal core. In addition, having a single ligand on each metal maximizes the number of valence electrons available for metal–metal bonding. Using bulky ligands and minimizing the number of ligand–metal interactions are design principles that have been applied in subsequent studies to achieve MM bond orders greater than 4.



Scheme 6.2

The structure of **1** is shown in Figure 6.21 and displays a *trans*-bent arrangement of the ligands about the dimetal core, with a Cr1'–Cr1–C1 angle of $102.78(3)^\circ$. In addition to the expected Cr–Ar' bond (Cr1–C7 = $2.131(1)\text{ \AA}$), there is also a weaker Cr–Ar' interaction with the *ipso* carbon of one of the terphenyl flanking rings (Cr1–C7' = $2.2943(9)\text{ \AA}$). The Cr–Cr bond distance is extremely short, $1.8351(4)\text{ \AA}$, which is a typical characteristic of all MM quintuply bonded compounds. Magnetic

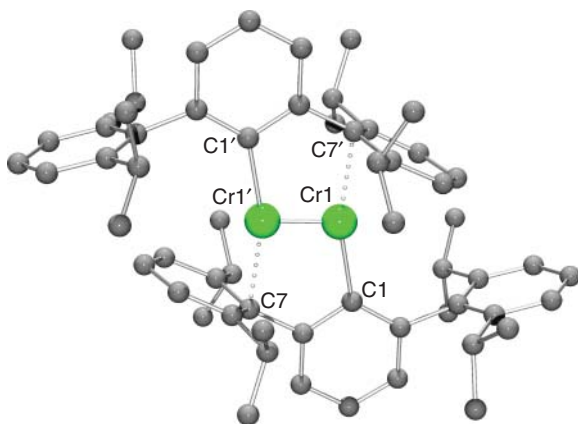


Figure 6.21 Crystal structure of **1** ($\text{Ar}'\text{CrCrAr}'$) [82].

measurements between 2 and 300 K showed temperature-independent, weak paramagnetism of $0.00112(5) \text{ emu mol}^{-1} \text{ Cr}$, which indicates there is no significant population of $S > 0$ states at room temperature and that there is strong coupling of the d^5-d^5 bonding electrons.

The electronic structure **1** was rationalized with the aid of density functional theory calculations (B3LYP/6-31G*). The HOMO and HOMO-1 are δ bonds, which have the weakest bonding interaction between the chromium ions. The HOMO-2 corresponds to the Cr_2 σ -bond, while the two π -bonding interactions (HOMO-3 and HOMO-4) have the lowest energy. Therefore, this compound can be thought to have a $\sigma^2\pi^4\delta^4$ electronic configuration.

Compound **1** forms a red solution in hexane, displaying an absorption at 488 nm ($\epsilon = 3200 \text{ mol}^{-1} \text{ l cm}^{-1}$), which, based on the computational results, is assigned as a $\text{Cr}_2-\delta \rightarrow \text{Cr}_2-\delta^*$ transition.

The isolation and characterization of **1** reignited the interest in synthesizing and characterizing compounds with high formal bond orders, as they are test beds to improve our understanding of the fundamentals of chemical bonding, provide the shortest metal–metal bond distances, and have also been found to be interesting reactivity. These experimental and theoretical studies are discussed in the following sections.

6.2.2

Synthesis

6.2.2.1 Arylchromium Dimers

A series of arylchromium(I) dimers of form $(4\text{-X-Ar}')\text{CrCr}(4\text{-X-Ar}')$ ($\text{X} = \text{H}$ (**1**), SiMe_3 (**2**), OMe (**3**), and F (**4**)) have been synthesized by Power and coworkers using the synthetic route shown in Scheme 6.2 [82, 83]. These compounds display broadened signals in their ^1H NMR spectra because of weak paramagnetism or the fluxional behavior of their terphenyl substituents. Adding electron-withdrawing and -donating groups only has a small effect on the properties of these compounds, with absorptions observed on the UV/vis spectra in the narrow range 482–490 nm. The compounds all exhibit similar magnetic behavior; a very small molar magnetic susceptibility is observed in the temperature range 2–300 K due to mixing of the fully spin-coupled ground state with Boltzmann-depopulated paramagnetic excited states.

While bulky ligands must be used to protect the quintuple bonds and prevent oligomerization, this study also highlighted problems associated with making a ligand too bulky. The treatment of $(3,5\text{-}i\text{Pr}_2\text{-Ar}')\text{CrCl}$ (see Figure 6.22 for terphenyl ligand structure) with KC_8 in THF results in the formation of monomeric $(3,5\text{-}i\text{Pr}_2\text{-Ar}')\text{Cr}(\text{THF})$, as opposed to the expected dimer. In this instance, the formation of a Cr-Cr bond is prevented by the steric bulk of the ligand.

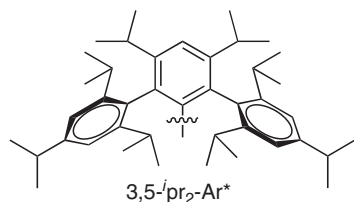
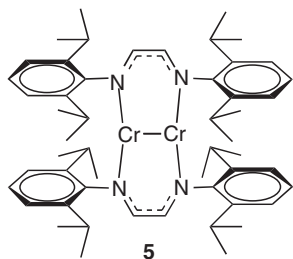
Figure 6.22 Structure of 3,5- $i\text{Pr}_2\text{-Ar}^*$.

Figure 6.23 Structure of compound 5.

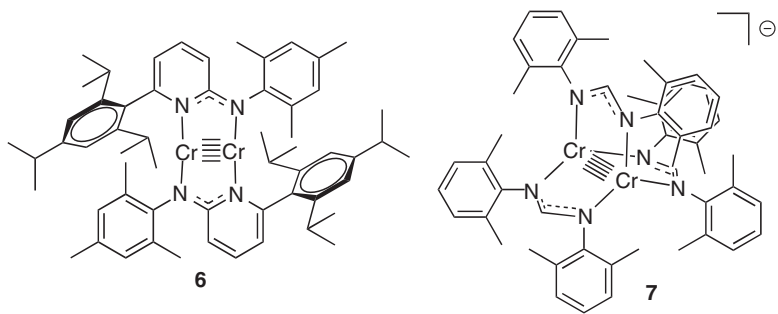


Figure 6.24 Structure of compounds 6 and 7.

6.2.2.2 Dichromium Compounds with N-Donor Ligands

In addition to aryl ligands, a variety of N-donor ligands have been used to bridge the dimetal core in quintuply bonded compounds. One of the first reported attempts at this was the dichromium diazadiene complex $\text{Cr}_2(\text{}^{\text{H}}\text{L}^{\text{iPr}})_2$ (Figure 6.23, 5; $\text{}^{\text{H}}\text{L}^{\text{iPr}} = N,N'$ -bis(2,6-diisopropylphenyl)-1,4-diazadiene) [84]. This compound was isolated by addition of $\text{Na}_2[\text{}^{\text{H}}\text{L}^{\text{iPr}}]$ to $\text{CrCl}_3(\text{THF})_3$ in THF to generate the $[\text{}^{\text{H}}\text{L}^{\text{iPr}}\text{Cr}(\mu\text{-Cl})]_2$ precursor, which was reacted with KC_8 to yield 5. While this compound could potentially have five bonding electron pairs and a formal quintuple bond, theoretical studies, *vide infra*, have shown that extensive mixing of one of the Cr_2 - δ orbitals with the ligand- π system makes assigning a formal Cr–Cr bond order complicated.

A variety of dichromium compounds containing monoanionic, three-atom bridging N-donor ligands have been isolated (Figure 6.24). The first two reports appeared simultaneously from independent groups and used a bulky 2-phenyl pyridine ligand, $\text{Cr}_2(\text{NN}^1)_2$ ($\text{HNN}^1 = [6-(2,4,6\text{-triisopropylphenyl})\text{pyridin-2-yl}](2,4,6\text{-triisopropylphenyl})\text{amide}$, 6) [85], or bulky amidinate ligand, $\text{Cr}_2(\text{Ar}^{\text{Xyl}}\text{-NC(R)N-Ar}^{\text{Xyl}})_3$ ($\text{Ar}^{\text{Xyl}} = 2,6-(\text{CH}_3)_2\text{-C}_6\text{H}_3$, 7) [86]. Compound 6 was isolated by the reaction of a chromium(III) chloride precursor with KC_8 . To generate 7, the precursor $[\{\text{Cr}(\text{THF})_2(\mu\text{-Cl})_2(\mu\text{-Ar}^{\text{Xyl}}\text{NC(H)NAr}^{\text{Xyl}})\}_2]$ was first reacted with 1.5 equiv. of KC_8 to yield the mixed-valent Cr_2^{3+} complex $[\text{Cr}(\mu\text{-Ar}^{\text{Xyl}}\text{NC(H)NAr}^{\text{Xyl}})]_2$, which has a formal Cr–Cr bond order of 4.5 [86]. Reduction

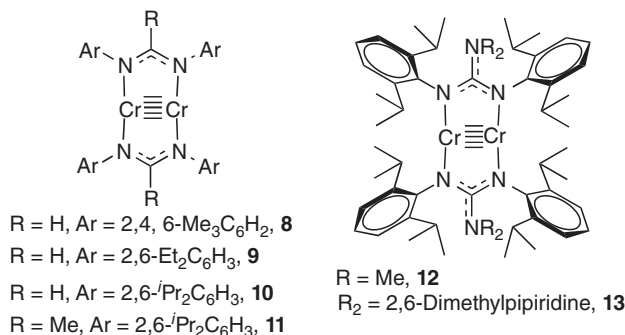


Figure 6.25 Structure of compounds 8–13.

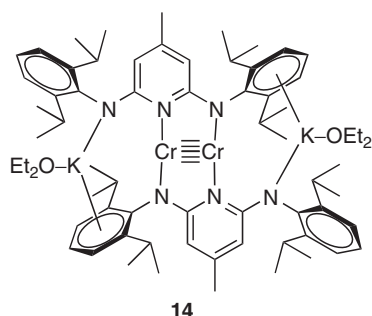


Figure 6.26 Structure of compound 14.

of this compound with a further equivalent of KC_8 yields the quintuply bonded anion **7**, in which there is a lantern arrangement of the ligands about the dichromium core.

Besides anionic compounds with three amidinate ligands, quintuple bonds have been found in neutral compounds with two amidinate ligands (Figure 6.25). For example, treatment of the mononuclear precursors $\text{CrCl}_2(\eta^2\text{-Ar-NC(R)N-Ar})(\text{THF})_2$ with KC_8 yields a range of bis-substituted compounds of form $\text{Cr}_2(\text{Ar-NC(R)N-Ar})_2$ (**8–11**) [87]. Another addition to this family of compounds are the guanidinate derivatives **12** and **13** [88]. As noted earlier for the diaryl dichromium bonded compounds, if the guanidinate ligand is too bulky, steric interactions result in the formation of coordination isomers other than the desired quintuply bonded bimetallic complex.

Compound **14** (Figure 6.26) was prepared from sequential reduction of a halide-free dinuclear chromium precursor [89]. The encapsulated potassium ions play a critical role in the formation of the Cr–Cr quintuple bond; reaction of **14** with 1 equiv. of [18]crown-6 yields a mononuclear Cr(II) compound.

6.2.2.3 Dimolybdenum Compounds

The chemistry of quintuply bonded compounds was extended to another group 6 metal, molybdenum, in 2009 with the synthesis and characterization of the diamido compounds $\text{Mo}_2(\mu\text{-RC}\{\text{N-2,6-}^i\text{Pr}_2\text{-C}_6\text{H}_3\}_2)_2$ (Figure 6.27, $R = \text{H}$ (**15**) or Ph (**16**)) [90]. These compounds were prepared by reducing a quadruply bonded chloride precursor with KC_8 , and their solid-state structures display extremely short Mo–Mo bonds of 2.02 Å, consistent with a formal quintuple bond between the Mo atoms. DFT calculations on this compound (BP86/def2-TZVP) predict a $\pi^4\sigma^2\delta^4$ electronic configuration for this compound, similar to its dichromium analogs. Compound **15** has also been prepared from the quadruply bonded hydride complex $\text{Mo}_2(\text{H})_2(\text{THF})_2(\mu\text{-RC}\{\text{N-2,6-}^i\text{Pr}_2\text{-C}_6\text{H}_3\}_2)_2$ by UV irradiation in cyclohexane solution [91]. Crystallization from benzene or toluene yields

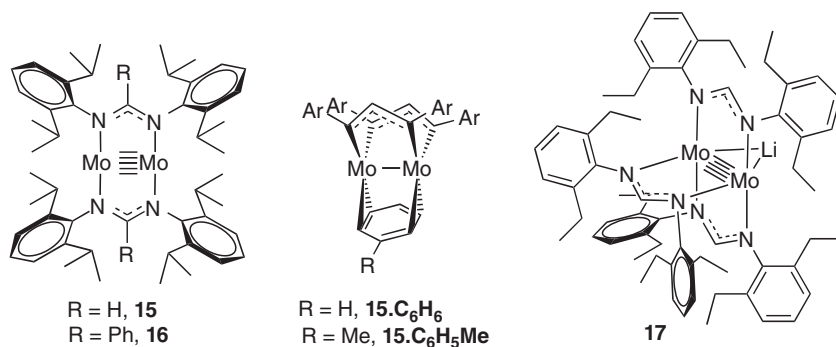


Figure 6.27 Structure of compounds 15–17.

the corresponding aryl adducts $\mathbf{15} \cdot \text{C}_6\text{H}_6$ and $\mathbf{15} \cdot \text{C}_6\text{H}_5\text{CH}_3$, in which the arene rings bridge the dimolybdenum core. The Mo–Mo bond lengths of these arene adducts are considerably longer than those found in the parent compound **15**, suggesting a decrease in the Mo–Mo bond order. Another dimolybdenum quintuply bonded compound with more than two bridging ligands has been synthesized by treatment of the diamagnetic trimolybdenum complex $\text{Mo}_2(\mu\text{-HC}\{N\text{-}2,6\text{-Et}_2\text{-C}_6\text{H}_3\}_2)(\mu\text{-Cl})\text{Mo}(\mu\text{-Cl})_2\text{Li}(\text{THF})(\text{OEt}_2)$ with 4 equiv. of KC8, resulting in the formation of $\text{Mo}_2(\mu\text{-HC}\{N\text{-}2,6\text{-Et}_2\text{-C}_6\text{H}_3\}_2)(\mu\text{-Li})$ (**17**, Figure 6.27) in low yield [92]. This compound is related to the dichromium analog **7**; however, the dimolybdenum core is so electron rich that it binds a lithium ion. The Mo–Mo bond length for **17** of 2.0612(4) Å is longer than that observed for **15** and **16** (2.02 Å), but DFT calculations show that a formal quintuple bond is maintained.

6.2.3

Structure

In the solid state, the majority of MM quintuply bonded compounds that have been isolated adopt one of the three structures shown in Chart 6.2 [92]. The *trans*-bent geometry of type **I** structures, where X is a bulky aryl ligand, is adopted by dichromium diaryl compounds. These compounds also display additional metal–ligand interactions with the C_{ipso} of one of the flanking aryl groups of terphenyl ligands. Type **II** structures are found in the compounds containing three- or four-atom bridging ligands. The donor atom (E) is exclusively nitrogen to date, and the ligands are arranged about the dimetal core with approximately D_{2h} symmetry. This is the most common arrangement displayed in the compounds found to date. Finally, type **III** compounds exhibit a D_{3h} arrangement of three-atom bridging about the dimetal core, although only compound **7** has been isolated with this arrangement of ligands. The isolation of **17**, which contains three formamidinate ligands and one lithium cation that bridge the dimolybdenum core in a paddlewheel arrangement, indicates that further geometries can be envisaged, although they are not necessarily easy to predict.

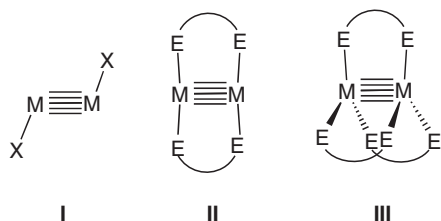


Chart 6.2 Possible structures of dimetal quintuply bonded compounds.

Table 6.7 Selected bond lengths and angles in dinuclear compounds with large formal bond orders.

Type I compounds	Cr–Cr (Å) ^a	Cr–C _{Ar} (Å) ^a	Cr···C _{ipso} (Å)	References	FSR
1 , Cr ₂ (Ar') ₂	1.8351(4)	2.131(1)	2.2943(9)	[82]	0.774
2 , Cr ₂ (4-SiMe ₃ -Ar') ₂	1.8077(2)	2.136(2)	2.322(2)	[83]	0.762
3 , Cr ₂ (4-OMe-Ar') ₂	1.8160(5)	2.131(2)	2.311(2)	[83]	0.766
4 , Cr ₂ (4-F-Ar') ₂	1.831(2)	2.135[8]	2.301[8]	[83]	0.772
Type II compounds	M–M (Å)	M–N (Å)			
5 , Cr ₂ (^H L ^{iPr}) ₂	1.8028(9)	1.914[3]	—	[84]	0.760
6 , Cr ₂ (NN ¹) ₂	1.749(2)	2.013[6]	—	[85]	0.737
22 , Cr ₂ (NN ³)	1.750(1)	2.014[4]	—	[93]	0.738
8 , Cr ₂ (Ar ^{Mes} NC{H}NAr ^{Mes}) ₂	1.7404(8)	2.000[3]	—	[87]	0.734
9 , Cr ₂ (Ar ^{Et} NC{H}NAr ^{Et}) ₂	1.7454(1)	2.015[6]	—	[87]	0.736
10 , Cr ₂ (Ar ^{iPr} NC{H}NAr ^{iPr}) ₂	1.7472[10]	2.005[2]	—	[87]	0.737
11 , Cr ₂ (Ar ^{iPr} NC{Me}NAr ^{iPr}) ₂	1.7395(7)	1.983[3]	—	[87]	0.733
12 , Cr ₂ (Ar ^{iPr} NC{NMe ₂ }NAr ^{iPr}) ₂	1.7293(12)	2.018[4]	—	[88a]	0.729
13 , Cr ₂ (Ar ^{iPr} NC{dmp}NAr ^{iPr}) ₂	1.7056(12)	2.001[5]	—	[88a]	0.719
14 , [(Et ₂ O)K] ₂ [Cr ₂ (NN ²) ₂]	1.7443(10)	2.014[6]	—	[89]	0.735
15 , Mo ₂ (Ar ^{iPr} NC{H}NAr ^{iPr}) ₂	2.0187(9)	2.117[6]	—	[90]	0.776
16 , Mo ₂ (Ar ^{iPr} NC{Ph}NAr ^{iPr}) ₂	2.0157(2)	2.117[2]	—	[90]	0.776
18 , Cr ₂ (Ar ^{Me} NC{H}NAr ^{Me}) ₂ (THF) ₂	1.8115(12)	2.041[4]	—	[89]	0.764
19 , Cr ₂ (Ar ^{Me} NC{H}NAr ^{Me}) ₂ (2-MeTHF)	1.7636(5)	2.031[2]	—	[89]	0.744
Type III and related	M–M (Å)	M–N (Å)	Mo–C (Å)		
15-C₆H₆	2.106(1)	2.180[3]	2.218	[91]	0.810
15-C₆H₅Me	2.105(1)	2.191[1]	2.216	[91]	0.810
7 , [Cr ₂ (Ar ^{Xyl} NC{H}NAr ^{Xyl}) ₃] [–]	1.7397(9)	2.092[3]	—	[86]	0.733
Cr ₂ (Ar ^{Xyl} NC{H}NAr ^{Xyl}) ₃	1.8169(7)	2.044[3]	Mo–Li (Å)	[86]	0.766
17 , Mo ₂ (Ar ^{iPr} NC{H}NAr ^{iPr}) ₃ (μ-Li)	2.0612(4)	2.156[2]	2.640(8)	[92]	0.793

a) The standard deviation for average bond lengths is given in square brackets and was calculated from $[] = [\sum_n (\text{esd})_i^2 / (n - 1)]^{1/2}$.

A summary of all the structural parameters associated with crystallographically characterized quintuply bonded compounds is given in Table 6.7. The formal shortness ratio (FSR) for a given bond was defined by Cotton [1] as follows:

$$\text{FSR}_{\text{AB}} = \frac{D_{\text{A-B}}}{(R_1^{\text{A}} + R_1^{\text{B}})}$$

where R_1^{A} and R_1^{B} are the atomic radii of A and B, and $D_{\text{A-B}}$ is the A–B bond distance. This is a useful parameter as it allows comparison between bonds consisting of different elements. The FSRs for the quintuply bonded compounds in Table 6.1 are typically smaller than that found for N₂ (FSR = 0.786) or HCCH (FSR = 0.783).

The Cr–Cr bond lengths for type **I** compounds range from 1.8077(2) to 1.8351(4) Å. The bond length in this class of compounds is not dominated by the electron-withdrawing or electron-donating ability of aryl ligands, but rather crystal packing effects appear to play a more dominant role. The Cr–Cr bond distances are longer than those associated with type **II** or **III** compounds and have FSRs ranging from 0.762 to 0.774.

Type **II** compounds all have aminopyridinate, amidate, or guanidinate bridging ligands, and as observed for type **I** compounds, the metal–metal bond length does not appear to be strongly correlated to the electronic nature of the bridging ligand [94]. The N–C–N bite angle in three-atom

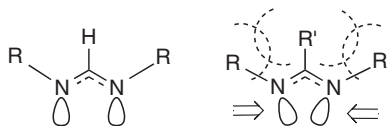


Figure 6.28 Diagram highlighting the affect on directionality of nitrogen lone pairs when using bulky ligands in the RNC(R')NR backbone of amidinate ligands.

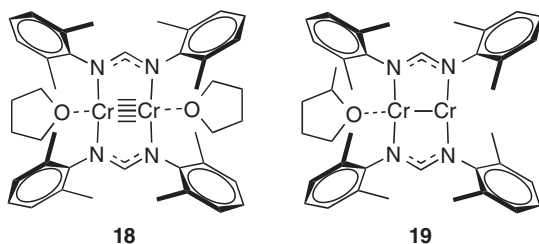


Figure 6.29 Structure of compounds **18** and **19**.

bridging ligands has been found to play a role in controlling the M–M bond lengths in some instances, as it can be modified by using suitably bulky groups on the RNC(R')NR backbone. As illustrated in Figure 6.28, for an amidinate ligand, when R' = H the N-donor lone pairs are likely to remain parallel to one another as expected. However, with sufficient steric interactions between R and R', a decrease in the N–C–N angle and convergence of the nitrogen lone pair orbitals will result, which essentially forces the two metal atoms being closer together. The M–M bond lengths in the compound pairs **10** and **11** and **15** and **16** are very similar and indicate that simply swapping H for R' = Me or Ph is not sufficient to induce this effect. However, guanidinate ligands (R' = NR''₂) are significantly more bulky, and it is possible to control the bite angle to some extent. This concept was used to generate compound **13**, which has the shortest M–M bond length reported to date for a quintuply bonded compound (1.7056(12) Å) [88b]. This ligand-based quintuple bond shortening concept does have its limitations, as if the bite angle is too small, other coordination isomers are formed instead. This effect has also been proposed to account for the slightly longer Cr–Cr bond length found in **6** by comparison to other complexes containing three-atom bridging ligands [94, 95]. In this instance, interligand repulsion is thought to give rise to a more divergent bite angle for the N–C–N ligand.

The metal–metal bond length in quadruply bonded paddlewheel complexes lengthens upon axial coordination of donor solvent molecules such as THF (Figure 6.29). A similar trend has been found in quintuply bond compounds [89]. Recrystallization of Cr₂(μ-HC{N-2,6-Me₂-C₆H₃}₂)₂ from THF or 2-MeTHF solutions yielded crystals Cr₂(μ-HC{N-2,6-Me₂-C₆H₃}₂)₂(THF)₂ (**18**) and Cr₂(μ-HC{N-2,6-Me₂-C₆H₃}₂)₂(2-MeTHF) (**19**). The Cr–Cr bond lengths of 1.8115(12) and 1.7636(5) Å are appreciably longer than those found in comparable species such as **8** (1.7404(8) Å), which have no axial ligation.

The Mo–Mo bond lengths in the adducts **15**·C₆H₆ (2.106(1) Å) and **15**·C₆H₅CH₃ (2.105(1) Å), in which the arene rings bridge the dimetal core resulting in a ligand rearrangement, are also considerably longer than those found in the parent compound **15** (2.0187(9) Å) [91]. Calculations suggest that the Mo–Mo elongation originates from strong mixing of the Mo₂-δ* orbitals with the benzene-π* orbitals resulting in a HOMO that is bonding with respect to the Mo–C bonds, but antibonding with respect to the Mo–Mo bond. As such, the Mo–Mo bonds in the arene adducts are closer to being quadruple bonds, rather than quintuple.

6.2.4

Theoretical Studies

The compounds described in the previous section can all potentially be described as quintuply bonded compounds, on the basis of the fact that both metal atoms have five electrons that are capable of interacting with one another. However, the bonding situation is often complicated by mixing of excited, less-bonding states with the ground state, or antiferromagnetic coupling (nonbonding interactions) between electron pairs. Electronic structure calculations are therefore a valuable tool to gain a fuller understanding of the nature of the chemical bonding in these compounds.

Some of the first calculations on quintuply bonded species examined the simple model compounds HMMH (M = Cr, Mo, W) [96]. The structures of these compounds were calculated using DFT methods, and a *trans*-bent structure (type I) as opposed to a linear structure was predicted. The origin for the preference of *trans*-bent as opposed to linear structures in these compounds arises from *sd*-hybridization of the metals [97]. The preference for the *trans*-bent isomer was also found in other RMMR (R = F, Cl, Br, CN, and CH₃) compounds, for which a quintuple bond is maintained between the metal atoms [98].

In order to obtain a proper description of the bonding in Ar'CrCrAr' complexes, multiconfigurational calculations are required. The simplified model compound PhCrCrPh has been examined using the high-level multiconfigurational complete active space self-consistent field (CASSCF)/CASPT2 level of theory [99]. The predominant contribution to the wavefunction was found to be the $\sigma^2\pi^4\delta^4$ electronic configuration, and an EBO of 3.52 was calculated for the Cr–Cr bond. Although the calculated bond order is less than 5, it is still a formally quintuple bond as five orbitals and five electrons from each chromium atom are involved in the bonding. The calculated Cr–Cr bond length for this simplified model (1.752 Å) is slightly shorter than that observed experimentally for **1** (1.8351(4) Å). Further calculations were performed using model compounds containing terphenyl ligands with the aim of seeing if the Cr–arene interactions present in **1** are in part responsible for the weakening of the Cr–Cr bond [99, 100]. Due to the complexity of the terphenyl ligands, these calculations were performed using DFT methods, which underestimate the Cr–Cr bond length because of their monodeterminantal character, but can be used to obtain information about the Cr–arene interaction. The DFT calculations yielded a Cr–Cr bond length of 1.708 Å for PhCrCrPh, which has no Cr–arene interaction, that increased slightly to 1.736 and 1.744 Å in the terphenyl model compounds Ar[§]CrCrAr[§] (Ar[§] = C₆H₄-2-C₆H₅) and Ar[#]CrCrAr[#] (Ar[#] = C₃H₃-2,6-(C₆H₃-2,6-Me₂)₂), which do have a Cr–arene interaction [100]. The small weakening of the Cr–Cr bond suggests that the Cr–Ar interaction in these types of compounds is relatively feeble. More recent studies combining the extended transition state energy decomposition method with the natural orbitals for chemical valence density decomposition scheme (ETS-NOCV) also show that different substituents on the terphenyl ligands do little to perturb the Cr–Cr bond [101]. However, it was found that the ⁱPr substituents on the aryl ligands provide considerable extra stability to the ArCrCrAr dimers with respect to the ArCr monomers through van der Waals dispersion interactions.

Multiconfigurational calculations on **20** (Figure 6.30), which is a model of the dichromium diazadiene complex **5** in which the ⁱPr groups were substituted for Me, generated an EBO of 3.43 [102]. Despite the similarity of this value to that obtained for **1** (EBO = 3.52) and the relatively short Cr–Cr bond length (1.8028(9) Å), the formal Cr–Cr bond order was assigned as four due to extensive mixing of one of the 3d δ -orbitals with the ligand- π system. Similar conclusions were made in other theoretical studies of this compound [103] and highlight the problem of trying to assign an integer value to bond orders in compounds with complicated electronic structures.

A series of dichromium model compounds containing amidinate (**21** and **9**), guanidinate (**12**), and aminopyridinate (**22**) bridging ligands (Figure 6.30), with geometries optimized at the CASPT2 level of theory, have been studied [104]. A linear correlation between the Cr–Cr bond length and EBO was found in these compounds, which all have a similar class of supporting ligand.

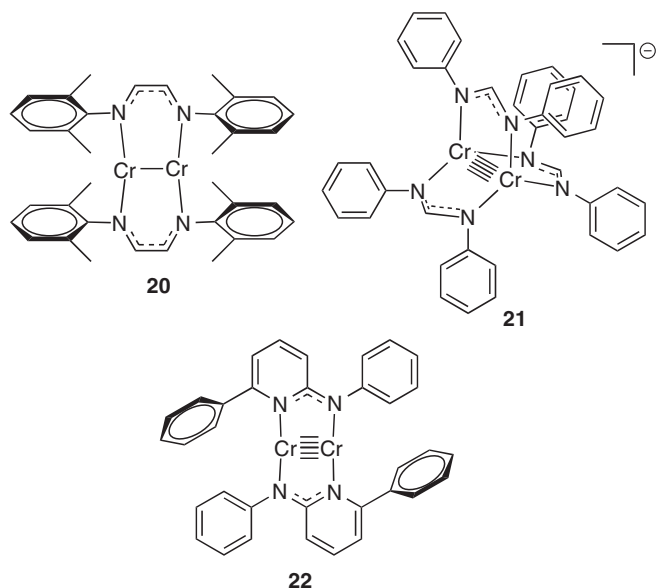


Figure 6.30 Structure of compounds 20–22.

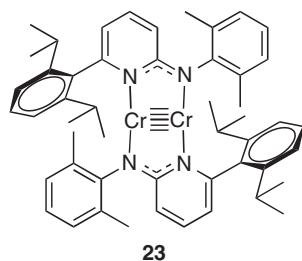


Figure 6.31 Structure of compound 23.

6.2.5

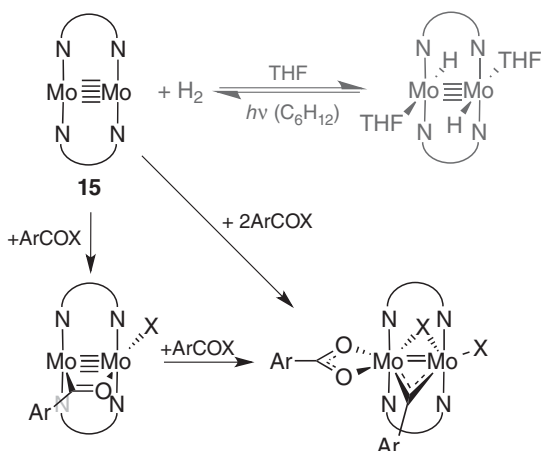
Reactivity

The first study probing the reactivity of MM quintuple bonds used the dichromium species **23** ($\text{Cr}_2(\mu\text{-NN}^3)_2$) (Figure 6.31) [93]. This compound reacts with dioxygen to generate the Cr(V) complex $[\text{Cr}(\text{O})(\text{NN}^3)]_2(\mu\text{-O})_2$, which has two bridging oxo ligands. Reaction with $\text{Al}(\text{Me})_3$ in hexane results in the formation of the carbalumination product $\text{Cr}_2(\mu\text{-NN}^3)_2(\mu\text{-CH}_3)(\mu\text{-AlMe}_2)$, which has a formal Cr–Cr quadruple bond. This chemistry is analogous to that found in organic compounds containing carbon–carbon double and triple bonds and highlights the potential of quintuply bonded compounds for use in small molecule activation as they can donate between two and eight electrons. For example, compound **23** has been shown to be capable of activating E_4 compounds ($\text{E} = \text{P}_4$, As_4 , and AsP_3) under mild conditions, and in a selective manner, to generate dichromium complexes with *cyclo*- E_4^{2-} ligands [105]. By contrast to its insertion reaction with oxygen, **23** undergoes addition reactions with other chalcogens leading to the formation of $\text{Cr}_2(\mu\text{-NN}^3)_2(\mu^2, \eta^2\text{-E}_2)$ ($\text{E} = \text{S}$, Se , and Te) [106]. Reaction with group 17 elements leads to the formation of $\text{Cr}_2(\mu\text{-NN}^3)(\mu\text{-X})_2$ ($\text{X} = \text{Cl}$, Br , and I), in which the quintuple bond undergoes an insertion reaction. This compound was also found

to undergo an insertion reaction when reacted with the dichalcogenides Ph_2S_2 and Ph_2Se_2 , forming the oxidative addition products $\text{Cr}_2(\mu\text{-NN}^3)_2(\mu\text{-EPh})_2$ [106].

Dichromium and dimolybdenum quintuply bonded compounds undergo reactions with alkenes and alkynes [107], resulting in the formation of cycloaddition products that have a reduced formal M–M bond order and a hydrocarbon bridge. The dichromium diazadiene complex **5** forms the expected [2+2] cycloaddition product upon reaction with electron-rich alkynes; electron poor alkynes add across the metal–ligand bond instead [108]. This difference in reactivity is believed to be a reflection of the unique ligand-based HOMO of **5**.

Treatment of the dimolybdenum quintuply bonded compound **15** with a stoichiometric amount of acyl halide results in the formation of a quadruply bonded dimolybdenum acyl complex in a reaction analogous to Friedel–Crafts insertion of alkynes [109]. The resulting dimolybdenum acyl complex shown in Scheme 6.3 can then react with another equivalent of acyl halide, yielding products in which there is a further reduction of the Mo–Mo bond order, and an unusual acyl disproportionation, which yields a metal carbyne complex that also contains a carboxylate ligand.



Scheme 6.3

Quintuple bonds can also activate small molecules. The reaction of **15** with hydrogen is illustrated in Scheme 6.3 and results in the oxidative addition of hydrogen across the quintuple bond to yield a bis(hydride) complex with a formal quadruple bond [91]. This reaction is reversible, and irradiation with UV light results in reductive elimination of H_2 to regenerate the quintuply bonded species. The reactivity of the quintuple bond was shown to be related to the steric bulk of the supporting ligand and nature of the metal. Reaction of the dichromium compound **9**, which is bridged by the ethyl-substituted amidinate ligand $\text{HC}(N\text{-}2,6\text{-Et}_2\text{C}_6\text{H}_3)_2$ (NN^4), with NO results in the formation of a mixture of a mononuclear, $\text{Cr}(\text{NO})_2(\kappa^2\text{-NN}^4)_2$, and dinuclear, $\text{Cr}_2(\mu\text{-}\kappa^1\text{-ONO})_2(\text{NO})_4(\mu\text{-}\kappa^2\text{-NN}^4)_2$ species [110]. Changing to the more sterically demanding isopropyl-substituted amidinate ligand $\text{HC}(N\text{-}2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)_2$ (NN^5) in **10**, the dinuclear product ($\kappa^2\text{-NO}_2$) $\text{Cr}(\mu\text{-NO})_2(\mu\text{-}\kappa^2\text{-NN}^5)_2\text{Cr}(\text{NO})$ is formed instead, which contains an axially coordinated, as opposed to bridging, NO_2 ligand. Changing the metal results in further differences; reaction of **16** with NO yields the quadruply bonded complex $\text{Mo}_2(\mu\text{-}\kappa^2\text{-NN})_2(\mu\text{-}\kappa^2\text{-ONO})_2$. The lack of axial ligation in this complex is believed to be a reflection of the stronger Mo–Mo quadruple bond than the chromium analogs. The reaction of the arylchromium dimer **1** with N_2O or the azide $\text{N}_3(1\text{-Ad})$ results in the formation of $\text{Ar}'\text{Cr}(\mu\text{-O})_2\text{Cr}(\text{O})\text{Ar}'$ and $\text{Ar}'\text{Cr}(\mu_2\text{-}\eta^1, \eta^3\text{-N}_3(1\text{-Ad}))\text{CrAr}'$ in which the Cr–Cr bond has been completely cleaved. This is in contrast to the behavior of quintuple bonds supported by N-donor bridging ligands in which the M–M bond is maintained to some extent in most instances [111].

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7

Group 7 Metal–Metal Bonds

Frederic Poineau, Alfred P. Sattelberger, Erli Lu, and Stephen T. Liddle

7.1

Manganese

7.1.1

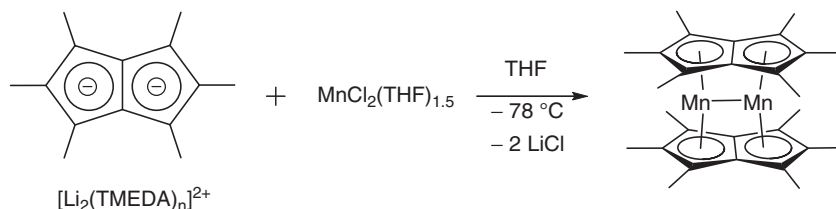
Introduction

The first manganese compound featuring a Mn–Mn bond, dimanganese decacarbonyl $[\text{Mn}_2(\text{CO})_{10}]$, was synthesized [1] and first structurally characterized [2] in the 1950s. Since then, the realm of Mn–Mn bonding species has significantly expanded. A search of the Cambridge Structural Database (CSD, version 03/2014) with the keyword Mn–Mn resulted in 512 hits. The vast majority of these are multimetallic cluster compounds, and therefore beyond the scope of this chapter. In contrast to its heavier group 7 congeners, (Tc and Re, *vide infra*) and other first-row congeners (e.g., Cr and Ni, see Chapters 6 and 10, respectively), there is a significant gap in knowledge of Mn–Mn bonded species reflecting the relative underdevelopment of the field, especially in the last decade. Instead of an encyclopedic coverage of the literature, this section will focus on representative advancements of homobimetallic complexes with Mn–Mn bonds published after 2000, while important historical aspects will be included as well. Heterometallic complexes with Mn–M (M = transition metal) interactions are not covered due to the page restrictions [3].

7.1.2

Complexes with Mn_2^{4+} Core

A “double metallocene” dimanganese permethylpentalene (Pn^+) complex $[\text{Pn}^+_2\text{Mn}_2]$ was reported in 2008, and was synthesized by salt metathesis, Scheme 7.1 [4]. The structure of the complex can be found in Figure 7.1 the ball and stick representation of $[\text{Pn}^+_2\text{Mn}_2]$. Both of the two Mn(II) centers bond with the Pn^+ ligand in a η^5 manner, and are almost symmetrical. The average Mn–C bond length is 2.170(2) Å, which is almost identical with that in $[\text{Cp}^+_2\text{Mn}]$ (2.169(5) Å) [5]. The Mn–Mn distance in the complex is rather short (2.277(5) Å). Actually, this is the second shortest Mn–Mn distance in the literature, only longer than the Mn–Mn triple bond (2.170 Å) in $[(\text{CpMn})_2(\mu\text{-CO})_3]$ [6]. Although the short Mn–Mn bond length indicates some multiple bond character, electron counting, however, suggests a Mn–Mn single bond. It should be noted that judging the bond order of any M–M bond with the presence of bridging ligand(s) only by internuclear distance is an oversimplification and should be treated with caution. The spin-state of the paramagnetic Mn(II) centers is postulated to be low-spin, which is evidenced not only by the similarity of the metric parameters between this complex and known low-spin manganocene $[\text{Cp}^+_2\text{Mn}]$ but also by magnetism and electron paramagnetic resonance (EPR) studies.



Scheme 7.1 Synthesis of $[\text{Pn}^*_2\text{Mn}_2]$.

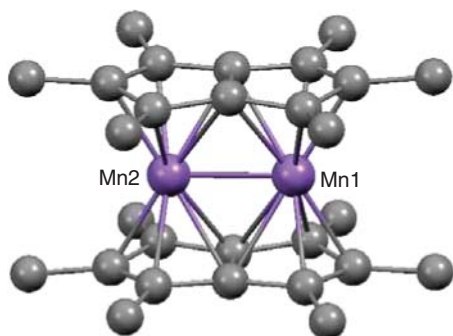
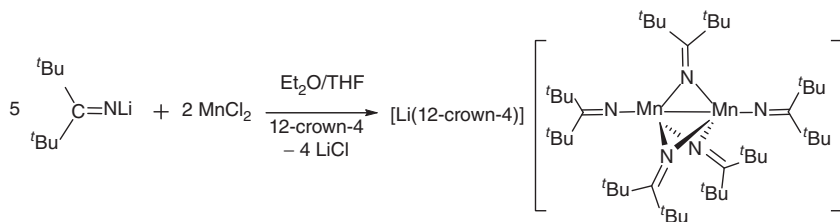


Figure 7.1 Ball and stick representation of $[\text{Pn}^*_2\text{Mn}_2]$. Hydrogen atoms are omitted for clarity.

A Mn_2^{4+} ketimide complex $\{[\text{Li}(12\text{-crown-4})][\text{Mn}_2(\text{N}=\text{C}t\text{Bu}_2)_5]\}$ was reported in 2012. This complex was synthesized straightforwardly by salt metathesis reaction in Scheme 7.2 [7]. The structure of the anion part of the complex can be found in Figure 7.2. Three among the five ketimides act as bridging ligands, while two act as terminal ligands. Thus, two co-facial tetrahedra are formed in the molecule. The Mn–Mn distance is $2.5965(7) \text{ \AA}$, significantly longer than that in the above-mentioned $[\text{Pn}^*_2\text{Mn}_2]$. The existence of a Mn–Mn bond is supported by a magnetism study: the two open-shell Mn(II) centers are found to be antiferromagnetically coupled, resulting in a diamagnetic ground state. The terminal Mn–N bond length ($1.971(2) \text{ \AA}$) is $\sim 0.1 \text{ \AA}$ shorter than that in a related Mn(II) ketimide $[\text{Mn}_3(\text{N}=\text{C}^t\text{Bu}_2)_6]$ [8] (in which a Mn–Mn bond is absent), indicating the presence of a *trans*-influence from the Mn–Mn bond.



Scheme 7.2 Synthesis of $\{[\text{Li}(12\text{-crown-4})_2][\text{Mn}_2(\text{N}=\text{C}t\text{Bu}_2)_5]\}$.

7.1.3

Complexes with Mn_2^{3+} Core

Recently, an elusive and intriguing example of a Mn_2^{3+} compound $\{[\text{Mn}_2(\mu\text{-}\kappa^2\text{-N,N'-Me}_2\text{Si}(\text{NDipp})_2)_2][\text{K}(18\text{-crown-6})(\text{THF})_2]\}$ was reported by Tsai and coworkers by the reduction of dimanganese(II) compound with 1 equiv. of KC_8 (Scheme 7.3) [9]. Further reduction of the Mn_2^{3+}

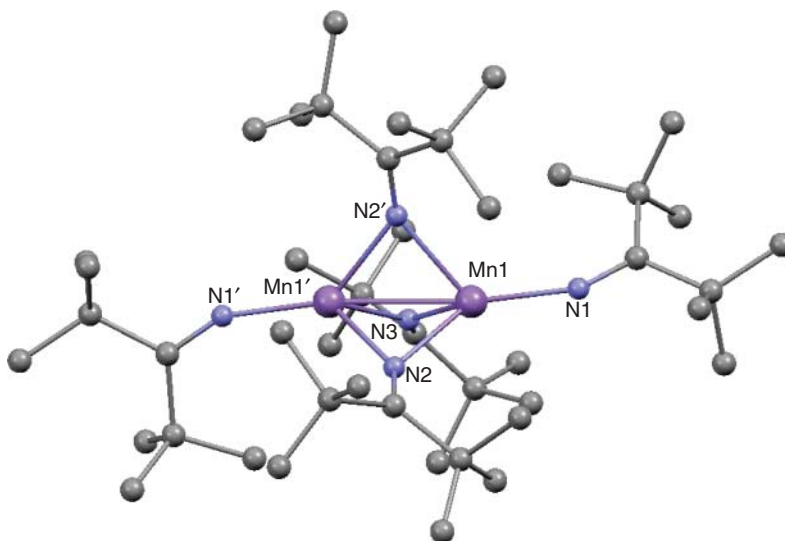
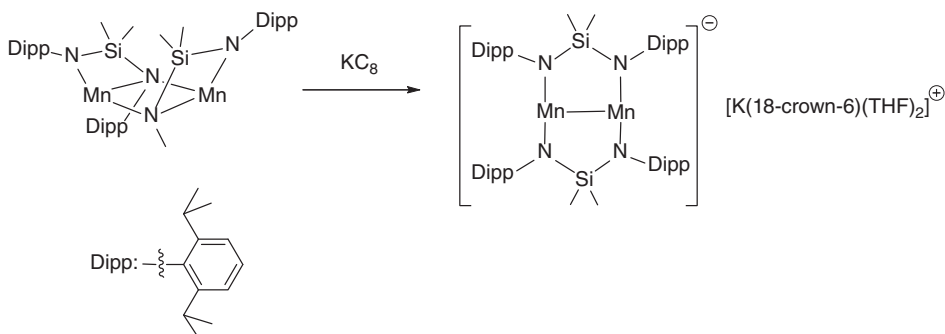


Figure 7.2 Ball and stick representation of $[\text{Li}(\text{12-crown-4})_2][\text{Mn}_2(\text{N}=\text{C}^t\text{Bu}_2)_5]$. Hydrogen atoms and cation are omitted for clarity.



Scheme 7.3 Synthesis of $[\text{Mn}_2(\mu\text{-}\kappa^2\text{-N,N'}\text{-Me}_2\text{Si}(\text{NDipp})_2)][\text{K}(\text{18-crown-6})(\text{THF})_2]$.

compound with one more equivalent of KC_8 can lead to a Mn_2^{2+} compound with Mn–Mn bond, or the Mn_2^{2+} compound can be alternatively made from the reaction of dimanganese(II) compound with 2 equiv. of KC_8 (*vide infra*).

The structure of the Mn_2^{3+} compound can be found in Figure 7.3. The coordination geometries in the compound for the two Mn centers are identical as T-shape, and the whole anion has an inversion center (C_i local symmetry). Thus, $(\text{Mn}^{+1.5})_2$ is an appropriate description of the Mn_2 core rather than mixed-valent ($\text{Mn}^{2+}\text{Mn}^{1+}$). The Mn–Mn bond length is 2.6848(8) Å. The room temperature effective magnetic moment (μ_{eff}) of the compound is $6.10 \mu_B$, which is smaller than the calculated values for two discrete noninteracting univalent Mn centers (9.8 and $6.9 \mu_B$ for ^7S and ^5D states, respectively).

7.1.4

Complexes with Mn_2^{2+} Core

7.1.4.1 Complexes with Carbene/Borylene Bridging Ligands

Mid- and late transition-metal Fischer carbene complexes, since first reported in the mid-twentieth century [10], have remained in the center-stage of coordination/organometallic chemistry for

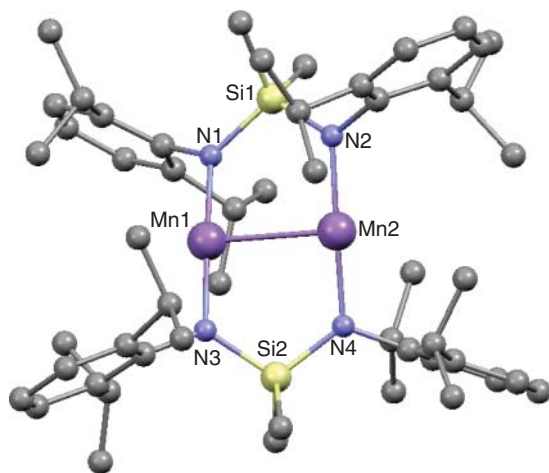


Figure 7.3 Ball and stick representation of $\{[\text{Mn}_2(\mu-\kappa^2\text{-}N,N'\text{-Me}_2\text{Si}(\text{NDipp})_2)_2][\text{K}(\text{18-crown-6})(\text{THF})_2]\}$. Hydrogen atoms, cation, and solvent molecule in lattice are omitted for clarity.

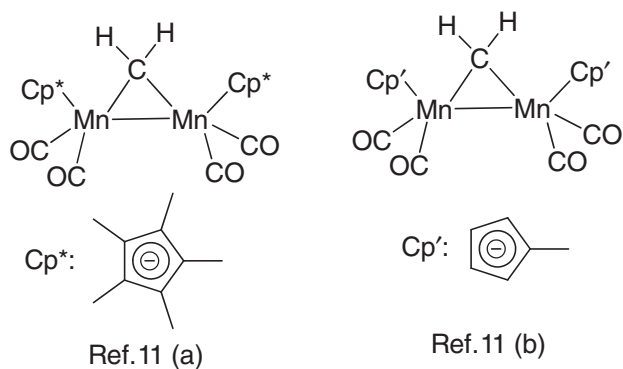


Figure 7.4 Carbene bridging dimanganese(I) complexes [11].

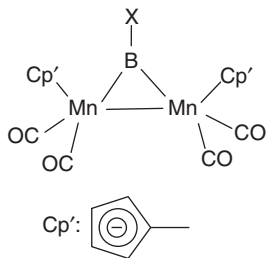
decades. A handful of carbene-bridged dimanganese(I) complexes with Mn–Mn bonds were synthesized and characterized in the early 1980s, and exemplars are listed in Figure 7.4. [11] Both of the complexes in Figure 7.4 were structurally characterized by X-ray crystallography, and the Mn–Mn bond lengths are 2.799 Å (for the Cp^* complex) and 2.779 Å (for the Cp' complex), respectively.

Borylene ($:\text{B}-\text{R}$) is isoelectronic to well-known CO and N_2 and thus can act in a similar role in coordination/organometallic chemistry as CO does [12]. But the development of metal borylene complex starts much later than metal carbonyl complexes.

In 1997, a series of borylene-bridged dimanganese(I) compounds were synthesized and characterized (Figure 7.5 Borylene bridging dimanganese(I) complexes.) [13]. Among them, the $-\text{OEt}$ [13] and $-\text{Mes}$ [14] substituted complexes were structurally characterized by X-ray crystallography. Reactivity studies of these complexes reveal that both Mn–Mn and B–X sites can be reactive to afford versatile products from Mn–Mn bond cleavage and B–B bond formation [15]. The Mn–Mn bond in these complexes is rather long, within the range of 2.79–2.85 Å.

7.1.4.2 Complexes with Unsupported Mn–Mn Bonds

In the last decade, sterically demanding β -diketiminates (BDI), diamide, or amidinates were used as capping ligands to stabilize unsupported Mn–Mn bonds in Mn_2^{2+} species (Figure 7.6) [9, 16, 17].



X = Cl, NH^tBu, NHPPh, OEt, OH, Mes

Figure 7.5 Borylene bridging dimanganese(I) complexes.

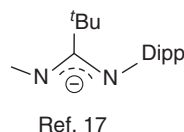
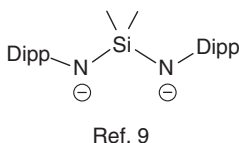
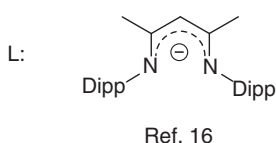
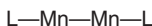
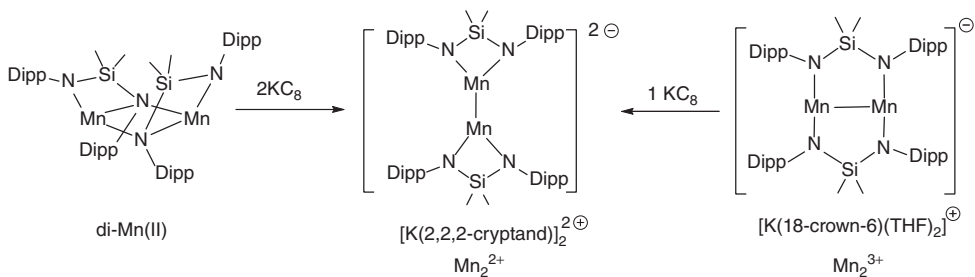


Figure 7.6 Capping ligands used to stabilize unsupported Mn–Mn bonds in Mn_2^{2+} species [9, 16, 17].

As mentioned earlier in Scheme 7.3, applying KC_8 as a reductant to dimanganese(II) compounds can afford Mn_2^{3+} or Mn_2^{2+} products, which depends on the equivalents of KC_8 [9]. The Mn_2^{2+} species can be produced from di-Mn(II) and 2 equiv. of KC_8 , or alternatively, from Mn_2^{3+} and 1 equiv. of KC_8 (Scheme 7.4). The structure of the Mn_2^{2+} species is shown in Figure 7.7 the ball and stick representation of $[\text{Mn}(\kappa^2\text{-}N,N'\text{-Me}_2\text{Si}(\text{NDipp})_2)]_2[\text{K}(2,2,2\text{-cryptant})]_2$. Hydrogen atoms, cations, and solvent molecules in lattice are omitted for clarity. The structure of the Mn_2^{2+} species is very different from its Mn_2^{3+} counterparts: the Mn–Mn distance in the former (2.7871(8) Å) is much longer than that in the latter (2.6851(9) Å). Two four-membered Mn–N–Si–N rings are connected by the Mn–Mn bond, and are coplanar with respect to each other.



Scheme 7.4 Synthesis of $\{[\text{Mn}(\kappa^2\text{-}N,N'\text{-Me}_3\text{Si(NDipp)}_2)_2]_2[\text{K}(2,2,2\text{-cryptant})]_2\}$.

A Mn_2^{2+} complex with a β -diketiminate ligand and unsupported Mn–Mn bond, $[\text{HC}(\text{CMeN})\text{Dipp}]_2[\text{Mn}]_2$, was synthesized by reduction of a Mn(II) iodide precursor (Scheme 7.5) [16]. It is noteworthy that this compound is the first three-coordinate Mn(I) compound. The X-ray structure of the compound can be found in Figure 7.8. The Mn–Mn bond length is reported as 2.721(1) Å. A magnetism study, in combination with density functional theory (DFT) calculations, reveals some intriguing features of the Mn–Mn bond and sheds lights on the nature of the Mn(I)–Mn(I) bond. The two Mn(I) centers are both high-spin ($S_1 = S_2 = 5/2$), which is elusive for the Mn(I) oxidation

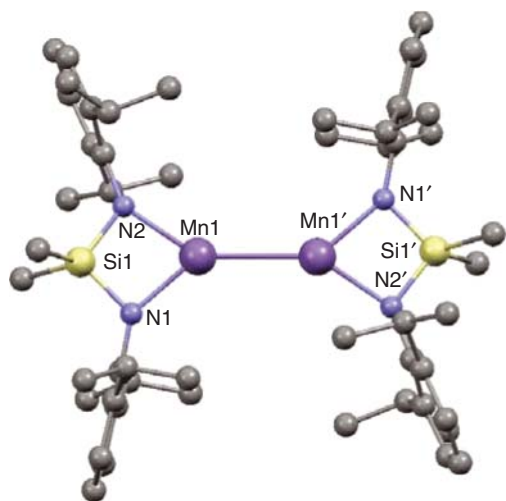
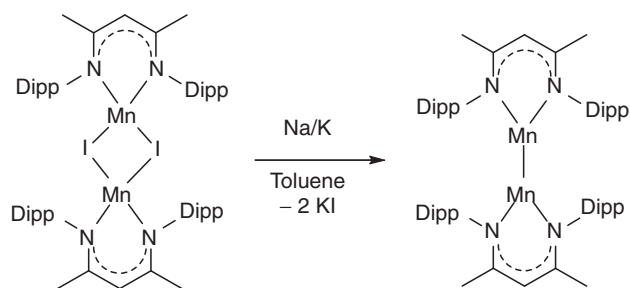


Figure 7.7 Ball and stick representation of $[\text{Mn}(\kappa^2\text{-}N,N'\text{-Me}_2\text{Si(NDipp)}_2)]_2[\text{K}(2,2,2\text{-cryptant})]_2$. Hydrogen atoms, cations, and solvent molecules in lattice are omitted for clarity.



Scheme 7.5 Synthesis of $[\{\text{HC}(\text{CMeNDipp})_2\}\text{Mn}]_2$.

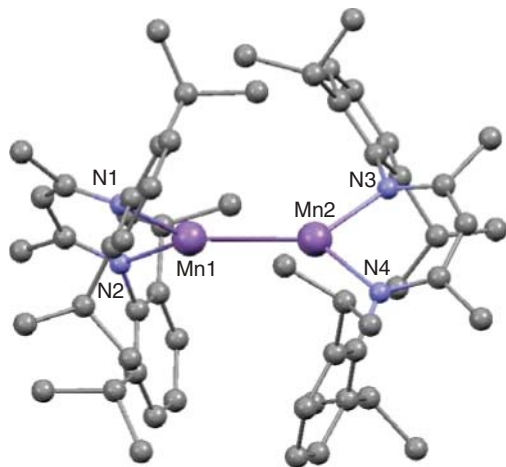
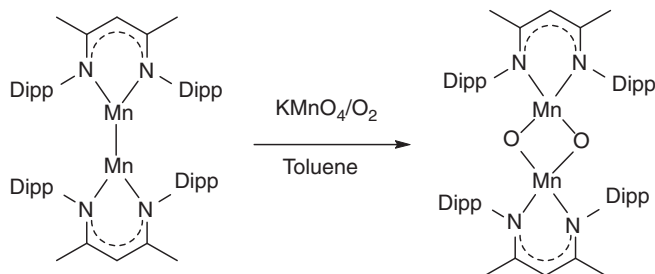


Figure 7.8 Ball and stick representation of $[\{\text{HC}(\text{CMeNDipp})_2\}\text{Mn}]_2$. Hydrogen atoms are omitted for clarity.

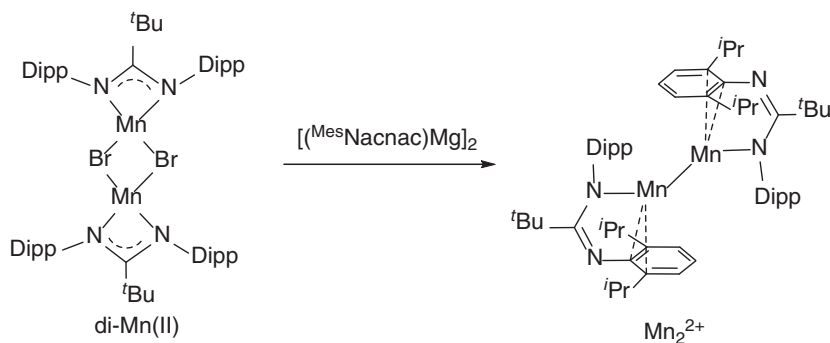
state; and the two Mn(I) centers are antiferromagnetically coupled to each other. DFT calculations suggests strong involvement of the 4s orbital in the Mn(I)–Mn(I) bonds, and the bond energy is estimated to be 44 kcal mol^{−1}.

The oxidation of the Mn₂²⁺ compound with an O-source (O₂ or KMnO₄) provides the Mn(III) bridging oxide dimer (Scheme 7.6), via Mn(I)–Mn(I) bond cleavage [16].



Scheme 7.6 Oxidation of $[\{\text{HC}(\text{CMeNDipp})_2\}\text{Mn}]_2$.

In 2012, a Mn₂²⁺ compound $[\text{Mn}(\eta^1:\eta^3\text{-}N\text{:C}_3\text{-(}^t\text{Bu)C(NDipp)}_2)]_2$ was made from the reduction of a Mn(II) bromide precursor using a Mg(I) dimer as reductant (Scheme 7.7) [17]. The molecular structure of the compound is shown in Figure 7.9 and the Mn–Mn bond length is 2.7170(9) Å. Magnetic susceptibility studies in the solid state suggest high-spin Mn(I) centers, like that in the β -diketiminato Mn₂²⁺ compound in Scheme 7.5. And DFT calculations also suggest antiferromagnetic coupling between two $S = 5/2$ Mn(I) centers.



Scheme 7.7 Synthesis of $[\text{Mn}(\eta^1:\eta^3\text{-}N\text{:C}_3\text{-(}^t\text{Bu)C(NDipp)}_2)]_2$.

7.1.4.3 Complexes with Chalcogenide and Related Bridging Ligands

$[\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2)]$, which is the simplest disulfide of iron carbonyl, was first reported in 1950s [18] and its reactivity was extensively studied [19]. The corresponding manganese compound $[\text{Mn}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-S}_2)]$ was made much later in 2001 from reaction between $[\text{Mn}_2(\text{CO})_9(\text{NCMe})]$ and thiirane (Scheme 7.8) by Adams and coworkers [20]. The molecular structure of this compound can be found in Figure 7.10 the ball and stick representation of $[\text{Mn}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-S}_2)]$. The Mn–Mn bond length is 2.6745(5) Å, while the S–S bond length in the disulfide (S_2^{2-}) ligand is 2.0474(11) Å, which is comparable with that in $[\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2)]$ (2.021(3) Å) [21]. In a theoretical investigation, the M–M bonds in both $[\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2)]$ and $[\text{Mn}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-S}_2)]$ were investigated using quantum theory of atoms in molecules (QTAIMs) [22], and the results suggest a strong Fe–Fe interaction in the former compound, while the Mn–Mn interaction in the later compound is minor.

In a subsequent reactivity study, Adams and coworkers demonstrated that the terminal coordinated CO ligand can be replaced by a tertiary phosphine and arsine, and an S-atom transfer to phosphine

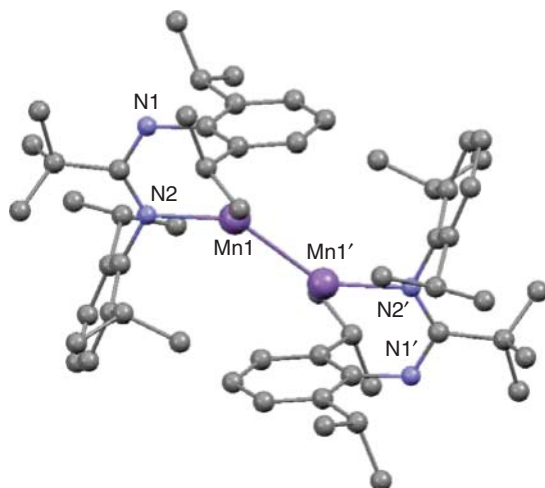
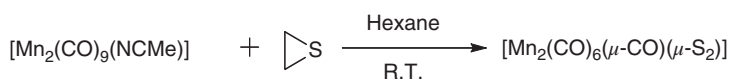


Figure 7.9 Ball and stick representation of $[\text{Mn}(\kappa:\eta^3\text{-N:C}_3\text{-(}^t\text{Bu)C(NDipp)}_2)]_2$. Hydrogen atoms and minor component of disorder are omitted for clarity.



Scheme 7.8 Synthesis of $[\text{Mn}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-S}_2)]$.

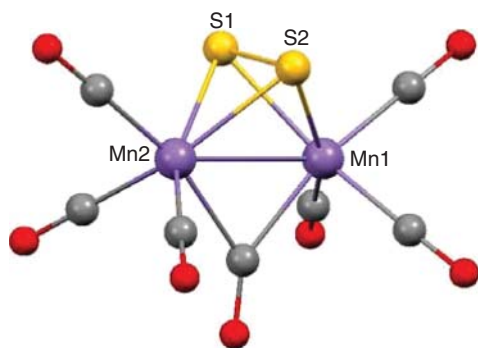
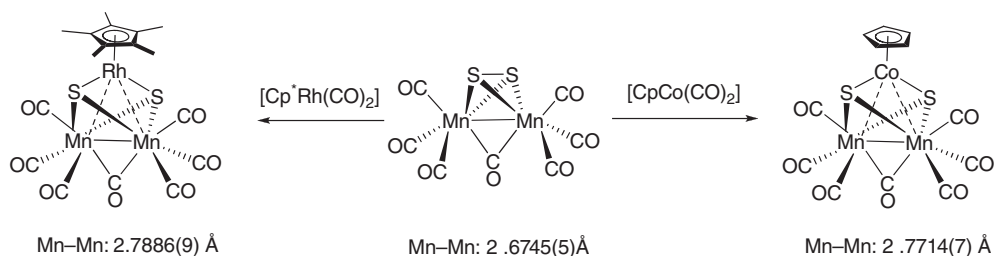


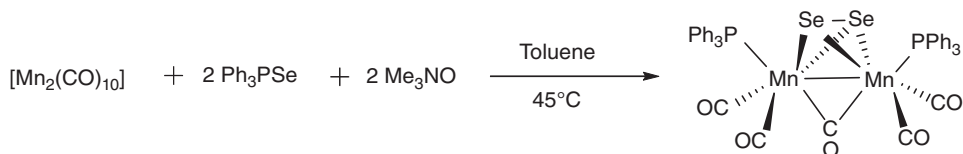
Figure 7.10 Ball and stick representation of $[\text{Mn}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-S}_2)]$.

to form $\text{R}_3\text{P}=\text{S}$ was observed [23]. If the Mn_2^{2+} compound $[\text{Mn}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-S}_2)]$ is treated with $[\text{CpCo}(\text{CO})_2]$ or $[\text{Cp}^*\text{Rh}(\text{CO})_2]$, insertions of the metal–cyclopentadienyl group into the S–S bond were observed to produce heterotrimetallic compounds with the retention of the Mn–Mn bond, but longer than their precursor (Scheme 7.9) [24].

The corresponding Mn_2^{2+} diselenide compound $[\text{Mn}_2(\text{CO})_4(\mu\text{-CO})(\mu\text{-Se}_2)(\text{PPh}_3)_2]$ was reported in 2004 by multicomponent reaction between $[\text{Mn}_2(\text{CO})_{10}]$, Ph_3PSe , and Me_3NO (Scheme 7.10) and its structure is shown in Figure 7.11 [25]. The compound has a tetrahedral Mn_2Se_2 core, with the Mn–Mn bond length of 2.702(2) Å, which is slightly longer than the aforementioned disulfide counterparts.



Scheme 7.9 Synthesis of heterotrimetallic complexes with Mn–Mn bonds.



Scheme 7.10 Synthesis of $[\text{Mn}_2(\text{CO})_4(\mu\text{-CO})(\mu\text{-Se}_2)(\text{PPh}_3)_2]$.

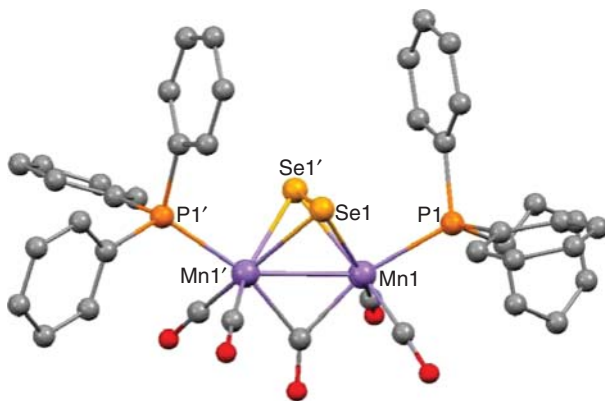


Figure 7.11 Ball and stick representation of $[\text{Mn}_2(\text{CO})_4(\mu\text{-CO})(\mu\text{-Se}_2)(\text{PPh}_3)_2]$. Hydrogen atoms are omitted for clarity.

Beside disulfide and diselenide, thiolate and selenolate can also act as bridges in Mn_2^{2+} compounds with Mn–Mn bonds (Figure 7.12) [26]. The Mn–Mn bond lengths in these compounds are within the range of 2.64–2.69 Å.

7.1.5

Complexes with Mn_2^0 Core

After the synthesis and characterization of $[\text{Mn}_2(\text{CO})_{10}]$ where the Mn–Mn bond length is 2.9042(8) Å [1, 2], several reports of unsupported Mn–Mn bonded species derived directly from $[\text{Mn}_2(\text{CO})_{10}]$, by replacing/functionalizing of one or more of the CO ligands, has been reported since 2000 (Figure 7.13) [27]. Generally speaking, the Mn(0)–Mn(0) bond is longer than the above-mentioned higher oxidation state Mn–Mn bonds.

Unusual polycyclic aromatic hydrocarbons (PAH)s supporting Mn(0)–Mn(0) bonded species were reported in 2005. These compounds were made from the chemical reduction of a Mn(I) PAH precursor with 1 equiv. of cobaltocene (Scheme 7.11) [33]. The molecular structure of these compounds is

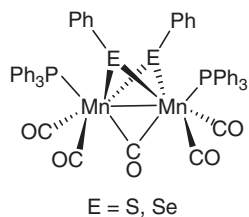


Figure 7.12 Thiolate and selenolate bridges in Mn_2^{2+} compounds.

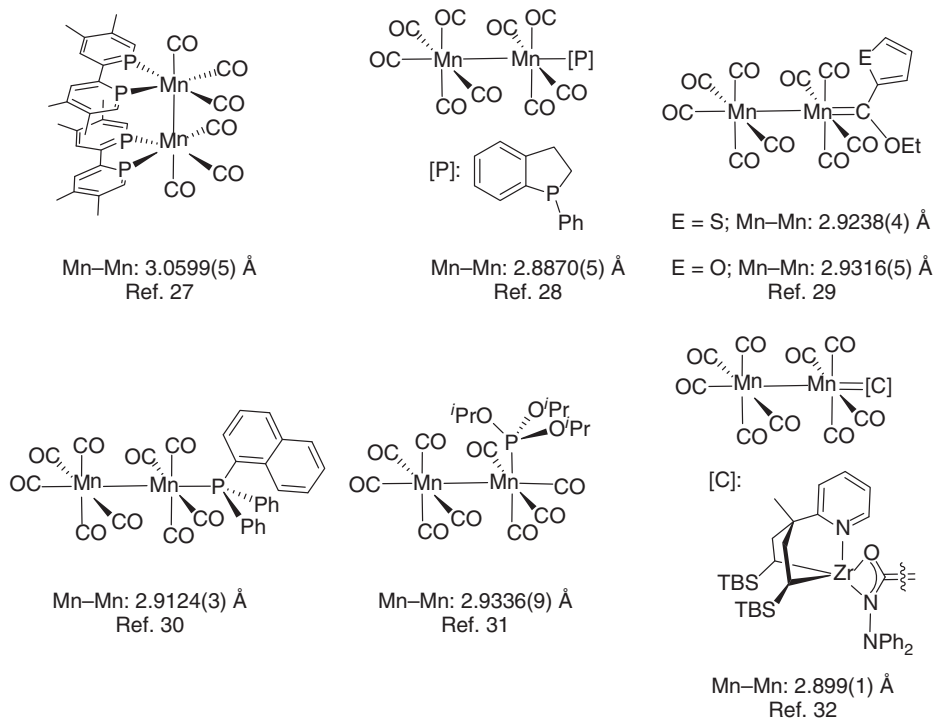
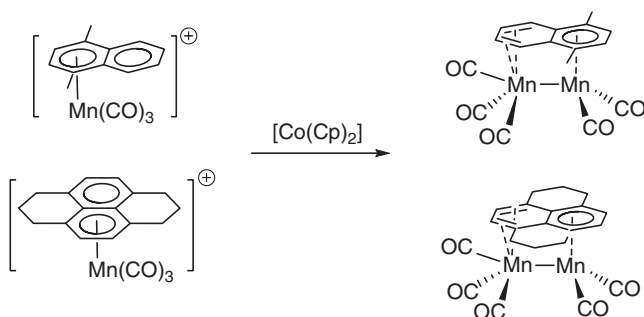


Figure 7.13 Unsupported Mn–Mn bonded species derived directly from $[Mn_2(CO)_{10}]$ [27–32].



Scheme 7.11 Synthesis of Mn–Mn complexes supported by polycyclic aromatic hydrocarbons.

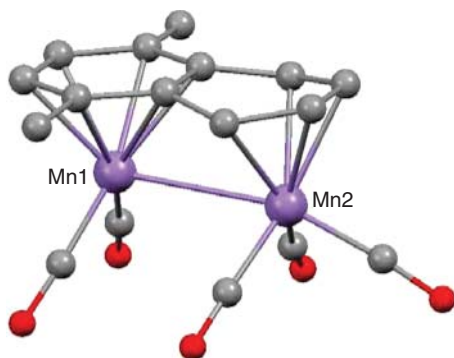


Figure 7.14 Ball and stick representation of $[\text{Mn}_2(\text{C}_{12}\text{H}_6\text{Me}_2)(\text{CO})_5]$. Hydrogen atoms are omitted for clarity.

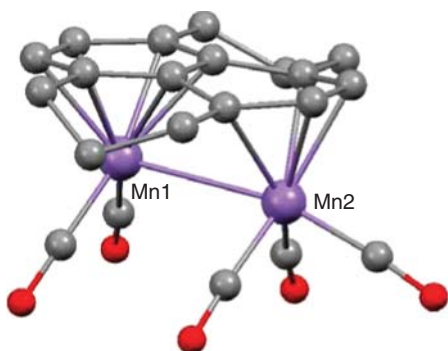


Figure 7.15 Ball and stick representation of $[\text{Mn}_2(\text{C}_{10}\text{H}_4(\text{CH}_2\text{CH}_2\text{CH}_2)_2)(\text{CO})_5]$. Hydrogen atoms are omitted for clarity.

presented in Figures 7.14 and 7.15, respectively. The Mn–Mn bond length in the two compounds is 2.9239(8) and 2.933(3) Å, respectively; this is in accordance with the above-mentioned Mn(0)–Mn(0) bond lengths. In both of the two compounds, one of the two Mn centers coordinates the arene in an η^6 -manner, while the other one is in an η^4 -manner. Upon treatment of Fc^+ ($[\text{Cp}_2\text{Fe}]^+$), the Mn–Mn bond is oxidatively cleaved and zwitterionic *syn*-facial bimetallic compounds are obtained as products.

7.2

Technetium

7.2.1

Introduction

In 1937 Perrier and Segré bombarded a molybdenum target with deuterons to produce technetium as the first man-made element [34]. This element has 31 known isotopes with mass numbers from 86 to 117, and all are radioactive. The most readily available isotope is ^{99}Tc ($t_{1/2} = 2.1 \times 10^5$ years), which can be isolated from spent nuclear fuel where it constitutes approximately 6% of the fission product yield of ^{235}U . In the recovery process, the pertechnetate anion, $[\text{TcO}_4]^-$, is extracted with pyridine from aqueous solution and ultimately isolated as $[\text{NH}_4][\text{TcO}_4]$ with a purity of better than 99.9% [35]. The ammonium salt is readily available at a reasonable cost from Oak Ridge National Laboratory [36].

All other starting materials trace their origins to this commercial source of the element. Ammonium pertechnetate from the supplier is black in color rather than the expected pure white. This is due to self-reduction to TcO_2 over long periods of time. Fortunately, the TcO_2 coating represents only a small fraction of the total mass and is easily converted back to pertechnetate by the recrystallization of the salt from a warm basic aqueous peroxide solution.

The ^{99}Tc isotope is a weak β -emitter ($E_{\text{max}} = 0.292 \text{ MeV}$), but the decay properties of ^{99}Tc allow handling of the isotope in quantities of up to about 1 g during normal chemical synthesis. Special shielding precautions are not necessary since with the mass limitation the low energy β radiation is absorbed by laboratory glassware. It is important to note that ^{99}Tc is a potential health hazard and the wearing of protective gloves and safety glasses is essential when working with ^{99}Tc . Nevertheless, following locally approved handling and monitoring procedures two of the authors have carried out hundreds of synthetic reactions and spectroscopic characterizations in laboratories designed for low-level radioactivity using efficient fume hoods and Schlenk and glove box techniques.

Technetium bears a close electronic relationship to rhenium, and therefore the occurrence of similar compounds may be anticipated. The usual caveats apply when moving from second row to third row elements; that is, one should expect differences in redox properties to play a significant role in determining appropriate synthetic routes as well as the relative stabilities of analogs. As one example of the latter, the prototype rhenium quadruply bonded dimer, $[\text{Re}_2\text{Cl}_8]^{2-}$, is stable in solution for extended periods of time, whereas $[\text{Tc}_2\text{Cl}_8]^{2-}$ is readily oxidized to $[\text{TcCl}_6]^{2-}$. Sadly, the radioactive nature of technetium has served to limit the development of its chemistry relative to its heavier congener. Only recently have the binary halides of the element been reasonably well characterized [37]. The subsections in this part of the chapter are organized in a similar fashion to the rhenium subsections. While due acknowledgment is given to key historical results in the area we focus mainly on results in this area in the past decade or so. There are, as yet, no reports of molecules with Tc_2^{8+} or Tc_2^{7+} cores. We start with molecules containing the Tc_2^{6+} core.

7.2.2

Complexes with a Tc_2^{6+} Core

The synthesis of the known compounds $(\text{TBA})_2\text{Tc}_2\text{X}_8$ ($\text{TBA} = n\text{-Bu}_4\text{N}$; $\text{X} = \text{Cl}, \text{Br}$) [38] was reinvestigated and improved upon [39]. The chloride compound was prepared from $(\text{TBA})\text{TcOCl}_4$ and 2 equiv. of $(\text{TBA})\text{BH}_4$ in THF followed by treatment of the green-brown solid isolated from the reaction with HCl in dichloromethane. The exact nature of the green-brown solid is still undetermined, but it is clear from extended X-ray absorption fine structure (EXAFS) measurements that it contains the dinuclear Tc_2 unit. The bromide analog, $(\text{TBA})_2\text{Tc}_2\text{Br}_8$, was prepared by treating $(\text{TBA})_2\text{Tc}_2\text{Cl}_8$ in CH_2Cl_2 with HBr gas, and carmine-red $(\text{TBA})_2\text{Tc}_2\text{Br}_8$ was obtained in about 70% yield based on $(\text{TBA})_2\text{Tc}_2\text{Cl}_8$. The TBA salts are stable in the solid-state in air for at least a year, but decompose quickly (about 1 h) in organic solvents such as acetone and dichloromethane, even under an inert atmosphere. The decomposition process slows with decreasing temperature.

Beautiful single crystals of $(\text{TBA})_2\text{Tc}_2\text{X}_8$ were grown from acetone:ether solution and used for X-ray measurements. Both TBA salts of $\text{Tc}_2\text{X}_8^{2-}$ crystallize as acetone solvates. The structure of the emerald green $\text{Tc}_2\text{Cl}_8^{2-}$ anion in the solvate was determined by single crystal X-ray diffraction (SCXRD) and compared with its unsolvated analog [40]. The metal–metal separation in the solvate is $2.1560(3) \text{ \AA}$, which is only slightly larger than the $2.151(1) \text{ \AA}$ distance observed in the unsolvated crystal. The $\text{Tc}\text{--}\text{Tc}\text{--}\text{Cl}$ angle in the solvated system is $103.92(2)^\circ$.

The TBA salt of $\text{Tc}_2\text{Br}_8^{2-}$ crystallizes in the monoclinic space group $P2_1/n$ [41]. The asymmetric unit contains two acetone molecules, one TBA cation, and one half of a $\text{Tc}_2\text{Br}_8^{2-}$ anion that is completed by an inversion operation. The $\text{Tc}_2\text{Br}_8^{2-}$ anion (Figure 7.16) exhibits the expected D_{4h} symmetry; it consists of two TcBr_4 units (average $\text{Tc}\text{--}\text{Br} = 2.473(2) \text{ \AA}$) linked by a $\text{Tc}\text{--}\text{Tc}$ quadruple bond ($\text{Tc}\text{--}\text{Tc} = 2.1625(9) \text{ \AA}$, $\text{Tc}\text{--}\text{Tc}\text{--}\text{Br} = 104.97(5)^\circ$) and is isostructural to the $\text{Tc}_2\text{Cl}_8^{2-}$ anion. The distances found by SCXRD are in excellent agreement with those determined earlier by EXAFS, that

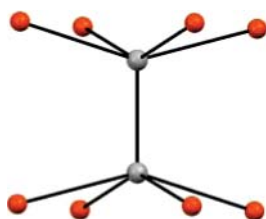


Figure 7.16 Ball and stick representation of the $\text{Tc}_2\text{Br}_8^{2-}$ anion.

Table 7.1 Average Tc–Tc, Tc–X and Tc–L bond distances (Å) found by SCXRD and EXAFS (bold font) for multiply metal–metal bonded technetium compounds.

Compound	Tc–Tc	Tc–X	Tc–L
$(\text{TBA})_2\text{Tc}_2\text{Cl}_8$	2.1560(3) 2.17(1)	2.3223[8] 2.34(1)	—
$(\text{TBA})_2\text{Tc}_2\text{Br}_8$	2.1625(9) 2.16(1)	2.473[2] 2.48(1)	—
$\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$	2.1758(3 Å) 2.18(2)	2.5078[5] 2.43(2)	2.021[1] 2.03(1)
$\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Br}_2$	2.19(1)	2.63(1)	2.03(1)
$\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$	2.1500(6) 2.15(2)	2.3121[9] 2.31(2)	2.022[2] 2.02(2)
$[\text{Cs}_{(2+x)}][\text{H}_3\text{O}_{(1-x)}]\text{Tc}_2\text{Br}_8$	2.1265(9) 2.12(2)	2.515[2] 2.51(3)	—
$\text{Cs}_3\text{Tc}_2\text{Cl}_8$	2.12(2)	2.38(2)	—
$\text{Tc}_2\text{Cl}_4(\text{PMe}_3)_4$	2.1318(2)	2.3858[4]	2.4356[4]
$\text{Tc}_2\text{Br}_4(\text{PMe}_3)_4$	2.1316(5)	2.5207[5]	2.4434[8]

is, $\text{Tc–Tc} = 2.16(1)$ Å and $\text{Tc–Br} = 2.48(1)$ Å [42]. The metal–metal separation and average Tc–Tc–X angle in $\text{Tc}_2\text{Br}_8^{2-}$ are slightly larger than the ones found in the $\text{Tc}_2\text{Cl}_8^{2-}$ anion (*vide supra*). Steric effects induced by the larger bromide ligands are likely the cause of these modest increases. The Tc–Tc distances in $\text{Tc}_2\text{X}_8^{2-}$ are longer than the ones in the $\text{Tc}_2\text{X}_8^{3-}$ anions *and* in the $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ (X = Cl, Br) complexes (*vide infra*). This phenomenon has been investigated by quantum chemical calculations and is discussed later. The average Tc–Tc, Tc–X and Tc–L separations found by SCXRD and EXAFS spectroscopy for all the complexes surveyed are summarized in Table 7.1. We include the EXAFS results to emphasize the overall reliability of the technique in cases where there is reasonable “guess” of the true structure.

Quantum chemical calculations on the $[\text{Tc}_2\text{X}_8]^{2-}$ ions were performed using DFT and multiconfigurational Complete Active Space SCF (CASSCF) methods, augmented by second-order perturbation theory (CASPT2) [43]. Geometry optimizations were performed using the valence triple zeta polarization (VTZP) basis set. For technetium, the VTZP basis set corresponds to the following contraction: 7s6p4d2f1g. The calculated Tc–Tc and Tc–X bond distances are in excellent agreement with the experimental values (Table 7.2) [44]. Noteworthy is the fact that the calculations confirm the experimental observation that the Tc–Tc bond distances are slightly shorter in $\text{Tc}_2\text{Cl}_8^{2-}$ than in $\text{Tc}_2\text{Br}_8^{2-}$. The Tc–Tc separation in $\text{Tc}_2\text{X}_8^{2-}$ is also larger than the ones calculated at the same level of theory in the $\text{Tc}_2\text{X}_8^{3-}$ systems.

The complete active space for $[\text{Tc}_2\text{Br}_8]^{2-}$ (Figure 7.17) contains 12 electrons in 12 active orbitals. The Tc–Tc bonding was quantified in terms of effective bond order (EBO), defined as $(\eta_b - \eta_a)/(\eta_b + \eta_a)$, where η_b is the occupation number for the bonding natural orbital, and η_a is the occupation number for the antibonding natural orbital. Analysis of the occupation numbers indicates that the σ bond is the strongest bond and has exactly the same strength in $\text{Tc}_2\text{Cl}_8^{2-}$ and

Table 7.2 Effective bond order, total bond order, Tc–Tc and Tc–X bond distances (Å) for the $\text{Tc}_2\text{X}_8^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) calculated at the CASPT2/VTZP level of theory.

Complexes	Tc–Tc	Tc–X	EBO σ	EBO π	EBO δ	Total B.O.
$\text{Tc}_2\text{Cl}_8^{2-}$	2.170 <i>2.1560(3)</i>	2.314 <i>2.3223[8]</i>	0.88	1.68	0.47	3.03
$\text{Tc}_2\text{Br}_8^{2-}$	2.173 <i>2.1625(9)</i>	2.448 <i>2.473[2]</i>	0.88	1.69	0.50	3.07

Experimental XRD results (italics) are also listed.

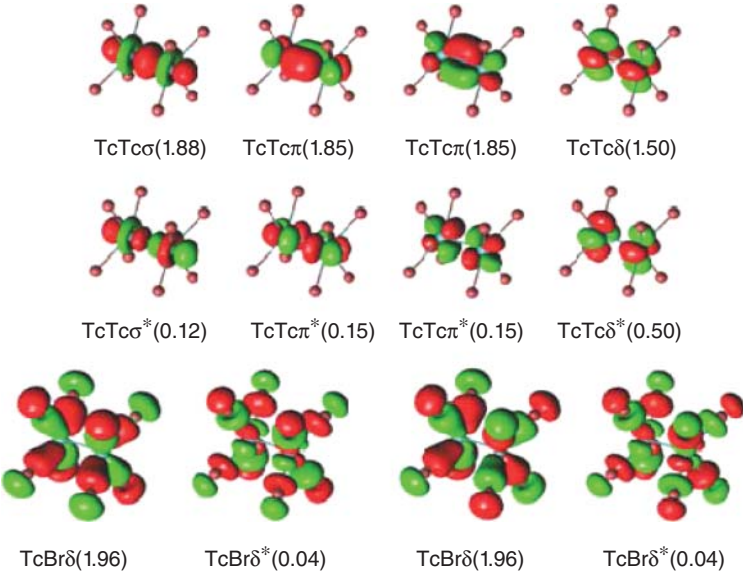


Figure 7.17 Active orbitals for $\text{Tc}_2\text{Br}_8^{2-}$ with their occupation numbers in the ground state.

$\text{Tc}_2\text{Br}_8^{2-}$. The corresponding value for the two π bonds is 1.68 for $\text{X} = \text{Cl}$ and 1.69 for $\text{X} = \text{Br}$. The δ/δ^* pair gives an EBO of only 0.50 for $\text{X} = \text{Br}$ and 0.47 for $\text{X} = \text{Cl}$. Adding up, these numbers result in a total bond order of 3.02 for $\text{X} = \text{Cl}$ and 3.07 for $\text{X} = \text{Br}$. Similar results were obtained on previous studies of analogous dirhenium(III) compounds [45].

The UV–visible spectra of the $(\text{TBA})_2\text{Tc}_2\text{X}_8$ salts dissolved in CH_2Cl_2 are shown in Figure 7.18. The spectrum of $\text{Tc}_2\text{Cl}_8^{2-}$ is identical to the one reported previously in the literature and exhibits three bands [40]. The band at $14\,713\text{ cm}^{-1}$ has been assigned as the $\delta \rightarrow \delta^*$ transition. The spectrum of $\text{Tc}_2\text{Br}_8^{2-}$ exhibits four intense bands (Table 7.3). The lowest energy transition at $13\,717\text{ cm}^{-1}$ is logically assigned to the $\delta \rightarrow \delta^*$ transition. The spectra of $\text{Tc}_2\text{Br}_8^{2-}$ and $\text{Tc}_2\text{Cl}_8^{2-}$ exhibit similar features to those of $\text{Re}_2\text{Br}_8^{2-}$ and $\text{Re}_2\text{Cl}_8^{2-}$, respectively [46]. The bands at the lowest energy ($\delta \rightarrow \delta^*$ transition) are nearly superimposable, while the other bands are shifted to higher energy for the Re compounds.

Multiconfigurational quantum chemical calculations on the $\delta \rightarrow \delta^*$ transitions were also performed for all four $\text{M}_2\text{X}_8^{2-}$ ($\text{M} = \text{Tc}, \text{Re}; \text{X} = \text{Cl}, \text{Br}$) anions [41]. The calculated excitation energies are higher than the measured values by $\sim 1000\text{ cm}^{-1}$. The calculations do not take into account solvation effects, but do capture the red shift of the $\delta \rightarrow \delta^*$ transition energy going from the chloride to the bromide and the near degeneracy of the $\delta \rightarrow \delta^*$ energies for each pair of $\text{M}_2\text{Cl}_8^{2-}$ and $\text{M}_2\text{Br}_8^{2-}$ ($\text{M} = \text{Tc}, \text{Re}$) anions (Table 7.4). We believe that these are the best model calculations to date on these systems.

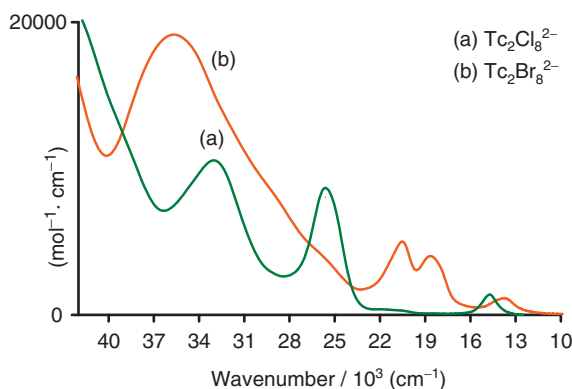


Figure 7.18 UV-visible spectra of (a) $\text{Tc}_2\text{Cl}_8^{2-}$ and (b) $\text{Tc}_2\text{Br}_8^{2-}$ in CH_2Cl_2 .

Table 7.3 Experimental band maxima (cm^{-1}) and proposed assignments for $\text{Tc}_2\text{Cl}_8^{2-}$ (top) and $\text{Tc}_2\text{Br}_8^{2-}$.

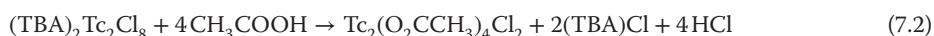
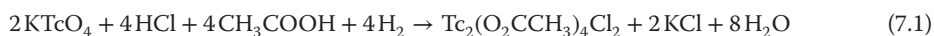
Experimental	14 713	25 623	—	33 016
	13 717	18 647	20 518	35 714
Assignment	$\delta \rightarrow \delta^*$	$\pi(\text{X}) \rightarrow \delta^*$	—	$\pi(\text{X}) \rightarrow \pi^*$

Table 7.4 Experimental and calculated band maxima (cm^{-1}) for the $\delta \rightarrow \delta^*$ transitions in $\text{M}_2\text{X}_8^{2-}$ ($\text{M} = \text{Tc}$, Re ; $\text{X} = \text{Cl}$, Br).

Complexes	$\text{Tc}_2\text{Cl}_8^{2-}$	$\text{Re}_2\text{Cl}_8^{2-}$	$\text{Tc}_2\text{Br}_8^{2-}$	$\text{Re}_2\text{Br}_8^{2-}$
Experimental	14 713	14 589	13 717	13 957
Calculated	15 836	15 628	14 714	14 841

The emission spectra of the $(\text{TBA})_2\text{Tc}_2\text{X}_8$ ($\text{X} = \text{Cl}$, Br) solids have been investigated at 77 K. The emission spectra (with excitation at 645 nm) exhibit a band centered around 750 nm for both compounds (Figure 7.19) [47]. The emission decay times are respectively 46 and 30 ns for the chloride and bromide salts, respectively. The small Stokes shifts in the emission spectra are consistent with the emission being spin-allowed fluorescence from the low-energy singlet $\delta-\delta^*$ excited state.

The acetate derivative $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ can be synthesized by two very distinct methods: (i) treatment of a solution of KTcO_4 in a 2 : 1 mixture of acetic acid and concentrated aqueous hydrochloric acid under excess hydrogen for 14 h at 210 °C in a stainless steel autoclave (Eq. (7.1)) [48], or (ii) reaction of $(\text{TBA})_2\text{Tc}_2\text{Cl}_8$ in refluxing acetic acid/acetic anhydride (v : v, 4 : 1) for 5 min (Eq. (7.2)) [49]. The former method gives a higher yield (~70%) and a crystalline red product. Method 2 provides an amorphous red powder in about 20–30% yield. We note in passing that the analogous rhenium reaction provides orange red amorphous $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ in essentially quantitative yield. $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$, like $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$, is insoluble in all common solvents.



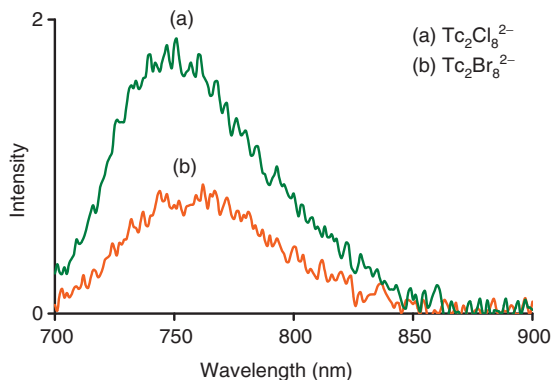


Figure 7.19 Emission spectra at 77 K of crystalline $(\text{TBA})_2\text{Tc}_2\text{Cl}_8$ (a) and $(\text{TBA})_2\text{Tc}_2\text{Br}_8$ (b) after excitation at 645 nm.

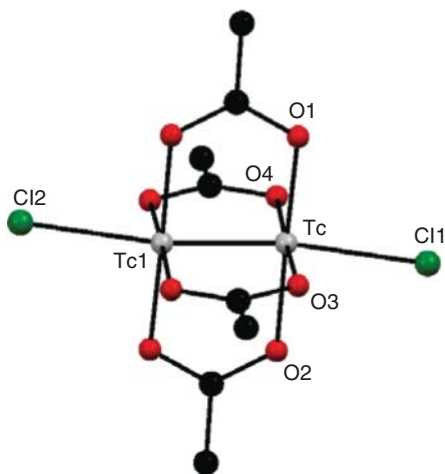


Figure 7.20 Ball and stick representation of $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$. Carbon atoms are in black, oxygen in red, chlorine in green, and technetium in gray. Hydrogen atoms are omitted for clarity. Selected

distances in Å: $\text{Tc}-\text{Tc1} = 2.1758(3)$, $\text{Tc}-\text{O1} = 2.0164(12)$, $\text{Tc}-\text{O2} = 2.0390(12)$, $\text{Tc}-\text{O3} = 2.0034(12)$, $\text{Tc}-\text{O4} = 2.0259(12)$, and $\text{Tc}-\text{Cl1} = 2.5078(4)$.

The orange $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Br}_2$ complex can be prepared, also in low yield, by refluxing $(\text{TBA})_2\text{Tc}_2\text{Br}_8$ in an acetic acid/acetic anhydride mixture [49].

The complex $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ crystallizes in the monoclinic space group $P2_1/n$ and is isostructural to $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ [50]. The compound (Figure 7.20) exhibits the familiar paddlewheel motif and consists of four bridging acetate ligands and two axial chlorides. The paddlewheel unit is quite regular. The capping chlorides are bent 8° from linear ($\text{Tc}-\text{Tc1}-\text{Cl2} = 171.903(13)^\circ$). A smaller distortion ($\sim 3.5^\circ$) is observed in the dirhenium analog, and no distortion is observed for the technetium pivalate complex. Crystal packing is likely the origin of these small distortions. The $\text{Tc}-\text{Tc}$ separation of $2.1758(3)$ Å in $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ is larger than the one in $\text{Tc}_2\text{Cl}_8^{2-}$. This result is probably due to the presence of strong axial ligands that weaken the $\text{Tc}-\text{Tc}$ σ -bond and increase the $\text{Tc}-\text{Tc}$ separation. The $\text{Re}-\text{Re}$ distance in $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ is $2.2240(5)$ Å [50]. A difference in the range of ~ 0.04 – 0.06 Å is typical for $\text{Tc}-\text{Re}$ pairs of metal–metal bonded compounds with identical ligands. The $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{X}_2$ compounds ($\text{X} = \text{Cl}, \text{Br}$) were also characterized by EXAFS [49]. The $\text{Tc}-\text{Tc}$ separation determined by EXAFS for $\text{X} = \text{Cl}$, that is, $2.18(2)$ Å, is essentially identical to the

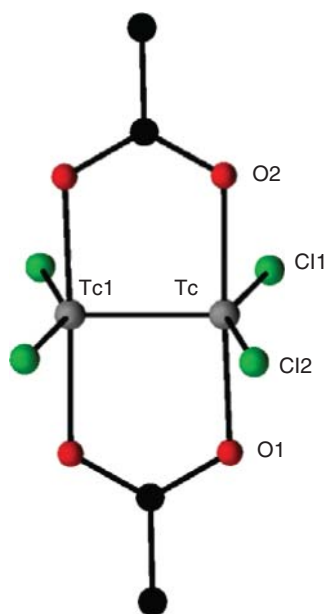


Figure 7.21 Ball and stick representation of $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$. Carbon atoms are in black, oxygen in red, chlorine in green, and technetium in gray. Hydrogen atoms are omitted for clarity. Selected distances in Å. $\text{Tc}-\text{Tc1} = 2.1500(6)$, $\text{Tc}-\text{O1} = 2.022(2)$, $\text{Tc}-\text{O2} = 2.021(1)$, $\text{Tc}-\text{Cl1} = 2.3339(7)$, and $\text{Tc}-\text{Cl2} = 2.2903(8)$.

one determined by SCXRD. For the related $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Br}_2$, the X-ray structure has not yet been reported, but EXAFS results indicate the following distances: $\text{Tc}-\text{Tc} = 2.19(1)$ Å, $\text{Tc}-\text{Br} = 2.63(1)$ Å and $\text{Tc}-\text{O} = 2.03(1)$ Å.

A green bis-acetate compound $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ can be prepared in essentially quantitative yield from the reaction of $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with gaseous hydrochloric acid at 150°C (Eq. (7.3)) [51]. In work described below, technetium trichloride ($\alpha\text{-TcCl}_3$) was obtained from the reaction of



$\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with HCl gas at a higher temperature, that is, 300°C . The mechanism of the formation of $\alpha\text{-TcCl}_3$ mimics the one described for rhenium [52]. The $\text{M}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ ($\text{M} = \text{Tc}, \text{Re}$) complexes are formed as intermediates in the early stages of both reactions. During the reaction of $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ and HCl gas, there was no evidence for a triacetate species. The emerald-green $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ complex is highly soluble in acetone and dichloromethane and stable as a solid in air for more than a month. $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ crystallizes in the triclinic space group $P\bar{1}$ and is isostructural to $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ [52]. The compound (Figure 7.21) exhibits an eclipsed conformation and consists of two *trans*-acetate ligands bridging the Tc_2^{6+} unit and four terminal chlorides. The four chlorine atoms are located in a plane perpendicular to the plane formed by the O atoms of the acetate ligands. The Cl atoms are not chemically equivalent, and two sets of $\text{Tc}-\text{Cl}$ distances are observed: $\text{Tc}-\text{Cl1} = 2.3339(7)$ Å and $\text{Tc}-\text{Cl2} = 2.2903(8)$ Å. The $\text{Tc}-\text{Tc}$ distance of $2.1500(6)$ Å in $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ is essentially identical to the one found in $(\text{TBA})_2\text{Tc}_2\text{Cl}_8$ and consistent with the presence of a quadruple $\text{Tc}-\text{Tc}$ bond. We note that the $\text{Re}-\text{Re}$ distance in $\text{Re}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ is $2.2084(3)$ Å [52].

A geometry optimization of $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ was performed using the Tao, Perdew, Staroverov, and Scuseria hybrid functional (TPSSH) at the triple-zeta valence plus polarization (TZVPP) basis set [53]. The results show that the calculated $\text{Tc}-\text{Tc}$, $\text{Tc}-\text{Cl}$, and $\text{Tc}-\text{O}$ bond distances are in good agreement with the experimental values (Table 7.5). The largest deviation is found for the $\text{Tc}-\text{Tc}$ distance,

Table 7.5 Effective bond order, total bond order, and Tc–Tc, Tc–Cl, and Tc–O bond distances (Å) for $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ and $\text{Tc}_2\text{Cl}_8^{2-}$ calculated at the TPSSh/TZVPP level of theory.

Complex	Tc–Tc	Tc–Cl	Tc–O	EBO σ	EBO π	EBO δ	Total B.O.
$\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$	2.080 <i>2.1500(6)</i>	2.278 <i>2.312(1)</i>	2.021 <i>2.022(2)</i>	0.90	1.71	0.59	3.20
$\text{Tc}_2\text{Cl}_8^{2-}$	2.124 <i>2.1560(3)</i>	2.392 <i>2.3223(8)</i>	—	0.88	1.68	0.47	3.03

Experimental XRD results (italics) are also shown.

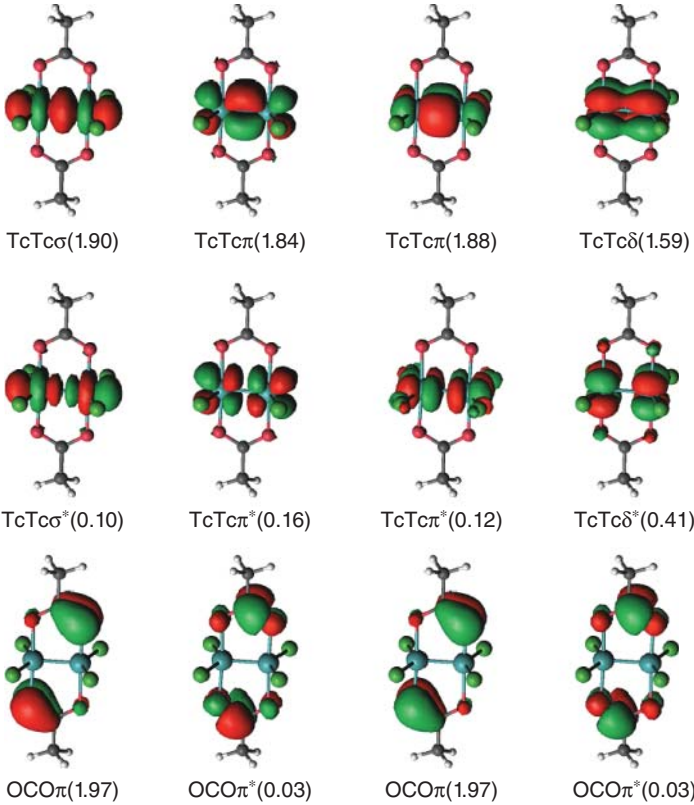


Figure 7.22 Active orbitals for $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ with their occupation numbers in the ground state.

which is still within 3%. The calculations performed on an isolated $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ complex result in 4 equiv. Tc–Cl distances. Packing effects may be responsible for the nonequivalent sets of Tc–Cl distances observed in the crystal structure. Comparison with the structure of $\text{Tc}_2\text{Cl}_8^{2-}$ optimized at the same level of theory (TPSSh/TZVPP) confirms the experimental observation that the Tc–Tc bond distances are indeed slightly shorter in $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ than in $\text{Tc}_2\text{Cl}_8^{2-}$.

The electronic structure of $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ was investigated at the CASSF/CASPT2 level [51]. The 12 molecular orbitals forming the active space and their occupation numbers are presented in Figure 7.22. The occupancy of δ and δ^* orbitals are respectively 1.59 and 0.41, which gives an EBO of 0.59 for the σ bond. The EBO value for the δ bond is 0.90 and the corresponding value for the

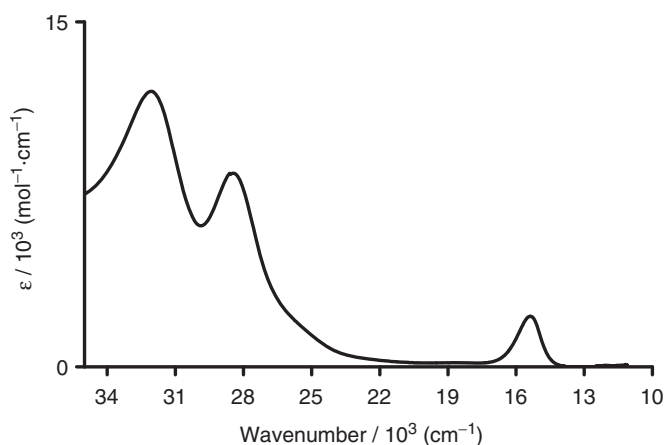


Figure 7.23 UV-visible spectrum of $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ in CH_2Cl_2 .

Table 7.6 Experimental band maxima (cm^{-1}), assignments, calculated excitation energies (cm^{-1}), and their intensities for $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ [51].

Experimental	Assignment	Excitation energies	Intensity
15 455	$\delta \rightarrow \delta^*$	17 733	0.41×10^{-2}
28 450	$\delta \rightarrow \pi^*$	27 553	0.36×10^{-3}
32 100	$\pi \rightarrow \delta^*$	31 721	0.31×10^{-3}

π bond is 1.71. The σ , π , and δ bonds are slightly stronger in $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ than in $\text{Tc}_2\text{Cl}_8^{2-}$ (Table 7.5) which is consistent with the decrease of the Tc–Tc distance observed. The total bond order in $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ is 3.20, which is the largest value reported so far for a multiply Tc–Tc bonded dimer. It is similar to the one calculated in $\text{Re}_2\text{Cl}_8^{2-}$ (i.e., 3.25) and consistent with the presence of a moderately strong quadruple bond.

The electronic absorption spectrum of $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ in CH_2Cl_2 (Figure 7.23) exhibits three bands at 15 455, 28 450, and 32 100 cm^{-1} and is similar to the one reported for $\text{Tc}_2\text{Cl}_8^{2-}$ with the lowest energy band shifted by $\sim 742 \text{ cm}^{-1}$ to higher energy in $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$. Computed excitation energies along with their intensities are reported in Table 7.6. Calculations confirm that the lowest energy band in the spectrum of $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ corresponds to the $\delta \rightarrow \delta^*$ transition [51]. The calculations reproduce the blue shift of the $\delta \rightarrow \delta^*$ transition observed experimentally for $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ relative to $\text{Tc}_2\text{Cl}_8^{2-}$. The next band is attributed to the $\delta \rightarrow \pi^*$ transition and its calculated position (27 553 cm^{-1}) matches well with the experimental value of 28 450 cm^{-1} . The transition located at 32 100 cm^{-1} is assigned to $\pi \rightarrow \delta^*$ transition and is predicted at 31 721 cm^{-1} .

7.2.3

Complexes with a Tc_2^{5+} Core

The cesium salts of $\text{Tc}_2\text{X}_8^{3-}$ were synthesized according to the method previously reported by Preetz *et al.* [38] The $\text{Tc}_2\text{Br}_8^{3-}$ anion was generated in warm concentrated HBr via disproportionation of the $\text{Tc}_2\text{Br}_8^{2-}$ anion and precipitated as a cesium salt using CsBr [44]. The $(\text{TBA})_2\text{Tc}_2\text{Br}_8$ salt is slightly soluble in cold HBr, but upon warming its solubility increases and the $\text{Tc}_2\text{Br}_8^{2-}$ anion disproportionates according to Eq. (7.4).



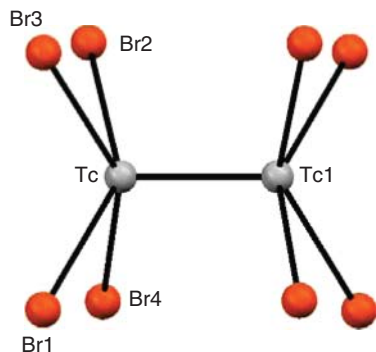


Figure 7.24 Ball and stick representation of the $\text{Tc}_2\text{Br}_8^{3-}$ anion. Technetium atoms are in gray and bromine in orange. Selected distances in Å: $\text{Tc-Tc} = 2.1265(9)$, $\text{Tc-Br1} = 2.5152(9)$, $\text{Tc-Br2} = 2.5192(9)$, $\text{Tc-Br3} = 2.5259(9)$, and $\text{Tc-Br4} = 2.5011(9)$.

The separation of TcBr_6^{2-} from $\text{Tc}_2\text{Br}_8^{3-}$ is performed by fractional crystallization using CsBr . The Cs_2TcBr_6 is considerably less soluble than $\text{Cs}_3\text{Tc}_2\text{Br}_8$, and after separation, an orange microcrystalline powder containing the $\text{Tc}_2\text{Br}_8^{3-}$ cesium salt is obtained in about 20% yield based on $(\text{TBA})_2\text{Tc}_2\text{Br}_8$.

The cesium salt of $\text{Tc}_2\text{Cl}_8^{3-}$ can be prepared using a method similar to the one used for the bromide analog. The synthesis involves the disproportionation of $(\text{TBA})_2\text{Tc}_2\text{Cl}_8$ in warm concentrated $\text{HCl}(\text{aq})$ followed by selective precipitation with CsCl . The cesium salts of $\text{Tc}_2\text{X}_8^{3-}$ are stable in air for a least a month, and they are stable in hydrohalic acids for several days, but rapidly hydrolyze in pure water to TcO_2 .

Single crystals of the bromo complex were grown in concentrated HBr . The cesium $\text{Tc}_2\text{Br}_8^{3-}$ salt crystallizes in the trigonal space group $P3_221$ [44]. The crystals contain $\text{Tc}_2\text{Br}_8^{3-}$ anions, cesium cations, hydronium ions, and water molecules. The stoichiometry $[\text{Cs}_{(2+x)}][\text{H}_3\text{O}_{(1-x)}]\text{Tc}_2\text{Br}_8 \cdot 4.6\text{H}_2\text{O}$, with $x = 0.221$ was obtained after refinement. The $\text{Tc}_2\text{Br}_8^{3-}$ anion (Figure 7.24) exhibits approximate D_{4h} symmetry. It consists of two TcBr_4 units linked by a Tc-Tc bond of $2.1265(9)$ Å and is isostructural to the $\text{Tc}_2\text{Cl}_8^{3-}$ anion. The bromine atoms are crystallographically independent and four Tc-Br distances are observed in the range of $2.5011(9)$ – $2.5259(9)$ Å. The eight bromine atoms form an approximate cube with edge lengths in the range of $3.400(1)$ – $3.514(1)$ Å. An internal rotation of 4.86° of the TcBr_4 unit along the Tc-Tc bond is noted; this type of twist was also observed for the $\text{Tc}_2\text{Cl}_8^{3-}$ anion (15.75°) in the yttrium salt [54].

The metal–metal separation and average Tc-Tc-X angle in $\text{Tc}_2\text{Br}_8^{3-}$ ($\text{Tc-Tc-Br} = 106.07(4)^\circ$) are slightly larger than the ones found in the $\text{Tc}_2\text{Cl}_8^{3-}$ anion (i.e., $\text{Tc-Tc} = 2.105(1)$ Å and $\text{Tc-Tc-Cl} = 104.34(6)^\circ$ in $\text{Y}_3\text{Tc}_2\text{Cl}_8$). Steric effects induced by the larger bromide ligands are presumably the cause of these modest increases; a similar trend was noted earlier in the $\text{Tc}_2\text{X}_8^{2-}$ system. The average Tc-Br distances in $\text{Tc}_2\text{Br}_8^{3-}$ ($2.515[2]$ Å) are longer than the ones in $\text{Tc}_2\text{Br}_8^{2-}$ ($2.473(2)$ Å) and probably due to a decrease of the effective charge on the Tc atoms. The Tc-Tc separation in $\text{Tc}_2\text{Br}_8^{3-}$ is ~ 0.04 Å shorter than in $\text{Tc}_2\text{Br}_8^{2-}$ possibly due to stronger π bonds in $\text{Tc}_2\text{Br}_8^{3-}$ (*vide infra*).

The X-ray structure of the cesium salt of $\text{Tc}_2\text{Cl}_8^{3-}$ is unknown, but the Tc-Tc and Tc-Cl distances found by EXAFS in the $\text{Tc}_2\text{Cl}_8^{3-}$ anion (i.e., $2.12(2)$ and $2.38(2)$ Å, respectively) are in good agreement with those found by SCXRD measurements for other $\text{Tc}_2\text{Cl}_8^{3-}$ salts.

Geometry optimizations of $\text{Tc}_2\text{X}_8^{3-}$ ($\text{X} = \text{Cl}, \text{Br}$) were performed at the CASPT2/VTZP level of theory [44]. The calculated Tc-Tc and Tc-X bond distances are in excellent agreement with the experimental values (Table 7.7). The calculations confirm the experimental observation that the Tc-Tc bond distances are shorter in $\text{Tc}_2\text{X}_8^{3-}$ compared to $\text{Tc}_2\text{X}_8^{2-}$ dimers. The 0.03 Å decrease of the Tc-Tc distance is in excellent agreement with the ones measured experimentally (0.039 Å for $\text{X} = \text{Cl}$ and 0.036 Å for $\text{X} = \text{Br}$). The calculations also confirm the Tc-X distances to be ~ 0.05 Å longer in $\text{Tc}_2\text{X}_8^{3-}$ than $\text{Tc}_2\text{X}_8^{2-}$.

Table 7.7 Effective bond order, total bond order, Tc–Tc, and Tc–X bond distances (Å) for the $\text{Tc}_2\text{X}_8^{n-}$ ($\text{X} = \text{Cl}, \text{Br}$; $n = 2, 3$) anions calculated at the CASPT2/VTZP level of theory.

Complexes	Tc–Tc	Tc–X	EBO σ	EBO π	EBO δ	Total B.O.
$\text{Tc}_2\text{Cl}_8^{3-}$	2.140 <i>2.117(4)</i>	2.369 <i>2.363[15]</i>	0.89	1.74	0.41	3.04
$\text{Tc}_2\text{Br}_8^{3-}$	2.143 <i>2.1265(9)</i>	2.496 <i>2.515[2]</i>	0.89	1.74	0.41	3.04
$\text{Tc}_2\text{Cl}_8^{2-}$	2.170 <i>2.1560(3)</i>	2.314 <i>2.3223[8]</i>	0.88	1.68	0.47	3.03
$\text{Tc}_2\text{Br}_8^{2-}$	2.173 <i>2.1625(9)</i>	2.448 <i>2.473[2]</i>	0.88	1.69	0.50	3.07

Experimental XRD results (italics) are also included.

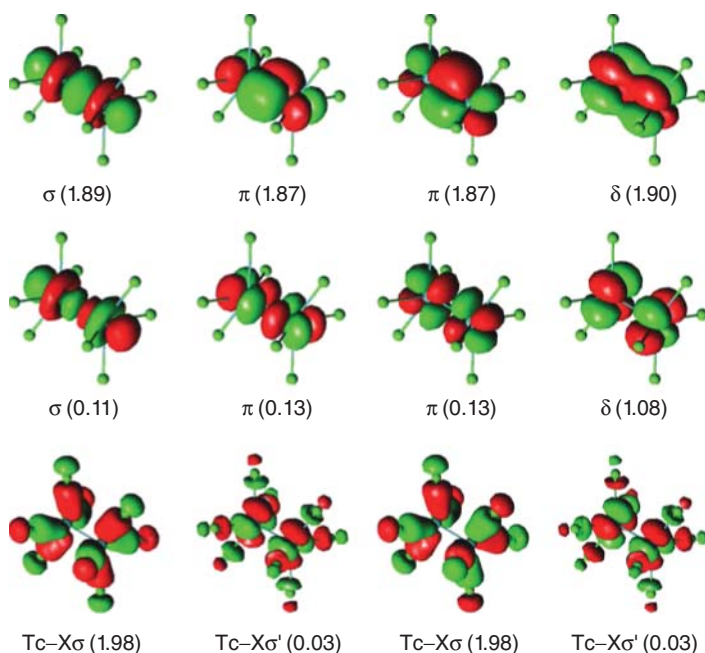


Figure 7.25 Active orbitals for $\text{Tc}_2\text{X}_8^{3-}$ ($\text{X} = \text{Cl}, \text{Br}$) with their occupation numbers in the ground state.

Multiconfiguration calculations at the CASSCF/CASPT2 level were performed in order to investigate the electronic structures of $\text{Tc}_2\text{X}_8^{n-}$ ($\text{X} = \text{Cl}, \text{Br}$; $n = 2, 3$) anions. For $\text{Tc}_2\text{X}_8^{3-}$, the complete active space (Figure 7.25) contains 13 electrons in 12 active orbitals. The molecular orbitals and the ground state wave functions for the two $\text{Tc}_2\text{X}_8^{3-}$ anions were compared. Both anions have identical orbital occupations indicating that their electronic structure is relatively insensitive to the nature of the coordinating ligands.

The EBOs in the $\text{Tc}_2\text{X}_8^{n-}$ systems were compared (Table 7.7). In all the four anions, the effective sigma bond order is identical. The π component of the Tc–Tc bond is larger in the $\text{Tc}_2\text{X}_8^{3-}$ dimers and may be the origin of shorter Tc–Tc separations in $\text{Tc}_2\text{X}_8^{3-}$. The δ bond order is lower in $\text{Tc}_2\text{X}_8^{3-}$ due to the single occupation of the δ^* orbital, which may also explain the small internal rotations in the

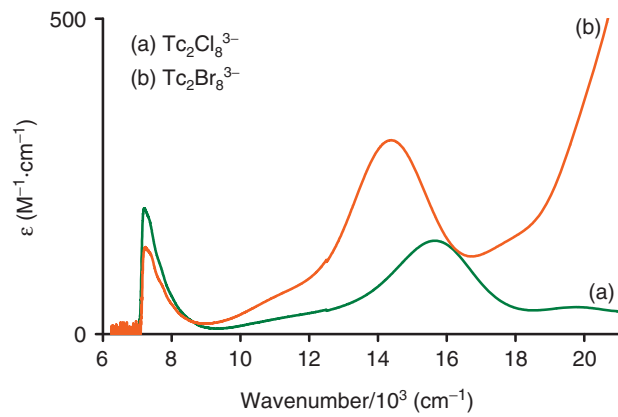


Figure 7.26 UV–visible spectra of (a) $\text{Tc}_2\text{Cl}_8^{3-}$ in HCl(aq) and (b) $\text{Tc}_2\text{Br}_8^{3-}$ in HBr(aq) .

Table 7.8 Experimental band maxima (cm^{-1}), assignments, calculated excitation energies (cm^{-1}) and their intensities for $\text{Tc}_2\text{X}_8^{3-}$ ($\text{X}=\text{Cl}$ in bold and $\text{X}=\text{Br}$).

Experimental	Assignment	Excitation energies	Intensity
<9000	$\delta \rightarrow \delta^*$	6132	0.91×10^{-2}
<9000		6344	0.13×10^{-1}
11 820	$\delta^* \rightarrow \text{Tc-X } \sigma^*$	9622	0.13×10^{-5}
10 830		9546	0.12×10^{-5}
15 620	$\delta^* \rightarrow \pi^*$	11 322	0.15×10^{-4}
14 420		11 942	0.17×10^{-4}

$\text{Tc}_2\text{X}_8^{3-}$ anions. Because of the face-to-face nature of the d_{xy} orbital overlap, the δ bonds are much weaker than either the σ or π bonds in these dimers. The total bond order in $\text{Tc}_2\text{X}_8^{3-}$ anions (~ 3) is similar to that found for the $\text{Tc}_2\text{X}_8^{2-}$ complexes, that is, changing the electronic configuration from $\sigma^2\pi^4\delta^2$ ($\text{Tc}_2\text{X}_8^{2-}$) to $\sigma^2\pi^4\delta^2\delta^*$ ($\text{Tc}_2\text{X}_8^{3-}$) has a negligible effect on the total bond order.

The UV–visible spectra of $\text{Tc}_2\text{Br}_8^{3-}$ and $\text{Tc}_2\text{Cl}_8^{3-}$ were recorded respectively in concentrated aqueous HBr and HCl . The spectrum of $\text{Tc}_2\text{Br}_8^{3-}$ between 7000 and 20 000 cm^{-1} is similar to the one reported for the $\text{Tc}_2\text{Cl}_8^{3-}$ ion (Figure 7.26). A continuous increase of absorption from 9000 to 7100 cm^{-1} with a sudden drop at 7100 cm^{-1} (absorbance of solvent) is noted. The bands in the spectrum of chloro-complex are shifted to slightly higher energy relative to those in its bromo-analog. The close resemblance of the spectra is expected given their similar electronic structures. Electronic transitions in $\text{Tc}_2\text{Br}_8^{3-}$ and $\text{Tc}_2\text{Cl}_8^{3-}$ were computed at the CASPT2 level (Table 7.8). For both species, the intense band in the region 14 000–16 000 cm^{-1} and the absorption between 7000 and 9000 cm^{-1} are assigned to the $\delta^* \rightarrow \pi^*$ and $\delta \rightarrow \delta^*$ transitions, respectively. These results are consistent with earlier SCF- $X\alpha$ calculations on $\text{Tc}_2\text{Cl}_8^{3-}$ [55].

7.2.4

Complexes with a Tc_2^{4+} Core

Chloro-phosphine compounds of the type $\text{Tc}_2\text{Cl}_4(\text{PR}_3)_4$ ($\text{R}_3=\text{Et}_3$, $n\text{-Pr}_3$, Me_2Ph , MePh_2) were described in the mid-1990s and were synthesized by the sonication of *trans*- $\text{TcCl}_4(\text{PR}_3)_2$ with zinc metal in THF or benzene [56]. The complex $\text{Tc}_2\text{Cl}_4(\text{PMe}_3)_4$ was not mentioned and attempts to synthesize this dimer via the sonication of the known *trans*- $\text{TcCl}_4(\text{PMe}_3)_2$ in benzene with zinc

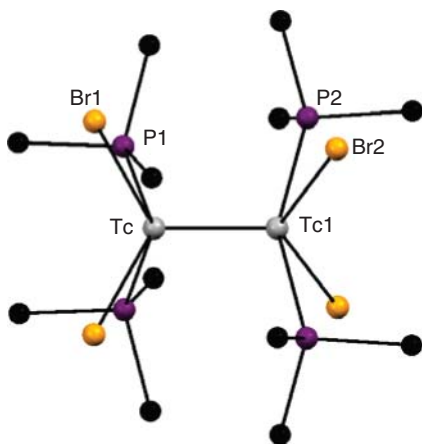


Figure 7.27 Ball-and-stick representation of $\text{Tc}_2\text{Br}_4(\text{PMe}_3)_4$. Carbon atoms are in black, phosphorous in purple, bromine in orange, and technetium in gray. Hydrogen atoms are omitted for clarity. Selected distances in Å: $\text{Tc}-\text{Tc1} = 2.1316(5)$, $\text{Tc}-\text{Br1} = 2.5218(4)$, $\text{Tc}-\text{P1} = 2.4454(8)$, $\text{Tc1}-\text{Br2} = 2.5196(4)$, $\text{Tc1}-\text{P2} = 2.4415(8)$.

were unsuccessful. The analogous rhenium complexes $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{R}_3 = \text{Me}_3, \text{Et}_3, n\text{-Pr}_3, \text{Et}_2\text{Ph}, \text{MePh}_2$) were obtained in high yield from the reactions between $\text{Re}_2\text{X}_8^{2-}$ and the corresponding tertiary phosphines in refluxing ethanol [57–60].

For technetium, the complexes $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ are obtained reproducibly in about 10% yield from the reaction between $\text{Tc}_2\text{X}_8^{2-}$ and PMe_3 in dichloromethane [61]. Dinuclear Tc_2^{4+} (i.e., $\text{Tc}_2\text{Cl}_4(\text{PMe}_3)_4$) and mononuclear Tc^{4+} species ($\text{TcCl}_4(\text{PMe}_3)_2$ and TcCl_6^{2-}) are observed immediately after mixing a solution of $\text{Tc}_2\text{Cl}_8^{2-}$ with PMe_3 , which indicates that disproportionation is the genesis of $\text{Tc}_2\text{Cl}_4(\text{PMe}_3)_4$. The complex $\text{Tc}_2\text{Br}_4(\text{PMe}_3)_4$ can also be obtained from the reduction of TcBr_3 with $\text{Na}(\text{Et}_3\text{BH})$ in THF/PMe_3 solution [62]. The $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ complexes are soluble in CH_2Cl_2 , hexane, and diethyl ether.

Single crystals of $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ ($\text{X} = \text{Cl}, \text{Br}$) were grown in hexane. The compounds $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ crystallize in the monoclinic space group $C2/c$ and are isostructural to $\text{M}_2\text{X}_4(\text{PMe}_3)_4$ ($\text{M} = \text{Re}, \text{Mo}$, $\text{X} = \text{Cl}, \text{Br}$) [63]. Both $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ complexes exhibit the eclipsed conformation with D_{2d} symmetry, the individual *trans*- $\text{TcX}_2(\text{PMe}_3)_2$ units are pyramidal (Figure 7.27). The average $\text{Tc}-\text{P}$ distances ($2.4356[4]$ Å for $\text{X} = \text{Cl}$ and $2.4434[8]$ Å for $\text{X} = \text{Br}$) are similar to the ones found in monomeric *trans*-dihalo $\text{Tc}(\text{II})$ phosphine complexes [64]. The $\text{Tc}-\text{X}$ distances ($2.3858[4]$ Å for $\text{X} = \text{Cl}$ and $2.5207[5]$ Å for $\text{X} = \text{Br}$) are shorter than in $\text{Tc}(\text{II})$ mononuclear complexes (i.e., $\text{Tc}-\text{Cl} = 2.424(2)$ Å in $\text{TcCl}_2(\text{DPPE})_2$ and $\text{Tc}-\text{Br} = 2.5925(7)$ Å in $\text{TcBr}_2(\text{PMe}_3)_4$) [62, 64]. This phenomenon is primarily due to steric congestion in the monomer.

The metal–metal distances in $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ ($2.1318(2)$ Å for $\text{X} = \text{Cl}$, and $2.1316(5)$ Å for $\text{X} = \text{Br}$) are consistent with the presence of an electron-rich $\sigma^2\pi^4\delta^2\delta^{*2}$ triple bond. The $\text{Tc}-\text{Tc}$ distances in $\text{Tc}_2\text{Cl}_4(\text{PR}_3)_4$ ($\text{R}_3 = \text{Et}_3, \text{Me}_3, \text{Me}_2\text{Ph}, \text{MePh}_2$) vary over a narrow range of $2.127(1)$ Å ($\text{R}_3 = \text{Me}_2\text{Ph}$) to $2.138(4)$ Å ($\text{R}_3 = \text{MePh}_2$) [54]. Apparently, the nature of the halogen and phosphine ligands does not have a strong influence on the metal–metal separations. The relative insensitivity of the Tc_2^{4+} unit to the nature of the coordinating ligand contrasts with Tc_2^{6+} . For the quadruply bonded dimers, an elongation of the $\text{Tc}-\text{Tc}$ distance is observed when replacing Cl by Br or by a carboxylate ligand. Currently, no quadruply bonded technetium(III) dimers containing tertiary phosphine ligands, for example, $\text{Tc}_2\text{Cl}_6(\text{PR}_3)_2$, are known, but we would expect them to be synthetically accessible.

Geometry optimizations of $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ reveal that the calculated $\text{Tc}-\text{Tc}$, $\text{Tc}-\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$), and $\text{Tc}-\text{P}$ bond distances are in excellent agreement with the experimental values (Table 7.9) [61]. Calculations confirm the experimental observation that the $\text{Tc}-\text{Tc}$ bond distance is identical in both

Table 7.9 Effective bond order, total bond order, and Tc–Tc, Tc–X, and Tc–P bond distances (Å) for $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ (X = Cl, Br) calculated at the CASPT2/VTZP level of theory.

Complexes	Tc–Tc	Tc–X	Tc–P	EBO σ	EBO π	EBO δ	Total B.O.
$\text{Tc}_2\text{Cl}_4(\text{PMe}_3)_4$	2.118 <i>2.1318(2)</i>	2.383 <i>2.3858[4]</i>	2.425 <i>2.4356[4]</i>	0.90	1.81	0.01	2.72
$\text{Tc}_2\text{Br}_4(\text{PMe}_3)_4$	2.117 <i>2.1316(5)</i>	2.532 <i>2.5207[5]</i>	2.437 <i>2.4434[8]</i>	0.90	1.81	0.01	2.72

Experimental XRD results (italics) are also included.

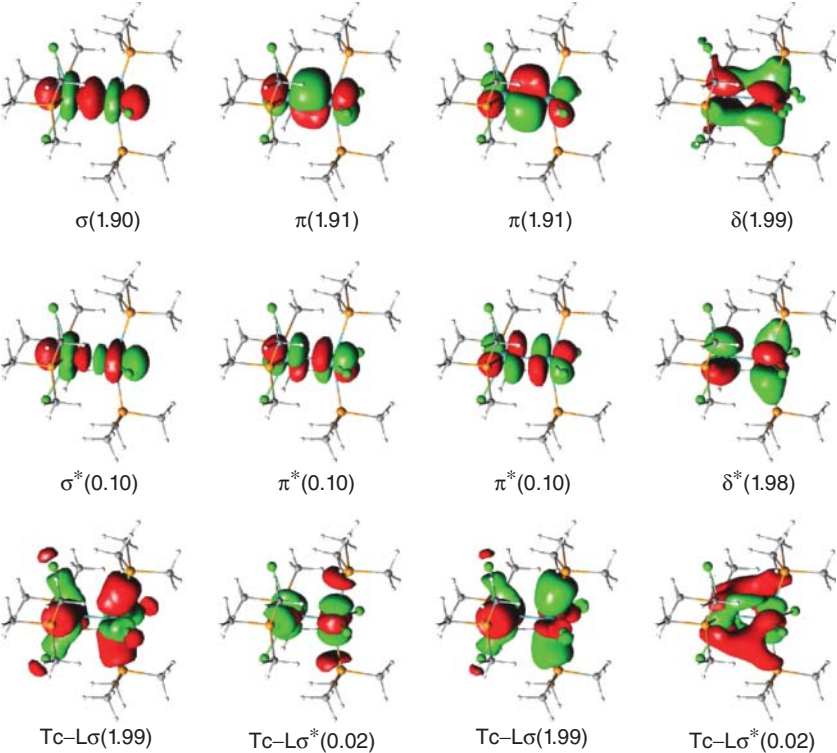


Figure 7.28 Active orbitals for $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ (X = Cl, Br) and their occupation numbers in the ground state.

complexes. The calculated Tc–Cl distance is 2.38 Å and the Tc–Br distance is 2.53 Å. The Tc–P distances vary in a very narrow range of 2.42–2.44 Å, independent of the nature of X. Examination of the Tc–Tc distances in the optimized structures of $\text{Tc}_2\text{X}_8^{2-}$ and $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ (X = Cl, Br) reveals a decrease of the metal–metal distance with a decrease in total bond order when moving from Tc_2^{6+} to Tc_2^{4+} and confirms the trend observed experimentally.

The CASSCF/CASPT2 calculations were performed in order to investigate the electronic structures of $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ (X = Cl, Br). The 12 molecular orbitals forming the active space along with their occupation numbers are presented in Figure 7.28. The two bonding Tc–L orbitals are mainly located on L (L = X and P), while the corresponding antibonding orbitals have a large contribution from the Tc $4d_{x^2-y^2}$ orbital. The occupancy of δ and δ^* orbitals is nearly identical, which gives no contribution to the δ bond (EBO of 0.01).

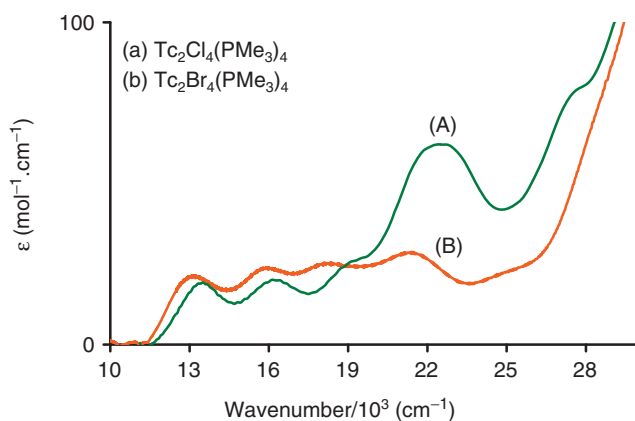


Figure 7.29 UV-visible spectra of (a) $\text{Tc}_2\text{Cl}_4(\text{PMe}_3)_4$ and (b) $\text{Tc}_2\text{Br}_4(\text{PMe}_3)_4$ in benzene.

Table 7.10 Experimental band maxima (cm^{-1}), assignments, calculated excitation energies (cm^{-1}), and their intensities for $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ ($\text{X}=\text{Cl}$ in bold and $\text{X}=\text{Br}$).

Experimental	Assignment	Excitation energies	Intensity
13 477	$\delta^* \rightarrow \sigma^*$	13 249	$<1.0 \times 10^{-8}$
13 072		12 206	$<1.0 \times 10^{-8}$
16 129	$\delta^* \rightarrow \pi^*$	16 370	0.14×10^{-4}
15 949		16 516	0.17×10^{-4}
19 200 (sh)	$\delta \rightarrow \sigma^*$	20 744	$<1.0 \times 10^{-8}$
18 281		19 836	$<1.0 \times 10^{-8}$
22 371	$\delta \rightarrow \pi^*$	24 163	0.21×10^{-3}
21 436		24 410	0.14×10^{-3}
27 777(sh)	$\delta \rightarrow \sigma^*$ (Tc–Cl)	27 215	$<1.0 \times 10^{-8}$

EBOs for the σ , π , and δ components in $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ are identical and indicate that the halide ligand has essentially no effect on metal–metal bonding in Tc_2^{4+} core (Table 7.9). A comparison between the EBO in $\text{Tc}_2\text{X}_8^{2-}$ and $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ indicates that the Tc_2^{4+} cores have stronger π bonds than the Tc_2^{6+} core, and is also consistent with the observed decrease of Tc–Tc distance associated with the reduction of total bond order in the Tc_2^{4+} unit.

The UV–visible spectra of $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ ($\text{X}=\text{Cl}, \text{Br}$) in benzene show a series of five low-intensity bands (Figure 7.29). The bands in the spectrum of the chloro-complex are shifted to slightly higher energy relative to those in its bromo-analog [61]. Attribution of the bands in $\text{Tc}_2\text{X}_4(\text{PMe}_3)_4$ ($\text{X}=\text{Cl}, \text{Br}$) spectra was performed at the CASPT2 level (Table 7.10).

The calculations predict that the lowest energy band corresponds to the dipole forbidden $\delta^* \rightarrow \sigma^*$ transition with the difference between calculated and experimental values being 228 cm^{-1} for $\text{X}=\text{Cl}$ and 866 cm^{-1} for $\text{X}=\text{Br}$. The calculations are also able to mimic the red shift of the $\delta^* \rightarrow \sigma^*$ transition observed for the bromo compound; the calculated shift (1043 cm^{-1}) being within a factor of ~ 2.5 to the experimental one ($\sim 400 \text{ cm}^{-1}$). The next band is attributed to the dipole allowed $\delta^* \rightarrow \pi^*$ transition and its calculated position matches well with the experimental values. The third transition appears as a shoulder in the $\text{Tc}_2\text{Cl}_4(\text{PMe}_3)_4$ spectrum ($\sim 19\,200 \text{ cm}^{-1}$) and as a distinct band ($18\,281 \text{ cm}^{-1}$) in the $\text{Tc}_2\text{Br}_4(\text{PMe}_3)_4$ spectrum. These bands are assigned to the $\delta \rightarrow \sigma^*$ transitions. The higher intensity bands located around $22\,000 \text{ cm}^{-1}$ are attributed to the $\delta \rightarrow \pi^*$ transition which is allowed in D_{2d} symmetry. The higher intensity of the $\delta \rightarrow \pi^*$ transition is also confirmed theoretically.

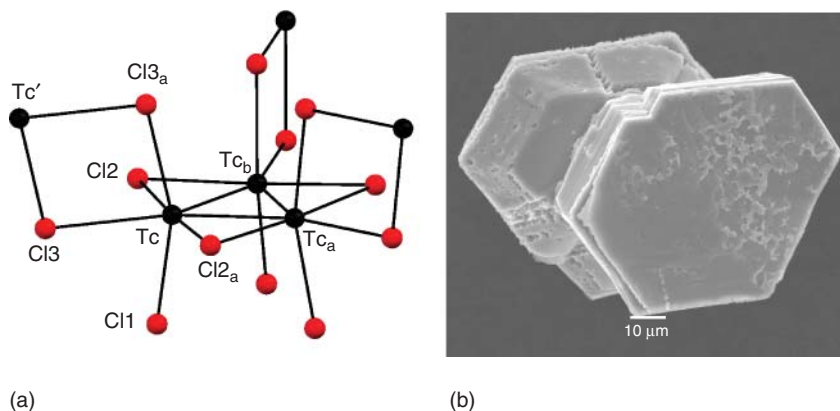


Figure 7.30 (a) Ball and stick representation of the structure of $\alpha\text{-TcCl}_3$. Color of atoms: Tc in black and Cl in red. Selected distances (Å): $\text{Tc-Cl1} = 2.238(2)$, $\text{Tc-Cl2}_{(a)} = \text{Tc-Cl3}_a = 2.373(2)$, $\text{Tc-Cl3} = 2.585(2)$, $\text{Tc-Tc}_{(a,b)} = 2.444(1)$, and $\text{Tc-Tc}' = 3.852(1)$. (b) SEM image of crystals $\alpha\text{-TcCl}_3$.

7.2.5

Miscellaneous Complexes with Tc–Tc Multiple Bonds

The compound $\alpha\text{-TcCl}_3$ (Tc_3Cl_9) can be obtained by the thermal decomposition of TcCl_4 under vacuum [65] or by reaction between $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ and flowing $\text{HCl}(\text{g})$ at 300°C [66]. The reaction of $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $\text{HCl}(\text{g})$ is the method of choice for the production of macroscopic amounts of $\alpha\text{-TcCl}_3$; during this reaction, a color change from pink to green ($\sim 100^\circ\text{C}$) and then black ($\sim 250^\circ\text{C}$) was noted. Analyses of the green compound revealed it to be $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$, while the black amorphous compound was identified as $\alpha\text{-TcCl}_3$. The formation of $\alpha\text{-TcCl}_3$ mimics the one described for rhenium; the dimers $\text{M}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$ ($\text{M} = \text{Tc}, \text{Re}$) are formed as intermediates in the early stages of the reactions, after which rhenium and technetium trichlorides are formed at 340 and 300°C , respectively (*vide supra*). What is not obvious is how incipient M_2Cl_6 isomerizes in the solid state to M_3Cl_9 . The structure consists of infinite layers of Tc_3Cl_9 units and is isostructural to ReCl_3 [67]. In the Tc_3Cl_9 unit (Figure 7.30), the Tc atoms form an equilateral triangle with Tc–Tc distances of $2.444(1)$ Å. This distance is 0.045 Å shorter than the Re–Re distance in Re_3Cl_9 and is indicative of a $\text{Tc}=\text{Tc}$ double bond. The Tc_3Cl_9 units are linked by the Cl atoms and the $\text{Tc}\cdots\text{Tc}'$ distance of $3.852(1)$ Å between Tc_3Cl_9 units precludes any metal–metal interaction. The bonding in the Tc_3Cl_9 cluster has been analyzed; the calculations indicate the presence of 1.99 electrons in both the σ and π orbitals, for an EBO of 2 [66]. The black solid dissolves in concentrated aqueous hydrochloric acid to form an orange solution, presumably containing $[\text{Tc}_3\text{Cl}_{12}]^{3-}$. There are no reports of other reactions involving $\alpha\text{-TcCl}_3$.

Technetium dichloride, TcCl_2 can be obtained by the reaction between the elements at elevated temperature [68, 69], or by the thermal decomposition of TcCl_4 or $\alpha\text{-TcCl}_3$ under vacuum at 450°C [65]. For the first route, single crystals of $\beta\text{-TcCl}_2$, $\beta\text{-TcCl}_3$, and TcCl_4 were congruently obtained. The $\beta\text{-TcCl}_2$ needles that were located in the center part of the tube were used for the structure determination. The dark powder containing technetium metal and TcCl_2 was sealed in a clean tube with AlCl_3 , and $\alpha\text{-TcCl}_2$ single crystals were obtained by sublimation after four days at 450°C . Solid $\beta\text{-TcCl}_2$ was analyzed by energy dispersive X-ray (EDX) spectroscopy and by XANES. These two techniques have proven very useful in determining stoichiometries and Tc oxidation states, respectively. Both $\beta\text{-TcCl}_2$ and $\alpha\text{-TcCl}_2$ exhibit new structure-types that consist of infinite chains of eclipsed $[\text{Tc}_2\text{Cl}_8]$ units (Figure 7.31). In the $[\text{Tc}_2\text{Cl}_8]$ units, the average Tc–Cl distance for $\beta\text{-TcCl}_2$ (i.e., $2.398(3)$ Å) is slightly larger than that found in $\alpha\text{-TcCl}_2$ ($2.372(9)$ Å) and the Tc–Tc separations – $2.136(3)$ Å for $\beta\text{-TcCl}_2$ and $2.127(2)$ Å for $\alpha\text{-TcCl}_2$ – are indicative of a $\text{Tc}\equiv\text{Tc}$ triple

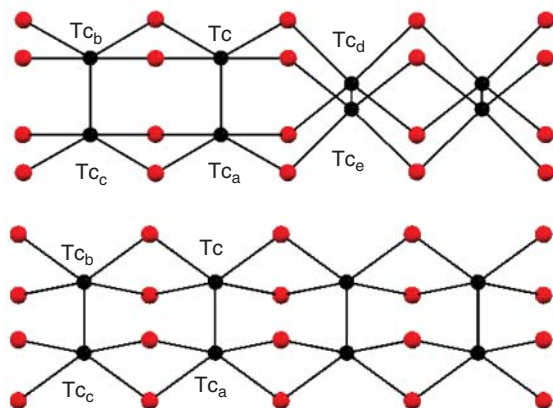


Figure 7.31 Ball-and-stick representation of portions of β - TcCl_2 chain (top) and α - TcCl_2 (bottom) chains. Color of atoms: Tc in black and Cl in red. Selected distances (Å) in β - TcCl_2 : $\text{Tc}-\text{Tc}_a = 2.136(3)$,

$\text{Tc}-\text{Tc}_b = 3.425(2)$, $\text{Tc}-\text{Tc}_c = 4.037(3)$, and $\text{Tc}-\text{Tc}_{(d,e)} = 3.744(2)$. Selected distances (Å) in α - TcCl_2 : $\text{Tc}-\text{Tc}_a = 2.136(3)$, $\text{Tc}-\text{Tc}_b = 3.417(2)$, and $\text{Tc}-\text{Tc}_c = 4.025(2)$.

bond (*vide infra*). It is surprising that TcCl_2 adopts a structure so different than the octahedral structures of MoCl_2 and WCl_2 . We note that ReCl_2 is currently unknown.

In a β - TcCl_2 chain, two orientations of the $\text{Tc}\equiv\text{Tc}$ bonds in the $[\text{Tc}_2\text{Cl}_8]$ unit are observed: the $\text{Tc}\equiv\text{Tc}$ bonds of two adjacent $[\text{Tc}_2\text{Cl}_8]$ units are either parallel or perpendicular (Figure 7.31), and the orientation of the $\text{Tc}\equiv\text{Tc}$ bonds changes every two $[\text{Tc}_2\text{Cl}_8]$ units. The distances between $\text{Tc}\equiv\text{Tc}$ bonds of parallel ($3.425(2)$ Å) and perpendicular $[\text{Tc}_2\text{Cl}_8]$ units ($3.744(2)$ Å) preclude any metal–metal interaction between adjacent units. In α - TcCl_2 , only one orientation of the $\text{Tc}\equiv\text{Tc}$ bonds is observed, and the $\text{Tc}\equiv\text{Tc}$ vectors of adjacent units are parallel. The distances between Tc atoms of the adjacent units ($3.417(2)$ Å) also preclude any metal–metal interaction.

The metal–metal separations in α/β - TcCl_2 are similar to those observed in a number of dinuclear technetium(II) complexes (*vide supra*) and are consistent with the presence of a metal–metal triple bond. Further quantification of the metal–metal bonding is provided by first-principles calculations of the natural bond orbital (NBO) occupancy of the $\text{Tc}-\text{Tc}$ bond; these results indicate an NBO of 5.30, which is close to the value expected for a perfect triple bond (i.e., 6.00). In α/β - TcCl_2 , the $\text{Tc}\equiv\text{Tc}$ triple bond should exhibit the $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration, which is also consistent with the experimental diamagnetism of the compound. Technetium dichloride crystals are stable in air and can be kept for a year without any evidence of decomposition. The β - TcCl_2 needles are insoluble in common organic solvents and aqueous HCl at ambient temperature. No reactions occur between TcCl_2 powder and neat PMe_3 . The compound disproportionates to Tc metal and TcCl_4 in a sealed tube at or above 600°C [69].

Because technetium tri- and tetrachloride decompose to TcCl_2 , it was expected that TcBr_2 would result from the thermal decomposition of TcBr_4 and TcBr_3 . This is not the case. Rather, TcBr_4 and TcBr_3 both decompose to $\text{Na}[\{\text{Tc}_6\text{Br}_{12}\}_2\text{Br}]$ in a sealed Pyrex tube under vacuum at 450°C [70]. In $\text{Na}[\{\text{Tc}_6\text{Br}_{12}\}_2\text{Br}]$, the hexanuclear $[\text{Tc}_6\text{Br}_{12}]$ cluster adopts a trigonal prismatic geometry and is composed of two identical parallel Tc_3Br_6 units linked by multiple $\text{Tc}\equiv\text{Tc}$ bonds (Figure 7.32). The thermal decomposition of TcBr_4 and TcBr_3 performed in a quartz tube did not provide a crystalline product, which suggests that the source of the sodium in the compound originates from the Pyrex tube. Questions remain on whether TcBr_2 is accessible by thermal decomposition and whether its structure is a “naked” $\text{Tc}_6\text{Br}_{12}$ cluster or one similar to TcCl_2 .

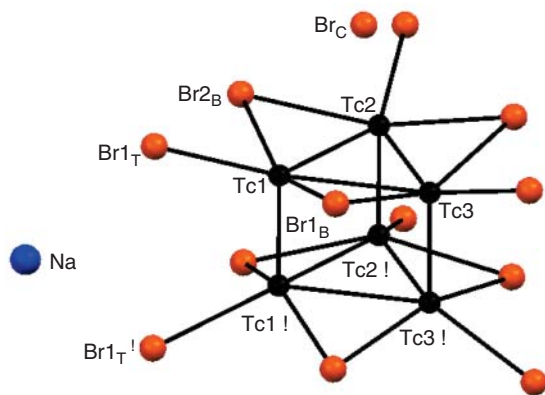


Figure 7.32 Ball and stick representation of $\text{Na}[\text{Tc}_6\text{Br}_{12}]_2\text{Br}$. Color of atoms: Tc in black, Br in orange, and Na in blue. Selected distances (Å): $\text{Tc1-Tc2} = 2.6879(5)$, $\text{Tc1-Tc3} = 2.6735(5)$,

$\text{Tc2-Tc3} = 2.6776(5)$, $\text{Tc1-Tc1}' = 2.1651(5)$, $\text{Tc2-Tc2}' = 2.1779(5)$, $\text{Tc3-Tc3}' = 2.1776(5)$, $\text{Tc1-Br1}_\text{T} = 2.5216(8)$, $\text{Tc1-Br2}_\text{B} = 2.4819(7)$ Å, and $\text{Tc1-BrC} = 3.0994(4)$.

7.3

Rhenium

7.3.1

Introduction

One of the landmark achievements of modern inorganic chemistry was the isolation and characterization of transition metal complexes that contain multiple metal–metal bonds. The groundbreaking observations of the early 1960s have now evolved into a field of considerable breadth, depth, and complexity and for this reason, we limit our discussions to homobimetallic species in this section [71]. One particularly noteworthy milestone near the dawn of the field was the synthesis and structural characterization of salts containing the octachlorodirhenate(III) anion, $\text{Re}_2\text{Cl}_8^{2-}$. This anion was first prepared via the high-pressure reduction of the perrhenate ion, ReO_4^- , by molecular hydrogen in concentrated aqueous hydrochloric acid [72]. This synthesis is not a particularly convenient method of preparing the binuclear rhenium(III) complex as it requires rather specialized and expensive high pressure equipment. It did, however, provide crystals of $\text{K}_2\text{Re}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$, whose X-ray structure revealed an eclipsed orientation of two square planar ReCl_4^- units as shown schematically (Figure 7.33). The observed Re–Re separation of 2.24 Å is considerably shorter than the Re–Re separation in rhenium metal [73]. The unusually short distance and eclipsed arrangement of chloride ligands led Professor F. A. Cotton and coworkers at the Massachusetts Institute of Technology to propose the existence of a quadruple metal-metal bond ($\sigma^2\pi^4\delta^2$ ground state electronic configuration) between the rhenium(III) centers [74].

The synthesis of a related *n*-butylammonium salt, $(\text{TBA})_2\text{Re}_2\text{Cl}_8$, was first achieved via the hypophosphorous acid (H_3PO_2) reduction of ReO_4^- in aqueous hydrochloric acid [75]. This reaction provided access to a salt of $\text{Re}_2\text{Cl}_8^{2-}$ that has good solubility properties in polar organic solvents and facilitated numerous studies of the chemical and physical properties of the anion. A major disadvantage of this otherwise reproducible synthesis was the relatively low yield of the desired salt (~30%). A straightforward, high-yield synthesis of $(\text{TBA})_2\text{Re}_2\text{Cl}_8$ was developed some years later by Barder and Walton [76]. It involves the reductive coupling of $(\text{TBA})\text{ReO}_4$ in either benzoyl or *p*-toluoyl chloride (*p*-methylbenzoyl chloride) for a predetermined period of time followed by treatment with a concentrated solution of $(\text{TBA})\text{Cl}$ in a mixture of ethanol and hydrochloric acid.

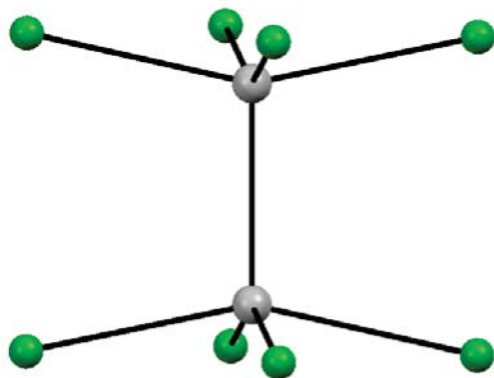


Figure 7.33 Ball and stick representation of the $\text{Re}_2\text{Cl}_8^{2-}$ anion.

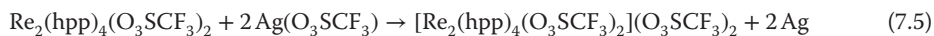
The blue salt is isolated in yields approaching 90% and it is soluble in polar organic solvents such as acetonitrile, dichloromethane, and methanol. In the solid state, it is stable in air and can be stored indefinitely without special precautions. It is readily converted into dozens of other compounds with Re–Re quadruple bonds. We refer to these compounds in shorthand as molecules with a Re_2^{6+} core. Other members of this family are described in Section 7.3.4.

The compounds described in Sections 12–16 are members of a particular class of Re_2^{n+} core molecules where $n = 4–8$. A final Section 17 describes triangular compounds that have Re_3^{9+} cores.

7.3.2

Complexes with the Re_2^{8+} Core

Only one compound containing the Re_2^{8+} unit has been reported in the period 2005–2014: $\{[\text{Re}_2(\text{hpp})_3(\text{OH})(\text{O}_3\text{SCF}_3)]_2(\mu\text{-O})_2(\text{O}_3\text{SCF}_3)_2\}$ [77]. The compound was obtained from the reaction of $\text{Re}_2(\text{hpp})_4(\text{O}_3\text{SCF}_3)_2$ with $\text{Ag}(\text{O}_3\text{SCF}_3)$ in dichloromethane (Eq. (7.5)) followed by crystallization with un-dried hexanes (Eq. (7.6)).



The compound consists of two $[\text{Re}_2(\text{hpp})_3]^{5+}$ fragments each having an axial OH and a triflate anion; the two $[\text{Re}_2(\text{hpp})_3]^{5+}$ fragments are held together by two bridging oxo-groups (Figure 7.18). The $[\text{Re}_2(\text{hpp})_3]^{5+}$ fragment consists of an electron-poor triple-bonded Re_2^{8+} unit (electronic configuration is $\sigma^2\pi^4$) bridged by three hpp ligands. The hpp ligand is 1,3,4,6,7,8-hexahydro-2*H*-pyrimido [1,2-*a*]pyrimidine (Figure 7.34).

The Re–Re distances in $\{[\text{Re}_2(\text{hpp})_3(\text{OH})(\text{O}_3\text{SCF}_3)]_2(\mu\text{-O})_2(\text{O}_3\text{SCF}_3)_2\}$ (i.e., 2.2058(11) and 2.2066(10) Å) are longer (by ~ 0.05 Å) than the one in $\text{Re}_2(\text{hpp})_4(\text{O}_3\text{SCF}_3)_2$ (i.e., 2.1562(7) Å), which is consistent with the decrease of bond order (Table 7.11 and Section 8). The decrease in the average Re–N distances (~ 0.02 Å) in $\{[\text{Re}_2(\text{hpp})_3(\text{OH})(\text{O}_3\text{SCF}_3)]_2(\mu\text{-O})_2(\text{O}_3\text{SCF}_3)_2\}$ relative to those in $\text{Re}_2(\text{hpp})_4(\text{O}_3\text{SCF}_3)_2$ is consistent with the increase in overall charge of the dimetal unit that leads to a stronger interaction with the ligands. The Re–Re distances in $\{[\text{Re}_2(\text{hpp})_3(\text{OH})(\text{O}_3\text{SCF}_3)]_2(\mu\text{-O})_2(\text{O}_3\text{SCF}_3)_2\}$ are shorter than those in electron-rich triple bonded Re_2^{4+} compounds with $\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configurations [78]. Cyclic voltammetry experiments in CH_2Cl_2 have shown that the $\{[\text{Re}_2(\text{hpp})_3(\text{OH})(\text{O}_3\text{SCF}_3)]_2(\mu\text{-O})_2(\text{O}_3\text{SCF}_3)_2\}$ complex is not redox active. The reason

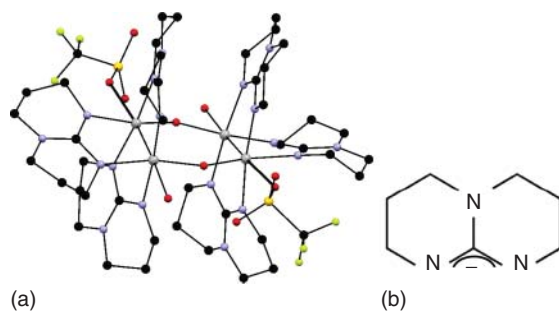


Figure 7.34 Ball and stick representation of $\{[\text{Re}_2(\text{hpp})_3(\text{OH})(\text{O}_3\text{SCF}_3)_2](\mu\text{-O})_2\}(\text{O}_3\text{SCF}_3)_2$ (a) and the hpp anion (b).

Table 7.11 Structural data for rhenium compounds containing the Re_2^{7+} and Re_2^{8+} cores.

Compounds	Unit	Re–Re (Å)
$[\text{Re}_2(\text{tbn})_4\text{Cl}_2]\text{PF}_6$	Re_2^{7+}	2.2691(14)
$[\text{Re}_2(\text{tbn})_4\text{Cl}_2]\text{Cl}$	Re_2^{7+}	2.2589(14)
$[\text{Re}_2(\text{hpp})_4(\text{O}_3\text{SCF}_3)_2](\text{O}_3\text{SCF}_3)$	Re_2^{7+}	2.1804(8)
$[\text{Re}_2(\text{hpp})_4\text{F}](\text{TFPB})_2$	Re_2^{7+}	2.1874(3)
$\{[\text{Re}_2(\text{hpp})_3(\text{OH})(\text{O}_3\text{SCF}_3)_2](\mu\text{-O})_2\}(\text{O}_3\text{SCF}_3)_2$	Re_2^{8+}	2.2058(11)
		2.2066(10)

of this lack of activity is probably the presence of OH ligands that react irreversibly (hydrogen production) upon reduction.

7.3.3

Complexes with the Re_2^{7+} Core

Four compounds containing the Re_2^{7+} core have been reported: $[\text{Re}_2(\text{tbn})_4\text{Cl}_2]\text{PF}_6$, $[\text{Re}_2(\text{tbn})_4\text{Cl}_2]\text{Cl}$, $[\text{Re}_2(\text{hpp})_4(\text{O}_3\text{SCF}_3)_2](\text{O}_3\text{SCF}_3)$ and $[\text{Re}_2(\text{hpp})_4\text{F}](\text{TFPB})_2$. The compounds $[\text{Re}_2(\text{tbn})_4\text{Cl}_2]\text{PF}_6$ and $[\text{Re}_2(\text{hpp})_4(\text{O}_3\text{SCF}_3)_2](\text{O}_3\text{SCF}_3)$ were respectively obtained via the oxidation of $\text{Re}_2(\text{tbn})_4\text{Cl}_2$ and $\text{Re}_2(\text{hpp})_4(\text{O}_3\text{SCF}_3)_2$ with $[\text{FeCp}_2]\text{PF}_6$ and $[\text{FeCp}_2]\text{O}_3\text{SCF}_3$ in dichloromethane [79]. Crystals of $[\text{Re}_2(\text{tbn})_4\text{Cl}_2]\text{Cl}$ were obtained after a sample of $\text{Re}_2(\text{tbn})_4\text{Cl}_2$ in CDCl_3 was left undisturbed for two weeks in an NMR tube. The tbn ligand is 2,3,5,6,7,8-hexahydroimidazo[1,2-*a*] pyrimidine (Figure 7.35).

These species exhibit the paddlewheel structure and consist of Re_2^{7+} units coordinated to four bridging bicyclic guanidates and two axial ligands. The compound $[\text{Re}_2(\text{tbn})_4\text{Cl}_2]\text{PF}_6$ has a Re–Re distance of 2.2691(14) Å. The increase of the Re–Re separation (~ 0.05 Å) relative to the one in $\text{Re}_2(\text{tbn})_4\text{Cl}_2$ is consistent with the removal of one electron from the δ orbital. In $[\text{Re}_2(\text{tbn})_4\text{Cl}_2]\text{PF}_6$, the Re_2^{7+} unit has a formal bond order of 3.5 ($\sigma^2\pi^4\delta^1$ electronic configuration). The $[\text{Re}_2(\text{tbn})_4\text{Cl}_2]^+$ cation (Figure 7.35) in $[\text{Re}_2(\text{tbn})_4\text{Cl}_2]\text{PF}_6$ is equivalent to the one in $[\text{Re}_2(\text{tbn})_4\text{Cl}_2]\text{Cl}$ (i.e., Re–Re = 2.2589(14) Å). The only substantive difference between $[\text{Re}_2(\text{tbn})_4\text{Cl}_2]\text{PF}_6$ and $[\text{Re}_2(\text{tbn})_4\text{Cl}_2]\text{Cl}$ is the presence of the uncoordinated anion.

The compound $[\text{Re}_2(\text{hpp})_4(\text{O}_3\text{SCF}_3)_2](\text{O}_3\text{SCF}_3)$ has a paddlewheel structure containing four equatorial hpp ligands and two axially coordinated triflate anions. The Re–Re distance (i.e., 2.1804(8) Å) is shorter by ~ 0.08 Å than the ones in $[\text{Re}_2(\text{tbn})_4\text{Cl}_2]\text{PF}_6$ and $[\text{Re}_2(\text{tbn})_4\text{Cl}_2]\text{Cl}$, but slightly longer than that the one in $\text{Re}_2(\text{hpp})_4(\text{O}_3\text{SCF}_3)_2$ (i.e., 2.1562(7) Å) which has the shortest Re–Re distance known. The increase of the metal–metal separation in Re_2^{7+} relative to the one

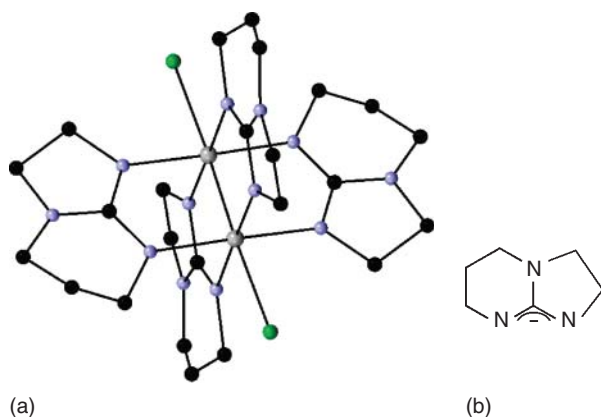


Figure 7.35 Ball and stick representation of the $\text{Re}_2(\text{tbn})_4\text{Cl}_2^+$ cation (a) and the tbn anion (b).

in Re_2^{6+} is consistent with the removal of an electron from the δ orbital. The shortening in the Re–Re distance in the hpp compounds, relative to those in the tbn compounds is due to two major factors: one of them is the increase in bite angle going from hpp to tbn, which pulls the rhenium atoms apart. The second factor is related to the p-type nonbonding electrons in the chlorine atoms that interact with the electrons in the π orbitals of the Re_2^{7+} unit. The short Re–Re distances for $[\text{Re}_2(\text{hpp})_4(\text{O}_3\text{SCF}_3)_2](\text{O}_3\text{SCF}_3)$ and its precursor, can be attributed to a decrease in electron density that is donated by the axial ligands. Variable-frequency, variable-temperature EPR studies of $[\text{Re}_2(\text{tbn})_4\text{Cl}_2]\text{PF}_6$ and $[\text{Re}_2(\text{hpp})_4(\text{O}_3\text{SCF}_3)_2](\text{O}_3\text{SCF}_3)$ in the solid and in frozen CH_2Cl_2 solution show the presence of one unpaired electron in a metal-based orbital consistent with the $\sigma^2\pi^4\delta^1$ electronic configuration.

The compound $[\text{Re}_2(\text{hpp})_4\text{F}](\text{TFPB})_2$ have been obtained from the reaction of $\text{Re}_2(\text{hpp})_4\text{Cl}_2$ with potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate in CH_2Cl_2 /diethylether mixture followed by the reaction of the resulting solid $[\text{Re}_2(\text{hpp})_4](\text{TFPB})_2$ with $[\text{Ag}(\text{CH}_3\text{CN})_2]\text{PF}_6$ in CH_2Cl_2 [80]. The compound exhibits the paddlewheel geometry and consists of a Re_2^{7+} unit coordinated to hpp equatorial ligands and fluoride axial ligands. The Re–Re distance in $[\text{Re}_2(\text{hpp})_4\text{F}](\text{TFPB})_2$ (i.e., 2.1874(3) Å) is significantly shorter than those in related Re_2^{7+} species (Table 7.11). The difference is attributable to the presence of only one axial ligand (disordered over two positions). The electronic spectra of $[\text{Re}_2(\text{hpp})_4\text{F}](\text{TFPB})_2$ in CH_2Cl_2 exhibits two bands at 424 nm ($\epsilon = 21\,200\text{ M}^{-1}\text{ cm}^{-1}$) and 597 nm ($\epsilon = 21\,900\text{ M}^{-1}\text{ cm}^{-1}$).

7.3.4

Complexes with the Re_2^{6+} Core

7.3.4.1 Compounds with No Bridging Ligands

Seven compounds containing the Re_2^{6+} unit with no bridging ligands have been reported. These include salts of $\text{Re}_2\text{Cl}_8^{2-}$, $(\text{Et}_3\text{NH})_2\text{Re}_2(\text{Cl}_4\text{Cat})_4$, and compounds with a Re_2^{6+} core coordinated by polyoxometalate (POM) ligands. Four new $\text{Re}_2\text{Cl}_8^{2-}$ salts of the radical cations of tetramethyltetraselenafulvalene (TMTSF), tetramethyltetratrathiafulvalene (TMTTF), bis-ethylenedithiotetrathiafulvalene (ET) and o-4,40-dimethyltetratrathiafulvalene (o- Me_2TTF) were reported: $(\text{TMTTF})_3\text{Re}_2\text{Cl}_8 \cdot 2\text{CH}_3\text{CN}$, $(\text{TMTSF})_5[\text{Re}_2\text{Cl}_8]_2 \cdot 6\text{CH}_2\text{Cl}_2$, $(\text{ET})_2\text{Re}_2\text{Cl}_8$, and $(\text{o-Me}_2\text{TTF})_2\text{Re}_2\text{Cl}_8$ [81]. These salts were prepared by the electrochemical oxidation of the neutral donors (ET), (TMTTF), (TMTSF), and (o- Me_2TTF) in the presence of $(n\text{-Bu}_4\text{N})\text{Re}_2\text{Cl}_8$ in either acetonitrile, dichloromethane, or benzonitrile. The structures of these salts consist of one-dimensional stacks of the donor molecules interleaved with $\text{Re}_2\text{Cl}_8^{2-}$ anions and interstitial solvent molecules. In the salts, the $\text{Re}_2\text{Cl}_8^{2-}$ anion

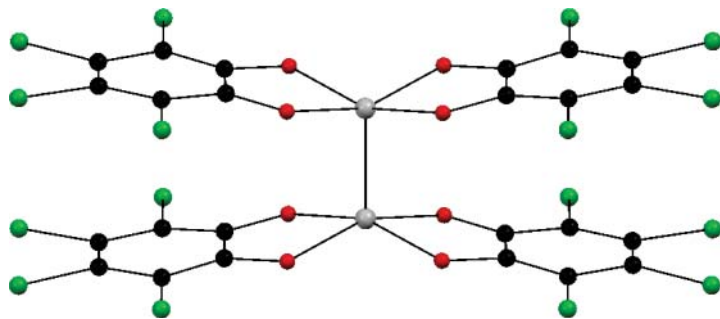


Figure 7.36 Ball and stick representation of the $\text{Re}_2\text{Cl}_8^{2-}$ anion (left) and the $\text{Re}_2(\text{Cl}_4\text{Cat})_4^{2-}$ anion (right).

exhibits the familiar eclipsed geometry. The Re–Re separation varies between 2.2249(4) Å for $(o\text{-Me}_2\text{TTF})_2\text{Re}_2\text{Cl}_8$ and 2.257(16) Å for $(\text{TMTTF})_3\text{Re}_2\text{Cl}_8 \cdot 2\text{CH}_3\text{CN}$. The electrical conductivities of solids $(\text{TMTTF})_3\text{Re}_2\text{Cl}_8 \cdot 2\text{CH}_3\text{CN}$ and $(\text{ET})_2\text{Re}_2\text{Cl}_8$ have been measured; both salts exhibit semiconducting behavior with room temperature conductivities of 2.2×10^{-4} and $3.0 \times 10^{-4} \text{ S cm}^{-1}$, respectively.

The compound $(\text{Et}_3\text{NH})_2\text{Re}_2(\text{Cl}_4\text{Cat})_4$ was prepared from the reaction of tetrachlorocatechol with $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ in THF, followed by the addition of triethylamine [82]. The structure of the $\text{Re}_2(\text{Cl}_4\text{Cat})_4^{2-}$ anion (Figure 7.36) consists of a Re_2^{6+} unit (Re–Re = 2.2067(7) Å) coordinated to four tetrachlorocatechol ligands. The planar tetrachlorocatechol ligands are eclipsed and bent away from the ReO_4 plane at each metal. The distances between two planar tetrachlorocatechol are in the range 3.00–3.75 Å. Distortions of the planar structure at the Re atoms are probably due to steric interactions between the tetrachlorocatechol ligands. Within $\text{Re}_2(\text{Cl}_4\text{Cat})_4^{2-}$, the average Re–O bond distances are 1.996[8] Å.

The compounds $\text{H}_2(\text{Bu}_4\text{N})_6[\text{Re}_2(\text{PW}_{11}\text{O}_{39})_2] \cdot 1.5\text{MeCN}$ and $\text{H}_2(\text{Bu}_4\text{N})_6[\text{Re}_2(\text{PW}_{11}\text{O}_{39})_2] \cdot 1.6\text{H}_2\text{O}$ were obtained from the reaction of $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ with the lacunary Keggin complex $[\text{PW}_{11}\text{O}_{39}]^{7-}$ in water [83]. Recrystallization of the product in acetonitrile produced $\text{H}_2(\text{Bu}_4\text{N})_6[\text{Re}_2(\text{PW}_{11}\text{O}_{39})_2] \cdot 1.5\text{MeCN}$, while $\text{H}_2(\text{Bu}_4\text{N})_6[\text{Re}_2(\text{PW}_{11}\text{O}_{39})_2] \cdot 1.6\text{H}_2\text{O}$ was obtained from water. The structure of the $[\text{Re}_2(\text{PW}_{11}\text{O}_{39})_2]^{8-}$ anion (Figure 7.37) contains a Re_2^{6+} unit coordinated to two Keggin-type $(\text{PW}_{11}\text{O}_{39})^{7-}$ subunits. The Re–Re separation is 2.2731(9) Å in $\text{H}_2(\text{Bu}_4\text{N})_6[\text{Re}_2(\text{PW}_{11}\text{O}_{39})_2] \cdot 1.5\text{MeCN}$ and 2.269(1) Å in $\text{H}_2(\text{Bu}_4\text{N})_6[\text{Re}_2(\text{PW}_{11}\text{O}_{39})_2] \cdot 1.6\text{H}_2\text{O}$. Each $(\text{PW}_{11}\text{O}_{39})^{7-}$ unit coordinates the Re atom in a pentadentate fashion and four short (i.e., 1.903(9), 1.905(9), 1.926(8), 1.931(6) Å), and one long (i.e., 2.436(8) Å) Re–O distances are observed. Electrospray ionization mass spectrometry (ESI-MS) studies of $\text{H}_2(\text{Bu}_4\text{N})_6[\text{Re}_2(\text{PW}_{11}\text{O}_{39})_2] \cdot 1.5\text{MeCN}$ in acetonitrile show that the dimeric moiety retains its integrity in solution. Multiple peaks observed in the negative ESI-MS spectrum were assigned to the $\{(\text{Bu}_4\text{N})_{5-n}[\text{Re}_2(\text{PW}_{11}\text{O}_{39})_2(\text{Hn})]\}^{3-}$ ($n = 1–3$) anions.

7.3.4.2 Compounds with (O, O) Bridging Ligands

Five compounds containing the Re_2^{6+} unit coordinated with (O, O) bridging ligands have been reported: *cis*- $[\text{Re}_2(\text{GABA})_2\text{Cl}_5(\text{H}_2\text{O})]\text{Cl} \cdot 2\text{H}_2\text{O}$, $(n\text{-Bu}_4\text{N})\text{Re}_2(\text{O}_2\text{C}(\text{CO})\text{Et})\text{Cl}_6$, $\text{Re}_2(\text{esp})_2\text{Cl}_2$, $[\text{Re}_2(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$, and *cis*- $\text{Re}_2[(\text{CH}_3)_3\text{CCOO}]_2\text{Cl}_4 \cdot 2\text{DMSO}$.

The *cis*- $[\text{Re}_2(\text{GABA})_2\text{Cl}_5(\text{H}_2\text{O})]\text{Cl} \cdot 2\text{H}_2\text{O}$ complex, which contains γ -aminobutyrate (GABA) ligands, was prepared after treatment of $[\text{GABA}]\text{Re}_2\text{Cl}_8$ in acetonitrile [84]. The structure of the $\text{Re}_2(\text{GABA})_2\text{Cl}_5(\text{H}_2\text{O})^+$ cation (Figure 7.38) consists of a Re_2^{6+} core (Re–Re = 2.2437(3) Å) bridged by two γ -aminobutyrate ligands in *cis*-positions, four equatorial Cl ligands (Re–Cleq = 2.3048(13)–2.3233(12) Å), one axial H_2O molecule (Re–Oax = 2.363(3) Å) and one axial Cl ligand (Re–Clax = 2.6735(12) Å). The UV–visible spectrum of the complex in methanol reveals three bands at: $15\,870 \text{ cm}^{-1}$ ($\epsilon = 725 \text{ M}^{-1} \text{ cm}^{-1}$), $21\,500 \text{ cm}^{-1}$ ($\epsilon = 120 \text{ M}^{-1} \text{ cm}^{-1}$) and $31\,920 \text{ cm}^{-1}$ ($\epsilon = 3610 \text{ M}^{-1} \text{ cm}^{-1}$). The band at $15\,870 \text{ cm}^{-1}$ was attributed to the $\delta \rightarrow \delta^*$ transition. The *cis*- $[\text{Re}_2(\text{GABA})_2\text{Cl}_5$

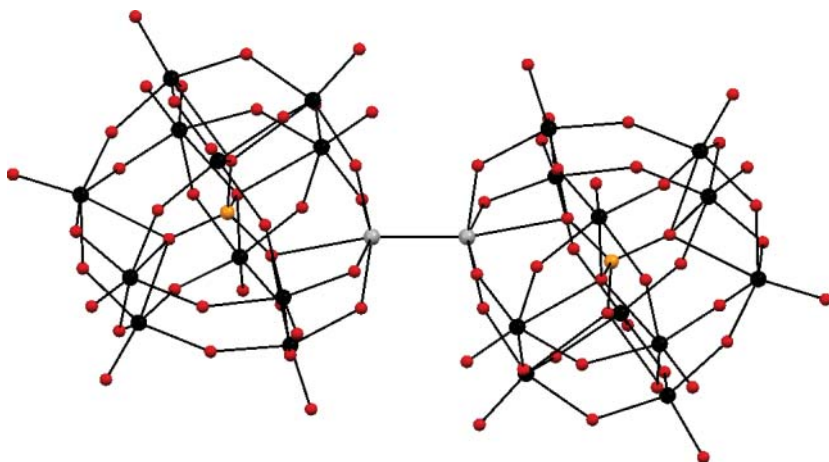


Figure 7.37 Ball and stick representation of the $[\text{Re}_2(\text{PW}_{11}\text{O}_{39})_2]^{8-}$ anion.

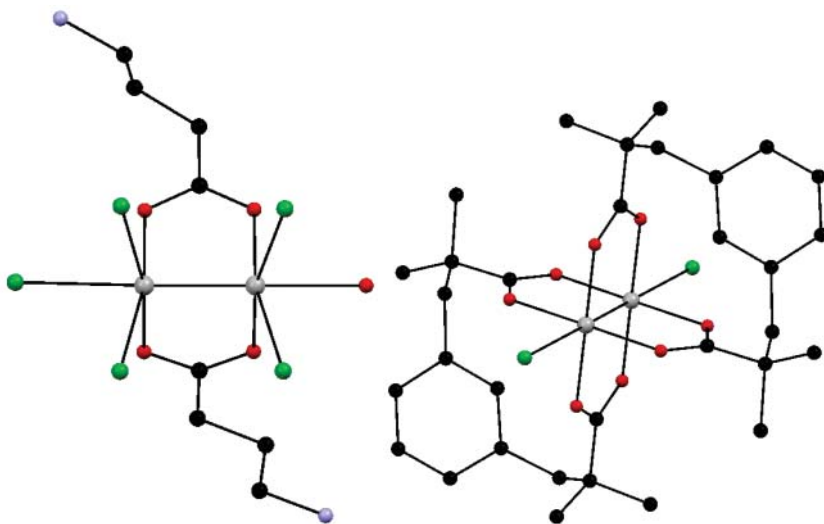


Figure 7.38 Ball and stick representations of the $\text{Re}_2(\text{GABA})_2\text{Cl}_5(\text{H}_2\text{O})^+$ cation (a) and $\text{Re}_2(\text{esp})_2\text{Cl}_2$ (b).

$(\text{H}_2\text{O})\text{Cl}\cdot 2\text{H}_2\text{O}$ complex exhibits antitumor properties. The introduction of the compound in rats inoculated by tumor carcinoma Guerink cells inhibited the tumor growth by about 60% and led to the stabilization of red blood cells in the tumor-bearing organisms.

The $\text{Re}_2(\text{esp})_2\text{Cl}_2$ was prepared from the reaction of $\text{Re}_2(\text{OAc})_4\text{Cl}_2$ and tetramethyl-1,3-benzenedipropionic acid (H_2esp) under reflux conditions [85]. The structure of $\text{Re}_2(\text{esp})_2\text{Cl}_2$ consists of a Re_2^{6+} ($\text{Re}-\text{Re} = 2.2304(6) \text{ \AA}$) unit coordinated to two axial Cl ligands ($\text{Re}-\text{Cl} = 2.447(3) \text{ \AA}$) and two esp ligands (Figure 7.38). The asymmetric unit contains one half of the molecule with an inversion center that bisects the Re_2^{6+} unit. The $\text{Re}-\text{O}$ distances are in the range $2.010(6) - 2.043(6) \text{ \AA}$. The two esp ligands are coordinated in a strapped arrangement, a geometry already observed in $\text{Rh}_2(\text{esp})_2(\text{acetone})_2$ [86]. The redox behavior of $\text{Re}_2(\text{esp})_2\text{Cl}_2$ was studied by cyclic voltammetry in $\text{THF}/(n\text{-Bu}_4\text{N})\text{PF}_6$ solution. The cyclic voltammogram exhibits a single reversible reduction wave at -0.35 V versus (Ag/AgCl), which corresponds to the process $\text{Re}_2^{6+} \rightarrow \text{Re}_2^{5+}$. The redox potentials for rhenium compounds containing a Re_2^{6+} unit are summarized in Table 7.12.

Table 7.12 Structural data for rhenium compounds containing the Re_2^{6+} unit.

Compounds	Re–Re (Å)
Compounds with no bridging ligands	
$(\text{TMTTF})_3\text{Re}_2\text{Cl}_8 \cdot 2\text{CH}_3\text{CN}$	2.2253(8)
$(\text{TMTSF})_5[\text{Re}_2\text{Cl}_8]_2 \cdot 6\text{CH}_2\text{Cl}_2$	2.257(16)
$(\text{Et})_2\text{Re}_2\text{Cl}_8$	2.231(19)
$(o\text{-Me}_2\text{TTF})_2\text{Re}_2\text{Cl}_8$	2.2249(4)
$(\text{Et}_3\text{NH})_2\text{Re}_2(\text{Cl}_4\text{Cat})_4$	2.2067(7)
$\text{H}_2(\text{Bu}_4\text{N})_6[\text{Re}_2(\text{PW}_{11}\text{O}_{39})_2] \cdot 1.5\text{MeCN}$	2.2731(9)
$\text{H}_2(\text{Bu}_4\text{N})_6[\text{Re}_2(\text{PW}_{11}\text{O}_{39})_2] \cdot 1.6\text{H}_2\text{O}$	2.269(1)
Compounds with (O, O) bridging ligands	
<i>cis</i> - $[\text{Re}_2(\text{GABA})_2\text{Cl}_5(\text{H}_2\text{O})]\text{Cl} \cdot 2\text{H}_2\text{O}$	2.2437(3)
<i>(n</i> -Bu ₄ N) $\text{Re}_2(\text{O}_2\text{C}(\text{CO})\text{Et})\text{Cl}_6$	2.2263(3)
$\text{Re}_2(\text{esp})_2\text{Cl}_2$	2.2304(6)
$[\text{Re}_2(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$	2.2168(8)
<i>cis</i> - $\text{Re}_2[(\text{CH}_3)_3\text{CCOO}]_2\text{Cl}_4 \cdot 2\text{DMSO}$	2.2532(2)
Compounds with (O, O) and (N, N) bridging ligands	
$\text{Re}_2(\text{OAc})_2(\text{DmAniF})_2\text{Cl}_2$	2.2468(7)
$[\text{Re}_2(\text{TPG})_3(\text{OAc})\text{Cl}]\text{Cl}$	2.1967(5)
Compounds with (N, N) bridging ligands	
$\text{Re}_2(\text{tbn})_4\text{Cl}_2$	2.216(2)
$\text{Re}_2(\text{tbo})_4\text{Cl}_2$	2.2901(11)
$\text{Re}_2(\text{tbn})_4(\text{SO}_3\text{CF}_3)_2$	2.1900(16)
$\text{Re}_2(\text{tbo})_4(\text{SO}_3\text{CF}_3)_2$	2.2384(13)
$\text{Re}_2(3,5\text{-(CH}_3)_2\text{ap})_4\text{Cl}_2$	2.2214(4)
$\text{Re}_2(\text{ap})_4\text{Cl}_2$	2.2216(6)
$\text{Re}_2(3\text{-Clap})_4\text{Cl}_2$	2.2262(11)
$\text{Re}_2(3,5\text{-Cl}_2\text{ap})_4\text{Cl}_2$	2.2252(6)
$\text{Re}_2(\text{DCyBA})_2\text{Cl}_4$	2.1679(6)
$\text{Re}_2(\text{DmAniF})_2\text{Cl}_4$	2.1804(5)
$[\text{Re}_2(\text{DMBA})_4(\text{WO}_4)]\infty$	2.207(1), 2.202(1), 2.206(1)
$[\text{Re}_2(\text{DMBA})_4(1,4\text{-(O}_2\text{C)}_2\text{C}_6\text{H}_4)]\infty$	2.1944(6)
$\text{Re}_2(\text{hpp})_4(\text{CF}_3\text{SO}_3)_2$	2.1562(7)
$\text{Re}_2(\text{hpp})_4(\text{CF}_3\text{CO}_2)_2$	2.1711(5)
$\text{Re}_2(\text{hpp})_4\text{F}_2$	2.1959(4)

The complex $(n\text{-Bu}_4\text{N})\text{Re}_2(\text{O}_2\text{C}(\text{CO})\text{Et})\text{Cl}_6$ was obtained from the reaction of $(\text{TBA})_2\text{Re}_2\text{Cl}_8$ with molten 2-oxobutanoic acid [87]. The complex $(\text{TBA})\text{Re}_2(\text{O}_2\text{C}(\text{CO})\text{Et})\text{Cl}_6$ and the already known $(\text{TBA})\text{Re}_2(\text{O}_2\text{CCF}_3)\text{Cl}_6$ are the only examples of monocarboxylato-hexahalido compounds containing a Re_2^{6+} unit [88]. The $\text{Re}_2(\text{O}_2\text{C}(\text{CO})\text{Et})\text{Cl}_6^-$ anion consists of a Re_2^{6+} unit bridged by one 2-oxobutanoato ligand and coordinated to six chloro ligands in an eclipsed configuration ($\text{Cl}\cdots\text{Cl} = 3.30\text{--}3.36\text{ \AA}$) (Figure 7.39). The Re–Re separation (i.e., 2.2263(3) Å) is characteristic of a quadruple bond. Each $\text{Re}_2(\text{O}_2\text{C}(\text{CO})\text{Et})\text{Cl}_6^-$ anion is linked via two $\text{Re}\cdots\text{Cl}$ contacts (i.e., 2.897(2) Å) to dimeric $\{[\text{Re}_2(\text{O}_2\text{C}(\text{CO})\text{Et})\text{Cl}_6]_2\}^{2-}$. In the crystal, the dinuclear complexes are separated from each other by $(n\text{-Bu}_4\text{N})^+$ cations. The compound is air stable, it is insoluble in diethyl ether, and decomposes at about 170 °C without melting.

The compound $[\text{Re}_2(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ was synthesized from the reaction of $\text{Re}_2(\text{O}_2\text{C}_3\text{H}_5)_4\text{Cl}_2$ with mixture of phosphoric acid, propanoic acid, and water at 100–110 °C under an inert atmosphere [89]. The $\text{Re}_2(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_2(\text{H}_2\text{O})_2$ complex exhibits the paddlewheel motif

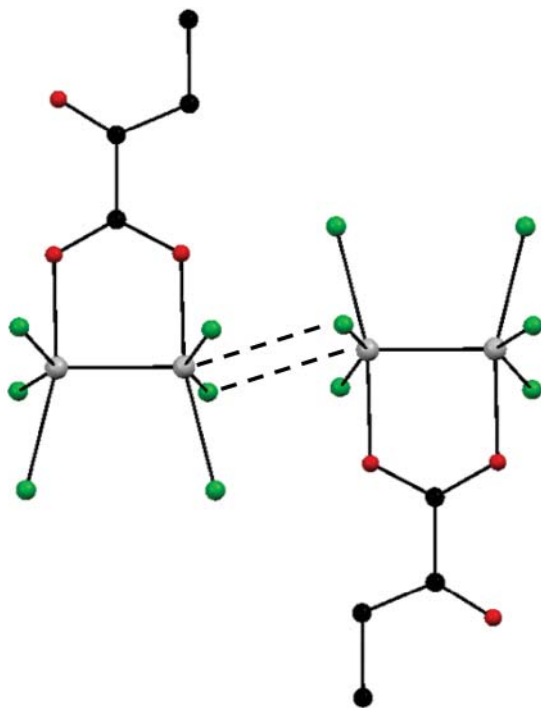


Figure 7.39 Ball and stick representation of two units of the $\text{Re}_2(\text{O}_2\text{C}(\text{CO})\text{Et})\text{Cl}_6^-$ anion. $\text{Re}\cdots\text{Cl}$ contacts are represented in dashed line.

and consists of a Re_2^{6+} unit (i.e., $2.2168(8) \text{ \AA}$) coordinated to four bidentate bridging phosphate ligands in *trans* positions and two axial water molecules (Figure 7.40). The $\text{Re}-\text{O}_{\text{ax}}$ distance (i.e., $2.299(6) \text{ \AA}$) is significantly longer than the $\text{Re}-\text{O}_{\text{eq}}$ distances (i.e., $2.000(6) - 2.026(7) \text{ \AA}$). The electronic absorption spectrum of the complex in aqueous solution exhibits a band at $15\,625 \text{ cm}^{-1}$, which is attributed to the $\delta \rightarrow \delta^*$ transition. The thermal stability of $[\text{Re}_2(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ was studied by thermogravimetric analysis; the loss of the four crystallization water molecules occurred at 196°C , while the loss of the two water molecules coordinated to the Re_2^{6+} unit occurred at 240°C .

The compound $\text{cis-Re}_2[(\text{CH}_3)_3\text{CCOO}]_2\text{Cl}_4 \cdot 2\text{DMSO}$ was obtained from the reaction of $(n\text{-NBu}_4)_2\text{Re}_2\text{Cl}_8$ with pivalic acid in methanol under inert atmosphere followed by treatment of the solution with DMSO [90]. The compound contains a Re_2^{6+} unit ($2.2532(2) \text{ \AA}$) coordinated to four chloride ligands, two bridging pivalate ligands oriented in *cis*-position and two weakly bonded axial DMSO ligands (Figure 7.40). The orientation of the coordinated DMSO ligands induces short intramolecular $\text{S}\cdots\text{O}$ contacts (i.e., $2.916(2)$ and $2.923(3) \text{ \AA}$). The compound exhibits antitumor properties, but its activity is accompanied by the significant elimination of red blood cells and kidney damage. The combination of $\text{cis-Re}_2[(\text{CH}_3)_3\text{CCOO}]_2\text{Cl}_4 \cdot 2\text{DMSO}$ with *cis*-platin led to the suppression or complete elimination of carcinoma Guerink cells. Electronic absorption titrations, electrophoretic mobility, and viscosity measurements indicate that the compound interacts strongly with DNA.

7.3.4.3 Compounds with (O, O) and (N, N) Bridging Ligands

Two compounds containing a Re_2^{6+} unit coordinated to (N, N) and (O, O) bridging ligands have been reported: $\text{cis-Re}_2(\text{OAc})_2(\text{DmAniF})_2\text{Cl}_2$ and $[\text{Re}_2(\text{TPG})_3(\text{O}_2\text{CCH}_3)\text{Cl}]\text{Cl}$.

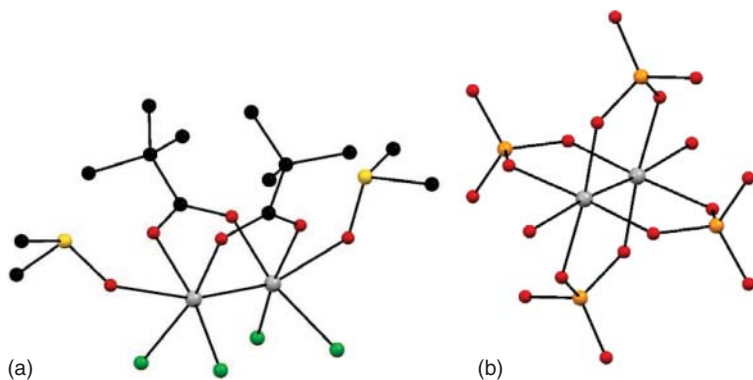


Figure 7.40 Ball and stick representation of *cis*-Re₂[(CH₃)₃CCOO]₂Cl₄·2DMSO (a) and Re₂(HPO₄)₂(H₂PO₄)₂(H₂O)₂ (b).

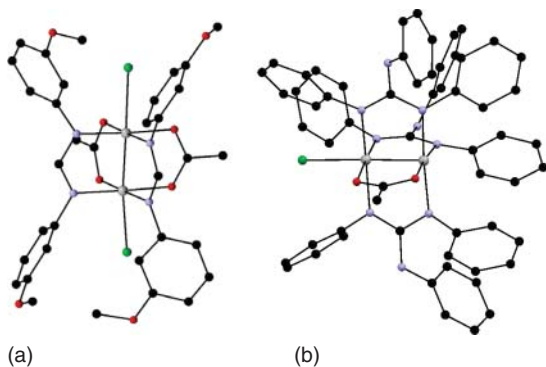


Figure 7.41 Ball and stick representation of *cis*-Re₂(OAc)₂(DmAniF)₂Cl₂ (a) and the Re₂(TPG)₃(OAc)Cl⁺ cation (b).

The compound Re₂(OAc)₂(DmAniF)₂Cl₂ was obtained from the reaction of *cis*-Re₂(OAc)₂Cl₄ with di(3-methoxyphenyl)formamidine (HDmAniF) under reflux conditions [85]. The compound exhibits the paddlewheel geometry and consists of a Re₂⁶⁺ unit coordinated to two axial Cl ligands, two acetates, and two DmAniF ligands in *cis*-positions (Figure 7.41). The Re–Re separation (i.e., 2.2468(7) Å) is slightly longer than the one in Re₂(OAc)₄Cl₂ (i.e., 2.2240(5) Å) [50]. The average Re–N separation is about 2.05 Å. The average Re–O distance (about 2.07 Å) is slightly longer than the one in Re₂(OAc)₂Cl₄ (i.e., 2.02 Å), while the Re–Cl distance (i.e., 2.502(4) Å) is slightly shorter than in Re₂(OAc)₂Cl₄ (i.e., 2.521(3) Å). The redox behavior of Re₂(OAc)₂(DmAniF)₂Cl₂ was probed by cyclic voltammetry in THF/(*n*-Bu₄N)PF₆ solution. The cyclic voltammogram exhibits a reversible reduction wave at –0.87 V versus (Ag/AgCl) and an irreversible reduction at –1.78 V versus (Ag/AgCl).

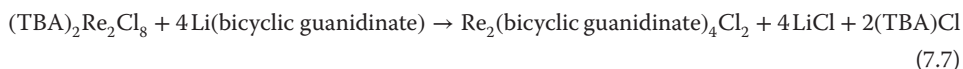
The compound [Re₂(TPG)₃(O₂CCH₃)Cl]Cl was obtained after the reaction of Re₂(OAc)₂Cl₄ with 1,2,3-triphenylguanidine (TBG) in methanol under reflux conditions [91]. The Re₂(TPG)₃(O₂CCH₃)Cl⁺ cation adopts the paddlewheel structure and consists of a Re₂⁶⁺ unit (Re–Re = 2.1967(5) Å) coordinated to three TPG ligands and one axial chlorine atom (Figure 7.41). One axial position on the Re atoms is vacant and the Re–O and Re–N distances for the axially non-coordinated Re atom (i.e., 2.067(4) and 2.032(5) Å) are longer than the one for the axially coordinated Re atom (i.e., 2.119(4) and 2.054(4) Å). In the structure, the three NHPg groups are arranged such that the phenyl rings are pointed away from the axially coordinated chloride side of the molecule. The average Re–O distance (about 2.09 Å) is longer than the one in Re₂(OAc)₂Cl₄ (i.e., 2.02 Å), while the Re–Cl distance

(2.3946(14) Å) is shorter than in $\text{Re}_2(\text{OAc})_2\text{Cl}_4$. The compound is soluble in dichloromethane, acetone, acetonitrile, and tetrahydrofuran. In contrast to $[\text{H}_2\text{TPG}]\text{ReO}_4$, which exhibits luminescence properties in solution, $[\text{Re}_2(\text{TPG})_3(\text{O}_2\text{CCH}_3)\text{Cl}]\text{Cl}$ does not show any emission activity.

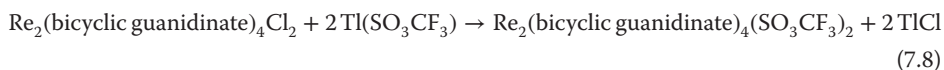
7.3.4.4 Compounds with (N, N) Bridging Ligands

Compounds coordinated to (N, N) bridging ligands are the most numerous among complexes with a Re_2^{6+} unit reported in the period 2005–2014. Fifteen complexes have been reported: those include dinuclear complexes coordinated to bicyclic guanidinate ligands, hpp ligands, anilopyridinate derivatives, and one-dimensional polymers containing Re_2^{6+} units coordinated to dimethylbenzaminate (DMBA) ligands.

Four compounds with equatorial bicyclic guanidinate ligands have been reported: $\text{Re}_2(\text{tbn})_4\text{Cl}_2$, $\text{Re}_2(\text{tbn})_4(\text{SO}_3\text{CF}_3)_2$, $\text{Re}_2(\text{tbo})_4\text{Cl}_2$, $\text{Re}_2(\text{tbo})_4(\text{SO}_3\text{CF}_3)_2$ [92]. The tbn anion is presented in Figure 7.35 the ball and stick representation of the $\text{Re}_2(\text{tbn})_4\text{Cl}_2^+$ cation (a) and the tbn anion (b) and the tbo anion is an analogous species with two five-membered rings (1,4,6-triazabicyclo[3.3.0]oct-4-ene). The compounds $\text{Re}_2(\text{tbn})_4\text{Cl}_2$ and $\text{Re}_2(\text{tbo})_4\text{Cl}_2$ were obtained from the reaction of $(n\text{-NBu}_4)_2\text{Re}_2\text{Cl}_8$ with the lithium salt of the ligand in acetonitrile (Eq. (7.7)).



The compounds $\text{Re}_2(\text{tbn})_4(\text{SO}_3\text{CF}_3)_2$ and $\text{Re}_2(\text{tbo})_4(\text{SO}_3\text{CF}_3)_2$ were respectively synthesized from the reaction of $\text{Re}_2(\text{tbn})_4\text{Cl}_2$ and $\text{Re}_2(\text{tbo})_4\text{Cl}_2$ with $\text{Ti}(\text{SO}_3\text{CF}_3)_3$ in CH_2Cl_2 (Eq. (7.8)).



All four bicyclic guanidinate complexes exhibit the paddlewheel motif with four equatorial bicyclic guanidinate ligands and two axially coordinated anions. The Re–Re separation in $\text{Re}_2(\text{tbo})_4\text{Cl}_2$ (i.e., 2.2901(11) Å) is the longest known for a quadruply bonded dirhenium paddlewheel species. The $\text{Re}_2(\text{tbn})_4\text{Cl}_2$ and $\text{Re}_2(\text{tbo})_4\text{Cl}_2$ complexes are presented in Figure 7.42. Replacement of the axial chloride ligands by triflate anions leads to a significant decrease of the Re–Re separations. The Re–Re separations decrease from 2.216(2) Å in $\text{Re}_2(\text{tbn})_4\text{Cl}_2$ to 2.1900(16) Å in $\text{Re}_2(\text{tbn})_4(\text{SO}_3\text{CF}_3)_2$, and for the tbo analog, it decreases from 2.2901(11) Å in $\text{Re}_2(\text{tbo})_4\text{Cl}_2$ to 2.2384(13) Å in $\text{Re}_2(\text{tbo})_4(\text{SO}_3\text{CF}_3)_2$. A comparison with the hpp compounds reveals a similar trend with the metal–metal distances decreasing from 2.189(2) Å in $\text{Re}_2(\text{hpp})_4\text{Cl}_2$ to 2.1562(7) Å in $\text{Re}_2(\text{hpp})_4(\text{SO}_3\text{CF}_3)_2$. The Re–Re distance in $\text{Re}_2(\text{hpp})_4(\text{SO}_3\text{CF}_3)_2$ is the shortest distance reported between rhenium atoms in a quadruple bonded unit. The Re–Re separations for the triflate species are shorter than for the chloride analogs; this is primarily due to a destabilization of the π bonds of the Re_2^{6+} unit by the Cl ligand.

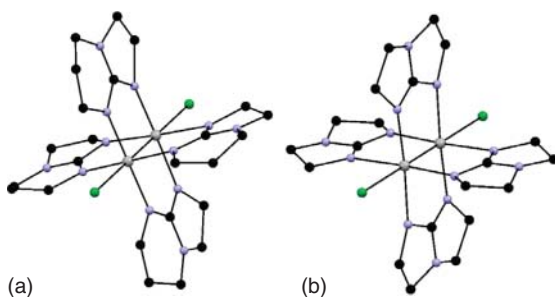


Figure 7.42 Ball and stick representation of $\text{Re}_2(\text{tbn})_4\text{Cl}_2$ (a) and $\text{Re}_2(\text{tbo})_4\text{Cl}_2$ (b).

Analysis of the Re–X axial distances ($X = \text{Cl}$, triflate) for the hpp, tbn, and tbo system was performed. For the chlorine compounds, results show that the Re–Cl distances follow the trend: hpp (2.749(5) Å) > tbn (2.645(7) Å) > tbo (2.566(2) Å); a similar trend was observed for the Re–O distances in the triflate compounds: hpp (2.484(5) Å) > tbn (2.398(8) Å) > tbo (2.291(10) Å). The electronic spectra of the complexes were recorded in dichloromethane, the lowest absorption band ($\delta \rightarrow \delta^*$ transition) is located at 567 nm for $\text{Re}_2(\text{tbn})_4\text{Cl}_2$, 569 nm for $\text{Re}_2(\text{tbn})_4(\text{SO}_3\text{CF}_3)_2$, 545 nm for $\text{Re}_2(\text{tbo})_4\text{Cl}_2$ and 559 nm for $\text{Re}_2(\text{tbo})_4(\text{SO}_3\text{CF}_3)_2$. Electrochemical measurements show two redox waves for each set of compounds corresponding to the $\text{Re}_2^{6+} \rightarrow \text{Re}_2^{7+}$ and $\text{Re}_2^{7+} \rightarrow \text{Re}_2^{8+}$ processes. The redox processes are affected by the bite angle of the guanidinate ligand as well as the ability of the axial ligands to interact with the π orbitals of the dirhenium unit. For $\text{Re}_2(\text{tbn})_4\text{Cl}_2$ and $\text{Re}_2(\text{tbo})_4\text{Cl}_2$, the first redox couples occur at 0.146 and 0.487 V, respectively, while for $\text{Re}_2(\text{tbn})_4(\text{SO}_3\text{CF}_3)_2$ and $\text{Re}_2(\text{tbo})_4(\text{SO}_3\text{CF}_3)_2$ these are at 0.430 and 0.698 V, respectively (Table 7.12).

Five compounds coordinated to anilopyridinate derivatives were reported: $\text{Re}_2(3,5\text{-(CH}_3)_2\text{ap})_4\text{Cl}_2$, $\text{Re}_2(\text{ap})_4\text{Cl}_2$, $\text{Re}_2(3\text{-MeOap})_4\text{Cl}_2$, $\text{Re}_2(3\text{-Clap})_4\text{Cl}_2$, and $\text{Re}_2(3,5\text{-Cl}_2\text{ap})_4\text{Cl}_2$ [93]. The ligands 3,5-(CH_3)₂ap, ap, 3-MeOap, 3-Clap, and 3,5- Cl_2 ap are respectively 2-(3,5-dimethylanilino)pyridinate, 2-anilopyridinate, 2-(3-methoxyanilino)pyridinate, 2-(3-chloroanilino)pyridinate and 2-(3,5-dichloroanilino)pyridinate. These complexes were prepared from the reaction of $\text{Re}_2(\text{OAc})_4\text{Cl}_2$ with the anilopyridine ligand in inert atmosphere under molten conditions.

The complexes exhibit the paddlewheel geometry with two axial chloride ligands and four 2-anilopyridinate ligands attached in the equatorial positions. The Re–Re separations are consistent with the presence of a Re–Re quadruple bond, and do not vary significantly in the series $\text{Re}_2(3,5\text{-(CH}_3)_2\text{ap})_4\text{Cl}_2$ (i.e., 2.2214(4) Å, Figure 7.43), $\text{Re}_2(\text{ap})_4\text{Cl}_2$ (i.e., 2.2216(6) and 2.2190(6) Å, Figure 7.43), $\text{Re}_2(3\text{-Clap})_4\text{Cl}_2$ (i.e., 2.2262(11) Å, Figure 7.44), and $\text{Re}_2(3,5\text{-Cl}_2\text{ap})_4\text{Cl}_2$ (i.e., 2.2252(6) Å, Figure 7.44). Similar invariance was also observed for the Re–Cl separations: 2.5804(14) Å in $\text{Re}_2(3,5\text{-(CH}_3)_2\text{ap})_4\text{Cl}_2$, 2.564(2)–2.586(2) Å in $\text{Re}_2(\text{ap})_4\text{Cl}_2$, and 2.549(4) Å in $\text{Re}_2(3\text{-Clap})_4\text{Cl}_2$. In $\text{Re}_2(3,5\text{-Cl}_2\text{ap})_4\text{Cl}_2$, one of the Re–Cl distance (i.e., 2.596(3) Å) is slightly longer than the other one

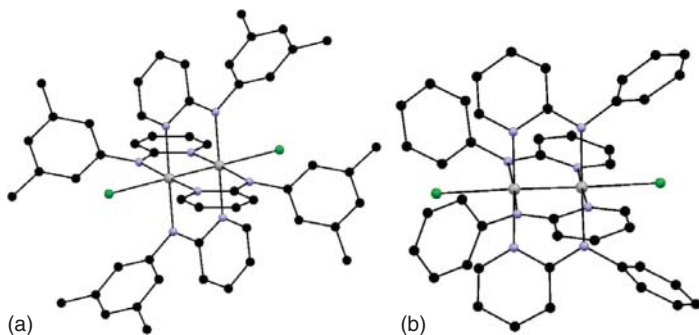


Figure 7.43 Ball and stick representation of $\text{Re}_2(3,5\text{-(CH}_3)_2\text{ap})_4\text{Cl}_2$ ((a) and $\text{Re}_2(\text{ap})_4\text{Cl}_2$ (b).

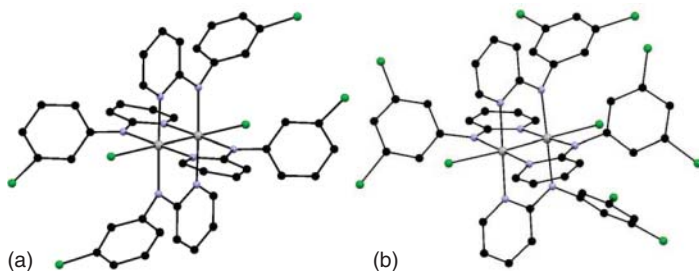


Figure 7.44 Ball and stick representation of $\text{Re}_2(3\text{-Clap})_4\text{Cl}_2$ (a) and $\text{Re}_2(3,5\text{-Cl}_2\text{ap})_4\text{Cl}_2$ (b).

Table 7.13 Redox potentials $E_{1/2}$ for rhenium compounds containing the Re_2^{6+} unit.

Compounds	$E_{1/2}$ (red1) ^{a)}	$E_{1/2}$ (ox1) ^{b)}	$E_{1/2}$ (ox2) ^{c)}
Compounds with (O, O) bridging ligands			
$\text{Re}_2(\text{esp})_2\text{Cl}_2^{\text{d)}$	−0.35 V	—	—
Compounds with (O, O) and (N, N) bridging ligands			
$\text{Re}_2(\text{OAc})_2(\text{DmAniF})_2\text{Cl}_2^{\text{d)}$	−0.87 V	—	—
Compounds with (N, N) bridging ligands			
$\text{Re}_2(\text{tbn})_4\text{Cl}_2^{\text{e)}$	—	0.148	0.716
$\text{Re}_2(\text{tbo})_4\text{Cl}_2^{\text{e)}$	—	0.430	0.812
$\text{Re}_2(\text{tbn})_4(\text{SO}_3\text{CF}_3)_2^{\text{e)}$	—	0.486	0.885
$\text{Re}_2(\text{tbo})_4(\text{SO}_3\text{CF}_3)_2^{\text{e)}$	—	0.698	0.992
$\text{Re}_2(3,5\text{-(CH}_3)_2\text{ap})_4\text{Cl}_2^{\text{e)}$	−1.077	0.802	1.152
$\text{Re}_2(\text{ap})_4\text{Cl}_2^{\text{e)}$	−1.108	0.860	1.260
$\text{Re}_2(3\text{--Clap})_4\text{Cl}_2^{\text{e)}$	−1.057	0.971	1.321
$\text{Re}_2(3,5\text{--Cl}_2\text{ap})_4\text{Cl}_2^{\text{e)}$	−1.030	1.102	1.405
$\text{Re}_2(\text{DCyBA})_2\text{Cl}_4^{\text{d)}$	−1.08 V	—	—
$\text{Re}_2(\text{DmAniF})_2\text{Cl}_4^{\text{d)}$	−0.69 V	—	—

Values are given in V versus/(Ag/AgCl).

a) $E_{1/2}$ (red1) corresponds to the reaction $\text{Re}_2^{6+} \rightarrow \text{Re}_2^{5+}$.

b) $E_{1/2}$ (ox1) corresponds to the reaction $\text{Re}_2^{6+} \rightarrow \text{Re}_2^{7+}$.

c) $E_{1/2}$ (ox2) corresponds to the reaction $\text{Re}_2^{7+} \rightarrow \text{Re}_2^{8+}$.

d) Performed in THF/(*n*-Bu₄N)PF₆ solution.

e) Performed in CH₂Cl₂/(*n*-Bu₄N)PF₆ solution.

(i.e., 2.522(3) Å). In those complexes, the Re–Nan (anilino nitrogen) separation is shorter than the Re–Np (pyridino nitrogen) one.

Electronic absorption spectra of the five compounds in CH₂Cl₂ are similar. For each compound, three bands are observed in the region of 350–620 nm. The lowest absorption band ($\delta \rightarrow \delta^*$ transition) is located at 615 nm for $\text{Re}_2(3,5\text{-(CH}_3)_2\text{ap})_4\text{Cl}_2$ and $\text{Re}_2(3,5\text{--Cl}_2\text{ap})_4\text{Cl}_2$, 611 nm for $\text{Re}_2(\text{ap})_4\text{Cl}_2$ and $\text{Re}_2(3\text{--MeOap})_4\text{Cl}_2$ and 614 nm for $\text{Re}_2(3\text{--Clap})_4\text{Cl}_2$. All five compounds display three quasi-reversible one electron waves: two oxidations ($\text{Re}_2^{6+} \rightarrow \text{Re}_2^{7+}$ and $\text{Re}_2^{7+} \rightarrow \text{Re}_2^{8+}$) and one reduction ($\text{Re}_2^{6+} \rightarrow \text{Re}_2^{5+}$) and their redox potentials (Table 7.13) correlate linearly with the Hammett constant of the aniline substituent.

The compounds $\text{Re}_2(\text{DCyBA})_2\text{Cl}_4$ and $\text{Re}_2(\text{DmAniF})_2\text{Cl}_4$ were respectively obtained from the reaction of $\text{Re}_2(\text{OAc})_4\text{Cl}_2$ and *N,N'*-dicyclohexylbenzamidine (HDCyBA) and from the reaction (*n*-Bu₄N)₂Re₂Cl₈ with *N,N'*-di(3-methoxyphenyl)formamidine (HDmAniF) in inert atmosphere under molten conditions [85]. Single crystals were obtained after recrystallization from CH₂Cl₂/hexane for $\text{Re}_2(\text{DCyBA})_2\text{Cl}_4$ and from THF/hexane for $\text{Re}_2(\text{DmAniF})_2\text{Cl}_4$. The structures of $\text{Re}_2(\text{DCyBA})_2\text{Cl}_4$ and $\text{Re}_2(\text{DmAniF})_2\text{Cl}_4$ consist of two bidentate bridging ligands in *trans*- positions and four chlorine ligands in equatorial positions (Figure 7.45). The relatively short Re–Re separations in $\text{Re}_2(\text{DCyBA})_2\text{Cl}_4$ and $\text{Re}_2(\text{DmAniF})_2\text{Cl}_4$ (i.e., 2.1679(6) and 2.1804(5) Å) are probably due to the absence of axial chloro ligands that donate electron density into the σ orbital and weaken the Re–Re quadruple bond. Compounds $\text{Re}_2(\text{DCyBA})_2\text{Cl}_4$ and $\text{Re}_2(\text{DmAniF})_2\text{Cl}_4$ contain four equatorial chloro ligands that could act as the entries for Re_2 -alkynyl species. The average Re–C_{leq} distances in $\text{Re}_2(\text{DCyBA})_2\text{Cl}_4$ and $\text{Re}_2(\text{DmAniF})_2\text{Cl}_4$ (i.e., 2.3318[25] and 2.3267[25] Å) are shorter than the Re–Cl_{ax} separation in $\text{Re}_2(\text{OAc})_2(\text{DmAniF})_2\text{Cl}_2$ (i.e., 2.5029(4) Å, *vide supra*). The redox behavior of $\text{Re}_2(\text{DCyBA})_2\text{Cl}_4$ and $\text{Re}_2(\text{DmAniF})_2\text{Cl}_4$ was probed by cyclic voltammetry in THF/(*n*-Bu₄N)PF₆ solution. The voltammogram of $\text{Re}_2(\text{DCyBA})_2\text{Cl}_4$ exhibits a quasi-reversible reduction wave at −1.08 V versus (Ag/AgCl) and an irreversible reduction at −2.19 V versus (Ag/AgCl).

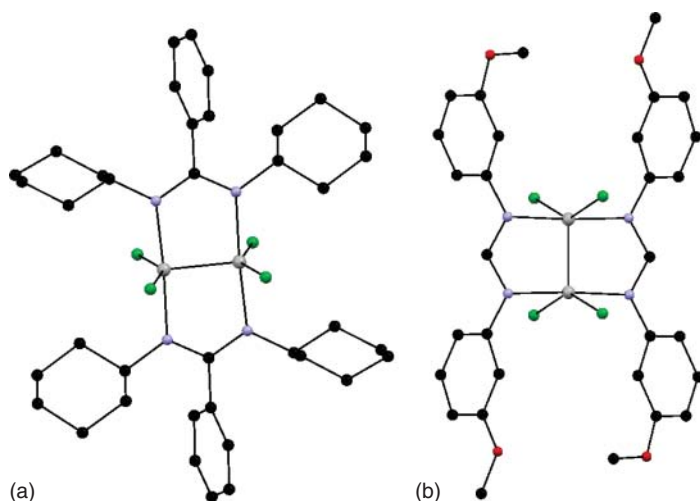


Figure 7.45 Ball and stick representation of $\text{Re}_2\text{DCyBA})_2\text{Cl}_4$ (a) and $\text{Re}_2(\text{DmAniF})_2\text{Cl}_4$ (b).

The irreversibility of the second process is possibly due to the decomposition of the compound via the loss of the equatorial chloride ligand. The voltammogram of $\text{Re}_2(\text{DmAniF})_2\text{Cl}_4$ exhibits a single quasi-reversible reduction at -0.69 V versus (Ag/AgCl).

The one-dimensional polymers $[\text{Re}_2(\text{DMBA})_4(\text{WO}_4)]_\infty$ and $[\text{Re}_2(\text{DMBA})_4(1,4-(\text{O}_2\text{C})_2\text{C}_6\text{H}_4)]_\infty$ were prepared from a slow diffusion of a CH_3CN solution of $\text{Re}_2(\text{DMBA})_4(\text{NO}_3)_2$ into an aqueous solution of Na_2WO_4 and $(n\text{-Bu}_4\text{N})_2(1,4\text{-O}_2\text{CC}_6\text{H}_4\text{CO}_2)$, respectively [94].

The structure of $[\text{Re}_2(\text{DMBA})_4(\text{WO}_4)]_\infty$ consists of one-dimensional infinite chains of $[\text{Re}_2(\text{DMBA})_4]^{2+}$ cations linked by WO_4^{2-} anions (Figure 7.46). In the compound, three independent Re–Re distances are observed (i.e., 2.207(1), 2.202(1), and 2.206(1) Å). These Re–Re distances are slightly longer than the one in $\text{Re}_2(\text{DMBA})_4(\text{NO}_3)_2$ (i.e., 2.173(1) Å) [95]. The increase of the Re–Re distance in $[\text{Re}_2(\text{DMBA})_4(\text{WO}_4)]_\infty$ is attributed to the stronger axial coordination of the tungstate than the nitrate ligand. Two sets of W–O distances are observed: the longer one is associated with the oxygen atoms axially coordinated to Re (avg. W–O = 1.802(9) Å) and the shorter one with the non-coordinated oxygen (avg. W=O = 1.737(10) Å). The average Re–O distance is 2.225(9) Å and the average Re–N distance is 2.07(2) Å. For $[\text{Re}_2(\text{DMBA})_4(1,4-(\text{O}_2\text{C})_2\text{C}_6\text{H}_4)]_\infty$, the structure is a one-dimensional chain of $[\text{Re}_2(\text{DMBA})_4]^{2+}$ cations linked by terephthalate groups. The Re–Re separation (i.e., 2.1944(6) Å) lies between those of $\text{Re}_2(\text{DMBA})_4(\text{NO}_3)_2$ and $[\text{Re}_2(\text{DMBA})_4(\text{WO}_4)]_\infty$, and the order is consistent with the donor strength of axial ligands: $\text{WO}_4^{2-} > (\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2)^{2-} > \text{NO}_3^-$.

Despite the weak coordinating ability of the tungstate and terephthalate anions, both chains are insoluble in common polar and nonpolar solvents. In the solid state, both compounds display phosphorescence from the $^3(\delta \rightarrow \delta^*)$ state, the emission maxima of $[\text{Re}_2(\text{DMBA})_4(\text{WO}_4)]_\infty$ and $[\text{Re}_2(\text{DMBA})_4(1,4-(\text{O}_2\text{C})_2\text{C}_6\text{H}_4)]_\infty$, respectively occur at 795 and 780 nm.

Three compounds that contain the hpp ligand have been reported: $\text{Re}_2(\text{hpp})_4(\text{CF}_3\text{SO}_3)_2$, $\text{Re}_2(\text{hpp})_4(\text{CF}_3\text{CO}_2)_2$, and $\text{Re}_2(\text{hpp})_4\text{F}_2$. The compounds $\text{Re}_2(\text{hpp})_4(\text{CF}_3\text{SO}_3)_2$ and $\text{Re}_2(\text{hpp})_4(\text{CF}_3\text{CO}_2)_2$ were respectively synthesized from reaction of $\text{Re}_2(\text{hpp})_4\text{Cl}_2$ with $\text{Ti}(\text{SO}_3\text{CF}_3)_3$ and $\text{Ti}(\text{CF}_3\text{CO}_2)_3$ in CH_2Cl_2 (Eq. (7.9)). The compound $\text{Re}_2(\text{hpp})_4\text{F}_2$ was obtained from the reaction of $\text{Re}_2(\text{hpp})_4(\text{CF}_3\text{SO}_3)_2$ with $[(\text{CH}_3)_2\text{N}]_3\text{S}[(\text{CH}_3)_3\text{SiF}_2]$ in CH_2Cl_2 .



All the three hpp complexes exhibit the paddlewheel motif with a Re_2^{6+} unit coordinated to four equatorial hpp ligands and two axial anions. The three molecules have a crystallographic inversion center at the midpoint of each Re–Re bond. The ring conformation of the hpp ligands is disordered

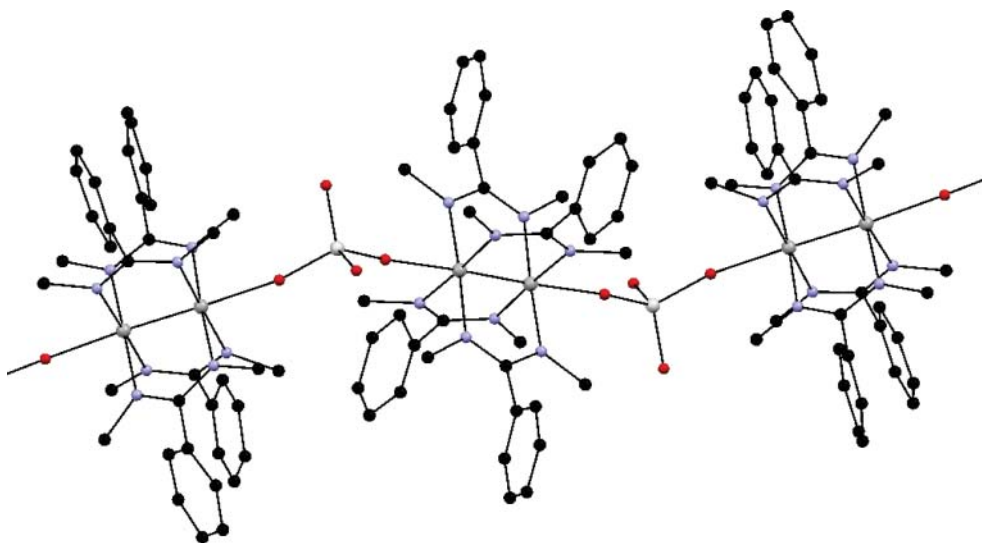


Figure 7.46 Ball and stick representation of $[\text{Re}_2(\text{DMBA})_4(\text{WO}_4)]_\infty$.

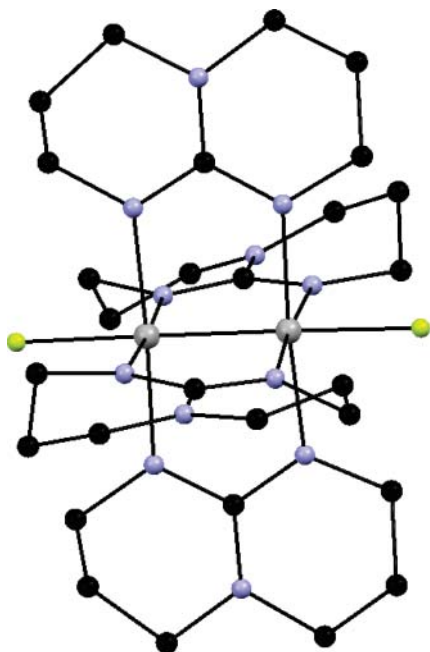


Figure 7.47 Ball and stick representation of $\text{Re}_2(\text{hpp})_4\text{F}_2$.

in all the molecules. The Re–Re separations in $\text{Re}_2(\text{hpp})_4(\text{CF}_3\text{SO}_3)_2$, $\text{Re}_2(\text{hpp})_4(\text{CF}_3\text{CO}_2)_2$, and $\text{Re}_2(\text{hpp})_4\text{F}_2$ (Figure 7.47) are respectively 2.1562(7), 2.1711(5), and 2.1959(4) Å. These distances are shorter than the ones observed for other quadruply bonded Re_2^{6+} compounds (Table 7.12). The longest Re–Xax distance (i.e., 2.484(5) Å) is observed in $\text{Re}_2(\text{hpp})_4(\text{CF}_3\text{SO}_3)_2$, which has the shortest Re–Re separation. The shortest Re–Xax distance (i.e., 2.209(2) Å) is observed in $\text{Re}_2(\text{hpp})_4\text{F}_2$, which has the longest Re–Re distance among the three $\text{Re}_2(\text{hpp})_4^{2+}$ compounds. The Re–O distances

in $\text{Re}_2(\text{hpp})_4(\text{CF}_3\text{SO}_3)_2$ are considerably longer than those in other Re_2^{6+} species with axially coordinated anions containing O-donor atoms. These structural studies emphasize the effect of the axial ligand on the Re–Re separation in $\text{Re}_2(\text{hpp})_4^{2+}$ compounds.

7.3.5

Complexes with the Re_2^{5+} Core

New complexes with the Re_2^{5+} core have not been reported in the 2005 – 2014 period and published studies focused on the spectroscopy and electronic structure of known species. The electronic structure of the paramagnetic complexes $\text{Re}_2\text{X}_4(\text{PMe}_3)_4^+$ ($\text{X} = \text{Cl}, \text{Br}$) has been investigated by magnetic circular dichroism (MCD) and electronic absorption spectroscopies [96]. The compounds $[\text{Re}_2\text{Cl}_4(\text{PMe}_3)_4]\text{PF}_6$ and $[\text{Re}_2\text{Br}_4(\text{PMe}_3)_4]\text{PF}_6$ were obtained from the oxidation of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_4$ with NOPF_6 in acetonitrile/ether mixtures.

The room temperature electronic absorption and 5 K MCD spectra of $[\text{Re}_2\text{Cl}_4(\text{PMe}_3)_4]\text{PF}_6$ and $[\text{Re}_2\text{Br}_4(\text{PMe}_3)_4]\text{PF}_6$ (Figure 7.48) display two prominent bands between 6000 and 25 000 cm^{-1} . The band in the near-IR region of the electronic absorption spectrum ($\epsilon \sim 4000 \text{ M}^{-1} \text{ cm}^{-1}$) is assigned to the $\delta \rightarrow \delta^*$ transition. The corresponding band in MCD is a positive, temperature-dependent C term that possesses a well-resolved vibrational fine structure. This $\delta \rightarrow \delta^*$ C-term band is of interest because it is z-polarized and is therefore formally forbidden in MCD. A violation of the MCD sum rule indicates the presence of ground-state contributions to the MCD intensity. The energy and intensity of the $\delta \rightarrow \delta^*$ transition directly probe the nature of the Re–Re δ and Re–L bonding interactions, and the near-equivalent energies and intensities for this transition in $\text{Re}_2\text{X}_4(\text{PMe}_3)_4^+$ ($\text{X} = \text{Cl}, \text{Br}$) ($\Delta E \sim 200 \text{ cm}^{-1}$) indicate that there is a negligible difference in the δ bond order.

7.3.6

Complexes with the Re_2^{4+} Core

Five compounds containing a Re_2^{4+} unit with bridging ligands and one compound containing a Re_2^{4+} unit with no bridging ligands have been reported. In those complexes, the non-bridging ligand is acetonitrile, while the bridging ligands are bis(diphenylphosphino)methane (dppm), *p*-nitrobenzoic acid and naphthyridine.

The compound $\text{Re}_2(\text{dppm})_2(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-NO}_2)_2\text{Cl}_2$ was prepared from the reaction of $\text{Re}_2(\text{dppm})_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_2$ with *p*-nitrobenzoic acid in refluxing methanol [97]. The structure of the compound consists of a Re_2^{4+} unit coordinated to two Cl axial ligands, two bridging dppm and two bridging *p*-nitrobenzoate ligands in *cis*-positions (Figure 7.49). The Re–Re distance (i.e., 2.320(8) Å) is similar to the one in $\text{Re}_2(\text{dppm})_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_2$ (i.e., 2.315(1) Å) and is expected for a Re–Re triple bond with the $\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configuration. The central paddlewheel unit is not eclipsed and the O–Re–Re–O torsion angle is 14.5(3)°. In the structure, the $(\text{O}_2\text{C-C}_6\text{H}_4\text{-}p\text{-NO}_2)$ groups are planar.

The absorption spectrum of $\text{Re}_2(\text{dppm})_2(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-NO}_2)_2\text{Cl}_2$ has been investigated in dichloromethane. The most intense absorption is located at $\sim 370 \text{ nm}$ ($\epsilon \sim 10\,000 \text{ M}^{-1} \text{ cm}^{-1}$) and there is a weaker absorption at $\sim 790 \text{ nm}$ ($\epsilon \sim 200 \text{ M}^{-1} \text{ cm}^{-1}$). Calculations were performed in order to assign the nature of the transitions in the electronic spectra of $\text{Re}_2(\text{dppm})_2(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-NO}_2)_2\text{Cl}_2$. These calculations predict that the lowest energy transition is due to electronic transitions from the HOMO (δ^*) orbital to combinations of the LUMO, LUMO+1, LUMO+2 orbitals. The LUMO and LUMO+1 are π^* orbitals with some Cl p π -anti-bonding character. The redox behavior of the compound was studied by cyclic voltammetry in the THF/(*n*-Bu₄N)PF₆ solution. The cyclic voltammogram exhibits a reversible oxidation wave at -0.08 V versus/(Cp₂Fe/Cp₂Fe⁺), which corresponds to the $\text{Re}_2^{4+} \rightarrow \text{Re}_2^{5+}$ process. The structural data for rhenium compounds containing the Re_2^{4+} unit are presented in Table 7.14 and their redox potentials are summarized in Table 7.15.

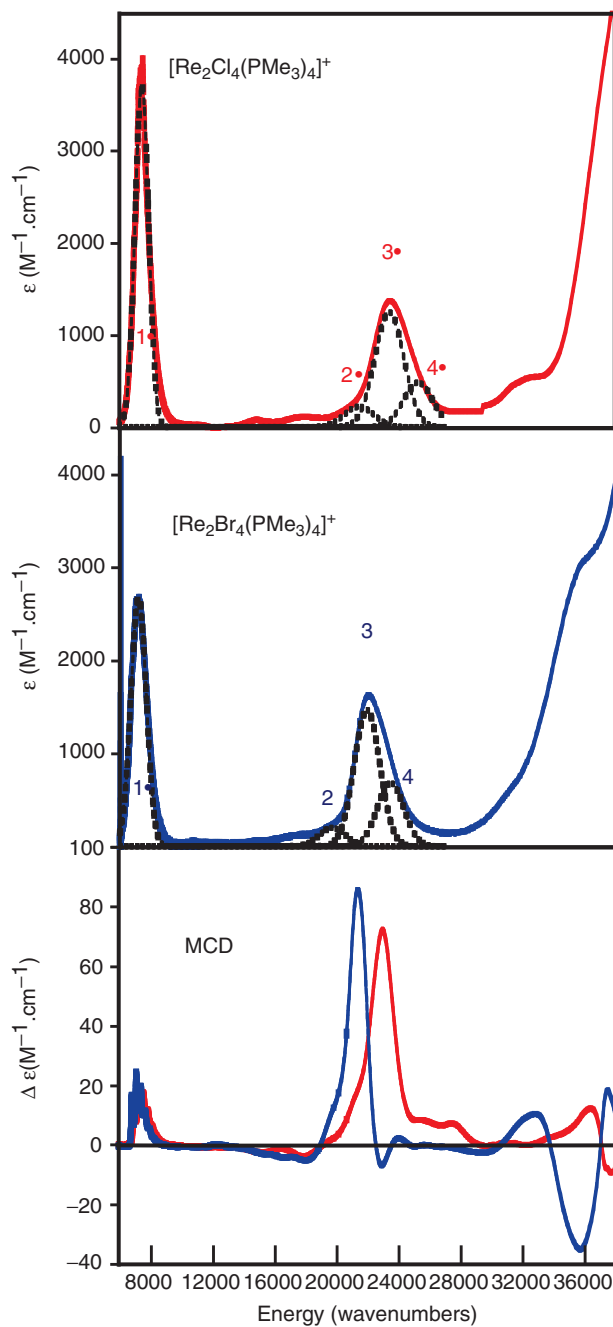


Figure 7.48 Electronic absorption and MCD spectra of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_4^+$ (red) and $\text{Re}_2\text{Br}_4(\text{PMe}_3)_4^+$ (blue).

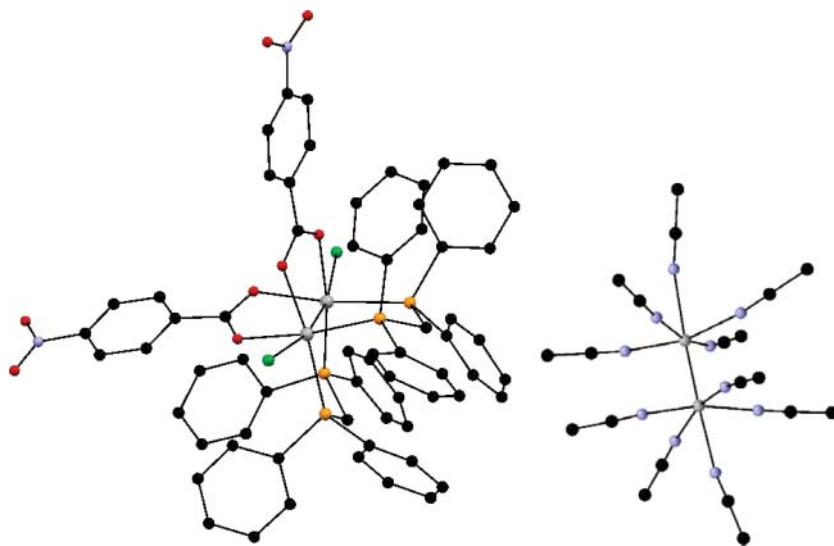


Figure 7.49 Ball and stick representation of $\text{Re}_2(\text{dppm})_2(\text{O}_2\text{CC}_6\text{H}_4\text{-p-NO}_2)_2\text{Cl}_2$ (a) and the $\text{Re}_2(\text{CH}_3\text{CN})_{10}^{4+}$ cation (b).

Table 7.14 Structural data for rhenium compounds containing the Re_2^{4+} unit.

Compounds	Re–Re (Å)
$\text{Re}_2(\text{dppm})_2(\text{O}_2\text{CC}_6\text{H}_4\text{NO}_2)_2\text{Cl}_2$	2.3208(9)
$[\text{Re}_2(\text{CH}_3\text{CN})_{10}][\text{BARf}]_4$	2.2628(4)
<i>cis</i> - $\text{Re}_2(\text{dppm})_2(\text{CH}_3\text{CN})_6[\text{BF}_4]_4$	2.3010(7)
<i>trans</i> - $\text{Re}_2(\text{dppm})_2(\text{CH}_3\text{CN})_6[\text{BF}_4]_4$	2.3109(13)
<i>trans</i> - $\text{Re}_2(\text{pynp})_2(\text{CH}_3\text{CN})_4[\text{BF}_4]_4$	2.2844(7)
<i>trans</i> - $\text{Re}_2(\text{tznP})_2(\text{CH}_3\text{CN})_4[\text{PF}_6][\text{BF}_4]_3$	2.2730(8)

Table 7.15 Redox potentials $E_{1/2}$ for rhenium compounds containing the Re_2^{4+} unit.

Compounds	$E_{1/2}$ (ox1) ^{a)}
$\text{Re}_2(\text{dppm})_2(\text{O}_2\text{CC}_6\text{H}_4\text{NO}_2)_2\text{Cl}_2$ ^{b)}	−0.08
<i>cis</i> - $\text{Re}_2(\text{dppm})_2(\text{CH}_3\text{CN})_6[\text{BF}_4]_4$ ^{c)}	0.27
<i>trans</i> - $\text{Re}_2(\text{dppm})_2(\text{CH}_3\text{CN})_6[\text{BF}_4]_4$ ^{c)}	0.32
<i>trans</i> - $\text{Re}_2(\text{pynp})_2(\text{CH}_3\text{CN})_4[\text{BF}_4]_4$ ^{c)}	0.56
<i>trans</i> - $\text{Re}_2(\text{tznP})_2(\text{CH}_3\text{CN})_4[\text{PF}_6][\text{BF}_4]_3$ ^{c)}	0.61

Values are given in V versus $(\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+)$.

a) $E_{1/2}$ (ox1) corresponds to the reaction $\text{Re}_2^{4+} \rightarrow \text{Re}_2^{5+}$.

b) Performed in THF/ $(n\text{-Bu}_4\text{N})\text{PF}_6$ solution.

c) Performed in $\text{CH}_3\text{CN}/(n\text{-Bu}_4\text{N})\text{PF}_6$ solution.

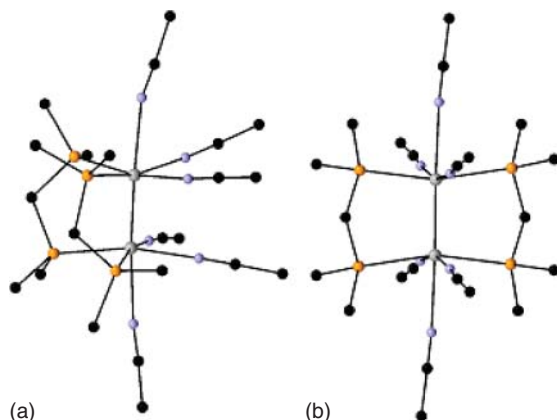


Figure 7.50 Ball and stick representation of the *cis*- $\text{Re}_2(\text{dppm})_2(\text{CH}_3\text{CN})_6^{4+}$ (a) and the *trans*- $\text{Re}_2(\text{dppm})_2(\text{CH}_3\text{CN})_6^{4+}$ cations (b). Phenyl groups are omitted for clarity.

Five solvated dirhenium acetonitrile complexes with the Re_2^{4+} unit have been reported: $[\text{Re}_2(\text{CH}_3\text{CN})_{10}][\text{BArf}]_4$, *cis*- $\text{Re}_2(\text{dppm})_2(\text{CH}_3\text{CN})_6[\text{BF}_4]_4$, *trans*- $\text{Re}_2(\text{dppm})_2(\text{CH}_3\text{CN})_6[\text{BF}_4]_4$, *trans*- $\text{Re}_2(\text{pynp})_2(\text{CH}_3\text{CN})_4[\text{BF}_4]_4$, and *trans*- $\text{Re}_2(\text{tzn})_2(\text{CH}_3\text{CN})_4[\text{PF}_6][\text{BF}_4]_3$ [98].

The complex $\text{Re}_2(\text{CH}_3\text{CN})_{10}[\text{BArf}]_4$ was prepared after the treatment of $[\text{Re}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ with potassium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (KBArf) in acetonitrile. The complex is soluble in CH_3CN , CH_2Cl_2 , and THF. The structure of the $\text{Re}_2(\text{CH}_3\text{CN})_{10}^{4+}$ cation consists of a Re_2^{4+} unit coordinated to acetonitrile ligands in staggered geometry (Figure 7.49). The Re–Re distance (i.e., 2.2628(4) Å) is consistent with the presence of an electron-rich Re–Re triple bond ($\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configuration). The equatorial CH_3CN ligands are staggered with the torsion angles ranging from 40° to 50°. The N equatorial ligands are more strongly bonded ($\text{Re}-\text{N}_{\text{eq}} = 2.045(6) - 2.075(7)$ Å) than the N axial ligands ($\text{Re}-\text{N}_{\text{ax}} = 2.375(5)$ and 2.410(5) Å).

The compound *cis*- $\text{Re}_2(\text{dppm})_2(\text{CH}_3\text{CN})_6[\text{BF}_4]_4$ was prepared via treatment of *cis*- $\text{Re}_2\text{Cl}_2(\text{dppm})_2(\text{O}_2\text{CCH}_3)_2$ with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in acetonitrile. The structure of the *cis*- $\text{Re}_2(\text{dppm})_2(\text{CH}_3\text{CN})_6^{4+}$ cation consists of a Re_2^{4+} unit coordinated to two bridging dppm ligands in *cis*-positions, two equatorial and four axial CH_3CN ligands (Figure 7.50). The Re–Re distance in *cis*- $\text{Re}_2(\text{dppm})_2(\text{CH}_3\text{CN})_6[\text{BF}_4]_4$ (i.e., 2.3010(7) Å) is shorter than the one in *cis*- $\text{Re}_2\text{Cl}_2(\text{dppm})_2(\text{O}_2\text{CCH}_3)_2$ (i.e., 2.3151(7) Å). The axial chlorides and the bridging acetate ligands in *cis*- $\text{Re}_2\text{Cl}_2(\text{dppm})_2(\text{O}_2\text{CCH}_3)_2$ lead to longer Re–Re distance in comparison to the weakly coordinated CH_3CN ligands in *cis*- $\text{Re}_2(\text{dppm})_2(\text{CH}_3\text{CN})_6[\text{BF}_4]_4$. The N equatorial ligands are more strongly bonded ($\text{Re}-\text{N}_{\text{eq}} = 2.082(10) - 2.101(9)$ Å) than the N axial ligands ($\text{Re}-\text{N}_{\text{ax}} = 2.364(9)$ and 2.401(7) Å). The compound *trans*- $\text{Re}_2(\text{dppm})_2(\text{CH}_3\text{CN})_6[\text{BF}_4]_4$ was prepared by treatment of *trans*- $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in acetonitrile. Two molecular units with two different Re–Re distances (i.e., 2.3126(12) and 2.3109(13) Å) are observed. The *trans*- $\text{Re}_2(\text{dppm})_2(\text{CH}_3\text{CN})_6^{4+}$ cation is presented in Figure 7.50. Structural parameters of the molecular unit having the shorter Re–Re distance are similar to the one in *cis*- $\text{Re}_2(\text{dppm})_2(\text{CH}_3\text{CN})_6[\text{BF}_4]_4$.

The reaction of $[\text{Re}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ with 2-(2-pyridyl)-1,8-naphthyridine (pynp) in acetonitrile provides *trans*- $\text{Re}_2(\text{pynp})_2(\text{CH}_3\text{CN})_4[\text{BF}_4]_4$. The analogous reaction with 2-(2-thiazolyl)-1,8-naphthyridine (tzn) and recrystallization with $(n\text{-Bu}_4\text{N})\text{PF}_6$ yielded *trans*- $\text{Re}_2(\text{tzn})_2(\text{CH}_3\text{CN})_4[\text{BF}_4]_3[\text{PF}_6]$.

The *trans*- $\text{Re}_2(\text{pynp})_2(\text{CH}_3\text{CN})_4^{4+}$ and *trans*- $\text{Re}_2(\text{tzn})_2(\text{CH}_3\text{CN})_4^{4+}$ cations are isomorphous (Figure 7.51). Both cations have inversion centers located at midpoint of the Re_2^{4+} unit. In *trans*- $\text{Re}_2(\text{pynp})_2(\text{CH}_3\text{CN})_4[\text{BF}_4]_4$, the N–C–N unit of the naphthyridine fragment bridges the two Re atoms, and the site *trans* to the Re–Re bond is occupied by the N atom of the pyridine. Two pynp

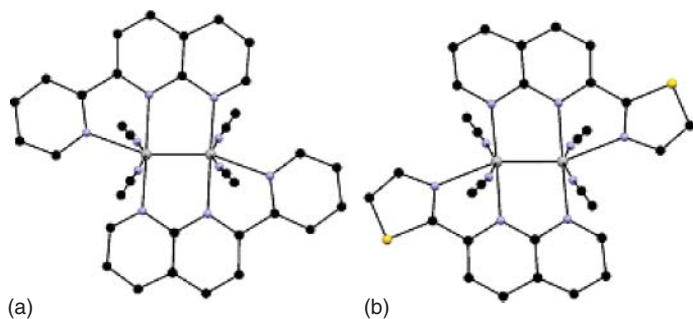


Figure 7.51 Ball and stick representation of the $trans\text{-Re}_2(\text{pynp})_2(\text{CH}_3\text{CN})_4^{4+}$ (a) and $trans\text{-Re}_2(\text{tznp})_2(\text{CH}_3\text{CN})_4^{4+}$ (b) cations.

ligands occupy four equatorial and two axial sites of the Re_2^{4+} unit. Each rhenium atom is further coordinated to two acetonitrile molecules. The Re–Re distance (i.e., 2.2844(7) Å) is typical of an electron-rich triple bond. The Re–N (naphthyridine) distances are 2.076(5) and 2.143(5) Å, and the Re–N (pyridine) axial distance is much longer (i.e., 2.267(5) Å). The Re–N (CH_3CN) distances are 2.044(4) and 2.048(4) Å.

In $\text{Re}_2(\text{tznp})_2(\text{CH}_3\text{CN})_4[\text{BF}_4]_3[\text{PF}_6]$, the tznp ligands are *trans*-oriented. The Re–Re distance is 2.2730(8) Å, the Re–N (naphthyridine) distances are 2.081(4) and 2.148(4) Å, the Re–N (thiazolyl) distance is 2.295(4) Å and the Re–N (CH_3CN) distances are 2.050(4) and 2.047(4) Å. The redox properties of the five solvated dirhenium acetonitrile complexes were studied by cyclic voltammetry in $\text{CH}_3\text{CN}/(n\text{-Bu}_4\text{N})\text{PF}_6$ solutions. Results show that all voltammograms exhibit a quasi-reversible oxidation wave ($\text{Re}_2^{4+} \rightarrow \text{Re}_2^{5+}$). The redox potentials are in the range 0.27–0.61 V versus $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ (Table 7.15).

7.3.7

Complexes with the Re_3^{9+} Core

In the 2005–2014 period, four new complexes containing the Re_3^{9+} unit were reported: $(4,4'\text{-bipyH}_2)\text{Re}_3\text{Cl}_8\text{I}_3\text{H}_2\text{O} \cdot 2\text{H}_2\text{O}$, $[\text{Na}(\text{THF})_2][\text{Re}_3\text{Cl}_5\{\text{OCMe}(\text{CF}_3)_2\}_5]$, $\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})_2$, and $\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})$.

The compound $(4,4'\text{-bipyH}_2)\text{Re}_3\text{Cl}_8\text{I}_3\text{H}_2\text{O} \cdot 2\text{H}_2\text{O}$ was obtained from the thermal reaction of $(\text{NH}_4)_4\text{Re}_2\text{OCl}_{10}$ with 4,4'-bipyridine triiodide in a sealed quartz ampoule under nitrogen atmosphere [99]. In the $\text{Re}_3\text{Cl}_8\text{I}_3\text{H}_2\text{O}^{2-}$ anion (Figure 7.52), the Re–Re separations are 2.4707(14),

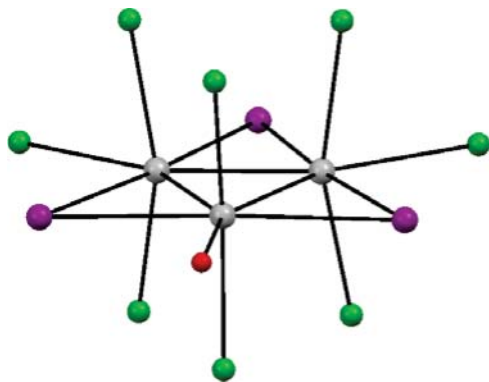
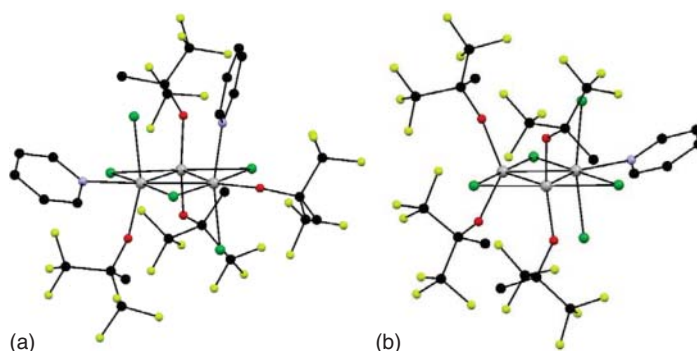


Figure 7.52 Ball and stick representation of the $\text{Re}_3\text{Cl}_8\text{I}_3\text{H}_2\text{O}^{2-}$ anion.

Table 7.16 Structural data for rhenium compounds containing the Re_3^{9+} unit.

Compounds	Re–Re (Å)
$(4,4'\text{-bipyH}_2)\text{Re}_3\text{Cl}_8\text{I}_3\text{H}_2\text{O}\cdot 2\text{H}_2\text{O}$	2.4707(14), 2.4766(12) 2.4772(11)
$\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})_2$	2.4522(3), 2.4800(4) 2.4498(3)
$\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})$	2.4232(5), 2.4310(5) 2.4318(5)

**Figure 7.53** Ball and stick representation of $\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})_2$ (a) and $\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})$ (b).

2.4766(12), and 2.4772(11) Å (Table 7.16). The Re–Cl distances are in the range 2.303(4)–2.334(4) Å for the atoms out of plane with respect to the Re_3^{9+} core. The bridging Re–I bond distances are in the range 2.728(16)–2.7593(16) Å. In the crystal structure packing, a layered arrangement of the $\text{Re}_3\text{Cl}_8\text{I}_3\text{H}_2\text{O}^{2-}$ anions is observed. Water molecules and 4,4'-bipyridyl cations are located between the layers formed by the $\text{Re}_3\text{Cl}_8\text{I}_3\text{H}_2\text{O}^{2-}$ anions. The structure is stabilized by N–H···Cl, O–H···O, O–H···Cl, and C–H···Cl hydrogen bonding networks. The stability of the complex was studied by thermogravimetric analysis; the loss of the water molecules occurred around 65 °C and the compound decomposed at 269 °C. The $(4,4'\text{-bipyH}_2)\text{Re}_3\text{Cl}_8\text{I}_3\text{H}_2\text{O}\cdot 2\text{H}_2\text{O}$ compound is the first example of a Re_3^{9+} iodo-complex with an aromatic ammonium cation as counterion.

Three complexes with the Re_3^{9+} unit coordinated to fluoroalkoxide ligands have been reported: $[\text{Na}(\text{THF})_2][\text{Re}_3\text{Cl}_5\{\text{OCMe}(\text{CF}_3)_2\}_5]$, $\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})_2$, $\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})$ [100]. The compound $[\text{Na}(\text{THF})_2][\text{Re}_3\text{Cl}_5\{\text{OCMe}(\text{CF}_3)_2\}_5]$ was prepared from the reaction of $\text{Re}_3\text{Cl}_9(\text{THF})_3$ with $\text{NaOCMe}(\text{CF}_3)_2$ in THF. The compound $\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})_2$ was obtained after the reaction of $[\text{Na}(\text{THF})_2][\text{Re}_3\text{Cl}_5\{\text{OCMe}(\text{CF}_3)_2\}_5]$ with a large excess of pyridine in CH_2Cl_2 . The mono-pyridine adduct $\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})$ was obtained as a side product in reactions between $[\text{Na}(\text{THF})_2][\text{Re}_3\text{Cl}_5\{\text{OCMe}(\text{CF}_3)_2\}_5]$ and pyridine.

Preliminary refinement of the X-ray data indicate that the structure of $[\text{Na}(\text{THF})_2][\text{Re}_3\text{Cl}_5\{\text{OCMe}(\text{CF}_3)_2\}_5]$ consists of two terminal alkoxide ligands on two Re atoms and a terminal alkoxide on the third Re atom. No structural parameters have been reported for this compound. The compound $\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})_2$ has two terminal alkoxide ligands on one Re atom, a terminal alkoxide ligand lying in the Re_3^{9+} plane on the second Re atom, and a terminal alkoxide ligand lying perpendicular to the Re_3^{9+} plane on the third Re atom (Figure 7.53). The compound $\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})$ exhibits the C_{2v} symmetry with four terminal alkoxide ligands attached to two rhenium atoms (Figure 7.53). The Re–Re distances in $\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})_2$ and $\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})$ are in the range 2.4232(5)–2.4800(4) Å (Table 7.16). The Re–Cl bond distances in the bridges are in the range 2.4027(15)–2.4105(15) Å for $\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})_2$ and in the range 2.386(3)–2.415(2) Å for $\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})$. The Re–O distances are in the range 1.903(4)–2.025(4) Å for $\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})_2$ and 1.881(6)–1.925(6) Å for

$\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})$. In $\text{Re}_3\text{Cl}_5[\text{OCMe}(\text{CF}_3)_2]_4(\text{py})_2$, the Re–O distance for the alkoxide in the plane of the Re_3^{9+} unit is ~ 0.08 Å longer than the Re–O distance for the alkoxide lying perpendicular to the Re_3^{9+} unit. These complexes are the first examples of Re_3^{9+} clusters coordinated to fluorinated alkoxide ligands.

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- group 6: Complex with Mn–M (M = transition-metal) heterometallic interaction is prosperous, especially if M is group 6, 8, 9, and 10 metals. A search in Cambridge Structural Database (CSD, version 03/2014) with keyword Mn–M: M = group 6, 96 hits; M = group 8, 104 hits; M = group 9, 58 hits; M = group 10, 68 hits. For representative examples, see: (a) Hart, I.J., Jeffery, J.C., Lowry, R.M., and Stone, F.G.A. (1988) *Angew. Chem., Int. Ed. Engl.*, **27**, 1703; group 8: (b) Harakas, G.N. and Whittlesey, B.R. (1996) *J. Am. Chem. Soc.*, **118**, 4210; group 9: (c) Beckers, H.-G., Flörke, U., and Haupt, H.-J. (1995) *Angew. Chem., Int. Ed. Engl.*, **34**, 1325; group 10: (d) Komiya, S., Muroi, S., Furuya, M., and Hirano, M. (2000) *J. Am. Chem. Soc.*, **122**, 170.
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8

Group 8 Metal–Metal Bonds

Stephen J. Tereniak and Connie C. Lu

8.1

Introduction

Cognization of metal–metal bonding arose from the structural elucidation of metal clusters, where two or more metals were in close proximity [1]. For Group 8 metals, some of the early examples were polynuclear carbonyl clusters, for example, $\text{Fe}_2(\text{CO})_9$, $\text{Ru}_3(\text{CO})_{12}$, and $\text{Os}_3(\text{CO})_{12}$, where the consideration of metal–metal bonds is requisite to achieve electronically saturated (18-electron) metal centers [2]. Another early precedent of a Group 8 bimetallic is the Ru_2^{5+} paddlewheel complex, $\text{Ru}_2(\text{OAc})_4\text{Cl}$, where multiple Ru–Ru bonds were first implicated [3, 4]. Since these early discoveries, the breadth and understanding of Group 8 metal–metal bonds have advanced significantly. Fundamental MO bonding pictures have been successfully implemented to understand electronic and magnetic properties. Beyond understanding, applications are increasingly being sought and developed for molecular electronic devices, magnetic materials, and catalysis.

The vast collection of coordination complexes in this chapter attests to the fact that Group 8 metals are highly versatile at forming metal–metal bonds. Of the Group 8 triad, Ru_2 complexes remain the most studied. In the past decade, the coordination chemistry of Os_2 has stagnated, but that for Fe_2 has flourished. While homobimetallics form the first part of this chapter, heterobimetallics with Group 8–metal bonds complete it. Throughout the chapter, we characterize the metal–metal interactions by their formal shortness ratio (FSR), which is defined as the ratio of the metal–metal bond distance to the sum of the single bond radii [5, 6].

8.2

Group 8 Homobimetallics

8.2.1

Diiron

Coordination complexes with Fe–Fe bonds are plentiful, although the majority are carbonyl clusters. An interesting minority of Fe_2 complexes do not contain any carbonyl ligands, and as their numbers have increased substantially in recent years, they are the focus of this section. Collectively, these Fe_2 complexes have a great diversity of oxidation states, coordination numbers, geometries, and spin states. Spectroscopy and theory have been key to revealing their complex electronic structures, and one advantage in studying Fe_2 complexes is their amenability to interrogation by ^{57}Fe Mössbauer spectroscopy. Until recently, different redox states of Fe_2 complexes were virtually unknown. New classes of Fe_2 complexes show promising redox flexibility as well as chemical reactivity.

In the following sections, the Fe_2 complexes are presented according to their coordination geometries. The most prevalent geometry for non-organometallic Fe_2 complexes is the trigonal paddlewheel. Diiron complexes have been isolated in related geometries, such as the classic tetragonal

paddlewheel and twofold planar, where a bridging ligand is formally added or removed. Figure 8.1 shows the qualitative d-orbital splitting diagram for Fe_2 complexes in tetragonal, trigonal, and twofold symmetries.

In trigonal paddlewheels, all five d-orbitals may participate in metal–metal bonding. The π - and δ -symmetric orbitals are doubly degenerate. This is opposed to the tetragonal symmetry, where the $d_{x^2-y^2}$ atomic orbitals are destabilized by M–L anti-bonding interactions and are not available for metal–metal bonding. Only one δ bond is possible, which is derived from the d_{xy} orbitals. The d-orbital splitting for twofold planar complexes can be derived by removing a pair of *trans* ligands from the tetragonal paddlewheel. The most affected orbitals are the δ orbitals with $d_{x^2-y^2}$ parentage; they drop in energy as half of the M–L anti-bonding interactions are removed. Since the energy differences between σ^* , π^* , and δ/δ^* orbitals can be subtle for trigonal paddlewheels and twofold planar complexes, their d-orbital manifolds appear qualitatively similar, though degeneracy is not required for the latter.

8.2.1.1 Tetragonal Complexes (Paddlewheel and Non-Paddlewheel)

Despite being a classical geometry for other metal–metal bonds, tetragonal paddlewheels with an iron–iron bond remain rare. At the time of writing, the only tetragonal paddlewheel complex is the Fe_2^{4+} tetraformamidinate $\text{Fe}_2(\text{PhNCHNPh})_4$, which was prepared by adding 2 equiv. of MeLi to $\text{FeCl}_2(\text{PhN=CHNHP})_2$ (Figure 8.2) [7, 8]. The complex has an Fe–Fe distance of 2.462(2) Å (FSR 1.06) and a measured magnetic moment of 8.8 μ_B by Evans' method at room temperature. The spin state was thus assigned as $S = 4$, which is the highest possible spin for an Fe_2^{4+} core.

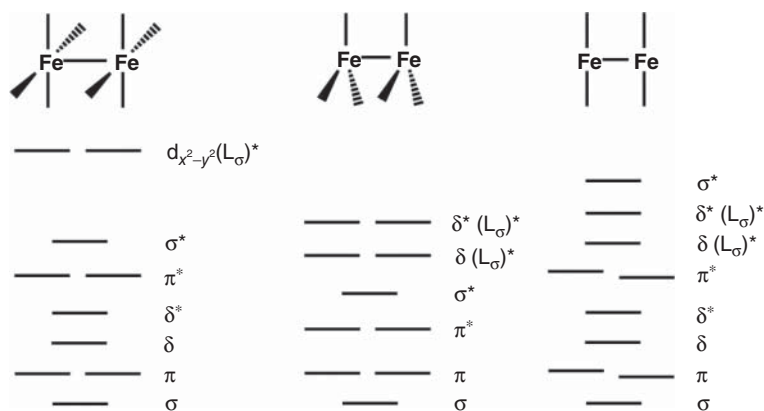


Figure 8.1 Qualitative d-orbital manifolds for Fe–Fe complexes in tetragonal, trigonal, and twofold planar symmetries. Orbitals that are anti-bonding with σ -ligands are indicated by $(L_{\sigma})^*$.

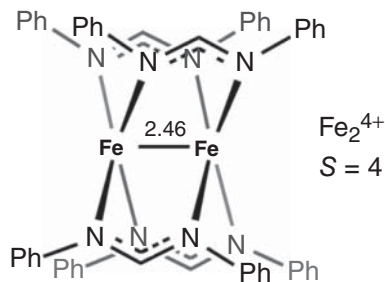


Figure 8.2 $\text{Fe}_2(\text{PhNCHNPh})_4$.

The solid-state structure of this complex reveals a significant distortion, where the formamidinate ligands are “stretched” toward one of the iron centers, in alternating fashion. The symmetry of the complex is thus reduced from the ideal D_{4h} symmetry to D_{2d} . A density functional theory (DFT) investigation of the complex provided an electronic basis for the distortion. In ideal D_{4h} symmetry, the electronic configuration $(\sigma)^2(\pi)^3(\delta)^1(\delta^*)^1(\pi^*)^2(\sigma^*)^1(d_{x^2-y^2(1)})^1(d_{x^2-y^2(2)})^1$ is unstable to Jahn–Teller distortion [9]. By lowering the symmetry to D_{2d} , the degeneracy of the π orbitals is lost, relaxing the $(2\pi)^3$ occupation to $(\pi)^2(\pi)^1$. Moreover, as the $d_{x^2-y^2}$ orbitals lose some Fe–ligand anti-bonding character, they become available for metal–metal bonding, generating the more delocalized configuration $(\sigma)^2(\pi)^2(\pi)^1(\delta)^1(\delta^*)^1(\pi^*)^1(\pi^*)^1(\sigma^*)^1(\delta)^1(\delta^*)^1$.

Considering the scarcity of tetragonal paddlewheel Fe_2 complexes, it is notable that a tetragonal complex has been discovered with an unsupported iron–iron bond [10]. The complex is a dimer of two square-planar iron centers that are coordinated by a N_4 -macrocylic ligand (tim), as shown in Figure 8.3. The dimer was isolated from the sodium amalgam reduction of the monoiron precursor, $[\text{Fe}(\text{tim})(\text{NCCCH}_3)_2](\text{PF}_6)_2$. In the solid-state structure of $\text{Fe}_2(\text{tim})_2$, the Fe–Fe bond distance is long at 2.6869(6) Å (FSR 1.15), demonstrating that Fe–Fe bonds within coordination complexes can be significantly longer than the sum of their single bond metallic radii (2.33 Å) [6], as well as the interatomic distance in the metal lattice (2.48 Å) [11].

The redox-active nature of the diimine units poses a significant challenge not only in assigning the oxidation states of the iron centers but also in understanding the iron–iron bonding. The presence of ligand radicals is suggested by the complex’s dark purple color, which arises from an intense band at 598 nm that is characteristic of the diimine π -radical state [12]. Moreover, structural changes in the diimine group, namely the shortening of the C–C backbone coupled to the elongation of C=N bonds, support ligand reduction. The Mössbauer spectrum showed a single doublet with an isomer shift (IS) of 0.18 mm s^{−1} and a quadruple splitting (QS) of 2.54 mm s^{−1}. The two iron centers are thus equivalent on the Mössbauer timescale ($\sim 10^{-8}$ s). Additionally, the IS values are akin to $S = 3/2$ Fe(III) complexes with π -radical ligands [12]. Finally, the measured magnetic moment of $2.9\mu_B$, that is invariant from 50 to 300 K, indicated an $S = 1$ ground state.

The collective experimental data is consistent with either Fe_2^{6+} or Fe_2^{5+} cores, which are charge-balanced by the ligand radical states, $(\text{L}^{3-})_2$ and $(\text{L}^{3-})(\text{L}^{2-})$, respectively. DFT calculations favor a delocalized mixed-valent Fe_2^{5+} description. Since the d-electron configuration $(d_{xy(1)})^2(d_{xy(2)})^2(\sigma)^2(d_{xz(1)})^1(d_{xz(2)})^1(\sigma^*)^1(d_{yz(1)})^1(d_{yz(2)})^1$ predicts five unpaired d-electrons, the $S_{\text{tot}} = 1$ state arises from strong, antiferromagnetic coupling to three unpaired ligand electrons. The metal–metal bonding interactions are limited, manifesting as $(\sigma)^2(\sigma^*)^1$, with π and δ bonds being notably absent. Due to the staggering of the ligands, the d_{xz} orbitals are orthogonal, and π -bonding is precluded. This unsupported Fe–Fe bond has a formal bond order of 0.5, and therefore, it may represent the lowest extreme in Fe–Fe covalent bonding.

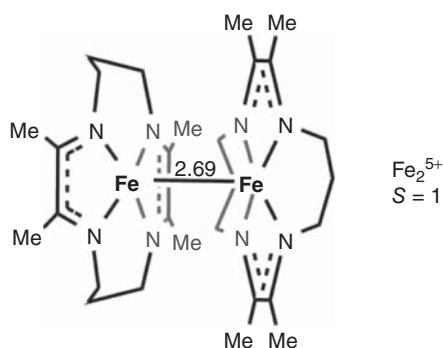


Figure 8.3 $\text{Fe}_2(\text{tim})_2$.

8.2.1.2 Trigonal Paddlewheel

Fe_2 trigonal paddlewheels are more prevalent than their tetragonal counterparts. The metal cores are typically Fe_2^{3+} or Fe_2^{4+} . The bridging ligands are monoanionic, and their charge delocalization occurs to varying extents depending on the similarity of the two donors. For example, the donor atoms in amidinates are electronically equivalent, whereas in phosphinoamides, the charge is localized at the amide.

Amidinate The classic trigonal Fe_2 paddlewheel, $\text{Fe}_2(\text{PhNCHNPh})_3$, was first prepared by Murillo, Cotton, and coworkers. The benzamidinate analog, $\text{Fe}_2(\text{PhNCPhNPh})_3$ is also known [13, 14]. These Fe_2^{3+} paddlewheel complexes were isolated via crystallization from a one-pot reaction: to $\text{FeCl}_2(\text{PhN}=\text{CRNHPH})_2$, NaHBEt_3 was added as a reducing agent with MeLi as a base [13, 14]. The solid-state structures revealed short Fe–Fe bond distances of 2.2318(8) Å (FSR 0.96) in $\text{Fe}_2(\text{PhNCHNPh})_3$ and 2.198(2) Å (FSR 0.94) in $\text{Fe}_2(\text{PhNCPhNPh})_3$ (Figure 8.4). At the time of the report, these Fe–Fe bonds were considered short and suggested multiple bonding between the iron centers.

The electron paramagnetic resonance (EPR) spectrum of $\text{Fe}_2(\text{PhNCHNPh})_3$ in toluene glass at 10 K showed an axial signal, with $g_{\perp} = 7.94$ and $g_{\parallel} = 1.99$, consistent with $S = 7/2$, the highest possible spin for Fe_2^{3+} . The $S = 7/2$ state was confirmed by magnetic susceptibility measurements, where the magnetic moment of 7.4 μ_B is invariant from 30 to 290 K [15]. Variable-field, variable-temperature (VTVH) Mössbauer spectra were globally fitted with $IS = 0.65 \text{ mm s}^{-1}$, $QS = 0.32 \text{ mm s}^{-1}$, and a zero-field splitting ($D_{7/2}$) of 8.2 cm^{-1} . As the fitting required only one unique iron, the Fe_2^{3+} core must be fully delocalized, or $\text{Fe}^{1.5}\text{Fe}^{1.5}$ [15]. The electronic absorption spectra contained two weak bands in the visible region (650 and 700 nm) and two weak absorptions in the near-infrared region (825 and 1250 nm). The higher energy transitions were assigned as $\pi \rightarrow \delta$ and $\pi \rightarrow \delta^*$ transitions, while the lowest energy band was assigned as $\pi \rightarrow \pi^*$ (*vide infra*).

Theoretical calculations were performed, initially with SCF- $X\alpha$ -SW methods on a truncated model [16], and later with the complete active space self-consistent field (CASSCF) and multiconfigurational complete active space second-order perturbation theory (CASPT2) methods on the full molecule [15]. The electronic structures from the two calculations were remarkably similar. The CASSCF/PT2 calculations predicted a single, dominant configuration (73%) with $(\sigma)^2(\pi)^4(\pi^*)^2(\sigma^*)^1(\delta)^2(\delta^*)^2$. Although the formal bond order is 1.5, the effective bond order, which considers minor configurations that contribute to the ground-state wavefunction, is lower at 1.15.

Aminopyridinate A trigonal Fe_2^{4+} paddlewheel compound is known with aminopyridinate donors. The diiron complex, $\text{Fe}_2\text{Cl}(\text{py}_3\text{tren})$ (shown in Figure 8.5), has a heptadentate ligand where three aminopyridinate groups are tethered to an amine linker, which is itself an axial donor to one of the iron centers [17]. (py_3tren refers to triply deprotonated N,N,N -tris(2-(2-pyridylamino)ethyl)amine). The Fe_2 complex was prepared by adding the monoiron(II) complex, $\text{K}[\text{Fe}(\kappa^4\text{-py}_3\text{tren})]$, to $\text{FeCl}_2(\text{THF})_{1.5}$ in THF. In the solid-state structure, the Fe–Fe bond distance is 2.2867(5) Å (FSR 0.98). While the

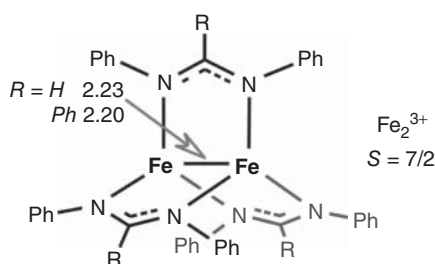


Figure 8.4 $\text{Fe}_2(\text{PhNCRNPh})_3$.

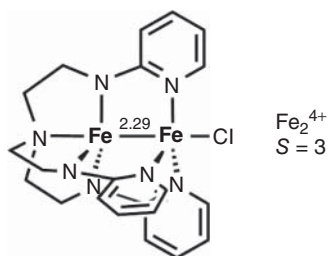


Figure 8.5 $\text{Fe}_2\text{Cl}(\text{py}_3\text{tren})$.

Fe–Fe distance is longer by 0.06–0.09 Å than that in tris(amidinate) Fe_2^{3+} paddlewheels, considerable lengthening of the Fe–Fe bond was expected with the addition of *trans* donors.

The Mössbauer spectrum of $\text{Fe}_2\text{Cl}(\text{py}_3\text{tren})$ contains two doublets of equal intensity. One doublet has an IS of 0.58 mm s^{−1} and QS of 0.38 mm s^{−1}, while the other has IS of 0.48 mm s^{−1} and QS of 1.69 mm s^{−1}. The latter was assigned to the Fe in the N_4 -pocket based on its similarity to a related complex, $\text{FeMnCl}(\text{py}_3\text{tren})$, where the iron resides in the N_4 -pocket (*vide infra*). The cyclic voltammogram of $\text{Fe}_2\text{Cl}(\text{py}_3\text{tren})$ showed a quasi-reversible, one-electron oxidation at −0.45 V and a reversible, one-electron reduction at −1.98 V (vs $\text{FeCp}_2^{+/0}$). The former was tentatively assigned as an Fe(II)/Fe(III) redox couple for the iron in the N_4 -pocket, while the latter was assigned as an Fe(II)/Fe(I) reduction of the other iron center. In the magnetic susceptibility plot (χT vs T), χT has a maximum value of 5.42 cm³ K mol^{−1} at 30 K, which is close to the spin-only value for $S = 3$ ($\chi T = 6.0$ cm³ K mol^{−1}). The χT value decreases gradually with increasing temperature, dropping to 4.42 cm³ K mol^{−1} at 290 K. CASSCF/PT2 calculations for the $S = 3$ ground state predicted $\text{Fe}_2\text{Cl}(\text{py}_3\text{tren})$ to be highly multi-configurational. The main configuration, which accounts only for 28% of the total wavefunction, is $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2(\pi^*)^2(\sigma^*)^0$. The *effective* bond order is 0.73, which is close to a single bond.

Phosphinoamide Thomas and coworkers have used phosphinoamides $(\text{R}_2\text{PNR}')^-$ to isolate trigonal Fe_2^{4+} and Fe_2^{3+} paddlewheels. Typically, the Fe_2^{4+} paddlewheels are synthesized by deprotonating the ligand (3 equiv.) with an appropriate base (e.g., KH or *n*BuLi) and mixing with FeCl_2 in THF. The Fe_2^{4+} complexes include $\text{Fe}(\text{NArP}^i\text{Pr}_2)_3\text{FeCl}$ (where $\text{Ar} = 2,4,6\text{-Me}_3(\text{C}_6\text{H}_2)$) and $\text{Fe}(\text{N}^i\text{PrP}^i\text{Pr}_2)_2(\text{P}^i\text{Pr}_2\text{N}^i\text{Pr})\text{FeCl}$, with Fe–Fe bond distances of 2.5855(4) Å (FSR 1.11) and 2.6112(7) Å (FSR 1.12), respectively (Figure 8.6) [18]. In $\text{Fe}(\text{NArP}^i\text{Pr}_2)_3\text{FeCl}$, all three phosphinoamide ligands are oriented in the same direction, giving a triamido iron and a triphosphine iron, which also binds to chloride. In $\text{Fe}(\text{N}^i\text{PrP}^i\text{Pr}_2)_2(\text{P}^i\text{Pr}_2\text{N}^i\text{Pr})\text{FeCl}$, one of the phosphinoamides is oriented in the opposite direction as the other two, creating two new coordination environments, $(\text{N}_2\text{P})\text{Fe}$ and $(\text{NP}_2)\text{FeCl}$.

The Mössbauer spectrum of $\text{Fe}(\text{NArP}^i\text{Pr}_2)_3\text{FeCl}$ contains two doublets. One doublet with an IS = 0.69 mm s^{−1} and QS = 2.63 mm s^{−1} is assigned to the triamido iron; while the other doublet

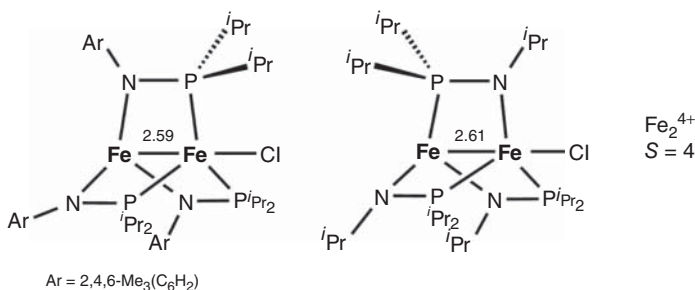


Figure 8.6 $\text{Fe}(\text{NArP}^i\text{Pr}_2)_3\text{FeCl}$ and $\text{Fe}(\text{N}^i\text{PrP}^i\text{Pr}_2)_2(\text{P}^i\text{Pr}_2\text{N}^i\text{Pr})\text{FeCl}$.

with $IS = 0.63 \text{ mm s}^{-1}$ and $QS = 1.16 \text{ mm s}^{-1}$ corresponds to the triphosphine iron. The Mössbauer spectrum of $\text{Fe}(\text{N}^i\text{PrP}^i\text{Pr}_2)_2(\text{P}^i\text{Pr}_2\text{N}^i\text{Pr})\text{FeCl}$ contains only a single doublet, $IS = 0.60 \text{ mm s}^{-1}$ and $QS = 1.80 \text{ mm s}^{-1}$. The apparent coincidence was attributed to the more similar coordination environments of the iron centers. Notably, all IS values indicate high-spin Fe(II) centers. Moreover, magnetic moments of 6.80 and $8.95 \mu_B$, measured by Evans' method, strongly suggest a high-spin ground state of $S = 4$ for these Fe_2^{4+} cores. Wiberg bond indices were calculated by DFT to be 0.42 and 0.43 , consistent with weak Fe–Fe bonding. Finally, the cyclic voltammogram of $\text{Fe}(\text{N}^i\text{PrP}^i\text{Pr}_2)_2(\text{P}^i\text{Pr}_2\text{N}^i\text{Pr})\text{FeCl}$ contains a reversible oxidation at -1.02 V (vs $\text{FeCp}_2^{+/0}$), suggesting possible access to an Fe_2^{5+} oxidation state.

The Fe_2^{3+} paddlewheels were prepared with the ligand variant, $(^i\text{PrNPPh}_2)^-$. The Fe_2^{3+} complexes (Figure 8.7), $\text{Fe}_2(^i\text{PrNPPh}_2)_3\text{L}$, contain different axial phosphines, $\text{L} = \text{PMe}_3$ or $\text{PPh}_2\text{NH}^i\text{Pr}$ [19]. The Fe_2^{3+} $\text{PPh}_2\text{NH}^i\text{Pr}$ -adduct was isolated directly from the reduction of the Fe_2^{4+} precursor, $\text{Fe}(^i\text{PrNPPh}_2)_3\text{Fe}(\eta^2-^i\text{PrNPPh}_2)$ with 1.5 equiv. sodium amalgam. Adding excess PMe_3 to $\text{Fe}(\mu-^i\text{PrNPPh}_2)_3\text{Fe}(\text{PPh}_2\text{NH}^i\text{Pr})$ then formed the Fe_2^{3+} PMe_3 -adduct. While the Fe_2^{4+} precursor has a negligible metal–metal interaction (Fe–Fe distance is $2.87 \text{ \AA}$), both Fe_2^{3+} complexes have considerably contracted Fe–Fe distances of $2.4545(5)$ (FSR 1.05 , $\text{L} = \text{PMe}_3$) and $2.4694(3) \text{ \AA}$ (FSR 1.06 , $\text{L} = \text{PPh}_2\text{NH}^i\text{Pr}$). The reduction is primarily localized at the $\text{Fe}(\text{P}_3)\text{L}$ site, as the Fe–P bond distances contract significantly from $2.49 \text{ \AA}$ in the Fe_2^{4+} precursor to 2.345 – $2.385 \text{ \AA}$ due to Fe–P backbonding. The Fe_2^{3+} paddlewheels have magnetic moments of 7.66 and $7.40 \mu_B$ (Evans' method), suggesting high-spin $S = 7/2$ ground states, akin to $\text{Fe}_2(\text{PhNCHNPh})_3$.

A highlight of these molecules is their ability to activate organic azides via oxidative group transfer to give Fe_2^{5+} imides (Figure 8.8). The addition of 2 equiv. N_3R (where $\text{R} = ^t\text{Bu}$, Ad , $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) to $\text{Fe}_2(^i\text{PrNPPh}_2)_3\text{L}$ affords $\text{Fe}(^i\text{PrNPPh}_2)_3\text{Fe}\equiv\text{NR}$, 2 equiv. N_2 , and the corresponding phosphinoamide, $\text{L} = \text{NR}$ [19]. The Fe_2^{5+} imides have reasonably short Fe–Fe distances of 2.54 – $2.56 \text{ \AA}$ (FSR 1.09 – 1.10). The $\text{Fe–N}(\text{imide})$ bond lengths of 1.64 – $1.67 \text{ \AA}$ are consistent with other C_3 -symmetric Fe-imide bonds in the literature. A Mössbauer spectrum of $\text{Fe}(^i\text{PrNPPh}_2)_3\text{Fe}\equiv\text{N}^t\text{Bu}$ showed a single doublet with $IS = -0.06 \text{ mm s}^{-1}$ and $QS = 0.54 \text{ mm s}^{-1}$, which was similar to the $S = 1/2$ Fe(III) imide, $\text{PhB}(\text{MesIm})_3\text{Fe}\equiv\text{NAd}$ [20]. Hence, the Fe_2^{5+} -imide core was proposed to be $\text{Fe}^{+2}\text{Fe}^{+3}\equiv\text{NR}$. The

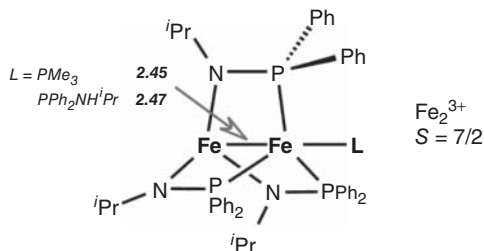


Figure 8.7 $\text{Fe}_2(^i\text{PrNPPh}_2)_3\text{L}$.

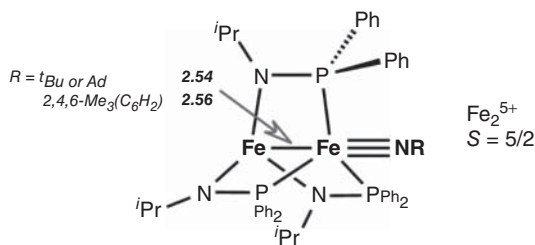


Figure 8.8 $\text{Fe}(^i\text{PrNPPh}_2)_3\text{Fe}\equiv\text{NR}$.

measured magnetic moment of $5.85 \mu_B$ is consistent with an $S = 5/2$ ground state, which arises from ferromagnetic coupling of high-spin Fe(II) and low-spin Fe(III). DFT calculations support the $S = 5/2$ ground state. Cyclic voltammetry shows reversible one electron oxidation and reduction waves at -0.32 and -1.94 V (vs $\text{FcP}_2^{+/0}$), respectively.

The bonding in the $\text{Fe}^{2+}\text{Fe}^{3+}\equiv\text{NR}$ core was investigated by DFT, as these are the first examples of metal-ligand multiple bonds that are *trans* to an M–M interaction involving *first-row* metals. Overall, the d-electrons are highly localized, and M–M bonding interactions are evident only in the $\sigma(\text{Fe}–\text{Fe})$ and the three-centered $\sigma^*(\text{Fe}–\text{Fe}–\text{N})$ orbitals. The Fe–Fe bond order is predicted to be low at 0.5, which is consistent with a weak Fe–Fe interaction.

8.2.1.3 Planar Paddlewheel

Currently, the shortest isolated Fe–Fe bond ($2.1270(7)$ Å, FSR 0.91) is found in the Fe_2^{2+} planar paddlewheel complex with two bridging guanidinate ligands (Pipiso) as shown in Figure 8.9 [21]. The dark red $\text{Fe}_2(\text{Pipiso})_2$ was isolated from the reduction of the diiron(II,II) bis(μ -bromide), $[(\text{Pipiso})\text{Fe}(\mu\text{-Br})_2]$, with $[\text{Mg}(\text{MesNacnac})_2]_2$ (see Chapter 2) in cyclohexane.

The complex has a magnetic moment of $7.95 \mu_B$, which is largely invariant from 150 to 300 K. CASSCF/PT2 calculations predict the ground spin state to be high spin, or $S = 3$. The calculations yield an effective bond order (EBO) of 1.19, suggesting a modest amount of multiple bonding despite the experimentally short Fe–Fe bond. The Mössbauer spectrum shows one quadrupole doublet with IS of 0.44 mm s^{-1} and QS of 2.39 mm s^{-1} .

8.2.1.4 Non-Paddlewheel

A small assortment of Fe_2 complexes have diverse geometries that do not fit into the above families. The first of these is a homoleptic iminoacyl Fe_2 complex shown in Figure 8.10, which was prepared by adding $\text{C}\equiv\text{N}^t\text{Bu}$ to $\text{Fe}_2(\text{Mes})_4$ at 0°C in THF [22]. The Fe–Fe bond distance is $2.371(4)$ Å (FSR: 1.02). From 20 to 300 K, the magnetic moment was essentially constant at $3.86 \mu_B$ per iron. A reasonable fit of the magnetic data was obtained using two $S = 3/2$ spins with g-values of 1.98 and magnetic coupling, $J = -0.45 \text{ cm}^{-1}$. A single Fe–Fe bond was deduced, as the strong coupling of only one unpaired electron per Fe(II) would be consistent with the magnetic data.

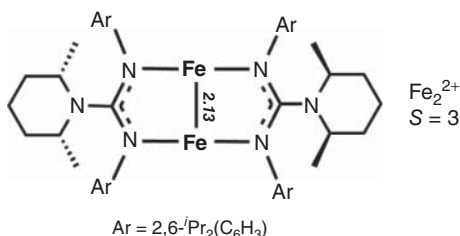


Figure 8.9 $\text{Fe}_2(\text{Pipiso})_2$.

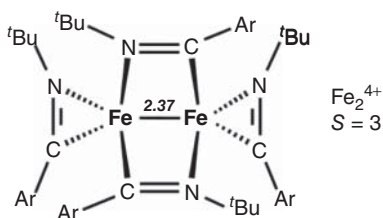


Figure 8.10 $\text{Fe}_2(\text{ArC}=\text{N}^t\text{Bu})_4$.

The anionic Fe₂ ketimide complex, [Li(12-crown-4)₂][Fe₂(NC^tBu)₅] (Figure 8.11), was prepared by adding 2.5 equiv. of Li(N = C^tBu₂) to FeCl₂ in THF, followed by 1 equiv. of 12-crown-4 [23]. The Fe–Fe distance is 2.443(1) Å (FSR: 1.05). The magnetic susceptibility data was modeled using two *S* = 1 spins with *g*-values of 2.30 and a magnetic coupling, *J* = 2.24 cm^{−1}. An Fe–Fe double bond was invoked, as strong coupling of two unpaired electrons per Fe(II) would be consistent with the magnetic data. An electronic configuration of σ²π⁴σ*²π*²δ²δ*⁰ was proposed, giving a net 1π + 1δ bond.

The use of sterically encumbered terphenyl ligands has also led to the isolation of Fe₂ complexes (Figure 8.12). The first is Fe₂(Ar')₂ (where Ar' = C₆H₃-2,6-(2,6-*i*Pr₂C₆H₃)₂) [24], where each terphenyl ligand coordinates to one iron through an Fe–C bond, while a flanking aryl ring forms an η⁶-arene interaction with the other iron. Dark red crystals of the complex were isolated in low yield from the reduction of [ArFe(μ-Br)]₂ with KC₈ in THF. The Fe–Fe bond distance is 2.515(9) Å (FSR: 1.08). The authors speculated that the complex ought to be diamagnetic, but magnetic susceptibility studies were inconclusive. On the other hand, multiconfigurational quantum chemical calculations predicted an *S* = 3 state [25].

The other terphenyl-stabilized Fe₂ analog, (3,5-*i*Pr₂-Ar*)FeFe(η⁵-Cp)(CO)₂ (where 3,5-*i*Pr₂-Ar* = C₆H₂-2,6-(C₆H₂-2,4,6-*i*Pr₃)₂-3,5-*i*Pr₂), was prepared from salt metathesis between K(η⁵-Cp)Fe(CO)₂ and a half equivalent of dimeric [(3,5-*i*Pr₂-Ar*)Fe(μ-Cl)]₂ [26]. This dark red molecule has a short, unsupported Fe–Fe bond (2.3931(8) Å, FSR: 1.03). The magnetic moment of 4.5–5.0 μ_B from 5 to 300 K is consistent with an *S* = 2 ground state. The Mössbauer spectrum for this complex contained two signals. One doublet with IS = 0.42 mm s^{−1} and QS = 0.96 mm s^{−1} was attributed to the terphenyl-supported iron, while the other with IS = 0.08 mm s^{−1} and QS = 1.73 mm s^{−1} was assigned to the carbonyl-supported Fe. DFT-computed natural charges of +1.12 for the iron in Fe(3,5-*i*Pr₂-Ar*) and −1.35 for the iron in Fe(η⁵-Cp)(CO)₂ indicate an intramolecular one-electron transfer from the former to the latter. Finally, the Wiberg bond order of 0.36 suggested that the Fe–Fe bonding is largely dative in nature.

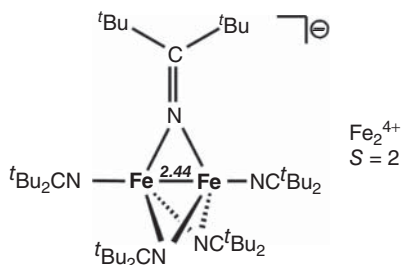


Figure 8.11 [Li(12-crown-4)₂][Fe₂(NC^tBu)₅].

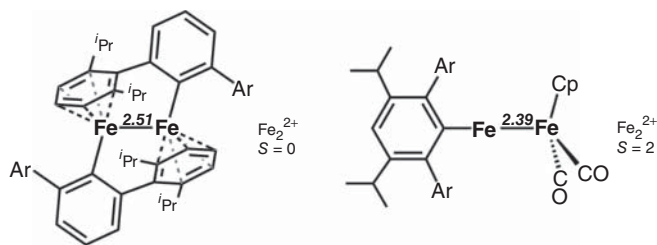


Figure 8.12 Fe₂(Ar')₂ and (3,5-*i*Pr₂-Ar*)FeFe(η⁵-Cp)(CO)₂.

8.2.1.5 Summary of Diiron

Non-organometallic diiron complexes are collected together as shown in Figure 8.13 to demonstrate the range of Fe–Fe bond lengths. Notably, the FSR values can be significantly higher than 1.0. Currently, the highest FSR value of 1.15 in this series is held by $\text{Fe}_2(\text{tim})_2$, which has an unsupported Fe–Fe bond. The oxidation states of the Fe_2 cores span from +2, for example, $\text{Fe}(\text{I})\text{Fe}(\text{I})$, to +5, for example, $\text{Fe}(\text{III})\text{Fe}(\text{II})$. Nearly all of these Fe_2 complexes are paramagnetic, and approximately half are high spin. Finally, the vast majority of these Fe_2 complexes require bridging ligands, with the two exceptions being $\text{Fe}_2(\text{tim})_2$ and $(3,5\text{-}^i\text{Pr}_2\text{-Ar}^*)\text{FeFe}(\eta^5\text{-Cp})(\text{CO})_2$.

8.2.1.6 Fe–Fe Bonding in Clusters

Beyond Fe_2 complexes, significant Fe–Fe interactions are also found within iron clusters. An overview of iron clusters (excluding those containing carbonyl or related ligands) is presented here, with a focus on their synthesis, properties, and reactivities.

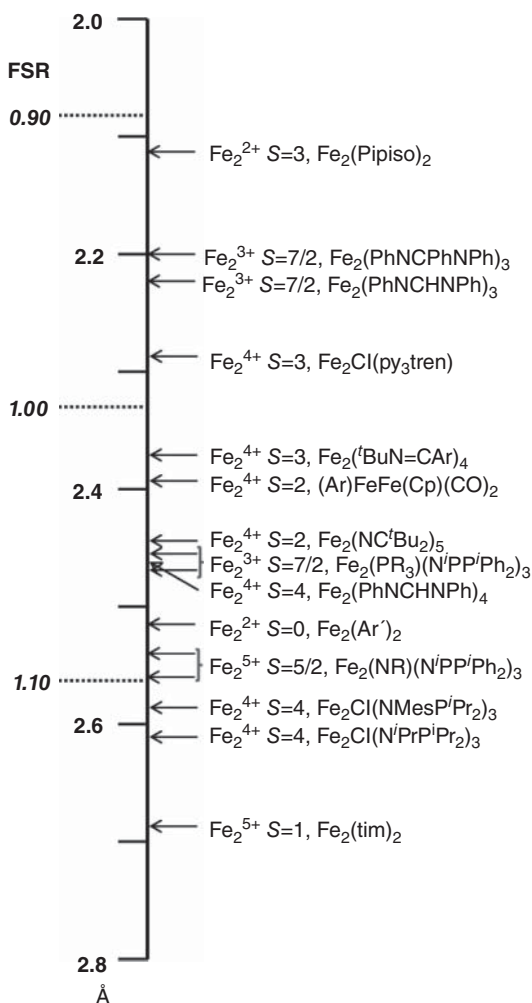


Figure 8.13 Non-organometallic Fe_2 complexes ranked according to the Fe–Fe bond length (in angstroms).

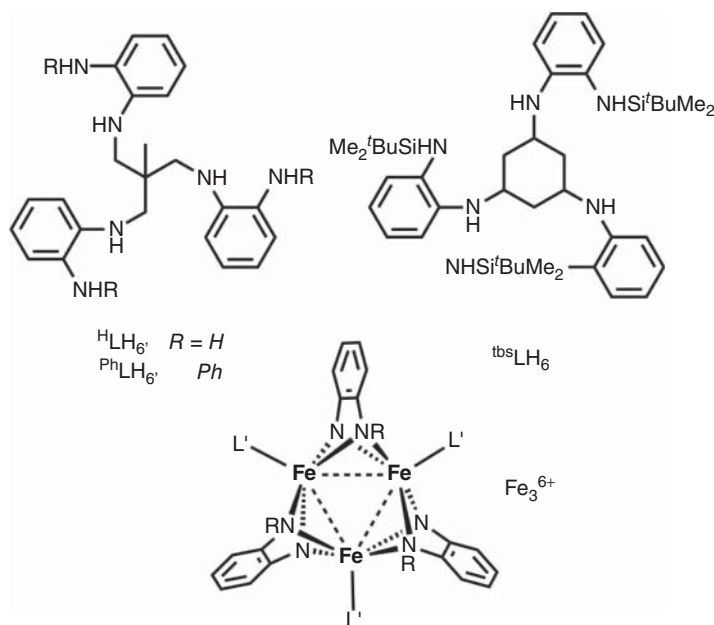


Figure 8.14 Ligands used for self-assembly of triiron cores, such as the Fe_3 complex, shown at bottom. The ligand backbone is omitted for clarity.

Trinuclear Fe_3 Clusters with Hexaamide Ligands Betley and coworkers have greatly expanded the coordination chemistry of Fe_3 complexes. Triiron cores were self-assembled within hexaamide ligands, which are shown in Figure 8.14. A typical metallation involves mixing the neutral ligand ($^R\text{LH}_6$) and $\text{Fe}_2(\text{N}(\text{SiMe}_3)_2)_4$ in a 2:3 stoichiometric ratio. For the less bulky ligands, an additional capping ligand (L') is needed to isolate the Fe_3^{6+} product, $(^R\text{L})\text{Fe}_3(\text{L}')_3$, where L' can be a phosphine, pyridine, or simply the THF solvent [27, 28]. For the bulky ligand, $(^{\text{tbs}}\text{L})^{6-}$, the metallation involved heating the neutral ligand and $\text{Fe}_2(\text{Mes})_4$ in benzene to afford $(^{\text{tbs}}\text{L})\text{Fe}_3(\text{THF})$, with only one capping ligand [29].

Both the ^RL ligand and the capping ligand affects the bonding and magnetic properties of the Fe_3^{6+} core. The $(^H\text{L})\text{Fe}_3(\text{PMe}_2\text{R}')_3$ complexes (where $\text{R}' = \text{Me}$ or Ph) are $S = 1$ with short Fe–Fe bond distances at 2.299 Å (FSR 0.99) [27]. The Mössbauer spectra of these compounds contain only one signal, with similar IS (0.38 and 0.39 mm s^{-1}) and QS values (1.03 and 0.96 mm s^{-1}), for $\text{R} = \text{Me}$ and Ph , respectively. While higher spin states were observed for the $(^{\text{Ph}}\text{L})\text{Fe}_3(\text{L}')_3$ complexes (where $\text{L}' = \text{THF}$, py , PMePh_2), the exact spin depended on L' [28]. For $\text{L}' = \text{THF}$, the $\chi_M T$ was measured by superconducting quantum interference device (SQUID) magnetometry to be temperature-independent at 18.5 $\text{cm}^3 \text{K mol}^{-1}$, which is near the expected value for $S = 6$. In contrast, for $\text{L}' = \text{py}$ or PMePh_2 , the $\chi_M T$ plots were temperature-dependent and were modeled as an equilibrium between an $S = 2$ ground state and a thermally accessible $S = 4$ excited state. The average Fe–Fe bond distances, which increase according to $\text{L}' = \text{THF} < \text{py} < \text{PMePh}_2$, are 2.49–2.59 Å (FSR 1.07–1.11), which are elongated compared to $(^H\text{L})\text{Fe}_3(\text{PMe}_2\text{R}')_3$. The Mössbauer spectra of the $(^{\text{Ph}}\text{L})\text{Fe}_3(\text{L}')_3$ have roughly similar ISs, 0.77–0.85 mm s^{-1} . The $(^{\text{Ph}}\text{L})\text{Fe}_3(\text{THF})_3$ is distinctive in that only one doublet is observed with $\text{QS} = 1.25 \text{ mm s}^{-1}$, whereas two signals are observed for $\text{L}' = \text{py}$ and PMePh_2 at 4 K. The two doublets, however, coalesce at higher temperatures. Finally, the solid-state structure of $(^{\text{tbs}}\text{L})\text{Fe}_3(\text{THF})$ revealed a unique coordination, with only one bridging silylamide group and one capping ligand. The average Fe–Fe bond distance was 2.58 Å (FSR 1.11). Consistent with the solid-state structure, $(^{\text{tbs}}\text{L})\text{Fe}_3(\text{THF})$ was characterized by three Mössbauer doublets: IS = 0.89, 0.49, and 0.50 mm s^{-1} , with the corresponding QS values of 1.68, 1.57, and 1.92 mm s^{-1} . The magnetic moment of $(^{\text{tbs}}\text{L})\text{Fe}_3(\text{THF})$

was determined by Evans' method to be $12.0(2) \mu_B$, which would be consistent with $S=6$, akin to $(^{Ph}L)Fe_3(THF)_3$ [29].

Rich reactivity was uncovered for the Fe_3^{6+} clusters. The cyclic voltammetry (CV) of $(^H L)Fe_3(PMe_3)_3$ showed two quasi-reversible, one-electron oxidations at -1.59 and -1.04 V (vs $FeCp_2^{+/0}$). Chemical oxidation with ferrocenium hexafluorophosphate afforded the Fe_3^{7+} complex, $[(^H L)Fe_3(PMe_3)_3](PF_6)$ [27]. The average Fe–Fe bond length contracted to $2.27 \text{ \AA}$ (FSR 0.97), a shortening by $0.03 \text{ \AA}$ relative to the Fe_2^{6+} analog. The Mössbauer IS decreased to 0.28 mm s^{-1} (from 0.38 mm s^{-1}) with $QS = 0.78 \text{ mm s}^{-1}$, which is consistent with a delocalized oxidation of all three iron centers. Chemical oxidation was also performed on $(^{Ph}L)Fe_3(THF)_3$ with 1 equiv. Ph_3CX ($X = Cl, Br$) or 0.5 equiv. I_2 , affording either halide-bridged hexairon clusters $[(^{Ph}L)Fe_3(\mu-X)]_2$ ($X = Cl$ or Br) or triiron clusters $(^{Ph}L)Fe_3X(L')$ ($X = Cl, L' = py$; $X = Br, L' = THF$; $X = I, L' = THF$). In the latter Fe_3^{7+} complexes, the halide and capping ligand are bound to the same iron center, leaving the other two iron centers to form a short bond of $2.308(1) \text{ \AA}$ (FSR 0.99) [30]. The oxidation was proposed to be localized on the diiron unit, and further, that the $S = 3/2$ Fe_2^{5+} unit coupled ferromagnetically to the $S = 2$ Fe^{2+} center. The different extent of delocalization upon oxidation was attributed to their different spin preferences, that is, low-spin $(^H L)Fe_3(PMe_3)_3$ versus high-spin $(^{Ph}L)Fe_3(THF)_3$.

The bulkier $(^{tBu}L)Fe_3(THF)$ system mediated a number of multi-electron processes that are potentially relevant to N_2 activation. A triiron μ^3 -nitride, $[(^{tBu}L)Fe_3(\mu^3-N)](Bu_4N)$, with a formal Fe_3^{8+} core, was generated by adding 1 equiv. $(Bu_4N)(N_3)$ to $(^{tBu}L)Fe_3(THF)$ [29]. This transformation was unusually facile at room temperature and did not require photolysis or heating, which are typically needed to extrude N_2 from a metal–azide intermediate. The functionalization of the capping nitride was performed with either MeI or lutidinium tetraphenylborate to give the Fe_3^{8+} μ^3 -imide complex, $(^{tBu}L)Fe_3(\mu^3-NR)$, where $R = Me$ or H . The Fe–Fe distance in both the Fe_3 nitride and the Fe_3 methylimide complexes is $2.48 \text{ \AA}$ (FSR 1.06), which is shorter than the average of $2.58 \text{ \AA}$ in $(^{tBu}L)Fe_3(THF)$. The average Fe–N bond length elongates slightly from $1.871(3)$ in the Fe_3 nitride to $1.892(3) \text{ \AA}$ in the Fe_3 methylimide. The magnetic moments of the Fe_3^{8+} cores in the nitride and imide complexes were determined by Evans' method to be $7.3(2)$ and $5.3(2) \mu_B$, which points to a dramatic lowering of spin states ($S = 2$ or 3) compared to the $S = 6$ Fe_3^{6+} starting material. The Mössbauer characterization of the Fe_3 nitride complex showed two signals with similar IS values of 0.37 and 0.39 mm s^{-1} ($QS = 1.78$ and 1.23 mm s^{-1}). For the Fe_3 imides, the IS values are also similar, ranging from 0.36 to 0.42 mm s^{-1} .

The $(^{tBu}L)Fe_3(THF)$ complex was found to cleave both N–N and N=N bonds. Hydrazine substrates, H_2NNHR ($R = H, Ph$), are reduced by $(^{tBu}L)Fe_3(THF)$ to form the Fe_3^{8+} μ^3 -imide, $(^{tBu}L)Fe_3(\mu^3-NH)$ and an amine byproduct, NH_2R ($R = H, Ph$) [31]. The use of the disubstituted hydrazine, $HPhNNHPh$, generates the phenyl imide, $(^{tBu}L)Fe_3(\mu^3-NPh)$, and aniline. Finally, adding azobenzene in different stoichiometries to $(^{tBu}L)Fe_3(THF)$ can generate either the capping imide, $(^{tBu}L)Fe_3(\mu^3-NPh)$ with 0.5 equiv., or the bis(imide) complex, $(^{tBu}L)Fe_3(\mu^3-NPh)(\mu^2-NPh)$ with 1 equiv. In both reactions, the N=N bond is fully cleaved, a rare feat for iron. Of interest, the latter reaction is formally a four-electron oxidation from Fe_3^{6+} ($3Fe(II)$) to Fe_3^{10+} ($2Fe(III), Fe(IV)$). The reactivity of the $(^{tBu}L)Fe_3$ system has thus far demonstrated metal cooperativity, redox flexibility, as well as ligand flexibility for potential applications in small-molecule activation.

Hexanuclear Fe_6 Clusters with Hexamide Ligands For the least bulky ligand system, ^HL , Betley and coworkers have also generated octahedral Fe_6 clusters. The octahedral clusters were favored over the triiron counterpart by metallating the ligand $^HLH_6$ with $Fe_2(Mes)_4$ in a mixture of benzene and pyridine, yielding the all-ferrous Fe_6^{12+} cluster, $(^HL)_2Fe_6$. The average Fe–Fe bond length was $2.597(2) \text{ \AA}$ (FSR 1.11). The CV of this complex was incredibly rich with five reversible redox events, including one reduction at -2.04 V (vs $FeCp_2^{+/0}$), and five oxidations between -1.55 and -0.72 V. In total, a six-membered redox series was isolated, containing Fe_6^{n+} cores with n ranging from 11 ($5Fe(II), Fe(I)$) to 16 ($4Fe(III), 2Fe(II)$). For the Fe_6^{11+} cluster, $[(^HL)_2Fe_6]^+$, the average Fe–Fe bond lengths slightly contracted to $2.580(1) \text{ \AA}$ (FSR 1.11). As the clusters were increasingly oxidized, the acetonitrile solvent bound as capping ligands. The number of acetonitrile ligands varied with the oxidation state:

two in $[(^H\text{L})_2\text{Fe}_6(\text{CH}_3\text{CN})_2]^+$, four in $[(^H\text{L})_2\text{Fe}_6(\text{CH}_3\text{CN})_4]^{2+}$, and a maximum of six, one per Fe, in $[(^H\text{L})_2\text{Fe}_6(\text{CH}_3\text{CN})_6]^{3+/4+}$. A qualitative trend was that the average Fe–Fe bond lengths increase with increasing positive charge, reaching upwards of 2.69–2.70 Å (FSR 1.15–1.16). Reactivity between $(^H\text{L})_2\text{Fe}_6$ and nitrite was reported. The Fe_6^{12+} cluster reduced 6 equiv. of nitrite in the presence of protons (12 equiv. benzoic acid) to generate the hexanitrosyl cluster, $(^H\text{L})_2\text{Fe}_6(\text{NO})_6$, in which the long Fe–Fe distances of 3.217(3) Å (FSR 1.38) suggest no Fe–Fe interactions. Interestingly, the nitro-ligated intermediate, $[(^H\text{L})_2\text{Fe}_6(\text{NO}_2)_6]^{2-}$ was isolated by adding 6 equiv. nitrite to the oxidized Fe_6^{16+} cluster, $[(^H\text{L})_2\text{Fe}_6(\text{CH}_3\text{CN})_6]^{4+}$. In the nitro intermediate, the average Fe–Fe bond distance of 2.727(4) Å (FSR 1.17) indicates weak Fe–Fe interactions. The lone quadrupole doublet in the Mössbauer spectrum ($\text{IS} = 0.38 \text{ mm s}^{-1}$, $\text{QS} = 2.38 \text{ mm s}^{-1}$) is consistent with fully delocalized d-electrons over the six iron centers [32–34].

Hydrocarbon-Supported Fe_3 and Fe_2 Clusters An interesting analog of $\text{Fe}_3(\text{CO})_{12}$, $\text{Fe}_3(\text{COT})_3$ (where COT = 1,3,5,7-cyclooctatetraene), was isolated by dissolving 10 mol% of *N,N'*-bis(2,6-diisopropyl)phenyl-substituted *N*-heterocyclic carbene (NHC) in a benzene solution of $\text{Fe}(\text{COT})_2$. By allowing the solution to rest, black crystals of $\text{Fe}_3(\text{COT})_3$ formed in good yield [35]. Gentle heating of the reaction at 45 °C increased the yield to 95%. The average Fe–Fe distance in $\text{Fe}_3(\text{COT})_3$ is 2.824 Å (FSR 1.21). As shown in Figure 8.15, each COT ligand bridges two Fe centers with η^5 and η^3 coordination modes, which may suggest an Fe_3^{6+} core. The complex exhibits a single ^1H NMR signal at –3.15 ppm, which indicated that the COT ligands are fluxional at rt. The ^1H NMR signal was interpreted to be paramagnetically shifted, though DFT studies favored a singlet ground state [36]. Intriguingly, the NHC was proposed to catalyze Fe–Fe bond formation. In support of this proposal, the reaction of $\text{Fe}(\text{COT})_2$ with the less bulky *N,N'*-bis(2,4,6-trimethyl)phenyl-substituted carbene produced a tetrairon cluster, $[(\text{MesNHC})\text{FeFe}(\text{cot})]_2(\mu\text{-C}_{16}\text{H}_{16})$, which contained two mixed-valent Fe_2^{1+} cores with shorter Fe–Fe bond distances of 2.508 Å (FSR 1.08). Follow-up work showed that using an abnormal *N*-heterocyclic carbene (aNHC), which is an imidazolyliene that binds the metal through a backbone carbon, the Fe_2^{2+} complex, $(\text{aNHC})\text{Fe}_2(\text{COT})_2$, was isolated [37]. The Fe–Fe bond length was even shorter at 2.4530(5) Å (FSR 1.05). A measured magnetic moment of $2.64 \mu_B$ by Evans' method suggested a spin state of $S = 1$.

Intermetallic Carbide Clusters Multiple bonding between iron centers have also been reported for the intermetallic carbide $\text{Gd}_{13}\text{Fe}_{10}\text{C}_{13}$ [38]. A new phase of the GdFeC intermetallic was prepared by annealing arc-melted pellets of elemental Gd, Fe, and C at 900 °C for 350 h. The crystal structure revealed an unsupported Fe–Fe bond in the C_2FeFeC_2 subunits, in which each iron center binds two carbides. The Fe–Fe bond lengths were 2.36 and 2.38 Å (FSR 1.01, 1.02). Bonding analysis using Hückel calculations suggested multiple bonding.

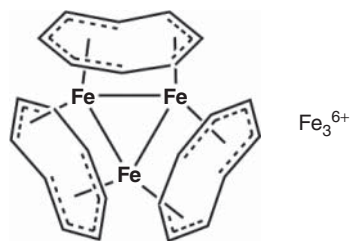


Figure 8.15 $\text{Fe}_3(\text{COT})_3$.

8.2.2

Diruthenium

Of the Group 8 homobimetallic complexes, those of diruthenium are the most numerous, perhaps because of their stability. Diruthenium complexes have many interesting electronic and redox properties. They can have multiple bonds, and they can be low or intermediate spin. Moreover, the spin states can be explained by the application of simple ligand field theory. Diruthenium complexes have been isolated in several redox states. Typically, oxidation state changes result in minimal reorganization of the diruthenium core, and hence, many of these complexes can transfer multiple electrons readily, albeit one at a time.

The vast majority of diruthenium complexes belong to the paddlewheel family. Non-paddlewheel diruthenium complexes include unsupported metal–metal bonds in both tetragonal and trigonal symmetry. Recent advances in Ru_2 paddlewheels focus on their applications as building blocks in molecular electronic wires and devices, as well as in magnetic materials. They also show increasing promise as catalysts in organic chemistry. This section does not delve into the detailed synthesis and bonding properties of Ru_2 paddlewheels, which have been reviewed comprehensively [39, 40]. Instead, the section will highlight the research discoveries since 2005, with a review of the electronic structures for understanding the evolving applications of Ru_2 complexes.

8.2.2.1 Paddlewheel

The first diruthenium paddlewheel complex, $\text{Ru}_2(\mu\text{-O}_2\text{CMe})_4\text{Cl}$, was prepared in 1966 by Stephenson and Wilkinson [3]. The paddlewheel geometry was validated in 1969 when Cotton and coworkers reported the X-ray crystal structure of an analogous complex, $\text{Ru}_2(\mu\text{-O}_2\text{C}^n\text{Pr})_4\text{Cl}$ [4]. In the crystal, $\text{Ru}_2(\mu\text{-O}_2\text{C}^n\text{Pr})_4\text{Cl}$ assembles in an infinite zig-zag chain, where each chloride atom bridges two diruthenium units. More significantly, a short Ru–Ru bond distance of 2.281(4) Å was revealed. The FSR of this bond is 0.92, which is consistent with a multiple bond order.

In addition to their historical role, Ru_2^{5+} tetracarboxylate complexes have broad synthetic utility. They can undergo ligand substitution reactions, and thus, are commonly used as reagents in the synthesis of other Ru_2^{5+} paddlewheels. Other ligands that can bridge the ruthenium centers in a similar fashion include amidates, amidinates, aminopyridinates, oxypyridinates, naphthyridines, carbonates, phosphonates, and sulfonates. The ligand substitution reactions typically occur at elevated temperatures in the molten, neutral form of the ligand, for example, the amide, amidine, or aminopyridine. Faster and higher yielding ligand substitution reactions of Ru_2^{5+} tetracarboxylates have recently been developed that use microwave irradiation or solvothermal techniques [41–43].

Electronic Structure and Properties

Ru_2^{5+} Most diruthenium paddlewheels contain Ru_2^{5+} cores, which are formally mixed-valent, Ru(II)Ru(III) . These cores are delocalized with Ru(2.5)Ru(2.5) oxidation states [44]. Two other redox states of the diruthenium core, Ru_2^{4+} and Ru_2^{6+} , have also been isolated, though only for a subset of the ligands listed above for Ru_2^{5+} . Generally, Ru_2^{5+} paddlewheels have weaker donors, for example, carboxylates and amidates, while Ru_2^{6+} paddlewheels have more electron-rich donors, for example, amidinates and aminopyridinates.

Nearly all Ru_2^{5+} paddlewheels possess an $S = 3/2$ spin ground states. The stability of the quartet spin has been attributed to the δ^* and π^* molecular orbitals being practically degenerate [45]. The electronic configuration of Ru_2^{5+} paddlewheels is $(\sigma)^2(\pi)^4(\delta)^2(\pi^*\delta^*)^3$ as shown in Figure 8.16. As is expected for tetragonal systems, only four d-orbitals participate in metal–metal bonding. The $d_{x^2-y^2}$ orbitals, which are not shown in Figure 8.16, are rendered inaccessible by their strong anti-bonding interactions with the ligands. The formal metal–metal bond order predicted by this electronic configuration is 2.5 (1 σ + 1 π + 0.5 δ), which is consistent with the short Ru–Ru bond distances (ave. 2.30 Å, FSR 0.93).

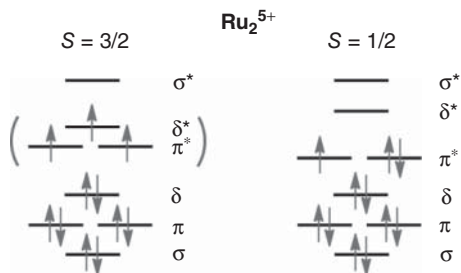


Figure 8.16 Qualitative d-orbital manifolds for Ru_2^{5+} paddlewheels.

Some exceptional Ru_2^{5+} paddlewheels have $S=1/2$ spin states. A few of these have in common highly basic, π -donating ligands such as aminothiazolates and triazenates, which further destabilize the δ^* orbital to give an electronic configuration $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^3$ [46, 47]. Others such as $\text{Ru}(\text{PhNCHNPh})_4(\text{CN})$ and $\text{Ru}(\mu\text{-O}_2\text{CMe})(\text{PhNCHNPh})_3(\text{SCN})$ have axial π -acceptors which stabilize the π^* orbitals relative to δ^* [48–50]. The $S=1/2$ Ru_2^{5+} paddlewheels tend to have longer Ru–Ru bond distances (ave. 2.40 Å, FSR 0.97), which is consistent with the stronger anti-bonding interactions (π^* vs δ^*).

Though rare, a few Ru_2^{5+} paddlewheels display spin transition from a doublet ground state to a low-lying quartet excited state. One example is $\text{Ru}_2(\text{ArNCHNAr})_4\text{Cl}$, where $\text{Ar} = p\text{-anisyl}$ [51]. The temperature dependence of the magnetic susceptibility (χT vs T) has a characteristic sigmoidal shape, starting at 0.5 emu K mol $^{-1}$ at 2 K and rising to 1.6 emu K mol $^{-1}$ at 300 K. Since Ru–Ru bond distances are sensitive to spin states, the temperature profile of the metal–metal bond can lend supporting evidence. The expectation is that the Ru–Ru bond will contract with increasing temperature as the electronic configuration changes from $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^3$ to $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2(\delta^*)^1$. Indeed, a significant shortening of the Ru–Ru bond by 0.0503(9) Å was observed in the solid-state structure obtained at 300 versus 27 K. Similar temperature dependence of the magnetic susceptibility and of the Ru–Ru bond distance have been reported for the diphosphine adduct $[\text{Ru}(\mu\text{-O}_2\text{CMe})_4(\text{PCy}_3)_2](\text{PF}_6)$ and $[\text{Ru}_2(\mu\text{-O}_2\text{CMe})(\text{PhNCHNPh})_3(\text{H}_2\text{O})](\text{SO}_3\text{CF}_3) \cdot \text{THF}$ [52, 53]. Of interest, $[\text{Ru}_2(\mu\text{-O}_2\text{CMe})(\mu\text{-PhNCHNPh})_3(\text{H}_2\text{O})](\text{BF}_4)$ displays more complex magnetic behavior that is inexplicable with spin crossover [54]. Instead, it is proposed that significant mixing of the $S=1/2$ and $S=3/2$ spin states via spin-orbital coupling results in a quantum chemical spin-admixed state.

Ru_2^{4+} Ru_2^{4+} paddlewheels are often synthesized by the chemical reduction of the Ru_2^{5+} precursor. Because of the mild reduction potentials of Ru_2^{5+} tetracarboxylates, most Ru_2^{4+} paddlewheels belong to this family [55–59]. One of the first isolated Ru_2^{4+} paddlewheels, $\text{Ru}_2(\mu\text{-O}_2\text{CMe})_4(\text{THF})_2$, was prepared by reducing the Ru_2^{5+} precursor with a Grignard reagent [60]. The Ru–Ru bond distance of 2.260(2) Å (FSR 0.91) suggested little to no change in the metal–metal bond order upon reduction. Ru_2^{4+} tetracarboxylates typically have $S=1$ spin states, which is consistent with either $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^3(\delta^*)^1$ or $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2(\delta^*)^2$. The temperature dependence of the magnetic moment of $\text{Ru}_2(\mu\text{-O}_2\text{CMe})_4$ was found to be consistent with the former interpretation [61]. The loss of a partial δ bond (0.5 δ) upon reduction is also consistent with the latter (Figure 8.17), as the Ru–Ru bond distance should be relatively similar in Ru_2^{5+} and Ru_2^{4+} tetracarboxylates (ave. 2.28 Å, FSR 0.92). Like their oxidized counterparts, Ru_2^{4+} tetracarboxylates are synthetic precursors to other Ru_2^{4+} paddlewheels via ligand substitution reactions.

For the more basic, N,N -donor ligands such as amidinates and triazenates, Ru_2^{4+} paddlewheels are diamagnetic and have a proposed configuration of $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^4$. As mentioned above, the higher ligand basicity destabilizes the δ^* orbital substantially. Because of the weakened metal–metal bond ($1\sigma + 1\delta$), the Ru–Ru bond distances are longer by 0.15 Å than in the Ru_2^{4+} tetracarboxylates (ave. 2.42 Å, FSR 0.98) [41, 42, 47, 62–66].

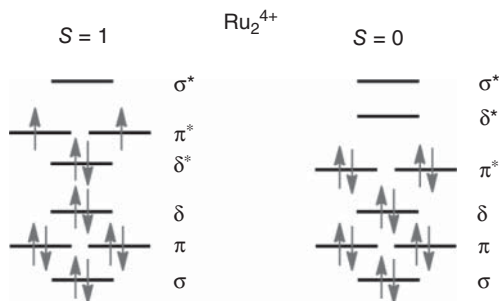


Figure 8.17 Qualitative d-orbital manifolds for Ru_2^{4+} paddlewheels.

Ru_2^{6+} Although no Ru_2^{6+} tetracarboxylates have been structurally characterized, Ru_2^{6+} paddlewheels are known with phosphate, sulfate, aminopyridinate, amidinate, and guanidinate ligands [67, 68]. A majority of the Ru_2^{6+} cores are additionally coordinated by axial, monoanionic ligands, such as halides and alkynyls, though there are examples where the axial sites are occupied by solvent or weakly coordinating anions. The spin ground states of Ru_2^{6+} paddlewheels seem to correlate well with the field strengths of the ligands. The Ru_2^{6+} sulfate and phosphate complexes, $[\text{Ru}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2]^{2-}$ and $[\text{Ru}_2(\text{HPO}_4)_3(\text{PO}_4)(\text{H}_2\text{O})_2]^{3-}$, have the highest observed spin $S = 2$, and hence, the electronic configuration is proposed to be $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2(\delta^*)^1$ (Figure 8.18) [69–71]. Only the sulfate complex has been structurally characterized, and the Ru–Ru bond distance is 2.343(1) Å [69].

For N,N -donor ligands, which accounts for nearly all Ru_2^{6+} paddlewheels, the spin states are either a triplet or singlet (Figure 8.18). When the axial ligands are Cl^- or a weakly coordinating anion, the $S = 1$ is favored [72–74]. In these cases, the Ru–Ru bond distances remain similar to those in the Ru_2^{5+} paddlewheels (ave. 2.32 Å, FSR 0.93), which is consistent with the electronic configuration of $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2$. With strong-field axial ligands, such as alkynyls and cyanides, the Ru_2^{6+} paddlewheels are diamagnetic. The low-spin state is the result of the significant disruption in the Ru–Ru σ -bond by the axial donors, giving a new configuration of $(\pi)^4(\delta)^2(\pi^*)^4$ [75, 76]. Consistent with this interpretation, the Ru–Ru bond distances are long (ave. 2.48 Å, FSR 1.00), as is expected for the net 1 δ bond.

An interesting exception to these general rules is a Ru_2^{6+} dichloride with four bridging guanidinate ligands. Specifically, the guanidinate ligand is the anionic state of 1,4,6-triaza-bicyclo-[3.3.0]oct-4-ene, which has two fused five-membered rings that considerably widen the ligand bite angle. The net

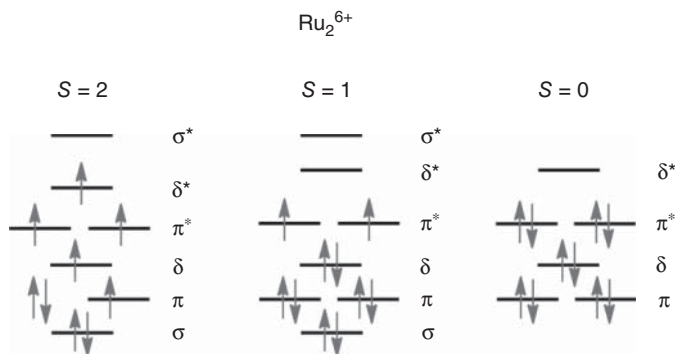


Figure 8.18 Qualitative d-orbital manifolds for Ru_2^{6+} paddlewheels.

outcome is a disruption in the Ru–Ru σ -bond (Ru–Ru 2.499(3) Å) such that the $(\pi)^4(\delta)^2(\pi^*)^4$ configuration becomes favored, giving rise to an $S=0$ ground state [77]. When the guanidinate ligand comprises at least one six-membered ring, the ligand bite angle relaxes, and their corresponding Ru_2^{6+} dichloride complexes are $S=1$.

Of note, Ren and coworkers have revisited the bonding picture of Ru_2^{6+} bis(alkynyl) species with DFT calculations [78]. Ru_2^{6+} bis(alkynyl) complexes are known to distort from the D_4 paddlewheel geometry, and one of the manifestations is the bending of the Ru–Ru–C(alkynyl) bond angle to $\sim 155\text{--}165^\circ$ [79]. DFT calculations reveal that this bending greatly alleviates one of the $\pi^*(\text{Ru–Ru})$ interactions, which then gains partial σ -bonding character (Figure 8.19). Hence, the authors surmise that the distortion arises to increase net Ru–Ru bonding.

An unusual spin transition has been observed for a Ru_2^{6+} paddlewheel that is covalently linked by butadienyl ligands to two terminal Ru_2^{5+} units, $\text{LRu}_2\text{--C}\equiv\text{C--C}\equiv\text{C--}(\text{MeNCPhNMe})_4\text{Ru}_2\text{--C}\equiv\text{C--C}\equiv\text{C--Ru}_2\text{L}$. The magnetic behavior of the linear Ru_2 -trimer is explained, in part, by a spin transition at the central Ru_2^{6+} unit from $S=0$ to $S=1$ with increasing temperature [80].

Summary of Ru–Ru Bond Distances in Ru_2 Paddlewheels The average Ru–Ru bond distances of paddlewheel complexes are shown in Figure 8.20. As discussed earlier, the metal–metal bond length is sensitive to both the spin state and oxidation state of the Ru_2 core. One qualitative trend is that the higher spin Ru_2 paddlewheels have shorter Ru–Ru bonds than their diamagnetic counterparts. Also, a notable difference from Fe_2 non-organometallic complexes is that for the metal–metal bond lengths in Ru_2 paddlewheels cover only a narrow range, from FSR 0.9 to ~ 1.0 .

Applications

Toward Electronic and Magnetic Materials and Devices One potential application of diruthenium paddlewheels is their use as building blocks in molecular electronic devices and magnetic materials.

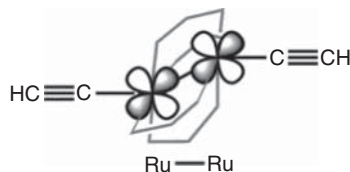


Figure 8.19 Bending of the Ru–Ru–C(alkynyl) bond angle gives partial σ -bonding character to the “ $\pi^*(\text{Ru–Ru})$ ” MO.

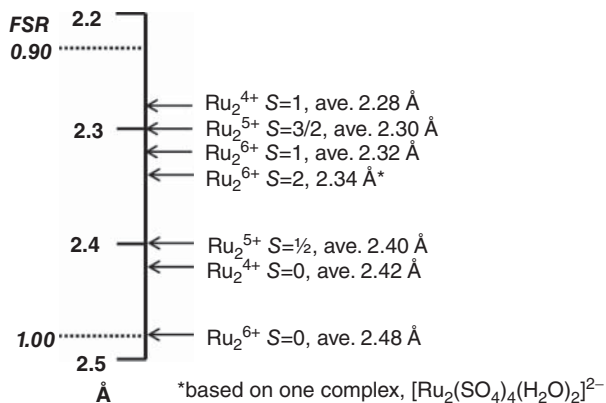
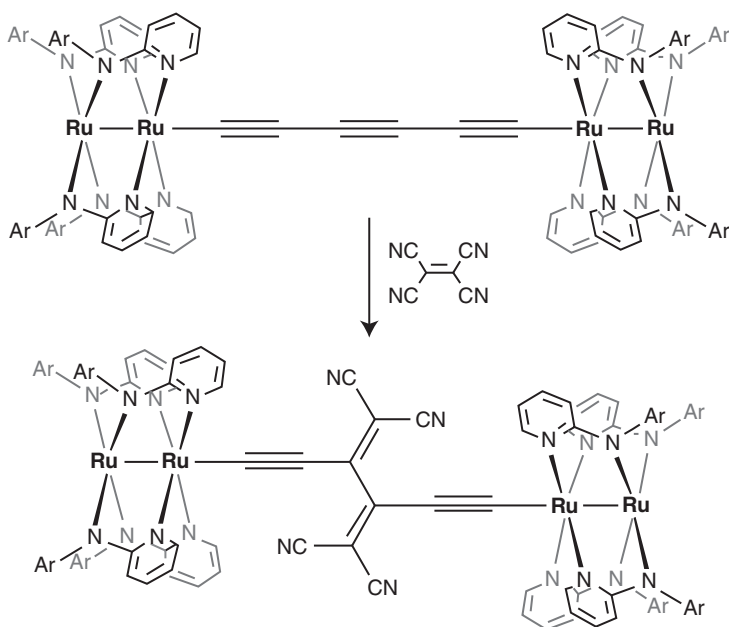


Figure 8.20 Average Ru–Ru bond lengths (Å) in Ru_2 paddlewheels.

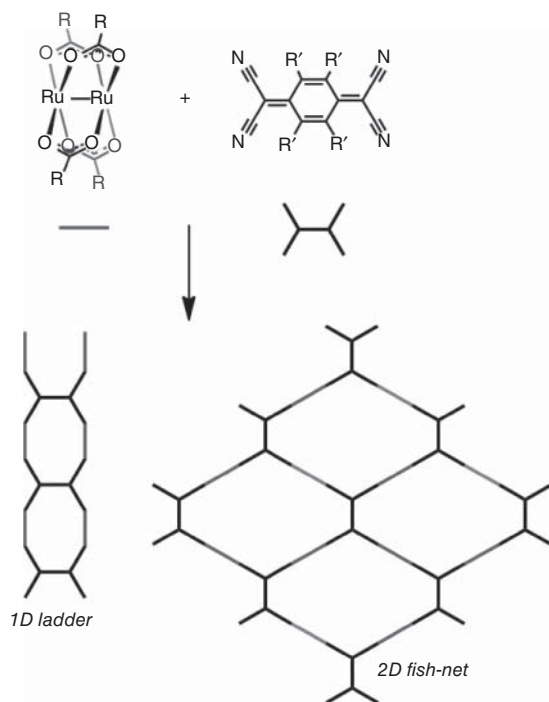
Historically, Ru_2^{5+} paddlewheels were targeted as molecular wires because of their paramagnetism and tendency to crystallize in chains via *interdimer* bridging ligands that coordinate in the axial positions. Solutions of $\text{Ru}_2(\mu\text{-O}_2\text{CEt})_4\text{X}$ adsorbed onto surfaces can self-assemble into long chains up to $8\ \mu\text{m}$ in length [81, 82]. Synthetic strategies aimed at controlling the magnetic and electronic properties of Ru_2 paddlewheels have primarily focused on tuning the interdimer bridging ligands. These interdimer ligands are conjugated, and ideally, their π -system energetically matches the $d\pi$ orbitals of the Ru_2 units, so as to facilitate electronic delocalization.

Both Ru_2^{5+} mono(alkynyl) and/or Ru_2^{6+} bis(alkynyl) units have been incorporated into linear conjugated molecules [83, 84]. The rigid alkynyl (or arylolethynyl) bridges can vary in length from simple acetylide monomers to tetramers (i.e., octadiynyl). The Ru_2 alkynyl complexes have multiple, accessible redox states, and high electron/hole mobility [85–88]. Quite promisingly, one variant $\text{Ru}_2(\text{aminopyridinate})_4(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4)_2\text{S}$ showed improved conductance in nano-junction measurements over the corresponding oligo(phenyleneethynylene) [89]. Further the chemical modification of the polyethynyl bridges within the Ru_2 alkynyl complexes can attenuate electron-transfer rates (Scheme 8.1), which may have applications in conductance switching [90].



Scheme 8.1 Disruption of electronic coupling between two Ru_2 units through chemical modification of alkynyl linker with tetracyanoethylene.

By adjoining Ru_2^{4+} paddlewheels with multitopic bridging ligands, two- and three-dimensional metal–organic frameworks have been assembled that are interesting as magnetic materials. Miyazaki and coworkers achieved long-range magnetic ordering and electrical conductivity through the self-assembly of Ru_2^{4+} tetracarboxylates with redox-active tetracyano-*p*-quinodimethane (TCNQ) derivatives [91–94]. One of the essential design elements is to match the redox potentials of the Ru_2^{4+} paddlewheels with the bridging ligand, so as to create a resonant charge-delocalized state, for example, $\text{Ru}_2^{5+}-(\text{TCNQ})^{\bullet-}-\text{Ru}_2^{4+} \leftrightarrow \text{Ru}_2^{4+}-(\text{TCNQ})-\text{Ru}_2^{4+} \leftrightarrow \text{Ru}_2^{4+}-(\text{TCNQ})^{\bullet-}-\text{Ru}_2^{5+}$, and thus, increasing conductivity. The multitopic TCNQ derivatives and the rigid Ru_2^{4+} paddlewheels create complex and structurally diverse networks, including one-dimensional ladders, two-dimensional hexagonal “fish-nets,” and three-dimensional bundles of helices (Scheme 8.2). The fish-net structure of $[\text{Ru}_2(\text{O}_2\text{CCF}_3)_4-(\text{TCNQF}_4)]$ further assembles into a layered, metamagnet



Scheme 8.2 Self-assembled structures of Ru_2^{4+} paddlewheels and TCNQ bridging ligands. 3-D helices are not shown. (Adapted from Ref. [95].)

material with antiferromagnetic ordering at 95 K (where TCNQF_4 is 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane). The metamagnetic behavior is attributed to antiferromagnetic coupling between layers, and long-range ferromagnetic ordering within each layer [91–94]. Three-dimensional networks of $[\text{Ru}_2(\text{O}_2\text{C}((p\text{-F})\text{-C}_6\text{H}_4))_4(\text{BTDA-TCNQ})]$ (where BTDA is bis(thiadiazole)) display long-range ferromagnetic coupling with a relatively high Curie temperature of 107 K [92].

Reactivity and Catalysis Developing catalysts based on Ru_2 paddlewheels is a burgeoning area. One of the first catalytic examples of a diruthenium paddlewheel was the hydrogenation of alkenes and alkynes by $\text{Ru}_2(\mu\text{-O}_2\text{CMe})_4$ [96]. Since then, numerous catalytic applications have been discovered, including: the cyclopropanation of alkenes; ring-opening metathesis polymerization (ROMP); and the aerobic oxidation of sulfide, alcohol, and amine substrates. Recently, Ru_2 paddlewheels have been scrutinized for catalytic C–H bond aminations. These studies offer detailed mechanistic insights into the reactivity of Ru_2 paddlewheels which may inspire new catalyst designs.

Another direction has been to develop heterogeneous applications of diruthenium paddlewheels [97]. By using multitopic carboxylate ligands, for example, 1,4-benzenedicarboxylate, Ru_2 tetracarboxylates are assembled into microporous networks. Interesting applications such as the catalytic hydrogenation of alkenes, the oxidation of primary aliphatic alcohols, and photocatalytic hydrogen production from water have been reported [98–101].

Cyclopropanation and Metathesis of Alkenes In a one-pot reaction containing ethyl diazoacetate, styrene, and norbornene, $\text{Ru}_2(\mu\text{-O}_2\text{CMe})_4$ was shown to catalyze cyclopropanation as well as the selective cross-metathesis of the two alkenes [102]. Since no metathesis occurs in the absence of ethyl diazoacetate, it is proposed that the diazoester initiates the catalyst by forming a reactive

diruthenium carbene species. Selectivity for cyclopropanation over metathesis can be achieved by altering the electronics of the diruthenium catalyst. $\text{Ru}_2(\mu\text{-O}_2\text{CCF}_3)_4$ is a highly selective catalyst for the cyclopropanation of cyclooctene [103]. However, when the alkene substrate is norbornene the selectivity of $\text{Ru}_2(\text{O}_2\text{CCF}_3)_4$ reverses and favors ROMP.

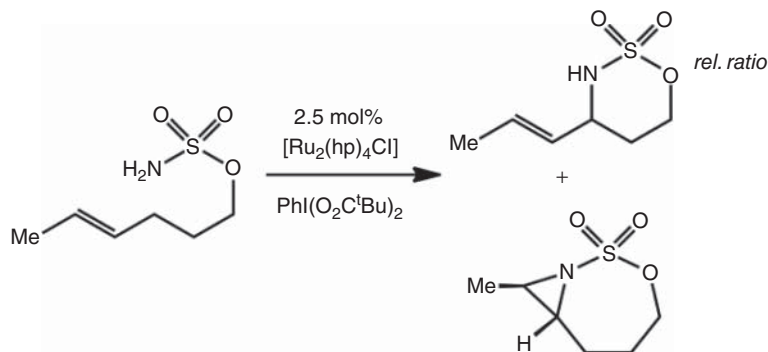
Organic Sulfide Oxidation The Ru_2^{5+} tetracarboxylate, $\text{Ru}_2(\text{esp})_2\text{Cl}$ (where esp = tetramethyl-1,3-benzenedipropionate), promotes the oxidation of organic sulfides to their corresponding sulfoxides and sulfones using $^t\text{BuO}_2\text{H}$ in acetonitrile [104]. When the catalysis is performed under neat conditions, the oxidation of MeSPh gives exclusively the sulfoxide product in nearly quantitative yield and at an enhanced rate. Ru_2^{5+} tetraamidate catalysts, $\text{Ru}_2(\mu\text{-NHCRO})_4\text{Cl}$ (where $\text{R} = \text{Et}, ^i\text{Pr}$), are also competent at oxidizing sulfides with $^t\text{BuO}_2\text{H}$ or H_2O_2 . These catalysts share similar initial rates, but the yields of the sulfoxide products are significantly worse for the Ru_2^{5+} tetraamidates relative to $\text{Ru}_2(\text{esp})_2\text{Cl}$ [105]. Hence, catalyst stability appears to be negatively impacted by the more electron-donating ligands. Aerobic oxidations of organic sulfides have also been reported for Ru_2^{5+} paddlewheels, but lengthy reaction times (72 h) were needed to obtain high conversion [106].

Aerobic Oxidation Ru_2^{5+} paddlewheels are known to catalyze the oxidation of alcohols and amines with O_2 . Under 1 atm O_2 , water-soluble $\text{Ru}_2(\mu\text{-O}_2\text{CMe})_3(\mu\text{-CO}_3)$ converts primary and secondary alcohols into aldehydes and ketones, respectively, in a biphasic water/toluene solution at 80 °C [107]. The catalyst can be recycled, by reusing the aqueous layer. High conversions are typical for activated alcohols, including benzylic, allylic, and α -keto alcohols. In the case of benzyl alcohol, over-oxidation to benzoic acid was observed. However, benzaldehyde was obtained in high yield by adding butylhydroxytoluene (BHT). The catalyst has a high chemoselectivity for primary over secondary alcohols (14 : 1). Consistent with this observation, a ruthenium alkoxide is proposed as an intermediate species that undergoes β -hydride elimination to release product.

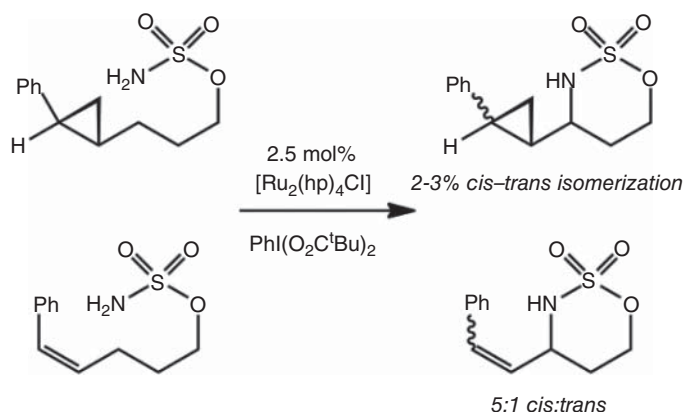
A similar mechanism has been proposed for the oxidation of secondary amines to imines using catalytic $\text{Ru}_2(\mu\text{-O}_2\text{CMe})_4\text{Cl}$ and O_2 in toluene [108]. The substrate scope includes a number of five- and six-membered cyclic amines, including tetrahydroquinolines, tetrahydroisoquinolines, and indolines. Dibenzylamine converted cleanly to the imine. Of interest, the primary amine benzylamine is oxidized completely to benzonitrile. Several monoruthenium complexes were also evaluated for catalysis, but their reaction yields were significantly lower, supporting an intact diruthenium catalyst.

Allylic C–H Bond Amination $\text{Ru}_2^{4+/5+}$ tetracarboxylates catalyze the insertion of carbenoids derived from diazoester reagents into O–H and N–H bonds [109, 110]. Recently, diruthenium paddlewheels have been shown to catalyze the intramolecular insertion of nitrenes derived from sulfamate esters (ROSO_2NH_2) into C–H bonds [111, 112]. The reaction conditions consist of a 2.5 mol% diruthenium catalyst, the oxidant $\text{PhI}(\text{O}_2\text{C}^t\text{Bu})_2$, and molecular sieves at 40 °C in CH_2Cl_2 . For unsaturated sulfamate esters, for example, *trans*-4-hexenyl sulfamate, the Ru_2^{5+} tetra-2-oxyppyridinate, $\text{Ru}_2(\text{hp})_4\text{X}$ (where $\text{hp} = 2\text{-oxyppyridinate}$, $\text{X} = \text{Cl}$ or SbF_6) was highly selective for allylic C–H amination over aziridination (Scheme 8.3). Intramolecular competition studies further indicate that amination selectivity of $\text{Ru}_2(\text{hp})_4\text{Cl}$ follows the order: allyl > benzyl > tertiary.

Some key experimental insights were obtained regarding the mechanism of $\text{Ru}_2(\text{hp})_4\text{Cl}$, as shown in Scheme 8.4. A substrate containing the *cis*-cyclopropane radical clock revealed a detectable amount (2–3%) of *cis*–*trans* isomerization. The *cis*–*trans* isomerization was attributed to a short-lived radical that can reversibly fragment the cyclopropane ring prior to fast radical recombination. *cis*–*trans* Isomerization became much more significant (5 : 1 *cis*:*trans*) for the *cis*-styrenyl substrate. Finally, a substrate used to probe the intramolecular competition of C–H versus C–D amination gave a kinetic isotope effect (KIE) of 4.9 ± 0.2 , suggesting considerable C–H bond breaking in the transition state. Based on these findings, the Ru_2 -catalyzed C–H amination likely involves



Scheme 8.3 Selective Ru_2 -catalyzed intramolecular allylic C–H amination. (Adapted from Ref. [111].)



Scheme 8.4 Observations that support a stepwise C–H abstraction/radical-rebound mechanism in Ru_2 catalyzed aminations.

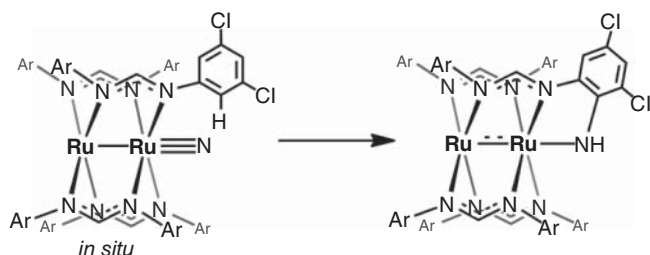
two discrete steps, homolytic C–H bond cleavage followed by radical recombination to form the C–N bond.

The reaction mechanism has also been investigated by DFT calculations, lending support for the stepwise mechanism [111, 112]. The first key intermediate is the diruthenium nitrenoid species ($S = 1/2$). In the transition state of the C–H bond scission, the coordinated nitrenoid interacts with the allylic H atom, polarizing the C–H bond. Subsequent H atom transfer to the N atom generates a diradical species comprising a diruthenium amide tethered to an allylic radical ($S = 3/2$). Of interest, the unpaired electrons are primarily localized at the two Ru centers (and the allylic fragment), with little spin density (0.14) at the N atom. Finally, radical rebound forms the cyclized amine.

The DFT mechanism shows that the quartet and doublet transition state species are close in energy, which is understandable since both $S = 3/2$ and $1/2$ ground states are known for Ru_2^{5+} paddlewheels. Considering the Ru–Ru–N core, the spin density at the N atom is minimal, despite its participatory role in C–H bond cleavage and N–H/N–C bond formations. Instead, both Ru centers harbor most of the spin density during the catalytic cycle. The spin flexibility afforded by the two Ru centers joined by a metal–metal bond may potentially be exploited in other catalytic applications.

Stoichiometric Aryl C–H Bond Amination Toward the goal of developing catalysts that can activate strong C–H bonds, Berry and coworkers have investigated diruthenium terminal nitrides supported by formamidinate ligands in a paddlewheel arrangement. Unlike mononuclear Ru nitrides, the Ru_2^{7+}

nitride species are extremely reactive and mediate intramolecular aryl C–H bond amination below room temperature [113]. The final product is a diruthenium amide, in which the nitride atom has formally inserted into an aryl C–H bond of the formamidinate ligand (Scheme 8.5). The KIE of 1.1 rules out typical C–H functionalization schemes such as H-atom abstraction. Instead, the mechanism based on DFT studies is electrophilic aromatic substitution, through which a strongly electrophilic Ru_2 nitride moiety engages the π -electron density of the proximal aryl ring to form an N–C bond followed by proton migration from C to N, generating the Ru_2 amide product.



Scheme 8.5 *In situ* diruthenium nitride formally inserts into an intramolecular aryl C–H bond.

The Ru_2^{7+} nitride, $\text{Ru}_2\text{N}(\mu\text{-PhNCHNPh})_4$, was generated *in situ* from the Ru_2^{5+} azide precursor by photolytic extrusion of N_2 in frozen solutions at 77 K [114]. Following the reaction by EPR spectroscopy showed that the initial axial $S = 3/2$ signals of the azide were replaced by new signals of an $S = 1/2$ spin with axial symmetry. The spectroscopic characterization of $\text{Ru}_2\text{N}(\mu\text{-PhNCHNPh})_4$ supported the Ru_2^{7+} nitride formulation. Relative to the Ru_2^{5+} azide, the Ru_2 nitride species showed a significant shift of the Ru K-edge to higher energy, consistent with a higher oxidation state of the Ru_2 core. To reasonably fit the extended X-ray absorption fine structure (EXAFS) spectrum, an additional short Ru–N vector of 1.76 Å and an elongated Ru–Ru vector (2.42 Å) were needed. Resonance Raman spectroscopy revealed a $\nu(\text{Ru}\equiv\text{N})$ band at 847.2 cm^{-1} that shifts to 822.6 cm^{-1} in the ^{15}N -labeled species. The data strongly indicates a Ru–N multiple bond, though the $\text{Ru}\equiv\text{N}$ linkage is considerably weaker in the Ru_2 species than in mononuclear Ru complexes. DFT investigations of the diruthenium nitride reveal highly delocalized bonding in the Ru–Ru–N core, as evident in the electronic structure, $(\sigma_{\text{Ru-Ru-N}})^2(\pi_{\text{Ru-Ru-N}})^4(\delta_{\text{Ru-Ru}})^2(\sigma_{\text{nb}})^4(\pi_{\text{nb}})^4(\delta_{\text{Ru-Ru}}^*)^1$. The overall bonding can be described as comprising multiple three-center four-electron bonds (1σ and 2π) and a 0.5δ bond between the two Ru centers. The lowest unoccupied molecular orbital (LUMOs) are degenerate $\text{RuRuN } \pi^*$ orbitals with significant N p orbital density, explaining the highly electrophilic nature of the nitride (Figure 8.21). Finally, in analogy to the Ru_2 -catalyzed allylic C–H amination, the spin flexibility of the diruthenium core is potentially significant in enhancing the reactivity of the nitride.

Of note, thermolyzing solid samples of diruthenium azides, $\text{Ru}_2(\mu\text{-ArNCHNAr})_4(\text{N}_3)_2$ (where $\text{Ar} = \text{Ph}$ and $3,5\text{-Cl}_2(\text{C}_6\text{H}_3)$), at $\sim 100^\circ\text{C}$ also affords the C–H bond amination products [113, 115]. Differential scanning calorimetry (DSC) coupled to thermal gravimetric analysis indicated a two-step process, in which N_2 is extruded in the first step. Despite the drastically different reaction

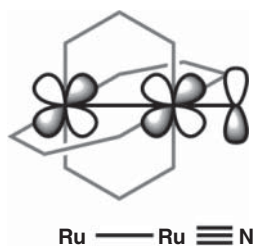


Figure 8.21 One of the degenerate $\text{RuRuN } \pi^*$ LUMOs.

conditions, the mechanism appears similar to the photolytic reactions, whereby a reactive Ru₂ nitride is generated prior to C–H bond insertion.

8.2.2.2 Non-Paddlewheel

The Ru₂ non-paddlewheel complexes can be classified by their geometry – tetragonal versus trigonal – and further classified by their supporting ligands. Nearly all the unsupported Ru₂ complexes are tetragonal.

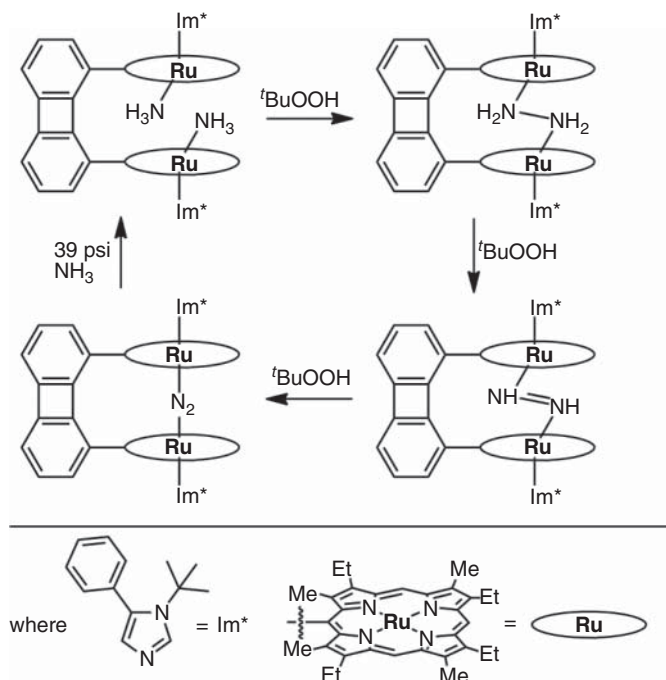
Tetragonal

Porphyrin The non-paddlewheel Ru₂ complexes consist primarily of binuclear Ru porphyrin dimers. Though the synthesis of Ru₂(OEP)₂ (where OEP = octaethylporphyrin dianion) was first formulated in 1975, evidence for the dimer was scant and primarily based on mass spectrometry [116]. The solid-state structure was reported almost a decade later in 1984 [117].

Reinvestigation of the binuclear Ru(II) porphyrin dimer, Ru₂(OEP)₂, revealed that the complex is paramagnetic with an $S = 1$ ground state ($\mu_{\text{eff}} = 2.8 \mu_{\text{B}}$, Evans' method). Solid-state magnetic susceptibility measurements confirmed the triplet state and also revealed exceedingly large zero-field splitting values of $240 \pm 45 \text{ cm}^{-1}$ [118]. Analytically pure Ru₂(OEP)₂ was prepared by vacuum pyrolysis (10^{-5} torr, $\sim 200^\circ\text{C}$) of the dipyrindine adduct, Ru(py)₂(OEP). The pyrolysis method was found to be general for other porphyrin ligands as well as other metalloporphyrins, for example, Os and Mo [117, 119]. The solid-state structure of Ru₂(OEP)₂ showed a Ru–Ru bond distance of $2.408(1) \text{ \AA}$ (FSR 0.97). The porphyrin ligands were essentially parallel with a twist of 23.8° . Moreover, each Ru porphyrin half shows a significant distortion with a domed conformation where the Ru center lies out of the N₄-plane by $0.30 \text{ \AA}$. The CV of Ru₂(OEP)₂ was quite rich, though four of the six one-electron processes were ascribed to the ligand. The first two oxidations, however, are metal-centered, and correspond to the Ru₂⁴⁺/Ru₂⁵⁺ and Ru₂⁵⁺/Ru₂⁶⁺ redox couples at -0.46 and 0.50 V , respectively (vs Ag/AgCl in CH₂Cl₂) [120]. Chemical oxidations were effected by adding 1 and 2 equiv. of an oxidant, such as AgBF₄, FcPF₆, or N(*p*-Br(C₆H₄))₃SbCl₆, in benzene to precipitate the purple mono- and dications.

Based on an MO analysis, the Ru₂⁴⁺ diporphyrin complex has an electronic configuration of $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2(\pi^*)^2$ with a formal bond order of 2. Removing one and two π^* -electron(s) to generate Ru₂⁵⁺ and Ru₂⁶⁺ analogs should increase the bond order to 2.5 and 3, respectively. To validate this hypothesis, the [Ru₂(OEP)₂]^{*n*+} (where $n = 0, 1, 2$) redox series were studied by K-edge EXAFS and resonance Raman spectroscopy [121, 122]. Indeed, the Ru–Ru bond distance as determined by EXAFS spectroscopy progressively decreased from $2.40 \text{ \AA}$ for $n = 0$, to $2.29 \text{ \AA}$ (FSR 0.92) for $n = 1$, to $2.23 \text{ \AA}$ (FSR 0.90) for $n = 2$. Consistent with this trend, the Ru–Ru stretching frequency increased upon oxidation, from 285 cm^{-1} for $n = 0$, to 301 cm^{-1} for $n = 1$, to 310 cm^{-1} for $n = 2$. A solid-state structure of a Ru₂⁵⁺ core, [Ru₂(TPP)₂]PF₆ (TPP = tetraphenylporphyrin dianion), showed a Ru–Ru bond distance of $2.293(2) \text{ \AA}$ (FSR 0.92), which is similar to that found for [Ru₂(OEP)₂]⁺ in the EXAFS study. In the structure, the metalloporphyrin rings were twisted (29.4°) and domed (Ru–N₄ plane distance of $0.378 \text{ \AA}$), similar to Ru₂(OEP)₂. The spin state of [Ru₂(TPP)₂]PF₆ was assigned as $S = 1/2$ based on a solution magnetic moment of $1.85 \mu_{\text{B}}$ and an axial EPR signal at 77 K , with $g_{\parallel} = 1.953$ and $g_{\perp} = 1.993$ [123]. While the Ru–Ru bond distance in [Ru₂(TPP)₂]PF₆ is comparable to Ru₂⁵⁺ paddlewheels, the latter are typically spin quartets.

Reactivity of binuclear Ru porphyrin dimers generally involves cleavage of the Ru–Ru bond. The addition of ligands ranging from CO to THF leads to the formation of the mono- or bis-ligand adduct of a mononuclear Ru porphyrin [124]. One interesting observation is the formation of a bimetallic dihydrogen adduct (Ru–H₂–Ru) using a Ru₂⁴⁺ compound where the two metalloporphyrins are tethered by a biphenylene backbone and where bulky imidazole ligands coordinate the external axial sites [125]. This system was also successful at interconverting amine with N₂ via bridging hydrazine and diazene intermediates (Scheme 8.6) [126].



Scheme 8.6 Six-electron oxidation of ammonia to dinitrogen using a Ru_2 diporphyrin system.

Tetra-aza[14]annulene Tetragonal Ru_2 dimers supported by tetra-aza annulenes were reported as early as 1978, though the solid-state structure was obtained only in 2000 [127, 128]. By mixing dibenzotetraaza[14]annulene ($\text{C}_{22}\text{H}_{22}\text{N}_4\text{H}_2$) with $\text{Ru}_2(\text{OAc})_4\text{Cl}$, the mixed-valent Ru_2^{5+} complex, $[\text{Ru}(\text{C}_{22}\text{H}_{22}\text{N}_4)]_2\text{Cl}$, was isolated as a dark green salt. The Ru_2^{5+} species had a doublet ground state ($\mu_{\text{eff}} = 1.55 \mu_{\text{B}}$) and two reversible one-electron transfer processes, an oxidation at -0.20 V and a reduction at -1.03 V (vs $\text{Ag}-\text{AgClO}_4$ in CH_3CN). Chemical reduction with NaBH_4 and oxidation with ferrocenium tetrafluoroborate generated the triplet Ru_2^{4+} ($\mu_{\text{eff}} = 2.88 \mu_{\text{B}}$) and diamagnetic Ru_2^{6+} complexes, respectively. Similar to the Ru_2 diporphyrin systems, the $\text{Ru}-\text{Ru}$ bond order should increase from two in Ru_2^{4+} to three in Ru_2^{6+} .

The subsequent investigation of the Ru_2 dimers with the dibenzotetramethyltetraaza[14]annulene dianion (abbreviated as *tmtaa*) resulted in solid-state structures of the Ru_2^{4+} and Ru_2^{5+} redox members [128]. The Ru_2^{4+} complex was prepared by refluxing a toluene solution of the cyclooctadiene-bridged diruthenium compound, $(\text{Ru}(\text{tmtaa}))_2(\text{COD})$ ($\text{COD} = 1,5\text{-cyclooctadiene}$). A subsequent oxidation with FcBPh_4 afforded the Ru_2^{5+} analog. The solid-state structures revealed $\text{Ru}-\text{Ru}$ bond distances of 2.3829(4) and 2.2782(4) Å for the Ru_2^{4+} and Ru_2^{5+} complexes, respectively (FSR 0.96 and 0.92). The contraction of the $\text{Ru}-\text{Ru}$ bond upon oxidation is consistent with the removal of a π^* electron. In both structures, the *tmtaa* ligands are staggered and domed with $\text{Ru}-(\text{N}_4\text{-plane})$ distances of 0.34 and 0.43 Å for the Ru_2^{4+} and Ru_2^{5+} complexes, respectively. The temperature dependence of the magnetic susceptibility was measured, and the magnetic moment of $1.96 \mu_{\text{B}}$ for $(\text{Ru}(\text{tmtaa}))_2$ at 298 K, was modeled as $S = 1$, remained fairly constant until 50 K. Below 50 K, the magnetic moment suddenly decreased, and a large zero-field splitting of 196 cm^{-1} was invoked. The Ru_2^{5+} analog had a magnetic moment of $\sim 1.50 \mu_{\text{B}}$ from 4 to 300 K, which is consistent with $S = 1/2$.

Corroles Binuclear Ru_2^{6+} corroles have been isolated by refluxing $[(\text{COD})\text{RuCl}_2]_2$ with the neutral corrole ligand in the presence of air and NEt_3 base with 2-methoxyethanol as a solvent [129]. The solid-state structures reveal short Ru–Ru bond distances of 2.166 and 2.182 Å (FSR 0.87–0.88), depending on the corrole substituents [129, 130]. The corrole rings are perfectly staggered with the Ru displaced from the N_4 -plane by ~ 0.50 Å. Their short Ru–Ru bond distances and diamagnetism are consistent with the electronic configuration, $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$, and a formal bond order of 3. The Ru_2^{6+} dicorrole complexes show multiple reversible electron-transfer processes, though only two to three of the redox processes are assigned as metal-centered. With alkyl-substituted corroles, the first oxidation to Ru_2^{7+} and reduction to Ru_2^{5+} occur at 0.13–0.20 V and -1.11 to -1.14 V (vs saturated calomel electrode (SCE), in CH_2Cl_2), respectively. The Ru_2^{7+} complex displayed a rhombic EPR signal at 77 K, with $g = (2.049, 1.991, 1.928)$ [131]. With C_6F_5 substituents on the corrole, the Ru_2^{6+} complex has a milder reduction at -0.48 V and more anodic oxidation at 0.76 V (vs Ag/AgCl, in CH_3CN) [130]. A second oxidation has been observed at 0.55 and 1.04 V for the alkyl- and C_6F_5 -substituted Ru_2^{6+} dicorrole systems, respectively, but it is not yet clear whether this redox process is a corrole-centered oxidation or the $\text{Ru}_2^{8+}/\text{Ru}_2^{7+}$ couple.

Catecholates Similar to porphyrin and related N_4 -ligand analogs, catecholate (Cat) ligands can stabilize Ru–Ru bonds between two, cofacial $\text{Ru}(\text{Cat})_2$ units. Ru_2^{5+} and Ru_2^{6+} cores have been isolated and well characterized for several catecholates [132, 133]. For the parent catechol and the tetrahalide-substituted variants ($o\text{-(OH)}_2\text{C}_6\text{X}_4$, where $\text{X} = \text{F}, \text{Cl}, \text{and Br}$), the Ru_2^{5+} complexes, $\text{Na}_3[\text{Ru}_2(\text{Cat})_4]$, were generated by stirring $\text{Ru}_2(\text{OAc})_4\text{Cl}$ with 4 equiv. of catechol and 8 equiv. of NaOH in THF. The Ru_2^{5+} complexes are red-purple to violet in color. Solid-state characterization revealed Ru–Ru bond lengths of 2.246(1)–2.273(1) Å (FSR 0.90–0.92). The $\text{Ru}(\text{Cat})_2$ units are domed with Ru–(O_4 -plane) distances of 0.271(3)–0.388(3) Å. Most of the Ru_2^{5+} complexes have nearly eclipsed $\text{Ru}(\text{Cat})_2$ units, though the Br_4Cat derivative stands out with a twist angle of 19.5° . Other structural variations include the presence or absence of an axial THF ligand, as well as the precise sites of the Na^+ ions, which bind to the oxygen atoms of the catecholates and thus, bridge adjacent Ru_2 complexes, creating an infinite polymeric chain [134]. The Ru_2^{5+} complexes with tetrahalide-substituted catecholates have $S = 1/2$ ground states, determined by solution-state magnetic moments of 1.59–1.67 μ_B , as well as rhombic EPR signals at 77 K with $g \sim (1.5, 1.8, 2.1)$; for the parent catecholate complex, the values are $g = (1.79, 1.93, 2.01)$. The CV of the $\text{Na}_3[\text{Ru}_2(\text{X}_4\text{Cat})_4]$ complexes showed a quasi-reversible one-electron oxidation and reduction near -0.6 and -1.7 V (vs $\text{FeCp}_2^{+/0}$), respectively; for the parent catecholate analog, these values are approximately -1.4 and -2.1 V, respectively. Chemical oxidation with Ag^+ generated the Ru_2^{6+} counterparts, $\text{Na}_2[\text{Ru}_2(\text{Cat})_4]$. As predicted by removing a π^* -electron, the Ru–Ru bond contracts slightly to 2.196(1) and 2.223(6) Å (FSR 0.88 and 0.90) for the Cl_4Cat and Br_4Cat systems, though each Ru center also binds a THF in the axial position. The diamagnetism of the Ru_2^{6+} complexes is consistent with the $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$ configuration.

Of note, use of the electron-donating catechols, 3,5- $t\text{Bu}_2\text{Cat}$ and 3,6- $t\text{Bu}_2\text{Cat}$, in the synthesis of the Ru_2^{5+} complexes ($\text{Ru}_2(\text{OAc})_4\text{Cl}$ and NaOH) leads directly to Ru_2^{6+} cores, despite the absence of an external oxidant [134]. Presumably, the oxidation potentials of the Ru_2^{5+} intermediates are sufficiently low to become *in situ* oxidized by the $\text{Ru}_2(\text{OAc})_4\text{Cl}$ reagent. Indeed, the CV of $\text{Na}_2[\text{Ru}_2(3,5\text{-}t\text{Bu}_2\text{Cat})_4]$ shows a low redox potential near -1.4 V (vs $\text{FeCp}_2^{+/0}$) for the $\text{Ru}_2^{6+}/\text{Ru}_2^{5+}$ couple. From the solid-state structures of $\text{Na}_2[\text{Ru}_2(3,5\text{-}t\text{Bu}_2\text{Cat})_4]$ and $\text{Na}_2[\text{Ru}_2(3,6\text{-}t\text{Bu}_2\text{Cat})_4]$, the Ru–Ru bond distances of 2.1698(6) and 2.140(2) Å (FSR 0.87 and 0.86) are more contracted relative to the complexes with halide substituents described above. Additionally, the Ru–(O_4 -plane) distances are quite long at ~ 0.5 Å. Unlike the X_4Cat complexes, the axial sites of the Ru_2^{6+} core are not occupied by THF. Hence, the catecholates with electron-donating substituents favor shorter Ru–Ru bonds and disfavor THF binding to the Ru_2^{6+} cores. The Na^+ counteranion can be replaced with $\text{M} = \text{Li}^+, \text{K}^+, \text{and Rb}^+$ by using the appropriate MOH base in the synthesis [134]. The non-coordinating $\text{N}(t\text{Bu})_4^+$ can also be swapped in by mixing $\text{Na}_2[\text{Ru}_2(3,6\text{-}t\text{Bu}_2\text{Cat})_4]$ with 2 equiv. $\text{N}(t\text{Bu})_4\text{PF}_6$. Despite the large variations in counteranions, the Ru–Ru bond distances are all within 0.012 Å. The $\text{Ru}_2^{6+}/\text{Ru}_2^{5+}$ redox potential, however,

is strongly cation-dependent, with shifts as large as 1.18 V. The changes in reduction potentials parallel the trend in charge density, that is, charge/size ratio, of the counteranions. The mildest potential was measured for Li^+ , while the N^nBu_4^+ analog showed the most negative potential. The authors reasoned that the smaller ions bind more closely to the Ru_2^{6+} core and thereby better stabilize the reduction.

Trigonal Trigonal Ru_2 complexes are highly unusual. At the time of writing, the only structurally characterized examples are hexakis(neopentyl) and hexakis(trimethylsilylmethyl) diruthenium complexes with a Ru_2^{6+} core [135]. The complexes were prepared by alkylating $\text{Ru}_2(\text{OAc})_4\text{Cl}$ with 6 equiv. of the corresponding Grignard reagent. A disproportionation of the Ru_2^{5+} intermediate with $\text{Ru}_2(\text{OAc})_4\text{Cl}$ was proposed to explain the isolation of the Ru_2^{6+} complex in ~50% yield. In support, the Ru_2^{4+} byproduct, $\text{Ru}_2(\text{OAc})_4(\text{soln})_2$, was also isolated in approximately 50% yield. The Ru_2R_6 solid-state structures show a staggered arrangement of the bulky alkyl groups and Ru–Ru bond distances of 2.311(3) Å (FSR 0.93) and 2.265(3) Å (FSR 0.91) for $\text{Ru}_2(\text{CH}_2\text{CMe}_3)_6$ and $\text{Ru}_2(\text{CH}_2\text{SiMe}_3)_6$, respectively [136]. The ^1H NMR spectra of these complexes are characteristically diamagnetic. Of interest, using only 4 equiv. of Grignard and shorter reaction times lead to the isolation of the red Ru_2^{6+} intermediate, $\text{Ru}_2\text{R}_4(\mu\text{-OAc})_2$.

Summary of Ru_2 Non-Paddlewheels The Ru–Ru bond distances of non-paddlewheel complexes are collected in Figure 8.22. Most of the complexes are tetragonal and adhere to the canonical d-orbital splitting of $(\sigma)(\pi)(\delta)(\delta^*)(\pi^*)(\sigma^*)$. One consequence is that the spin states for the Ru_2 oxidation states Ru_2^{4+} , Ru_2^{5+} , and Ru_2^{6+} are $S = 1$, $1/2$, and 0, respectively. Another consequence is that the Ru–Ru

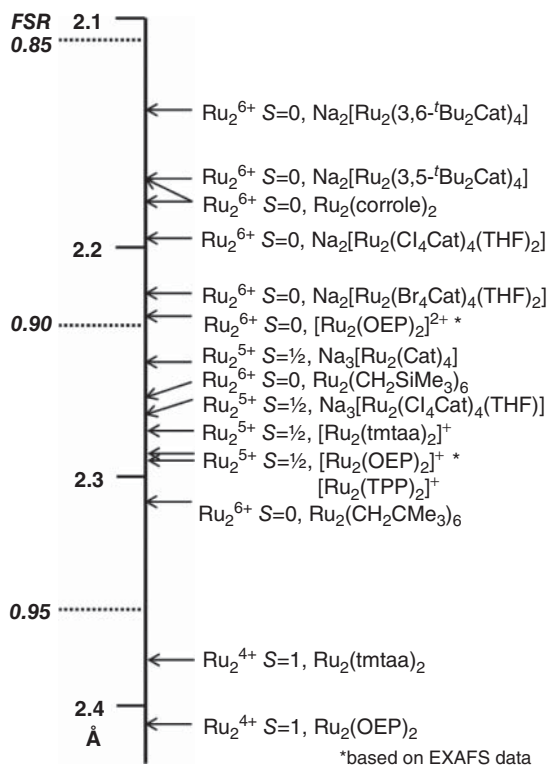


Figure 8.22 Ru–Ru bond lengths (Å) in Ru_2 non-paddlewheels.

bond distances increasingly contract as the oxidation state of the Ru₂ increases, which is consistent with the expected trend in formal bond orders (increasing from two for Ru₂⁴⁺ to three in Ru₂⁶⁺). Some of the shortest Ru–Ru bond lengths (FSR 0.86–0.90) are found in the Ru₂⁶⁺ tetragonal non-paddlewheels. The Ru₂ dicorrole systems show promise for expanding the available redox states to Ru₂⁷⁺, which has so far been characterized definitively in paddlewheel Ru₂ nitride species.

8.2.3

Diosmium

Of the Group 8 metals, Os₂ complexes are the least well developed. In this section, we summarize the small family of Os₂ complexes, most of which have been reviewed previously [39, 137]. A majority of Os₂ complexes are paddlewheels or have tetragonal geometries, akin to their Ru₂ counterparts. They also occur in similar oxidation states, namely Os₂⁴⁺, Os₂⁵⁺, and Os₂⁶⁺. However, a key difference is that the Os₂⁶⁺ core is the most prevalent (stability of Os₂⁶⁺ > Os₂⁵⁺), whereas the lower oxidation state of Ru₂ is more common (stability of Ru₂⁶⁺ < Ru₂⁵⁺). Finally, an Os₂ complex has been isolated in the unusually high oxidation state of +7, which remains unknown for Ru₂ and Fe₂ cores, with the exception of the (Ru₂⁷⁺N³⁻) core in the diruthenium nitride complex (*vide supra*) [113, 115].

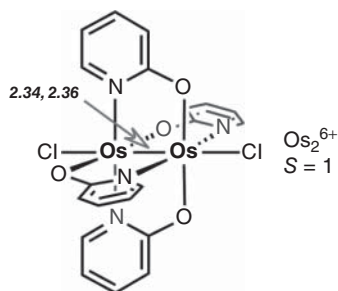
8.2.3.1 Paddlewheel

Os₂ paddlewheels are known for many bridging ligands, including carboxylate, oxypyridinate, amidate, guanidinate, and amidinate. They are typically coordinated by two axial X-type ligands. The Os₂ paddlewheels are organized by the bridging ligand type, which are ordered according to increasing π basicity.

Carboxylate Only a handful of Os₂ tetracarboxylates are structurally characterized. The first, Os₂(μ -O₂CMe)₄Cl₂, was prepared by reacting Na₂OsCl₆ in glacial acetic acid in the presence of acetic anhydride and a small amount of HCl [138]. The yield was later improved by generating a solution of OsCl₆²⁻ from OsO₄ and FeCl₂, and then heating in acetic acid/anhydride [139]. Os₂(μ -O₂CMe)₄Cl₂ is a versatile precursor for the synthesis of other Os₂⁶⁺ paddlewheels with bridging ligands by heating the diosmium precursor in the neutral ligand [39, 140]. The family of Os₂⁶⁺ tetracarboxylates, Os₂(μ -O₂CR)₄Cl₂, have similarly short Os–Os bond distances, 2.30–2.33 Å (FSR 0.92–0.93), for R = Me, Et, Pr, *o*-biphenyl, 2,4,6-triisopropylphenyl [141–144]. The magnetic moments of Os₂(μ -O₂CR)₄Cl₂ are between 1.60 and 2.1 μ_B at rt, and they drop with decreasing temperature. Analysis of the temperature-dependent magnetic susceptibility of Os₂(μ -O₂CMe)₄Cl₂ further revealed the ground-state electronic configuration to be (σ)²(π)⁴(δ)²(δ^*)¹(π^*)¹ ($S = 1$) with a zero-field splitting of 331 cm⁻¹ [145]. A resonance Raman study of Os₂(μ -O₂Me)₄Cl₂ reported an Os–Os stretching mode at 229 cm⁻¹ [146].

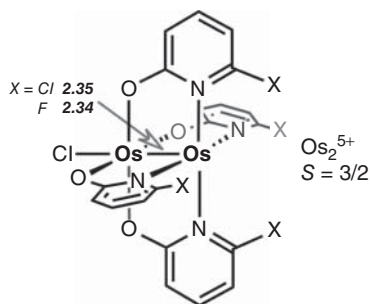
The CV of Os₂(μ -O₂CR)₄Cl₂ display reversible, one-electron reductions at mild potentials of –0.19 V (vs FeCp₂^{+/0}) for R = 2,4,6-triisopropylphenyl, and –0.03 and –0.07 V for R = Et and Pr, respectively [139, 144]. The latter complexes were reduced both electrochemically or with cobaltocene to form the Os₂⁵⁺ tetracarboxylates, [Os₂(μ -O₂CR)₄Cl₂]⁻, for R = Et and Pr [140]. Although solid-state structural characterization was lacking, the reduced complexes were characterized by solution-state magnetic measurements. The complex behavior of the magnetic moments, which increase from ~2.5 μ_B at rt to ~2.9 μ_B at ~200 K, was interpreted as a mix of quartet and doublet configurations in the ground state, (σ)²(π)⁴(δ)²(δ^*)¹(π^*)² ($S = 3/2$), (σ)²(π)⁴(δ)²(δ^*)²(π^*)¹ ($S = 1/2$), and/or (σ)²(π)⁴(δ)²(π^*)³ ($S = 1/2$).

Oxypyridinate The first structurally characterized Os₂ paddlewheel was the Os₂⁶⁺ tetra-2-oxypyridinate dichloride complex, Os₂(hp)₄Cl₂ (Figure 8.23). The complex was prepared by refluxing OsCl₃ with 2-hydroxypyridine [147]. The Os–Os bond distances are short, 2.344(2) and 2.357(1) Å (FSR 0.93, 0.94). The overall geometry is D_{2d}, where the oxypyridinates alternate in orientation

Figure 8.23 $\text{Os}_2(\text{hp})_4\text{Cl}_2$.

around each Os center in a *trans*(2,2) arrangement [148]. A magnetic moment of $1.70 \mu_{\text{B}}$ was measured at 280 K, and it declines with decreasing temperatures to $0.5 \mu_{\text{B}}$ at 6 K [143]. The temperature dependence was modeled as an $S=1$ ground state with an extraordinary zero-field splitting of 1196 cm^{-1} and a low g -value of 1.922. Two electronic configurations are possible, $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1(\pi^*)^1$ or $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2$. Both configurations implicate a triple bond between the Os centers, though the $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2$ configuration is generally favored for more π -basic ligands because $\text{L}(\pi)-\delta^*$ interactions destabilize the δ^* orbital. The CV of $\text{Os}_2(\text{hp})_4\text{Cl}_2$ shows one reversible reduction at 0.10 V (vs SCE in CH_2Cl_2). The Os_2^{5+} species, $[\text{Os}_2(\text{hp})_4\text{Cl}_2]^-$, was generated by chemical reduction with cobaltocene. The reduced $[\text{Os}_2(\text{hp})_4\text{Cl}_2]^-$ complex displayed an axial EPR signal with $g_{\perp} = 2.20$ and $g_{\parallel} = 2.14$, which are akin to the $S=3/2$ Ru_2^{5+} systems with large zero-field splitting [140].

While heating $\text{Os}_2(\mu\text{-O}_2\text{CMe})_4\text{Cl}_2$ with 2-hydroxypyridine provided an alternative route to $\text{Os}_2(\text{hp})_4\text{Cl}_2$, use of 6-halide-2-hydroxypyridine ligands did not yield Os_2^{6+} paddlewheels. Instead, the reduction of the Os_2 core occurred *in situ*, and Os_2^{5+} paddlewheels with 6-chloro-2-oxypyridinate (chp) and 6-fluoro-2-oxypyridinate (fhp) ligands, were isolated (Figure 8.24) [149, 150]. A later synthesis of $\text{Os}_2(\text{chp})_4\text{Cl}$ improved the yield by using a more soluble Os_2 precursor, $\text{Os}_2(\mu\text{-O}_2\text{CPr})_4\text{Cl}_2$ [151]. The solution-state magnetic moments of 2.90 and $3.70 \mu_{\text{B}}$ at rt indicate $S=3/2$ ground states, which would be consistent with $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2(\delta^*)^1$ with a formal bond order in the Os_2^{5+} paddlewheels of 2.5. However, the Os–Os bond distances of 2.348(1) and 2.341(1) Å (FSR 0.94 and 0.93) for $\text{Os}_2(\text{chp})_4\text{Cl}$ and $\text{Os}_2(\text{fhp})_4\text{Cl}$, respectively, are quite similar to that in $\text{Os}_2(\text{hp})_4\text{Cl}_2$. In both complexes, the ligands are oriented in the same orientation, that is, (4,0) arrangement, so that the N-donors are ligated to one Os center. The axial chloride ligand is bound to the oxygen-ligated Os center. The CV of $\text{Os}_2(\text{chp})_4\text{Cl}$ and $\text{Os}_2(\text{fhp})_4\text{Cl}$ both show a reversible reduction at nearly identical potentials of -0.60 V (vs Ag/AgCl). However, the former has a reversible oxidation at 0.90 V, whereas

Figure 8.24 $\text{Os}_2(\text{chp})_4\text{Cl}$ and $\text{Os}_2(\text{fhp})_4\text{Cl}$.

the oxidative process is irreversible in the latter. The Os_2^{6+} and Os_2^{4+} paddlewheels with four bridging chp/fhp ligands have not yet been reported, but an Os_2^{6+} analog, *trans*-(2,0)- $\text{Os}_2\text{Cl}_4(\text{chp})_2(\text{L})$ ($\text{L} = \text{py}$ or H_2O), with two bridging chp ligands is known [152].

Some limited reactivity has been reported. Ligand metathesis of $\text{Os}_2(\text{chp})_4\text{Cl}$ with NaN_3 provided the azide complex [151]. The axial chloride can also be abstracted with AgBF_4 in the presence of pyridine (py) or pyrazine (pyz). In the case of pyridine, the discrete salt $[\text{Os}_2(\text{chp})_4(\text{py})]\text{BF}_4$ was isolated and characterized with an Os–Os bond distance of 2.336(1) Å (FSR 0.93). For pyrazine, a dimer with a bridging pyz ligand, $[(\text{Os}_2(\text{chp})_4)_2(\mu\text{-pyz})](\text{BF}_4)_2$, was generated with an identical Os–Os bond distance of 2.334(1) Å (FSR 0.93). Though temperature dependence of the magnetic moments proved too complex to model, the values indicated $S = 3/2$ ground states, with a proposed configuration of $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1(\pi^*)^2$ [153].

Amidate A couple Os_2^{6+} paddlewheels have been structurally characterized with benzamidate ligands, $\text{Os}_2(\mu\text{-NHCPHO})_4\text{Cl}_2$ and $\text{Os}_2(\mu\text{-NHCPHO})_4\text{Br}_2$ [154, 155]. The relative orientation of the four benzamidate ligands was not determinable by X-ray crystallography, though a *cis*(2,2)-arrangement was deemed the most probable. Os–Os bond distances of 2.367(2) and 2.384(2) Å (FSR 0.94, 0.95) were measured in the chloride and bromide derivatives, respectively. The chloride complex, $\text{Os}_2(\mu\text{-NHCPHO})_4\text{Cl}_2$, displayed a reversible reduction at -0.07 V (vs SCE in DMSO).

Aminopyridinate With aminopyridinate ligands, only Os_2^{6+} paddlewheels have been isolated. From the reaction of 8 equiv. 2-anilinoypyridine (Hap) and $\text{Os}_2(\mu\text{-O}_2\text{CMe})_4\text{Cl}_2$, two regioisomers of $\text{Os}_2(\text{ap})_4\text{Cl}_2$ were crystallized, the *cis*(2,2) and (3,1) isomers [156, 157]. Manipulating the solvent polarity gave moderate control in the precipitation of a specific regioisomer. A polar solvent mixture of CH_2Cl_2 and CH_3OH favored the deposition of the nonpolar *cis*(2,2) isomer, while use of CH_2Cl_2 and hexanes switched the preference to the polar (3,1) isomer. The Os–Os bond distances in the regioisomers are nearly identical at 2.3937(8) and 2.3909(8) Å (FSR 0.95). A solution-state magnetic moment of $2.76 \mu_B$ at rt was consistent with $S = 1$. Owing to the more electron-donating ligand nature of the *N,N*-donors and also the significantly longer Os–Os bond distances than Os_2^{6+} tetracarboxylates, a configuration of $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2$ may be more appropriate than $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1(\pi^*)^1$.

$\text{Os}_2(\text{ap})_4\text{Cl}_2$ can undergo facile ligand methathesis reactions with lithiated alkynyl reagents to form $S = 0$ $\text{Os}_2(\text{ap})_4(\text{C}\equiv\text{CR})_2$ complexes (for $\text{R} = \text{Ph}$, Fc , and SiMe_3), where the Os–Os bond elongates significantly from the dichloride precursor to 2.46–2.48 Å (FSR 0.98–0.99) [156]. In the $\text{Os}_2(\text{ap})_4(\text{C}\equiv\text{CR})_2$ complexes, the metal–metal σ -bonding becomes disrupted by the Os–alkynyl interactions, and the resulting electronic configuration of $(\pi)^4(\delta)^2(\pi^*)^4$ is consistent with their diamagnetism.

Formamidinate Similar to aminopyridinates, formamidinate ligands stabilize Os_2^{6+} paddlewheels. The $\text{Os}_2(\mu\text{-ArNCHNAr})_4\text{Cl}_2$ (where $\text{Ar} = p\text{-tolyl}$) was crystallized, and an X-ray diffraction study revealed a long Os–Os bond distance of 2.4672(6) Å (FSR 0.98) [158]. The CV showed a quasi-reversible reduction at -0.62 V (vs $\text{FeCp}_2^{+/0}$) and an irreversible oxidation at 0.60 V. The temperature dependence of the magnetic moment was simulated by adopting $S = 1$, $g_{\text{ave}} = 1.802$, and a zero-field splitting of 1350 cm^{-1} . An X α self-consistent field calculation of the model complex, $\text{Os}_2(\mu\text{-HNCHNH})_4\text{Cl}_2$, validated the configuration of $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2$. Reactivity was sparse, but the tetrakis(diphenylformamidinate) Os_2^{6+} paddlewheel, $\text{Os}_2(\mu\text{-PhNCHNPh})_4\text{Cl}_2$, was reported to form the bis(azide) analog, $\text{Os}_2(\mu\text{-PhNCHNPh})_4(\text{N}_3)_2$, in a metathesis reaction with NaN_3 [151]. The latter has been structurally characterized with a similarly long Os–Os bond distance of 2.4531(6) Å (FSR 0.98).

Guanidinate In stabilizing M_2^{n+} cores of transition metals, guanidinate ligands are generally more versatile than formamidinate ligands, especially for high oxidation states [159]. By refluxing OsCl_3

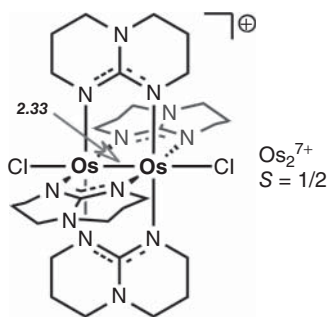


Figure 8.25 $\text{Os}_2(\text{hpp})_4\text{Cl}_2$.

with 4 equiv. of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2- α]pyrimidine (Hhpp) in ethanol, the Os_2^{6+} paddlewheel, $\text{Os}_2(\text{hpp})_4\text{Cl}_2$, was isolated as a dark red precipitate. An X-ray diffraction study of a single crystal showed an Os–Os bond distance of 2.379(2) Å (FSR 0.95), which is closer to Os_2^{6+} paddlewheels with *N,O*-donors than with other *N,N*-donors. The magnetic susceptibility (χ) was found to be independent of temperature from 2 to 300 K, consistent with an $S = 0$ ground state with temperature-independent paramagnetism ($\chi_{\text{TIP}} = 4.1 \times 10^{-5} \text{ emu mol}^{-1}$). Consistent with $S = 0$, the configuration $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$ was proposed. The CV of $\text{Os}_2(\text{hpp})_4\text{Cl}_2$ showed a reversible oxidation at -0.49 V (vs $\text{FcP}_2^{+/0}$) and a second, quasi-reversible oxidation at 0.57 V . The oxidized complex, $[\text{Os}_2(\text{hpp})_4\text{Cl}_2]\text{PF}_6$, was synthesized by adding ferrocenium to $\text{Os}_2(\text{hpp})_4\text{Cl}_2$ (Figure 8.25) [160]. The structural characterization of this Os_2^{7+} core revealed the contraction of the Os–Os bond by 0.05 Å upon oxidation, to 2.3309(4) and 2.3290(6) Å (two independent molecules) (FSR 0.93). The configuration of the Os_2^{7+} complex is proposed to be $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$ with a formal bond order of 3.5. The EPR spectrum contained an axial signal with low g -values, $g_{\perp} = 0.62$ and $g_{\parallel} = 1.38$ ($g_{\text{ave}} = 0.87$), which is characteristic of an $S = 1/2$ paramagnet with large spin–orbit coupling. A single-crystal EPR study was performed to determine the orientation of the g -values relative to the molecular axis, and $g_{\parallel}$ was found to lie along the vector defined by the Os–Os bond.

***P,C*-Bidentate Ligand** A family of Os_2^{6+} complexes with cyclometalated PPh_3 , *cis*-($\mu\text{-O}_2\text{CR}$) $_2\text{Os}_2(\mu\text{-Ph}_2\text{PC}_6\text{H}_4)_2\text{Cl}_2$, were prepared by warming $\text{Os}_2(\text{O}_2\text{CMe})_4\text{Cl}_2$ with 2 equiv. of PPh_3 in a carboxylic acid [161, 162]. The solid-state structures have been determined for $\text{R} = \text{Me}$ and Et variants. The Os–Os bond distances were identical, 2.271(1) and 2.272(1) Å (FSR 0.90), respectively. Their diamagnetism further supported a triple Os–Os bond with a configuration of $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$. The Cl ligands occupy the “axial” positions, but with Cl–Os–Os bond angles of $\sim 160^\circ$ that deviate significantly from linearity. The distortion was attributed to steric repulsion between the Cl ligands and the phenyl substituents on the phosphine.

8.2.3.2 Non-Paddlewheel

Unsupported Os–Os bonds have been isolated with halide, porphyrin, and carbanion-based ligands. The vast majority of these complexes are tetragonal, akin to Ru_2 .

Tetragonal

Halide Os_2^{6+} octahalide dianions are known for $\text{X} = \text{Cl}$, Br , and I , while the Ru_2 and Fe_2 octahalides remain unknown. The $[\text{Os}_2\text{X}_8]^{2-}$ complexes were prepared from exposing an ethanol solution of $\text{Os}_2(\mu\text{-O}_2\text{CMe})_4\text{Cl}_2$ to the gaseous HX for $\text{X} = \text{Cl}$ and Br [163]. The iodide variant was prepared from $[\text{Os}_2\text{Cl}_8]^{2-}$ and HI [164]. The complexes are all diamagnetic, with a proposed configuration of $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$. Several solid-state structures of $[\text{Os}_2\text{Cl}_8]^{2-}$ were determined with a variety of counteranions. Collectively, the Os–Os bond distance ranged from 2.182(1)–2.212(1) Å (FSR 0.87–0.88). The shorter Os–Os distances were associated with more staggered conformations (ave torsion angle

of 49.0° [163, 165], while the longer Os–Os distances corresponded to an eclipsed rotamer [164, 166]. Steric repulsion between chloride ligands attached to distinct $[\text{OsCl}_4]^{1-}$ halves presumably elongate the Os–Os bond in the eclipsed structure. Of interest, the two geometries give rise to different crystal colors. Green crystals of $[\text{Os}_2\text{X}_8]^{2-}$ (for X = Br, Cl) correspond to the staggered geometry, while eclipsed geometries are found in brown to pink crystals. The observation of both staggered and eclipsed geometries in the solid-state is consistent with the MO analysis that predicts a lack of δ -bonds. Moreover, crystal packing forces must be significant to override the steric repulsion of the chloride ligands in the eclipsed conformer.

For the Os_2^{6+} octabromide dianion, a few solid-state structures were determined. The first report revealed a staggered structure (ave torsion angle of 46.7°) for $[\text{N}(n\text{-Bu})_4]_2[\text{Os}_2\text{Br}_8]$ with an Os–Os bond distance of 2.196 Å (FSR 0.87) [163]. Structures were also reported for $[\text{OsH}(\text{C}_5\text{Me}_5)_2]_2[\text{Os}_2\text{Br}_8]$ and $[\text{OsBr}(\text{C}_5\text{Me}_4\text{H})_2]_2[\text{Os}_2\text{Br}_8]$, which were isolated from refluxing reactions of OsH_2Br_6 and the corresponding cyclopentadiene (and excess HBr for the former). In common, they have an eclipsed geometry with Os–Os bond distances of 2.219–2.229 Å (FSR), which are slightly longer than in the staggered structure [167, 168].

For the Os_2^{6+} octaiodide dianion, the solid-state structures obtained to date all show the staggered conformation with torsion angles $\sim 38^\circ$ and 47° , depending on the counteranion. The Os–Os bond distances are similar at 2.217(1) and 2.213 Å (FSR 0.89 to 0.88) [164, 169]. A periodic trend can be found by considering only the staggered structures in the $[\text{Os}_2\text{X}_8]^{2-}$ series, that is the Os–Os bond increases by ~ 0.02 Å down the halide group: $\text{Cl} < \text{Br} < \text{I}$.

The CV redox processes for $[\text{Os}_2\text{Cl}_8]^{2-}$ and $[\text{Os}_2\text{Br}_8]^{2-}$ were initially reported to be similar. Both halide species displayed an irreversible oxidation at ~ 1.15 V (vs Ag/AgCl, CH_2Cl_2) and an irreversible reduction at -0.90 to -0.75 V [166]. The CV of the $[\text{Os}_2\text{X}_8]^{2-}$ complexes were reinvestigated at 235 K in butyronitrile [170]. For $[\text{Os}_2\text{Cl}_8]^{2-}$, the first oxidation at 1.19 V becomes fully reversible, and a second, reversible oxidative process was observed at 1.82 V (vs Ag/AgCl), suggesting Os_2^{7+} and Os_2^{8+} cores. The oxidized Os_2^{7+} complex was generated *in situ* and characterized by spectroelectrochemistry. A distinctive band that is highly structured with vibronic coupling (220 cm^{-1}) was observed at 4600 cm^{-1} ($\epsilon = 1000\text{ M}^{-1}\text{ cm}^{-1}$). The band is highly characteristic of a $\delta \rightarrow \delta^*$ transition that couples to the Os–Os bond stretch. Though structural data was lacking, the observation of a δ/δ^* band implicates an eclipsed structure for $[\text{Os}_2\text{Cl}_8]^{2-}$ with a $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$ configuration. Under similar conditions, the CV of $[\text{Os}_2\text{Br}_8]^{2-}$ showed two reversible oxidations at 1.35 and 2.03 V, which are shifted anodically relative to $[\text{Os}_2\text{Cl}_8]^{2-}$. For oxidized $[\text{Os}_2\text{Br}_8]^{2-}$, a $\delta \rightarrow \delta^*$ transition was observed at 4630 cm^{-1} with a vibronic progression of 225 cm^{-1} .

Porphyrin The binuclear Os porphyrin dimers typically contain Os_2^{4+} cores, which is an uncommon oxidation state for Os_2 . Like their Ru counterparts, the synthesis involves vacuum pyrolysis of a mononuclear Os metalloporphyrin complex with two axially coordinated pyridines [119, 120, 171]. The CV of $\text{Os}_2(\text{OEP})_2$ is similar to $\text{Ru}_2(\text{OEP})_2$ in that six reversible redox processes are observed, though only the first two oxidations are localized at the M_2 core. The $\text{Os}_2^{4+}/\text{Os}_2^{5+}$ and $\text{Os}_2^{5+}/\text{Os}_2^{6+}$ redox potentials are at -0.77 and -0.01 V (vs Ag/AgCl, CH_2Cl_2), respectively [120]. The oxidized Os_2^{5+} and Os_2^{6+} complexes were prepared by adding 1 and 2 equiv. ferrocenium. The redox series, $[\text{Os}_2(\text{OEP})_2]^{n+}$ (where $n = 0, 1, 2$), was studied by resonance Raman spectroscopy [172]. The Os–Os stretching frequency increased upon oxidation, from 233 cm^{-1} for $n = 0$, to 254 cm^{-1} for $n = 1$, to 266 cm^{-1} for $n = 2$. The increase in Os–Os stretching mode frequency upon oxidation provides experimental support for the MO splitting diagram for the Os_2^{4+} diporphyrin complex as being $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2(\pi^*)^2$ with a formal bond order of 2. Removing one and two π^* -electron(s) to generate Os_2^{5+} and Os_2^{6+} analogs increases the bond order to 2.5 and 3, respectively. Magnetic susceptibility measurements of $\text{Os}_2(\text{OEP})_2$ showed that its magnetic moment reached $2.3\text{ }\mu_{\text{B}}$ at rt, but decreased steadily to $0.3\text{ }\mu_{\text{B}}$ at 5 K [118]. The data was fit as an $S = 1$ with a large zero-field splitting of $630 (\pm 210)\text{ cm}^{-1}$.

Alkyl Os_2^{6+} complexes containing alkyl ligands were isolated from reactions of Grignard/ MgR_2 reagents and $\text{Os}_2(\mu\text{-O}_2\text{CMe})_4\text{Cl}_2$. The $\text{Os}_2(\mu\text{-O}_2\text{CMe})_2\text{R}_4$ products incorporate only four alkyl groups even when a large excess of the alkylating reagents were used [136]. Attempts to further alkylate $\text{Os}_2(\mu\text{-O}_2\text{CMe})_2\text{R}_4$ were mostly unsuccessful, but with an important exception of allyl Grignard. In that case, a stable $\text{Os}_2(\eta^3\text{-allyl})_2(\text{CH}_2\text{CMe}_3)_4$ was isolated (Figure 8.26). The solid-state structure showed a tetragonal Os_2^{6+} core, where each allyl group is approximately planar with two neopentyl groups around a single Os center. Furthermore, the structure shows an eclipsed conformer, where each allyl group eclipses two neopentyl groups at the opposing Os center, which is suggestive of a δ -bond. Indeed, the Os–Os bond distance of 2.194(3) Å (FSR 0.87) is one of the shortest Os–Os bonds. The complex was reported to be diamagnetic. Based on the expected configuration of $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$, only a formal triple Os–Os bond is predicted, and so, the preference for the eclipsed versus staggered geometry is unclear.

Non-Tetragonal Non-tetragonal Os_2 complexes are rare, and to our knowledge, $\text{Os}_2(\text{Ph}_2\text{PC}_6\text{H}_4)_2\text{Cl}_4$ with cyclometalated PPh_3 ligands, is the only structurally characterized example (Figure 8.27) [173]. Brown microcrystals of $\text{Os}_2(\text{Ph}_2\text{PC}_6\text{H}_4)_2\text{Cl}_4$ were isolated from a refluxing reaction of *cis*-($\mu\text{-O}_2\text{CMe}$) $_2\text{Os}_2(\mu\text{-Ph}_2\text{PC}_6\text{H}_4)\text{Cl}_2$ and 2 equiv. Me_3SiCl in THF. The Os–Os bond in $\text{Os}_2(\text{Ph}_2\text{PC}_6\text{H}_4)_2\text{Cl}_4$ has contracted by 0.04–2.231(1) Å (FSR 0.89) from the precursor, $\text{Os}_2(\text{O}_2\text{CMe})_2(\text{Ph}_2\text{PC}_6\text{H}_4)\text{Cl}_2$. The Os centers have identical coordination environments. Each Os center is closer to trigonal bipyramidal, where the other Os atom is located in the equatorial plane. The P–Os–Cl linkages, which constitute the linear axis of the trigonal bipyramid, are oriented perpendicular to one another, so that the P–Os–Os–P torsion angle is 99.8°. A reversible, one-electron reduction was observed at 0.106 V (vs Ag/AgCl, CH_2Cl_2).

8.2.3.3 Summary of Diosmium

The Os–Os bond distances of Os_2 complexes are collected in Figure 8.28. With the one exception of $\text{Os}_2(\text{Ph}_2\text{PC}_6\text{H}_4)_2\text{Cl}_4$, the Os_2 complexes are tetragonal, and the vast majority contain Os_2^{6+} cores. The shortest Os–Os bonds are found in $S = 0$ Os_2^{6+} complexes without axial ligands, such as $\text{Os}_2(\eta^3\text{-allyl})_2(\text{CH}_2\text{CMe}_3)_4$ and staggered $[\text{Os}_2\text{Cl}_8]^{2-}$; both complexes contain a triple Os–Os bond,

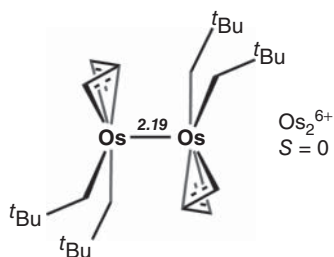


Figure 8.26 $\text{Os}_2(\eta^3\text{-allyl})_2(\text{CH}_2\text{CMe}_3)_4$.

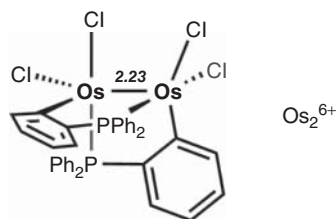


Figure 8.27 $\text{Os}_2(\text{Ph}_2\text{PC}_6\text{H}_4)_2\text{Cl}_4$.

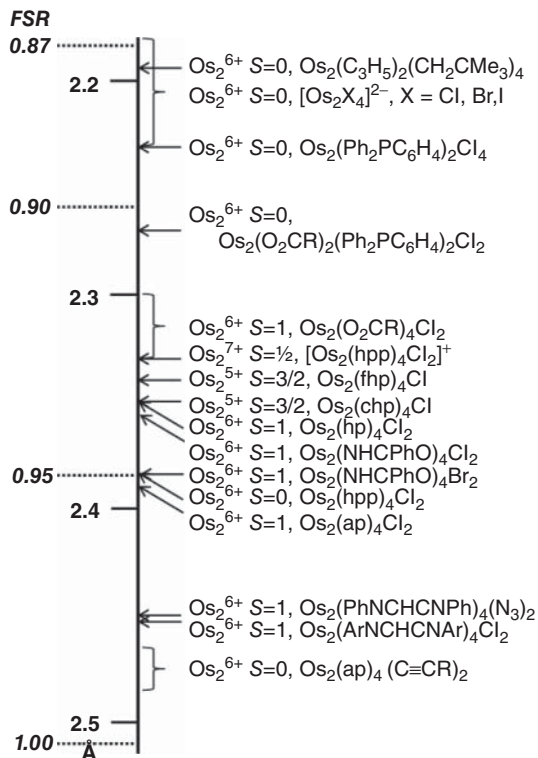


Figure 8.28 Os–Os bond lengths (Å) in Os_2 complexes.

formally. Os_2^{6+} paddlewheels with two axial halides tend to have Os–Os bond distances in the range of 2.3–2.4 Å and $S = 1$ ground states. The Os–Os bond distances in Os_2^{6+} paddlewheels increase as the π -basicity of the bridging ligands increase. The simple rationale is that π -basic ligands destabilize the δ^* orbital, so that only the π^* orbital becomes populated. Moreover, the π^* electrons elongate the M–M bond more effectively than the δ^* electrons. The Os_2^{6+} bis(alkynyl) complexes have the longest Os–Os bond characterized to date. Akin to the Ru_2 analogs, alkynyl ligands completely disrupt the Os–Os σ -bond, so that only one δ -bond is formally present.

8.3

Group 8 Heterometallics

Group 8 metals occupy a central position in the transition block, and as mid-metals, they form transition metal–metal bonds of various characters: mid-mid, mid-late, and early-mid. In addition, bonding between a Group 8 metal and an actinide, lanthanide, alkali, alkaline-earth, or main group metal have been demonstrated by several coordination complexes, attesting to their versatility in forming d–f, d–s, and d–p interactions. The focus of this section is *covalent* d–d bonds of Group 8 metals. For interactions involving Group 8 metals that are outside this scope, we refer readers to recent reviews on metal–metal bonds with f-elements [174, 175] and with main group metals [176, 177]. Donor–acceptor interactions, or dative bonding, for example, $\text{Cp}_2\text{Fe} \rightarrow \text{ML}_n$, are also excluded [178–184]. Furthermore, “xenophilic” compounds, which are characterized by electrostatic interactions between a low-valent, electronically saturated metal center (typically coordinated by carbonyls) and an open-shell, unsaturated metal center coordinated by hard donors, are not covered [185–187].

8.3.1

Intratriad Heterometallics

While there are a plethora of carbonyl clusters containing different Group 8 metals, they often contain bridging carbonyls and/or one-atom ligands, for example, hydride and sulfide. Such ligands can obfuscate metal–metal bonding by forcing the two metals into proximity [188, 189]. Warranting further consideration are borderline cases that have reasonably short metal–metal bonds, such as $[(\text{Me}_3\text{-TACN})\text{Ru}(\mu\text{-H})_3\text{OsHCP}^*][\text{PF}_6]$, $\text{Cp}^*\text{Ru}(\mu\text{-H})_4\text{OsCp}$, and $\text{Cp}^*\text{Ru}(\mu\text{-H})_2\text{OsCp}^*(\text{P}(\text{OMe})_3)$ with Ru–Os bond distances of 2.4110(3) Å (FSR 0.97), 2.4663(5) Å (FSR 0.99), and 2.5166(3) Å (FSR 1.01), respectively [190–192].

The clear cases are those of unsupported metal–metal bonds with reasonable FSR values. At the time of writing, only a small number of examples comply with this criterion. The mixed-metal trigonal carbonyl clusters, $\text{FeRu}_2(\text{CO})_{12}$ and $\text{Fe}_2\text{Ru}(\text{CO})_{12}$, possess unsupported Fe–Ru bonds in the range of 2.73–2.78 Å (FSR 1.13–1.16) [193, 194]. Another set of complexes is the Ru–Os diporphyrins, for example, $(\text{OEP})\text{OsRu}(\text{OETAP})$, where OETAP is octaethyltetraazaporphyrin dianion [171]. The heterometallic complex was generated in the co-pyrolysis of the mononuclear precursors, $\text{Os}(\text{OEP})(\text{py})_2$ and $\text{Ru}(\text{OETAP})(\text{py})_2$. To purify the heterometallic complex from the homobimetallic species, redox titration was employed to exploit the milder redox potentials of Os versus Ru and OEP versus OETAP in the $\text{M}_2(\text{porphyrin})_2$ species (Figure 8.29). The $\text{OsRu}^{4+/5+}$ redox potential of -0.73 V (vs $\text{FcCp}_2^{+/0}$)

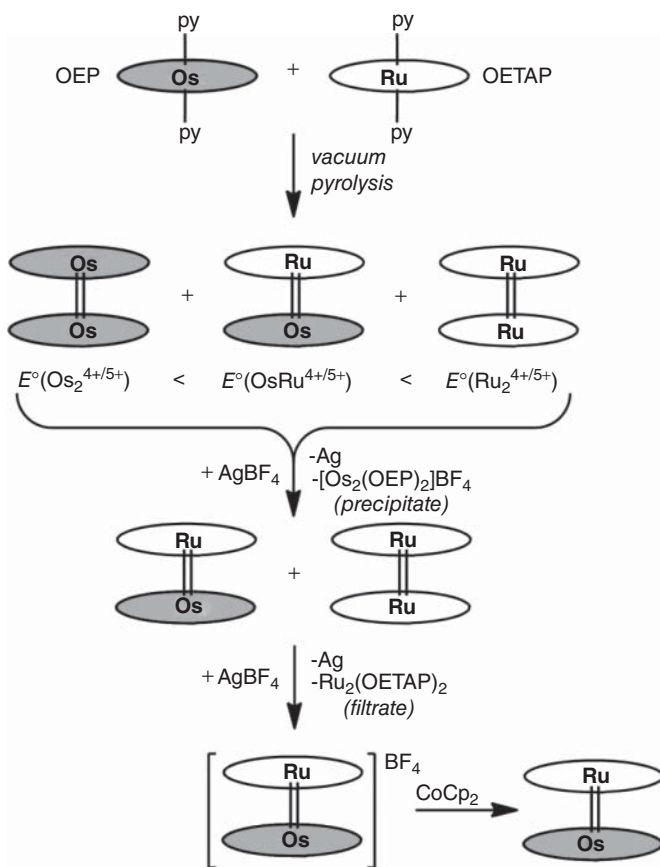


Figure 8.29 Purification of the OsRu heterobimetallic using redox titration.

is midway between that of $\text{Os}_2(\text{OEP})_2$ and $\text{Ru}_2(\text{OETAP})_2$. Thus, sub-stoichiometric oxidation with AgBF_4 of the crude mixture results in the separation of $[\text{Os}_2(\text{OEP})_2]^+$, followed by a second oxidation with AgBF_4 to isolate $[(\text{OEP})\text{OsRu}(\text{OETAP})]^+$, which was then reduced with CoCp_2 to furnish $(\text{OEP})\text{OsRu}(\text{OETAP})$. Based on its similar ^1H NMR profile as the homobimetallic counterparts, $(\text{OEP})\text{OsRu}(\text{OETAP})$ was assigned as $S = 1$ with a $(\sigma)^2(\pi)^4(\text{Ru } d_{xy})^2(\text{Os } d_{xy})^2(\pi^*)^2$ configuration and a formal bond order of 2. Another RuOs diporphyrin complex was prepared from the pyrolysis of $\text{RuOs}(\text{py})_4(\text{DPB})$, where DPB is a cofacial diporphyrin ligand linked by diphenylene [195]. A solution state magnetic moment of $1.3(3) \mu_B$ is consistent with an $S = 1$ state with a large zero-field splitting [118, 195].

8.3.2

Intertriad Heterometallics

Most of the Group 8 heterometallics contain Fe or Ru. In the Group 8-early metal and Group 8-late metal pairings, which make up the bulk of Group 8 heterometallics, the Fe and Ru centers often share similar, if not identical, coordination environments [196–199]. The Group 8-mid metal pairings are less known, but they represent an exciting area for accessing multiply bonded heterometallics. In 2013, the first Fe-mid metal pairings were reported, for example, Fe–Cr and Fe–V, which contain $\text{Fe}\equiv\text{M}$ triple bonds [200–202]. Notably, these complexes were the first examples of multiple bonds between *different* first-row metals. Mid-metal pairings with Ru and Os may also result in multiple bonding, such as $\text{RuM}(\text{porphyrin})_2$ and $\text{OsM}(\text{porphyrin})_2$ complexes where M is a Group 6 metal, Mo or W [196]. As in the case of intratriad metal–metal bonds, we exclude complexes with bridging carbonyls and one-atom ligands, as they make it more complicated to determine whether a metal–metal bond is present.

8.3.2.1 Fe–M Heterometallics

Fe–Group 4 Heterometallics Of the early transition metals, Group 4 metals are known to form single covalent bonds with both iron and ruthenium (see also Chapter 4). The historical developments of Fe and Ru heterobimetallics with early metals are intimately tied, as identical ligand systems and metalation strategies have been successful for both Fe and Ru [197, 198, 203]. The first discovery of direct metal–metal bonding between Groups 4 and 8 was $\text{Cp}_2(\text{O}^i\text{Bu})\text{ZrRu}(\text{CO})_2\text{Cp}$, which was formed by salt elimination from combining $\text{Cp}_2\text{Zr}(\text{O}^i\text{Bu})\text{Cl}$ and $\text{K}[\text{Ru}(\text{CO})_2\text{Cp}]$ [204]. In the same report, analogous Fe–Zr pairings were reported, albeit without solid-state characterization. A bridging ditopic ligand that adjoins a phosphine donor with a Cp ring, $\text{C}_5\text{H}_4\text{PPh}_2^-$, was also used to stabilize a related Fe–Zr complex, $\text{Cp}(\text{O}^i\text{Bu})\text{Zr}(\text{C}_5\text{H}_4\text{PPh}_2)\text{Fe}(\text{Cp})\text{CO}$, though again a solid-state structure was lacking [205].

The extension of Fe–Group 4 bonds to Ti required addressing the problem of an accessible Ti(IV)/Ti(III) redox couple. Single-electron transfer from a Group 8 metal to the Ti(IV) precursor was an undesirable reaction that competed with metal–metal bond formation. The first, isolated Fe–Ti complex was $(\text{NMe}_2)_3\text{TiFe}(\text{CO})_2\text{Cp}$. The basic, amide ligands at Ti were critical for lowering the Ti(IV)/Ti(III) redox potential. The complex was prepared via an amine elimination reaction between $\text{Ti}(\text{NMe}_2)_4$ and the iron hydride, $\text{Fe}(\text{CO})_2\text{CpH}$ [206]. The crystal structure showed unsupported Ti–Fe bonds that were $2.567(1)$ and $2.569(1)$ Å long ($\text{FSR} = 1.03$). This complex and other Ti alkoxide/aryloxide analogs, which were not structurally characterized, are unstable at room temperature and decompose into Fe_2 species and unidentified Ti byproducts [197, 198].

These early precedents set the stage for future developments in Fe–Group 4 bonding, where the Fe coordination environment has remained invariant as “ $\text{Fe}(\text{CO})_2\text{Cp}$,” and changes were made in the first coordination sphere of the Group 4 metal. For example, Gade and coworkers expanded the number of accessible unsupported bonds between Fe (as well as Ru) and Group 4 metals by using tripodal triamido ligands on the early metal to increase the stability of the Fe–metal bond [197]. One

reason for the stabilization is that the triamido donors function as both σ - and π -donors for the Lewis acidic, early metal [207]. In addition, the rigid, tripodal framework enforces a tetrahedral geometry, which gives additional thermodynamic stability against metal–metal bond homolysis, as the early metal fragment that forms upon dissociation would prefer to relax into a planar, trigonal geometry [208]. Several Fe–Ti complexes were formed in salt elimination reactions between $\text{K}[\text{Fe}(\text{CO})_2\text{Cp}]$ and a $\text{Ti}(\text{L})\text{X}$ precursor, where L is a tripodal triamido ligand, such as $\text{HC}(\text{SiMe}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4))_3$, $\text{MeC}(\text{CH}_2\text{NSiMe}_3)_3$, or $\text{PhC}(\text{CH}_2\text{NSiMe}_3)_3$. The Fe–Ti bond lengths range from 2.410(4) and 2.441(5) Å (FSR 0.97–0.98), which is consistent with a single bond [207, 209].

Switching to more sterically encumbered ligand variant with a trisilylsilane backbone, $\text{MeSi}(\text{SiMe}_2\text{NAr})_3$ where $\text{Ar} = 4\text{-CH}_3\text{C}_6\text{H}_4$ and $2\text{-FC}_6\text{H}_4$, a full suite of Fe–Group 4 pairings was isolated, including Ti–Fe, Zr–Fe, and Hf–Fe [210, 211]. By replacing Ti with Zr, the Fe–M bond elongated from 2.460(1)–2.605(2) Å for the $\text{Ar} = 4\text{-CH}_3\text{C}_6\text{H}_4$ complexes, as expected for the increased atomic radius of Zr relative to Ti. The FSR values for the Fe–Ti and Fe–Zr complexes, however, remained unchanged at 0.99 (Figure 8.30). Unfortunately, the Fe–Hf complex was not structurally characterized. However, all members of the series exhibited $\nu(\text{CO})$ IR bands, which are sensitive reporters of the electron density at iron that is perturbed to different extents by the Group 4 metals *through* Fe–M bonding. The Fe–Ti complex was the stand out in the series with the highest CO frequencies (1978, 1931 cm^{-1}), whereas the CO frequencies for Fe–Zr (1961, 1910 cm^{-1}) and Fe–Hf (1969, 1915 cm^{-1}) complexes were similarly lower [211]. To explain the trend, the Fe–Ti bond was deemed more covalent as Ti should be better matched to accept π -electron density from iron and thereby decrease π -back-bonding into the carbonyl ligands. The Fe–Zr and Fe–Hf bonds, on the other hand, are more ionic in nature.

Combining *both* Cp and amido ligands at the early metal has also successfully lead to the isolation of an Fe–Zr complex, $\text{Cp}(\text{L})\text{ZrFe}(\text{CO})_2\text{Cp}$, where L is the diamido ligand $\text{CH}_2(\text{CH}_2\text{NSiMe}_3)_2$. The Zr–Fe bond is 2.745(1) Å long (FSR 1.05) [212]. The same ligand also generated a ZrFe₂ trimetallic, $\text{LZr}(\text{Fe}(\text{CO})_2\text{Cp})_2$ where the two Zr–Fe bonds are both slightly shorter by comparison at 2.665(2) and 2.664(2) Å (FSR 1.02) [213].

Fe–Group 4 Bonding in Clusters Fe bonding to Group 4 metals has also been observed within molecular clusters and heterometallic solids. An example of the latter is Hf_5FeTe_3 , whose solid-state structure shows a central iron within a trigonal prism of Hf ions with short Hf–Fe interactions (2.617(5)–2.700(5) Å, FSR 1.00–1.04) [214]. The molecular cluster $[(\text{Zr}_6\text{Fe})\text{Cl}_{18}]^{4-}$ also has short Fe–Zr bonds (ave. 2.44 Å, FSR 0.93) where an interstitial Fe ion is centrally positioned within an octahedron of Zr ions [215, 216]. These clusters are structurally analogous to the $(\text{Zr}_6\text{Fe})\text{Cl}_{12}$ cubic building block of several solid-state materials, including $(\text{Zr}_6\text{Fe})\text{Cl}_{14}$ and $\text{K}(\text{Zr}_6\text{Fe})\text{Cl}_{15}$. Indeed, excision of an intact $(\text{Zr}_6\text{Fe})\text{Cl}_{12}$ unit by dissolving the inorganic materials in a melt of the ionic liquid, 1-ethyl-3-methylimidazolium (EMIm) with AlCl_3 , led to the isolation of $(\text{EMIm})_4[(\text{Zr}_6\text{Fe})\text{Cl}_{18}]$ [215].

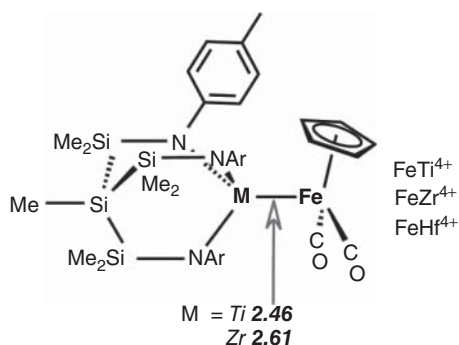


Figure 8.30 $\text{Fe}(\text{Cp})(\text{CO})_2\text{M}(\text{MeSi}(\text{SiMe}_2\text{NAr})_3)$, M = Ti, Zr, Hf.

Remarkably, using the same procedure to excise clusters from the bromide analog, $\text{Zr}_6\text{Br}_{14}\text{Fe}$, gave the same cluster product, wherein all bromide ligands were displaced by chlorides. A reverse halide exchange can be effected by dissolving $\text{K}(\text{Zr}_6\text{Fe})\text{Cl}_{15}$ in a mixture of EMImBr and AlBr_3 to yield $(\text{EMIm})[(\text{Zr}_6\text{Fe})\text{Br}_{18}]$, which has an average Zr–Fe bond distance of 2.469 Å (FSR 0.94) [217]. Hence, halide exchange can occur in either direction and is governed by the free halide present in the melt.

Fe–(Group 5–7) Heterometallics Only a few Fe–M systems are known where the pairing of Fe to an intertriad mid-metal produces short Fe–M bonds (FSR ≤ 1.10). The shortest known Fe–M bonds occur in the complexes, $[\text{FeCr}(\text{N}(\text{o}-(\text{NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4)_3)]^n$ (Figure 8.31), with Fe–Cr bond distances of 1.944(1) and 1.974(1) Å (FSR 0.83, 0.84) for $n = 0$ and -1 , respectively [200, 201]. The FSR values are both consistent with a triply bonded $\text{Fe}\equiv\text{Cr}$ core, and at the time of their report, these complexes were the first isolated examples of multiple bonds between different first-row metals. The FeCr^{3+} heterobimetallic was prepared via a two-step metallation, where the first metallation installs Cr into the tris(amide)amine-binding pocket, followed by a subsequent metallation of FeBr_2 and an *in situ* reduction with 2 equiv. of KC_8 . Further reduction with an additional equivalent of KC_8 in the presence of a chelating agent, for example, 2,2,2-cryptand (abbreviated as crypt-222), leads to the isolation of crystalline $\text{K}(\text{crypt-222})[\text{FeCr}(\text{N}(\text{o}-(\text{NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4)_3)]$.

The spin state of $\text{FeCr}(\text{N}(\text{o}-(\text{NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4)_3)$ was determined to be $S = 1/2$ based on an axial EPR signal that was modeled with $g = (1.944, 1.935, \text{ and } 1.759)$. The low g -values ($g_{\text{ave}} = 1.88$) are consistent with the unpaired spin residing at Cr, rather than Fe. The spin-state of the FeCr^{2+} analog was assigned as $S = 1$ based on magnetic susceptibility measurements showing a temperature-independent μ_{eff} of $2.65 \mu_B$ from 20 to 290 K. Mössbauer characterization of the two FeCr redox states provided some interesting electronic-structural comparisons. The similar IS of 0.25 and 0.29 mm s^{-1} for the FeCr^{3+} and FeCr^{2+} species suggested that the iron is *not* the site of reduction. A localized reduction at Cr was proposed, with the formal oxidation states changing from Fe(0)Cr(III) to Fe(0)Cr(II) . A surprising finding was the large QS of 5.92 and 5.20 mm s^{-1} , which had only been observed for high-valent iron nitrides [218–220]. CASSCF calculations of the FeCr^{3+} and FeCr^{2+} complexes indicated multiconfigurational ground-states. The dominant electronic configurations ($\sim 60\%$), $(\sigma)^2(\pi)^4(\text{Fe } d_{xy}, d_{x^2-y^2})^4(\text{Cr } d_{xy})^1$ for FeCr^{3+} and $(\sigma)^2(\pi)^4(\text{Fe } d_{xy}, d_{x^2-y^2})^4(\text{Cr } d_{xy}, d_{x^2-y^2})^2$ for FeCr^{2+} , are both consistent with a triply bonded $\text{Fe}\equiv\text{Cr}$ core, and unpaired spin density residing at Cr. However, the EBOs are predicted to be slightly lower at 2.21 and 2.30, respectively. The FeCr^{3+} complex was interrogated by cyclic voltammetry, and the $\text{FeCr}^{3+}/\text{FeCr}^{2+}$ redox couple was fully reversible at -2.33 V (vs $\text{FcP}_2^{+/0}$). Other notable redox processes are a reversible oxidation at -1.32 V , and a second, quasi-reversible oxidation at -0.62 V .

A family of Fe–V and Fe–Cr complexes supported by phosphinoamides ($\text{R}_2\text{PNR}'$)[−] in a trigonal coordination environment have been isolated and structurally characterized [202, 221, 222]. The Fe–V series is shown in Figure 8.32, including three redox states of the FeV core: FeV^{3+} , FeV^{4+} , and FeV^{5+} [202]. The monohalide complexes, $\text{XFeV}(\text{Ph}_2\text{PN}^i\text{Pr})_3$ (where $\text{X} = \text{Br}, \text{I}$), were generated by metallating the metalloligand, $\text{V}(\eta^2\text{-Ph}_2\text{PN}^i\text{Pr})_3$, with FeX_2 in the presence of Zn(s) . Subsequent reduction with KC_8 in the presence of PMe_3 provided the FeV^{3+} complex, $(\text{PMe}_3)\text{FeV}(\text{Ph}_2\text{PN}^i\text{Pr})_3$.

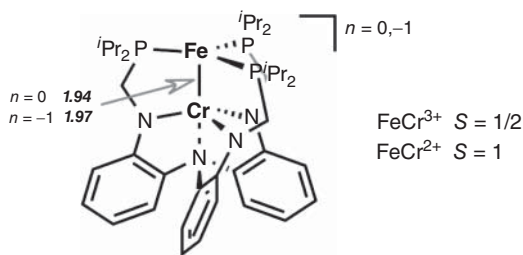


Figure 8.31 $[\text{FeCr}(\text{N}(\text{o}-(\text{NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4)_3)]^{0,1-}$.

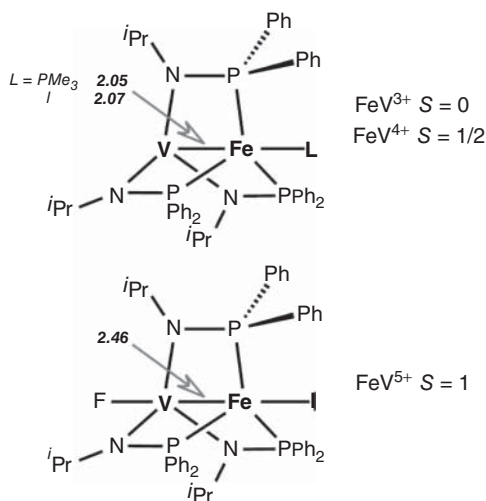


Figure 8.32 $(\text{PMe}_3)_2\text{FeV}(\text{Ph}_2\text{PN}^i\text{Pr})_3$ and $\text{IFeVF}(\text{Ph}_2\text{PN}^i\text{Pr})_3$.

The shortest Fe–V bond of 2.0495(5) Å (FSR 0.86) was found in $(\text{PMe}_3)_2\text{FeV}(\text{Ph}_2\text{PN}^i\text{Pr})_3$, which is diamagnetic. The FeV^{4+} complex, $\text{IFeV}(\text{Ph}_2\text{PN}^i\text{Pr})_3$, has a similarly short Fe–V bond (2.0745(5) Å, FSR 0.87) and is $S = 1/2$ based on the solution magnetic moment of 1.90 μ_B . These low FSR values are indicative of multiple bonding, and DFT calculations support the electronic configurations of $(\sigma)^2(\pi)^4(\text{Fe } d_{xy}, d_{x^2-y^2})^4$ and $(\sigma)^2(\pi)^4(\text{Fe } d_{xy}, d_{x^2-y^2})^3$, and triple bonds for the FeV^{3+} and FeV^{4+} cores, respectively. The Mayer bond orders were calculated to be slightly smaller at 2.53 for $(\text{PMe}_3)_2\text{FeV}(\text{Ph}_2\text{PN}^i\text{Pr})_3$ and 2.36 for $\text{IFeV}(\text{Ph}_2\text{PN}^i\text{Pr})_3$. The significant change in ISs in the Mössbauer spectra of $(\text{PMe}_3)_2\text{FeV}(\text{Ph}_2\text{PN}^i\text{Pr})_3$ (IS = 0.19, QS = 1.85 mm s^{−1}) and $\text{BrFeV}(\text{Ph}_2\text{PN}^i\text{Pr})_3$ (IS = 0.33, QS = 2.01 mm s^{−1}) is consistent with oxidation occurring primarily at the iron site.

Two reversible oxidations in the CV of $(\text{PMe}_3)_2\text{FeV}(\text{Ph}_2\text{PN}^i\text{Pr})_3$ corresponded to the $\text{FeV}^{4+}/\text{FeV}^{3+}$ and $\text{FeV}^{5+}/\text{FeV}^{4+}$ redox couples at −1.26 and −0.28 V (vs $\text{FeCp}_2^{+/0}$), respectively. Indeed, the FeV^{5+} dihalide species, $\text{IFeVF}(\text{Ph}_2\text{PN}^i\text{Pr})_3$, was formed in an oxidation reaction of $\text{IFeV}(\text{Ph}_2\text{PN}^i\text{Pr})_3$ with $[\text{FeCp}_2]\text{PF}_6$, whereby fluoride was inadvertently abstracted from the PF_6 counteranion. A solution magnetic moment of 2.80 μ_B suggested an $S = 1$ ground state for this dihalide species. The Fe–V bond elongated significantly upon oxidation to 2.4571(5) Å (FSR 1.03), which is consistent with a single bond. The introduction of fluoride into the V coordination sphere weakens the Fe–V σ -bond, but also disrupts all Fe–V π -bonding as σ - and π -electron density is donated from fluoride to V.

Using the $(\text{Ph}_2\text{PN}^i\text{Pr})^-$ ligand and adopting similar synthetic strategies, FeCr^{3+} and FeCr^{4+} complexes have also been isolated, namely, $\text{IFeCr}(\text{Ph}_2\text{PN}^i\text{Pr})_3$ and $(\text{PMe}_3)_2\text{FeCr}(\text{Ph}_2\text{PN}^i\text{Pr})_3$ [221]. The latter is assigned as $S = 2$ (4.83 μ_B) and the former as $S = 3/2$ (3.72 μ_B) based on solution magnetic moment measurements. Besides having higher spin states than $\text{FeCr}(\text{N}(o\text{-}(\text{NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4)_3)$, the FeCr phosphinoamide complexes have substantially elongated Fe–Cr bonds at 2.3696(10) and 2.3835(5) Å (FSR 1.00 and 1.01) for $L = \text{I}$ and PMe_3 , respectively. DFT calculations revealed electronic configurations of $(\sigma)^2(\pi)^4(\pi^*)^3(\text{Fe } d_{xy}, d_{x^2-y^2})^2$ and $(\sigma)^2(\pi)^4(\pi^*)^2(\text{Fe } d_{xy}, d_{x^2-y^2})^2$ for the FeCr^{3+} and FeCr^{4+} complexes. The occupation of the π^* orbitals lower the Fe–Cr formal bond orders to 1.5 and 2, respectively; and Mayer bond orders were slightly lower at 1.39 and 1.33. The CV of $\text{IFeCr}(\text{Ph}_2\text{PN}^i\text{Pr})_3$ showed a reversible oxidation at −0.58 V (vs $\text{FeCp}_2^{+/0}$), and an irreversible reduction at −1.93 V. The latter becomes increasingly reversible in the presence of excess NaI, confirming the lability of the axial halide upon reduction. The Mössbauer spectrum of $(\text{PMe}_3)_2\text{FeCr}(\text{Ph}_2\text{PN}^i\text{Pr})_3$ was fit with an IS of 0.15 mm s^{−1} and a QS of 0.31 mm s^{−1}. DFT calculations were used to compute the Mössbauer parameters of $\text{IFeCr}(\text{Ph}_2\text{PN}^i\text{Pr})_3$ and $(\text{PMe}_3)_2\text{FeCr}(\text{Ph}_2\text{PN}^i\text{Pr})_3$, revealing that upon reduction the IS

decreases from 0.23 mm s^{-1} for $\text{IFeCr}(\text{Ph}_2\text{PN}^i\text{Pr})_3$ to 0.15 mm s^{-1} for $(\text{PMe}_3)\text{FeCr}(\text{Ph}_2\text{PN}^i\text{Pr})_3$; this change is consistent with that observed for the analogous Fe–V pair.

The clear differences in spin states, bonding, and electronic structure between the FeCr complexes supported by three $(\text{Ph}_2\text{PN}^i\text{Pr})^-$ ligands versus $(\text{N}(o\text{-(NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4)_3)^{3-}$ are hypothesized to arise from the different coordination geometries imparted by these ligands [222]. Specifically, the phosphine donors in the phosphinoamide system prefer to stabilize a tetrahedral metal site, whereas the phosphine donors in the more flexible $(\text{N}(o\text{-(NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4)_3)^{3-}$ ligand tend toward a trigonal planar environment. The tetrahedral geometry in the Fe–Cr phosphinoamide complexes requires that π -symmetric d-orbitals engage in metal–ligand bonding to some degree, which weakens the metal–metal π -interactions. As a consequence, the π^* orbitals become energetically accessible and their occupation naturally gives rise to both the higher spin states and longer metal–metal bonds.

There are few iron–manganese complexes with reasonably small FSR values to suggest a bona fide metal–metal bond. One example is an FeMn^{4+} complex with the py_3tren ligand, as shown in Figure 8.33 [17]. The Fe–Mn complex was prepared by adding the monoiron(II) complex, $\text{K}[\text{Fe}(\kappa^4\text{-py}_3\text{tren})]$, to $\text{MnCl}_2(\text{THF})_{1.5}$ in THF at -78°C . Maintaining a low reaction temperature was necessary to prevent metal scrambling. In the solid-state structure, the Fe–Mn bond distance is $2.5283(5) \text{ \AA}$ (FSR 1.08), which despite being one of the shortest Fe–Mn bonds, is substantially longer than the Fe–V and Fe–Cr examples discussed earlier.

The Mössbauer spectrum of $\text{FeMnCl}(\text{py}_3\text{tren})$ showed a doublet with an IS of 0.46 mm s^{-1} and QS of 1.69 mm s^{-1} . The cyclic voltammogram had a quasi-reversible, one-electron reduction at -2.61 V and two irreversible, one-electron oxidations at 0.50 and 0.19 V (vs $\text{FcP}_2^{+/0}$). The first oxidation was tentatively assigned as an Fe(II)/Fe(III) redox couple based on its similarity to the diiron analog. The reductive couple was attributed to Mn(II)/Mn(I). In the magnetic susceptibility plot (χT vs T), χT has a minimum plateau value of $0.36 \text{ cm}^3 \text{ K mol}^{-1}$ at low T ($10\text{--}50 \text{ K}$), which is close to the spin-only value for $S = 1/2$ ($\chi T = 0.375 \text{ cm}^3 \text{ K mol}^{-1}$). The χT value increases gradually with increasing temperature, rising to $0.74 \text{ cm}^3 \text{ K mol}^{-1}$ at 290 K . The magnetic data was fit using a two-spin model comprising high-spin Fe(II) and Mn(II) that are antiferromagnetically coupled ($J = -145 \text{ cm}^{-1}$).

Because of the similar electron counts of Fe and Mn, conventional X-ray crystallography cannot differentiate these two metals. X-ray anomalous scattering experiments are thus useful and necessary to assess the metal atom purity at each binding site when similar transition metals are present in the same complex. Though high-spin Fe(II) and Mn(II) centers readily undergo ligand exchange, which could allow metal-scrambling between different sites, the Fe–Mn complex was found to be highly pure (95%). Thus, the py_3tren scaffold enabled heterometallics of similar metals to be accessed with high metal-site purity.

A stepwise metallation strategy was also used to successfully form a trinuclear heterometallic cluster featuring Fe–Mn interactions. The trigonal $\text{Fe}_2\text{Mn}^{6+}$ core in $(^{\text{tbs}}\text{L})\text{Fe}_2\text{Mn}(\text{THF})$ was assembled by heating the diiron intermediate $(^{\text{tbs}}\text{LH}_2)\text{Fe}_2$ and 0.5 equiv. $\text{Mn}_2(\text{N}(\text{SiMe}_3)_2)_4$ at 75°C in THF (Figure 8.34) [223]. The solid-state structure showed Fe–Mn distances of $2.7247(5)$ and $2.7485(5) \text{ \AA}$

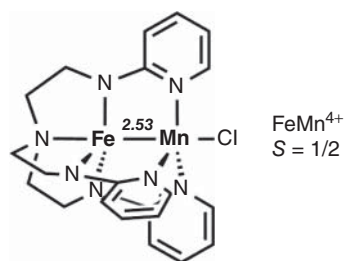


Figure 8.33 $\text{FeMnCl}(\text{py}_3\text{tren})$.

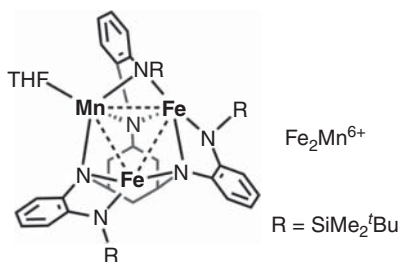


Figure 8.34 $\text{Fe}_2\text{Mn}(\text{THF})(^t\text{BuL})$.

(FSR ave 1.18), which are consistent with weak interactions. The complex is paramagnetic, and Mössbauer data showed two doublets with $\text{IS} = 0.35$ and 0.58 mm s^{-1} . X-ray anomalous scattering measurements pinpointed Mn at the metal site that coordinates THF.

Fe–Group 9 Heterometallics For FeCo heterometallics, one of the best known classes are the “xenophilic” Fe–Co complexes, $\text{TpFeCo}(\text{CO})_{4-n}(\text{PR}_3)_n$ (where Tp is a tris(pyrazolyl)borate and $n = 0, 1$). Because the Fe–Co interaction is primarily electrostatic (versus covalent), we will only briefly mention their relatively short Fe–Co bonds of $2.45\text{--}2.50 \text{ \AA}$ (FSR $1.05\text{--}1.08$) [186, 187]. The FeCo^{4+} complex, $\text{CoFeCl}(\text{py}_3\text{tren})$, has a similar Fe–Co bond distance of $2.4913(3) \text{ \AA}$ (FSR 1.07), though CASSCF calculations suggest a Co–Fe single covalent bond [17]. The complex is characterized with an $\text{IS} = 0.88 \text{ mm s}^{-1}$ ($\text{QS} = 2.62 \text{ mm s}^{-1}$). Akin to the FeMn analog (vide supra), the magnetic data is consistent with $S = 1/2$, where χT reaches a plateau value of $0.45 \text{ cm}^3 \text{ K mol}^{-1}$ at low T ($10\text{--}50 \text{ K}$) and gradually rises with increasing temperature. The magnetic data was fit using a two-spin model comprising high-spin Fe(II) and Co(II) that are antiferromagnetically coupled ($J = -184 \text{ cm}^{-1}$). The purity of $\text{CoFeCl}(\text{py}_3\text{tren})$ was determined to be only 88% by X-ray anomalous scattering studies, and the dicobalt species is the dominant impurity.

Using a tri(amidinate)amine ligand, an FeCo^{3+} complex was isolated with a significantly short Fe–Co bond ($2.1846(4) \text{ \AA}$, FSR 0.94) (Figure 8.35) [224]. The complex has a magnetic moment of $6.73 \mu_B$ from 20 to 290 K, which is consistent with a high-spin, $S = 3$ ground state. CASSCF/PT2 calculations revealed the main electronic configuration to be $(\sigma)^2(\pi)^4(\pi^*)^3(\sigma^*)^1(\text{Co } d_{xy}, d_{x^2-y^2})^2(\text{Fe } d_{xy}, d_{x^2-y^2})^2$, where the formal bond order is 1 ($0.5 \sigma + 0.5 \pi$). However, the configuration accounts for only 10% of the total wavefunction, so the Co–Fe interaction is weak. The Mössbauer IS for this complex is 0.65 mm s^{-1} ($\text{QS} = 0.64 \text{ mm s}^{-1}$). The IS value is exactly the same as the mixed-valent diiron complex, $\text{Fe}_2(\text{DPhF})_3$, which has a fully, delocalized Fe_2^{3+} core. Thus, by analogy, a delocalized CoFe^{3+} core was proposed.

Iron–cobalt bonds have also been studied within Fe–Co heterotrimetallics featuring $\text{Fe}_2\text{Co}^{7+}$ and FeCo_2^{7+} cores [225]. The mixed-metal clusters were synthesized using a novel strategy of metal atom substitution (Co) into a preexisting Fe_3^{7+} core, $[(\text{L}^{\text{Ph}})\text{Fe}_3(\mu\text{-Cl})]_2$. The addition of 2 and 5 equiv. of

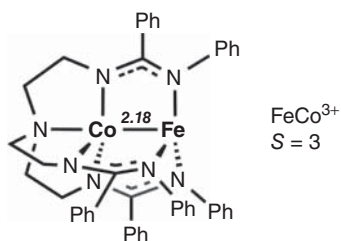
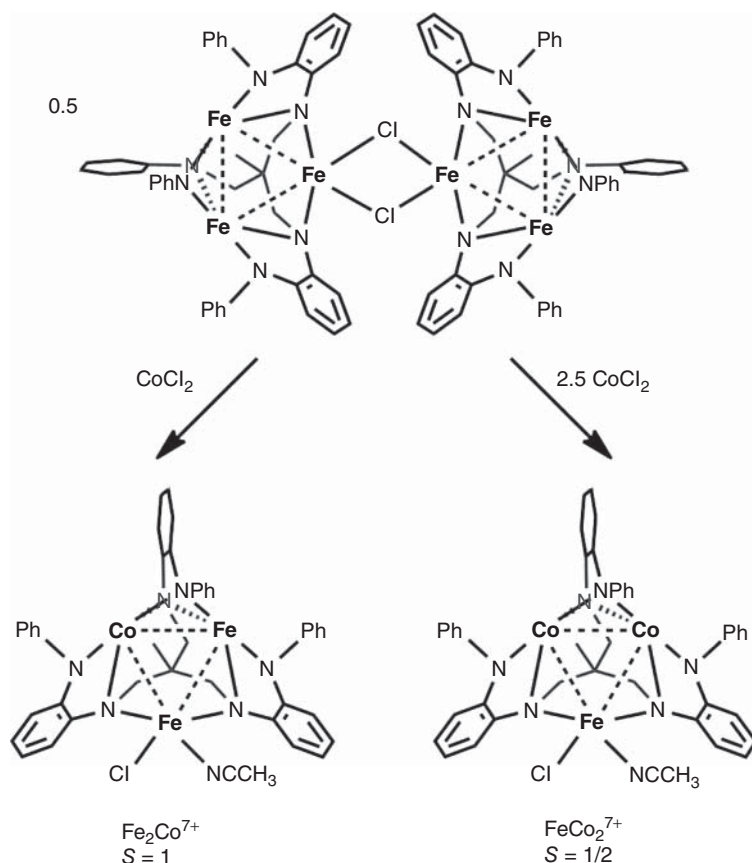


Figure 8.35 FeCo tri(amidinate)amine.



Scheme 8.7 Access to FeCo heterometallics via metal-atom substitution at a triiron core.

CoCl_2 effected the replacement of one and two iron centers in the triiron core with cobalt to generate $(\text{L}^{\text{Ph}})\text{CoFe}_2\text{Cl}(\text{CH}_3\text{CN})$ and $(\text{L}^{\text{Ph}})\text{Co}_2\text{FeCl}(\text{CH}_3\text{CN})$, respectively (Scheme 8.7). The reaction was performed in THF at rt for 3 h, and the dissolution of the reaction crude into acetonitrile resulted in the precipitation of the acetonitrile-cluster adducts as a crystalline material. Notably, no metal atom substitution occurs at the unique iron site, where chloride is bound.

Magnetic susceptibility of the $\text{Fe}_2\text{Co}^{7+}$ and FeCo_2^{7+} heterometallics were measured to gauge the effect of Co substitution on the overall magnetic properties of the cluster. The most dramatic change is the decrease in spin state, from $S = 7/2$ for the Fe_3^{7+} unit in $[(\text{L}^{\text{Ph}})\text{Fe}_3(\mu\text{-Cl})]_2$ to $S = 1$ and $1/2$ for the $\text{Fe}_2\text{Co}^{7+}$ and FeCo_2^{7+} clusters, respectively. The χT values vary with temperature, and the magnetic data was modeled as a two-spin system comprising high-spin Fe(II), $S = 2$, and a bimetallic $S = 1$ $[\text{FeCo}]^{5+}$ or $S = 1/2$ $[\text{Co}_2]^{5+}$ unit that are weakly coupled ($J = -4.25$ and -6.25 cm^{-1}). The Mössbauer spectra of the $\text{Fe}_2\text{Co}^{7+}$ complex showed three doublets, indicating that Co substitution occurs indiscriminately into two of the three iron sites. On the other hand, the FeCo_2^{7+} cluster exhibited a single doublet with $IS = 0.69 \text{ mm s}^{-1}$ and $QS = 1.38 \text{ mm s}^{-1}$, which corresponds to the unique Fe–Cl site. The shortest metal–metal bond in the trimetallic core is Co–Co at $2.286(1) \text{ \AA}$ (FSR 0.98). The two Fe–Co bonds are longer, ranging from 2.50 to $2.53 \text{ \AA}$ (FSR 1.08–1.09).

Fe–Group 10 Heterometallics The triad of Group 10 metals readily forms bonds with iron in a class of bimetallic complexes with related chemical formulas, $(\text{OC})_3\text{Fe}(\mu\text{-dppm})(\mu\text{-L})\text{MX}$, as shown

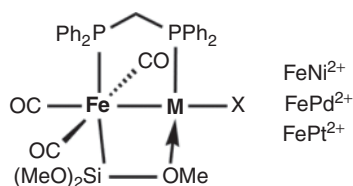


Figure 8.36 $(\text{OC})_3\text{Fe}(\mu\text{-dppm})(\mu\text{-L})\text{MX}$, $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$.

in Figure 8.36, where M is the Group 10 metal, and bis(diphenylphosphino)methane (dppm) is diphenylphosphinomethane. Typically, L is the anionic trialkoxysilylide, $\text{Si}(\text{OMe})_3$, and X can be a halide, alkyl, allyl, or acyl ligand. Many of the Fe-M bonds have FSRs in the vicinity of 1.05 [226–232]. In all cases, the geometry of the iron center is approximately octahedral with the three carbonyl ligands and the Group 10 metal occupying the equatorial plane. In the subfamily of $(\text{OC})_3\text{Fe}(\mu\text{-dppm})(\mu\text{-Si}(\text{OMe})_3)\text{MX}$ complexes, the two bridging ligands are *trans*-disposed, axial ligands at the octahedral Fe . The bridging silylide ligand attaches to Fe via the Si -atom and to M via the methoxy O -atom. Since the latter donor is potentially hemilabile, it masks an open site at the Group 10 metal. The hemilability is best demonstrated for Pd . For example, in the FePd complex, $(\text{OC})_3\text{Fe}(\mu\text{-dppm})(\mu\text{-Si}(\text{OMe})_3)\text{PdCl}$, all methoxy groups of the silylide ligand are equivalent on the NMR timescale [233], whereas two methoxy resonances are observed for the Pt analog.

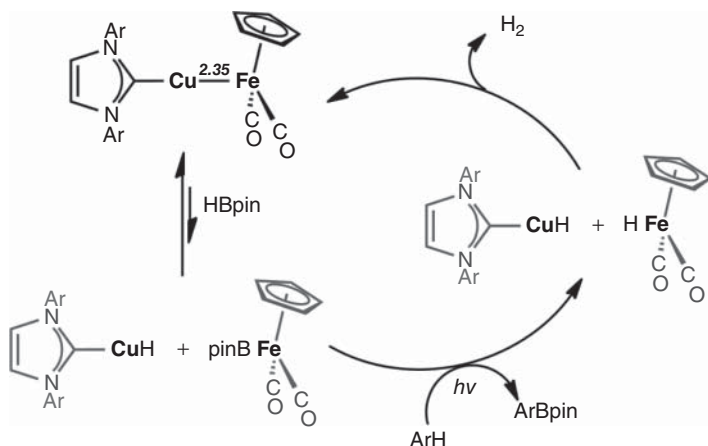
Reactivity of these complexes occurs primarily at the Group 10 metal. Metathesis with Grignard reagents transforms the MX linkages to their more reactive, organometallic MR variety. The hydrocarbyl ligands can undergo diverse transformations, which have been reviewed previously [234]. For instance, migratory insertions of CO and isocyanide into the MR bonds to generate $\text{MC}(\text{O})\text{R}$ and $\text{MC}(\text{NR})\text{R}$ species are well-known [226, 229, 235, 236]. Further insertions can ensue, generating oligomers of organic nitriles or an alternating sequence of CO and norbornene. Group 10 metal hydrides species have also been isolated, for example, $(\text{OC})_3(\text{Si}(\text{OMe})_3)\text{Fe}(\mu\text{-diphosphine})\text{Pt}(\text{H})\text{PPh}_3$ ($\text{Pt-Fe} = 2.670(2)/\text{FSR} = 1.09$) [232, 237], and terminal alkynes undergo insertion to give intermediary Pt -alkenyl complexes, for example, $(\text{OC})_3\text{Fe}(\mu\text{-Si}(\text{OMe})_3)(\mu\text{-dppm})\text{Pt}(\text{CH}=\text{CRH})\text{PPh}_3$, which subsequently rearranges *intramolecularly* to the bridging vinylidene complex, $(\text{CO})_3\text{Fe}(\mu\text{-C}=\text{CRH})(\mu\text{-dppm})\text{Pt}(\text{PPh}_3)$, with loss of silanol. An intermolecular process is observed for the electron-deficient alkyne, $\text{F}_3\text{CC}\equiv\text{CCF}_3$, wherein the derived Pt -alkenyl intermediate transforms into the bridging alkynyl complex, $(\text{OC})_3\text{Fe}(\mu\text{-dppm})(\mu\text{-F}_3\text{CC}\equiv\text{CCF}_3)\text{Pt}(\text{CO})$ [232]. Catalytic reactions have also been reported, including the dehydrogenative coupling of tin hydrides with Fe-Pd and Fe-Ni bimetallic complexes [226, 236, 238, 239].

An Fe-Pt interaction has been stabilized within a classical, tetragonal paddlewheel, $\text{PtFe}(\text{tba})_4(\text{OH}_2)_2$, with four bridging thiobenzoate (tba) ligands in a (4,0) arrangement: the S donors bind to Pt , while the O donors (and the H_2O) bind to Fe [240]. The Fe-Pt distance is $2.632(1) \text{ \AA}$ ($\text{FSR} = 1.07$). Solid-state magnetometry measurements were consistent with isolated, high-spin $\text{Fe}(\text{II})$: a Hamiltonian fit gave $g = 1.995$, $|D| = 6.399 \text{ cm}^{-1}$. DFT calculations on this molecule revealed an Fe-Pt bond order of 0.36, suggesting a weak donor (Pt)-acceptor (Fe) interaction.

Finally, switching to amide ligands, a linear Pt-Fe-Pt chain has been structurally characterized in $[\{\text{Pt}(\text{NH}_3)_2(\mu\text{-NHC}(\text{O})^t\text{Bu})_2\}_2\text{Fe}](\text{ClO}_4)_3$ [241]. The average Fe-Pt distance is $2.564 \text{ \AA}$ ($\text{FSR} = 1.04$). Iron has also featured in other linear heterotrimetallic complexes, such as $\text{Cr}_2\text{Fe}(\text{dpa})_4\text{Cl}_2$, where dpa = dipyridylamide and Cr_2 is a multiply bonded unit. However, the $\text{Fe-(Cr}_2)$ distance is quite long at $2.70 \text{ \AA}$ ($\text{FSR} = 1.16$), signifying a weak interaction at best [242]. The same general conclusion is true of other, related trimetallics, $\text{M}_2\text{Fe}(\text{dpa})_4\text{X}_2$ (where $\text{M}_2 = \text{Cr}_2, \text{Mo}_2, \text{W}_2$, $\text{X} = \text{Cl}$; $\text{M}_2 = \text{Cr}_2$, $\text{X} = \text{OTf}$, N_3): a strong M-M bond is present with a weak Fe-M interaction [242–244].

Fe-Group 11 Heterometallics The “ $\text{Fe}(\text{CO})_2\text{Cp}$ ” fragment, which was described earlier as a heterometallic partner with electrophilic Group 4 metals, also forms unsupported metal-metal bonds with Cu . The FeCu^+ complexes are formed in salt elimination reactions between various NHC-ligated

copper(I) chlorides and $\text{K}[\text{Fe}(\text{CO})_2\text{Cp}]$ [245]. The Fe–Cu bond distances in $(\text{IPr})\text{CuFe}(\text{CO})_2\text{Cp}$ and $(\text{SIMes})\text{CuFe}(\text{CO})_2\text{Cp}$ are 2.3462(5) and 2.3514(7) Å, respectively (FSR 1.00, 1.01), where IPr and SIMes are NHCs with the aryl substituents, 2,6-*i*-Pr₂(C₆H₃) and 2,4,6-Me₃(C₆H₂), respectively, as shown in Scheme 8.8. A low Wiberg bond order of 0.39 was computed by DFT, and a dative Fe → Cu bond with ionic character was proposed.



Scheme 8.8 Proposed catalytic mechanism for C–H borylation by an FeCu heterobimetallic.

An exciting application is catalytic C–H borylation promoted by $(\text{IPr})\text{Cu–Fe}(\text{CO})_2\text{Cp}$ [246]. While noble metal catalysts mediate C–H borylation, base metal compounds, such as the boryliron complex $\text{Cp}(\text{CO})_2\text{FeBcat}$, perform only stoichiometric aryl C–H borylation under irradiation [247, 248]. Turnover was inhibited in this precedent system by the generation of the inactive dimer, $\text{Cp}(\text{CO})_2\text{FeFe}(\text{CO})_2\text{Cp}$, which forms in the dehydrogenative coupling of two Fe hydride intermediates. The *key* to catalytic turnover in the FeCu system is the minute concentration of $\text{HFe}(\text{CO})_2\text{Cp}$ and its fast reaction with $(\text{IPr})\text{CuH}$ dimer, evolving H_2 and regenerating $(\text{IPr})\text{CuFe}(\text{CO})_2\text{Cp}$ as the catalyst resting state, and that its reaction with HBpin is a reversible equilibrium favoring the heterobimetallic reactant [246].

8.3.2.2 Ru–M Heterometallics

Ru–Group 4 Heterometallics As mentioned previously, the bonding of Ru to early metals share many similarities to Fe–early metal pairings [197, 198, 203]. The first structurally characterized example of direct metal–metal bonding between Groups 4 and 8 was $\text{Cp}_2(\text{O}^t\text{Bu})\text{ZrRu}(\text{CO})_2\text{Cp}$, which showcased an unsupported Zr–Ru bond length of 2.910(1) Å (FSR 1.08) [204]. Other Ru–Zr variants were isolated where the O^tBu^- ligand at Zr is replaced by a chloride, methyl, or ethyl group [203]. Unsupported Ru–Ti bonds have also been formed by the addition of $\text{RuH}(\text{CO})_2(\text{Cp})$ to $\text{Ti}(\text{NMe}_2)_4$ via amine elimination to give $(\text{NMe}_2)_3\text{TiRu}(\text{CO})_2(\text{Cp})$ [249]. A solid-state structure showed a Ru–Ti bond distance of 2.663(1) Å (FSR 1.04). In a similar manner, $(\text{NMe}_2)_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{O})\text{TiRu}(\text{CO})_2(\text{Cp})$ and $(\text{NMe}_2)(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{O})_2\text{TiRu}(\text{CO})_2(\text{Cp})$ were prepared from $\text{RuH}(\text{CO})_2(\text{Cp})$ with $(\text{NMe}_2)_3(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{O})\text{Ti}$ and $(\text{NMe}_2)_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{O})_2\text{Ti}$, respectively [250]. In $(\text{NMe}_2)(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{O})_2\text{TiRu}(\text{CO})_2(\text{Cp})$, the Ru–Ti bond length shortens to 2.573(1) Å (FSR 1.00). The shortening was attributed to the more electron-deficient character of the aryloxy-ligated Ti center, which can better accept electron-density from Ru.

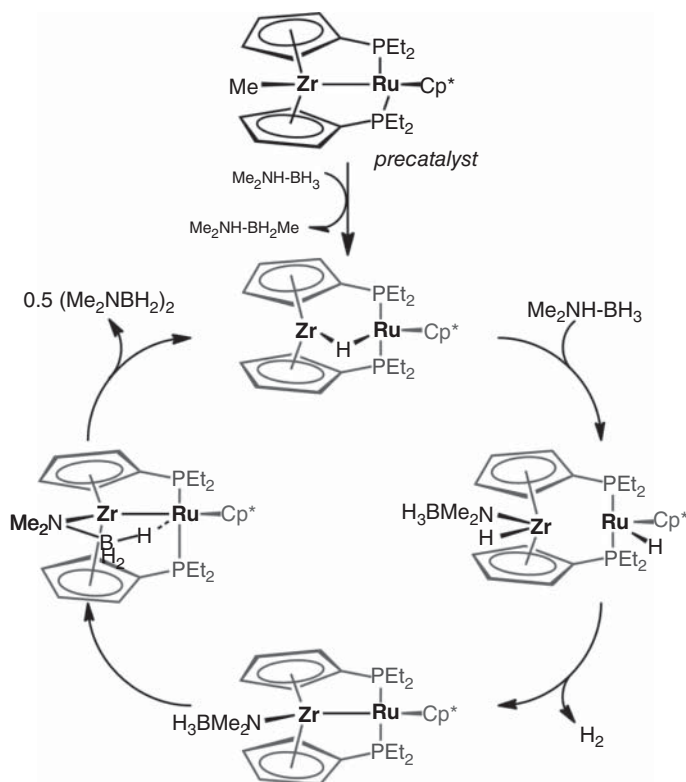
As was the case for Fe, stabilizing Ru–Group 4 complexes has benefited from the use of tripodal triamido ligands at the early metal. Several Ru–Ti complexes were formed in salt elimination reactions between $\text{K}[\text{Ru}(\text{CO})_2\text{Cp}]$ and a $\text{Ti}(\text{L})\text{X}$ precursor, where L is a tripodal triamido ligand, such

as $\text{HC}(\text{SiMe}_2\text{N}(p\text{-tol}))_3$, $\text{MeC}(\text{CH}_2\text{NSiMe}_3)_3$, or $\text{MeSi}(\text{SiMe}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4))_3$ [207, 209, 211]. Ru–Ti bond lengths range from 2.503(4) to 2.5609(8) Å (FSR 0.98–1.00), which is consistent with a single bond. The trisilylsilane-based ligands, $\text{MeSi}(\text{SiMe}_2\text{NAr})_3$ where $\text{Ar} = 4\text{-CH}_3\text{C}_6\text{H}_4$ and $2\text{-FC}_6\text{H}_4$, were also used to make a complete series of Ru–Group 4 complexes: Ti–Ru, Zr–Ru, and Hf–Ru [210, 211]. A similar trend in the $\nu(\text{CO})$ IR frequencies was observed in the Ru series, as was described previously for Fe. The Ru–Ti complex exhibits the highest CO frequencies (1991, 1937 cm^{-1}) compared to the Ru–Zr (1986, 1932 cm^{-1}) and Ru–Hf (1987, 1933 cm^{-1}) complexes, which are similar [210, 211]. As such, the Ru–Ti bond is more covalent because Ti is a better π -acceptor than Zr and Hf, which form more ionic bonds to Ru. With the bidentate, diamido ligand, $\text{CH}_2(\text{CH}_2\text{NSiMe}_3)_2$, several Ru–Zr complexes have been isolated, including $\text{Cp}(\text{CH}_2(\text{CH}_2\text{NSiMe}_3)_2)\text{ZrRu}(\text{CO})_2\text{Cp}$, where the Zr center is ligated by both Cp and amido ligands [212]. The Ru–Zr bond is 2.8297(14) Å long (FSR 1.05) [251]. The mixed Cp-amide donor set at the early metal followed a precedent, $(\text{C}_5\text{Me}_5)(\text{NMe}_2)_2\text{ZrRu}(\text{CO})_2\text{Cp}$, where the ligands on Ru are pentamethyl cyclopentadienyl and two monodentate amides [252]. The dipodal ligand also gave access to a rare Ru_2Zr trimetallic, $(\text{CH}_2(\text{CH}_2\text{NSiMe}_3)_2)\text{Zr}(\text{Ru}(\text{CO})_2\text{Cp})_2$, where the two Ru–Zr bonds are shorter at 2.7372(7) and 2.7452(7) Å (FSR 1.02) [213, 251]. The other Ru_2Zr species whose solid-state structure is known, $\text{Cp}_2\text{Zr}(\text{Ru}(\text{CO})_2\text{Cp})_2$, has significantly longer Ru–Zr bonds (2.938(1) and 2.948(1) Å, FSR 1.09) [253].

For Group 8 heterobimetallics, Hf is the least common among the Group 4 metals. For this reason, the family of Ru–Zr and Ru–Hf complexes with the bridging ditopic ligand, $\text{C}_5\text{H}_4\text{PEt}_2^-$, is interesting. They share a common chemical formula, $\text{M}'\text{X}(\text{C}_5\text{H}_4\text{PEt}_2)_2\text{Ru}(\text{C}_5\text{Me}_5)$, where $\text{M}' = \text{Zr}$ or Hf , and $\text{X} = \text{Cl}$, Me , $\kappa^2\text{-BH}_4$, and NMe_2 [254]. Because Hf and Zr have similar atomic radii, the Ru– M' bond distances are similar and primarily depend on X. For $\text{X} = \text{Cl}$ and Me , the Ru–Zr and Ru–Hf bond distances fall within a short range, 2.8396(2)–2.8620(10) Å (FSR 1.06). For $\text{X} = \kappa^2\text{-BH}_4$ or NMe_2 , the Ru–Zr bond distances are much longer (3.01 Å, FSR 1.12). Notably, the heterobimetallic complex, $\text{ZrMe}(\text{C}_5\text{H}_4\text{PEt}_2)_2\text{Ru}(\text{C}_5\text{Me}_5)$, is a precatalyst for the dehydrogenation of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ to give H_2 and the dimer, $(\text{Me}_2\text{NBH}_2)_2$. High yields of H_2 were achieved at catalyst loadings as low as 2 mol%, with a maximum turnover number of 47 in 6 h. The proposed catalytic cycle (Scheme 8.9) showcases the “early-late” cooperativity between Zr and Ru. The active species is proposed to be a bridged hydride complex, $\text{Zr}(\mu\text{-H})(\text{C}_5\text{H}_4\text{PEt}_2)_2\text{Ru}(\text{C}_5\text{Me}_5)$, which is generated from the precatalyst, $\text{ZrMe}(\text{C}_5\text{H}_4\text{PEt}_2)_2\text{Ru}(\text{C}_5\text{Me}_5)$, and $\text{Me}_2\text{NH}\cdot\text{BH}_3$. Notably, the reductive elimination of H_2 takes place across both metal centers to regenerate a Ru–Zr bond in the intermediate, $\text{Zr}(\text{NMe}_2\text{BH}_3)(\text{C}_5\text{H}_4\text{PEt}_2)_2\text{Ru}(\text{C}_5\text{Me}_5)$.

Ru–Group 6 Heterometallics Ru–M heterometallics, where M is a mid-transition metal, remain one of the least studied pairings. The limited examples are Ru–Mo and Ru–W diporphyrin complexes, which are prepared in the co-pyrolysis of $\text{Ru}(\text{porphyrin})(\text{py})_2$ (porphyrin = OEP or TPP) and $\text{Mo}(\text{OEP})(\text{PhC}\equiv\text{CPh})$ or $\text{W}(\text{OEP})(\text{PEt}_3)_2$, respectively, and purified by redox titration experiments (*vide supra*) [255–257]. The Ru– M^{4+} cores in $\text{RuM}(\text{porphyrin})_2$, which have (d–d)¹⁰ counts, display $S = 1$ ground states that are inconsistent with the typical tetragonal electronic configuration of $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$. Instead, two alternative configurations, $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2$ and $(\sigma)^2(\pi)^4(d_{xy}, d_{x^2-y^2})^2(\pi^*)^2$, were proposed for the heterometallics, in which formal bond orders range from 2 to 3, depending on the absence or presence of the δ -bond. The magnetic susceptibility of $\text{RuMo}(\text{OEP})_2$ was highly temperature dependent, with the effective magnetic moment rising from 0.44 μ_B at 2 K to 2.31 μ_B at 300 K. The data was modeled as $S = 1$ with a large zero-field splitting of 800 cm^{-1} . A resonance Raman study of $\text{RuMo}(\text{OEP})_2$ revealed a Ru–Mo bond vibration at 320 cm^{-1} . Substituting Mo with W in $\text{RuW}(\text{OEP})_2$, the Ru–W bond vibration decreases to 308 cm^{-1} . For comparison, $\text{Ru}_2(\text{OEP})_2$ exhibited a Ru=Ru bond stretch at 285 cm^{-1} .

The RuMo^{5+} and RuW^{5+} analogs were structurally characterized, but only in the case of a mixed porphyrin dimers. The $[(\text{TPP})\text{RuMo}(\text{OEP})]\text{PF}_6$ salt crystallized as two independent molecules in the asymmetric unit. Of interest, one molecule was an eclipsed conformer (torsion angle of 4.4°), while the other exhibited a staggered geometry (43.5°) [255]. The presence of both rotamers implicates a low energy barrier between the two conformations, and a steric energy difference of 5.5 kcal mol^{-1}



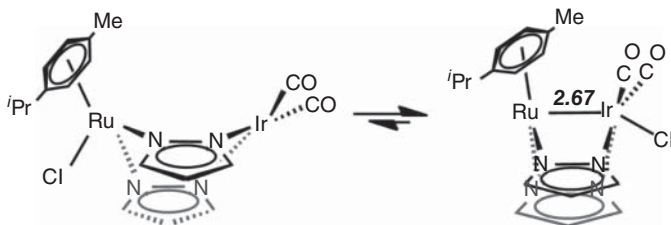
Scheme 8.9 Proposed catalytic cycle for the dehydrogenation of $\text{Me}_2\text{NH}\bullet\text{BH}_3$ with a Zr–Ru heterobimetallic system.

was computed using the MM2 force field. The staggered rotamer is favored energetically, which was expected as it should have less steric repulsion between the cofacial porphyrins than the eclipsed conformer. Indeed, the Ru–Mo bond is longer in the eclipsed structure (2.211(2) Å, FSR 0.87) than in the staggered one (2.181(2) Å, FSR 0.86), consistent with greater steric repulsion in the former. The spin state of a related RuMo^{5+} complex, $[\text{RuMo}(\text{OEP})_2]\text{PF}_6$, was assigned as $S = 1/2$ based on an axial EPR signal with $g_{\perp} = 1.973$ and $g_{\parallel} = 1.952$ [256]. In the Ru–W mixed-porphyrin analog, $[(\text{TPP})\text{RuW}(\text{OEP})]\text{PF}_6$, the Ru–W bond distance is 2.297(2) Å (FSR 0.90) and the torsion angle is 29.9° [257]. Depending on the strength of the δ -bond, the electronic configurations of the RuMo^{5+} and RuW^{5+} cores can be either $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^1$ or $(\sigma)^2(\pi)^4(d_{xy}, d_{x^2-y^2})^2(\pi^*)^1$, with respective bond orders of 3.5 and 2.5.

Resonance Raman measurements of $[(\text{TPP})\text{RuMo}(\text{OEP})]\text{PF}_6$ revealed a similar Ru–Mo bond vibration frequency as the RuMo^{4+} complex, $\text{RuMo}(\text{OEP})_2$ (318 cm^{-1} versus 320 cm^{-1}). To directly compare the effect of oxidation on the Ru–Mo bond vibrational frequency, one can compensate for the mass difference between OEP and TPP and extrapolate a value of 323 cm^{-1} for the non-existing RuMo^{5+} species, $[\text{RuMo}(\text{OEP})_2]^+$. As expected, the Ru–Mo bond vibrational frequency increases upon oxidation, though only by a few wavenumbers. The RuW^{5+} analog, $[(\text{TPP})\text{RuW}(\text{OEP})]\text{PF}_6$, showed a significantly higher Ru–W bond stretching frequency than the RuW^{4+} species, $\text{RuW}(\text{OEP})_2$ (327 cm^{-1} versus 308 cm^{-1}), which is consistent with increased bond order upon oxidation. The Ru–M bond strengths for the series were compared using force constants (k) that are calculated from the diatomic oscillator model, where $k = (3.55 \times 10^{17})\mu\nu^2$, μ is the reduced mass, and ν is the vibrational frequency from the Raman studies. The Ru–M complexes are ranked by the

strength of their force constants (mdyn/Å): RuW^{5+} 4.11 > RuW^{4+} 3.65 > RuMo^{4+} 2.97 ~ RuMo^{5+} 2.93 > Ru_2^{6+} 2.70 > Ru_2^{4+} 2.42. Of note, the heterometallic metal–metal bonds in $\text{RuM}^{4+/5+}$ species are significantly stronger than the homometallic bonds, including the (d–d)¹⁰ Ru_2^{6+} species.

Ru–Group 9 Heterometallics One of the most interesting Ru–heterometallics involves a Ru–Ir bond that breaks and forms reversibly in a pair of RuIr^{3+} isomers sharing the common formula, $(\eta^6\text{-p-cymene})\text{RuCl}(\mu\text{-pz})_2\text{Ir}(\text{CO})_2$, where pz is pyrazolyl [258]. The isomerization formally involves chloride migration between the two metals as shown in Scheme 8.10. Both isomers have been structurally characterized. In the isomer with a Ru–Cl bond, the two metals are 3.66 Å (FSR 1.47) apart, which is far too long to invoke an interaction. However, when the Cl is bound to Ir, the Ru–Ir distance contracts by nearly an angstrom to 2.6962(6) Å (FSR = 1.08). It is proposed that the Ru–Ir bond is a dative interaction between an Ir^{1+} donor and a Ru^{2+} acceptor, though a covalent Ru–Ir bond corresponding to formal oxidation states of $\text{Ru}^{1+}/\text{Ir}^{2+}$ was also considered. At rt in CDCl_3 , the isomerization has an equilibrium constant of 2.4(1), favoring the isomer with the Ru–Ir bond. The mechanism for the isomerization is proposed to be ionic with dissociation of the chloride ligand, since the reaction obeys a second-order rate law with respect to $(\eta^6\text{-p-cymene})\text{Ru}(\mu\text{-pz})_2\text{Ir}(\text{CO})_2\text{Cl}$ and is inhibited by the presence of chloride ions.



Scheme 8.10 Reversible formation and cleavage of an Ru–Ir bond upon chloride migration.

Several Ru–Group 9 heterobimetallics share related organometallic transformations of a bridging hydrocarbyl ligand. The complexes have in common two bridging dpmm ligands, which are *trans* disposed, and several carbonyl ligands. The transformations typically begin from the bridged methylene cations, $[(\text{CO})_2\text{Ru}(\mu\text{-CH}_2)(\mu\text{-CO})(\mu\text{-dpmm})_2\text{M}(\text{CO})]^+$ (where M = Rh, Ir), in which the Ru–M distances are too long to be considered a covalent bond (FSR ≥ 1.15) [259–261]. However, protonation of the methylene ligand with triflic acid provided the bridged acetyl salt, $[(\text{CO})_2\text{Ru}(\mu\text{-C}(\text{O})\text{CH}_3)(\mu\text{-dpmm})_2\text{Rh}(\text{OTf})]\text{OTf}$, in which the Ru–Rh bond distance contracted to 2.6953(4) Å (FSR 1.08) (Figure 8.37) [262]. The acetyl ligand binds through the acyl carbon to Rh and the O-atom to Ru. The reaction sequence presumably involves protonation to a methyl intermediate, migratory insertion of CO, and CO dissociation. Low-temperature NMR studies unraveled the sequence of hydrocarbyl transformations that is mediated cooperatively by both metals. At -80°C , the protonation yields a bridged methyl intermediate that is Ru-bound but has a C–H agostic interaction

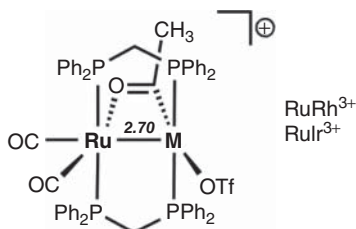


Figure 8.37 $[(\text{CO})_2\text{Ru}(\mu\text{-C}(\text{O})\text{CH}_3)(\mu\text{-dpmm})_2\text{M}(\text{OTf})]\text{OTf}$, M = Rh, Ir.

with Rh. Next, the intermediate isomerizes to a terminal Rh-methyl group, which then undergoes migratory insertion of a bridging CO, followed by the dissociation of a second bridging CO ligand.

The protonation of the corresponding methylene-bridged Ir–Ru bimetallic ultimately yielded several isolable RuIr^{3+} acetyl species, depending on the solvent and counterion [260]. One of these acetyl products, $[(\text{CO})_2\text{Ru}(\mu\text{-C}(\text{O})\text{CH}_3)(\mu\text{-dppm})_2\text{Ir}(\text{OTf}))\text{OTf}]$, is isostructural to the RuRh^{3+} species and possesses the shortest Ru–Ir bond (2.7037(6) Å, FSR 1.08) in this system. While the overall conversion (methylene to acetyl) is similar to that observed in the Rh–Ru system, there are some notable differences between the intermediates in these processes. Also, CO migratory insertion into the M-CH_3 bond is orders of magnitude slower for Ir than for Rh, which is a consequence of the greater M-C bond strengths for third-row versus second-row metals. Notably, the Ru–Ir acetyl complex is more reactive than its Rh counterpart, and reacts with H_2 to form the dihydride species, $[\text{H}(\text{CO})_2\text{Ru}(\mu\text{-C}(\text{O})\text{CH}_3)(\mu\text{-dppm})_2\text{IrH}(\text{OTf})]$, where the H–H bond is homolytically cleaved across both metals.

Ru–(Groups 10, 11) Heterometallics An early precedent of Ru–Group 10 bonding is the complex, $\text{Cl}(\text{CO})_2\text{Ru}(\mu\text{-Ph}_2\text{Ppy})_2\text{PdCl}$, with a Ru–Pd bond distance of 2.660(1) Å (FSR 1.06), as shown in Figure 8.38 [263]. Two *N,P*-ligands, Ph_2Ppy , bridge the two metal centers. The complex can be prepared by metallating the Ru(II) precursor, $\text{Ru}(\text{trans-PPh}_2\text{py})_2\text{Cl}_2(\text{CO})_2$, with Pd(0), or vice versa, by metallating the Ru(0) complex, $\text{Ru}(\text{trans-PPh}_2\text{py})_2(\text{CO})_3$ with (1,5-COD)PdCl₂.

Using a different Ru(II) metalloligand, $[\text{CpRu}(\eta^2\text{-dmpm})(\eta^1\text{-dmpm})]\text{PF}_6$ (where dmpm = dimethylphosphinomethane), the RuPt²⁺ complex, $[\text{CpRuPt}(\mu\text{-dmpm})_2(\text{PPh}_3)]\text{PF}_6$, was isolated from a reaction with $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ [264]. The Ru–Pt distance is 2.769(1) Å (FSR 1.09), and akin to the RuPd complex, the Group 10 metal is square planar.

A series of linear trimetallics with the formula $[\text{Ru}_2\text{M}(\text{dpa})_4\text{Cl}_2]^{0,1+}$ (M = Ni, Cu) have been prepared with $\text{Ru}_2\text{Ni}^{6+/7+}$ and $\text{Ru}_2\text{Cu}^{6+/7+}$ cores (Figure 8.39) [265]. The neutral complexes were isolated from a one-pot reaction comprising the neutral H(dpa) ligand, $\text{Ru}(\text{OAc})_4\text{Cl}$, Ni(II) or Cu(II) salts,

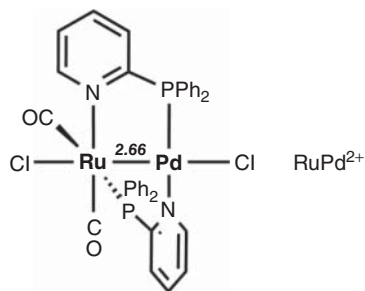


Figure 8.38 $\text{Cl}(\text{CO})_2\text{Ru}(\mu\text{-Ph}_2\text{Ppy})_2\text{PdCl}$.

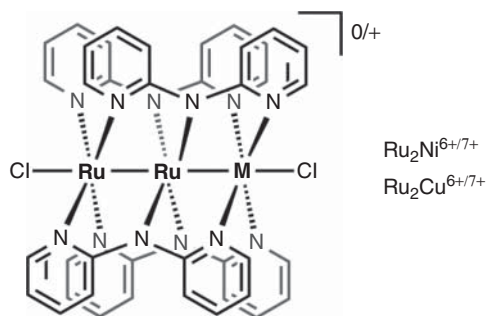


Figure 8.39 $[\text{Ru}_2\text{M}(\text{dpa})_4\text{Cl}_2]^{0,1+}$, M = Ni, Cu.

^tBuOK/^tBuOH, and LiCl heated in naphthalene. A separate oxidation with [FeCp₂]₂PF₆ gave access to the cationic analogs. The solid-state structures all show short Ru–Ru bonds (FSR 0.90–0.94) that are indicative of multiple bonds. The Ru–Ni and Ru–Cu bonds are longer, 2.349(5) Å (FSR 0.98) and 2.575(3) Å (FSR 1.07) in the neutral complexes, respectively. Upon oxidation, the Ru–Ni bond lengthens to 2.513(9) Å (FSR 1.05), while the Ru–Cu bond shortens to 2.51(1) Å (FSR 1.04).

Cyclic voltammetry of the neutral complexes showed two reversible oxidations each. For Ru₂Cu⁶⁺, these oxidations occur at –0.46 and 0.42 V (vs FeCp₂^{+/0}). The first oxidation was assigned to the Cu(I/II) redox couple because of a near-infrared absorbance at 900 nm, which is attributable to the mixed-valent Ru₂⁵⁺ core. For Ru₂Ni⁶⁺, the two oxidations occur at –0.63 and 0.41 V. Again, the first oxidation was assigned to the Ni(I/II) redox couple.

SQUID magnetometry experiments were also performed. The Ru₂Cu⁶⁺ complex was the most straightforward to interpret. Its magnetic data was modeled with parameters ($g_{\text{av}} = 2.08$, $D = 52.4 \text{ cm}^{-1}$) that are similar to Ru₂⁵⁺ species. Thus, the Ru₂Cu⁶⁺ core consists of an $S = 3/2$ Ru₂⁵⁺ subunit with d¹⁰ Cu⁺ center. Further confirmation of the spin state was obtained from an axial EPR signal with $g_{\perp} = 1.99$ and $g_{\parallel} = 3.99$. The Ru₂Cu⁷⁺ and Ru₂Ni⁶⁺ cores are isoelectronic, and their complexes have a similar magnetic profile, with a magnetic moment of 4.3 μ_{B} at 300 K that gently decreases below 100 K. An $S = 2$ state was proposed for both of these species, which could arise from ferromagnetic coupling of an $S = 3/2$ Ru₂⁵⁺ subunit and an $S = 1/2$ Cu²⁺ or Ni⁺ center. The Ru₂Ni⁷⁺ complex has a magnetic moment of 5.15 μ_{B} at 300 K that reaches a maximum of 5.80 μ_{B} at 88 K. A strong EPR signal at $g^e_{\perp} = 6.26$ and a weak signal at $g^e_{\perp} = 2.05$ suggests an $S = 5/2$ system with a large zero-field splitting.

8.3.2.3 Os–M Heterometallics

Os–Group 6 Heterometallics Os–M heterometallics, where M is a transition metal outside of Group 8, were isolated for the Group 6 metals, Mo and W. The Os–Mo and Os–W diporphyrin complexes were prepared in the co-pyrolysis of Os(OEP)(py)₂ and Mo(OEP)(PhC≡CPh) or W(OEP)(PEt₃)₂, respectively, and purified by redox titration experiments (*vide supra*) [256, 257, 266]. The OsM(OEP)₂ complexes are paramagnetic and solution-state magnetic measurements at room temperature indicate $S = 1$ ($\mu_{\text{eff}} = 2.72$ and 2.62 μ_{B} for OsMo and OsW). The Os–M bond vibrations were measured by resonance Raman spectroscopy at 304 cm^{–1} for OsMo(OEP)₂ and 267 cm^{–1} for OsW(OEP)₂. For comparison, Os₂(OEP)₂ exhibited an Os=Os bond stretch at 233 cm^{–1}. Thus, two different bonding schemes were proposed for the OsM⁴⁺ species, Os≡Mo and Os=W, with the corresponding electronic configurations of $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2$ and $(\sigma)^2(\pi)^4(\text{Os } d_{xy}, d_{x^2-y^2})^2(\pi^*)^2$.

A heteroporphyrin Os–Mo system has been isolated in two redox states, [(TPP)OsMo(OEP)]^{0/+}. A solid-state structure of the OsMo⁵⁺ complex showed an Os–Mo bond length of 2.238(3) Å (FSR 0.88) [257]. The porphyrin rings are staggered with a twist angle of 42.1°. A resonance Raman study of [(TPP)OsMo(OEP)]PF₆ revealed an Os–Mo bond vibration at 316 cm^{–1}, which is slightly larger than OsMo(OEP)₂. Thus, a bond order of 3.5 was proposed for [(TPP)OsMo(OEP)]PF₆ with a $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^1$ configuration. Though a staggered conformation often suggests an absence of δ -bonding, the relatively short Os–Mo bond length supports the higher bond order. As the energy difference between staggered and eclipsed rotamers can be quite small (5.5 kcal mol^{–1} in the MoRu⁵⁺ analog), subtle crystal packing forces may ultimately determine the molecular geometry.

The Os–M bond strengths were also compared using force constants (k) that are calculated from the diatomic oscillator model. The Os–M complexes are ranked by the strength of their force constants (mdyn Å^{–1}): [Os₂(OEP)₂]²⁺ 3.96 > OsW(OEP)₂ 3.93 > [(TPP)OsMo(OEP)]PF₆ 3.75 > OsMo(OEP)₂ 3.47 > Os₂(OEP)₂ 3.04. Notably, the heterometallic bonds of OsM⁴⁺ are significantly stronger than the corresponding homometallic bond of Os₂⁴⁺; but the isoelectronic Os₂⁶⁺ core has the strongest metal–metal bond force constant of 3.96 mdyn Å^{–1} in this series.

Os–Group 9 Heterometallics Analogous to the Ru–Rh system described earlier, the protonation of $[(\text{CO})_2\text{Os}(\mu\text{-CH}_2)(\mu\text{-CO})(\mu\text{-dppm})_2\text{Rh}(\text{CO}))\text{OTf}]$ with triflic acid yielded an isostructural, bridging acetyl complex, $[(\text{CO})_2\text{Os}(\mu\text{-C}(\text{O})\text{CH}_3)(\mu\text{-dppm})_2\text{Rh}(\text{OTf}))\text{OTf}]$, with a relatively short Os–Rh bond (2.7061(4) Å, FSR 1.08) [267]. The process was found to be similar to the RuRh analog, except that the dissociation of a bridging carbonyl ligand happened slowly at ambient temperatures (10% NMR conversion) and required refluxing conditions to go to completion quickly.

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9

Group 9 Metal–Metal Bonds

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9.1

Cobalt

9.1.1

Overview

Despite the abundance of dirhodium compounds, examples of which will be discussed in Section 9.2, comparatively few examples of analogous dicobalt compounds, with supported or unsupported Co–Co bonds, have been reported. The first dicobalt compound exhibiting a short Co–Co bond length, $\text{Co}_2(\text{NNN})_4$ ($[\text{NNN}]^- = (p\text{-CH}_3\text{C}_6\text{H}_4)\text{NNN}(\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)$; see Figure 9.1), was reported in 1987 [1]. This diamagnetic compound with a $\text{Co}_2(\text{II,II})$ core was prepared by the reaction of CoCl_2 with $\text{Li}(\text{NNN})$ in THF at -78°C . The crystal structure shows that the triazenido ligands adopt the expected tetragonal or paddlewheel arrangement, around the dimetal core. The short Co–Co bond length (2.265(2) Å) and diamagnetism indicated a $\sigma^2\pi^4\delta^2\delta'^2\pi'^4$ electronic configuration, and formal single σ -bonding interaction between the Co atoms. While early X α -SW calculations failed to predict the expected single σ -bond [2], later *ab initio* calculations employing the configuration interaction methods confirmed the expected $\sigma^2\pi^4\delta^2\delta'^2\pi'^4$ electronic configuration for $\text{Co}_2(\text{HNNNH})_4$ and $\text{Co}_2(\text{HNC}\{\text{H}\}\text{NH})_4$ model compounds [3].

By contrast to the diamagnetic tetragonal dicobalt compounds of the types $\text{Co}_2(\text{form})_4$ or $\text{Co}_2(\text{NNN})_4$ ($[\text{form}]^- = \text{formamidinate-type ligands}$, $[\text{NNN}]^- = \text{triazenido ligands}$) [1, 3, 4], the closely related trigonal compounds $\text{Co}_2(\text{form})_3$, are paramagnetic [5]. The cobalt atoms in the Co_2^{3+} cores have formal Co(I) and Co(II) oxidation states, although it is important to remember that the electron density is actually shared equally between both metal atoms. In these systems, the *pseudo*- D_{3h} symmetry of the dicobalt core results in two degenerate δ -bonding interactions between the d_{xy} and $d_{x^2-y^2}$ Co atomic orbitals. This results in compounds that have five unpaired electrons in a $\sigma^2\pi^2\pi'^2\pi''^2\sigma'^1\delta^1\delta'^1\delta''^1$ electronic configuration and a formal Co–Co bond order of 0.5 [6].

Prior to 2005, only six crystal structures of dicobalt compounds with short Co–Co distances had been reported [7]. This section describes advances in the field of Co–Co bonding since this time. There is a significant amount of literature on cobalt clusters containing π -acid ligands, such as carbonyls, which have Co–Co bonds. However, these types of systems are outside the scope of this book so they will not be discussed in any detail.

9.1.2

Dicobalt Compounds with Short Co–Co Bonds

The syntheses of the tetragonal paddlewheel compound, $\text{Co}_2(\text{DAniF})_4$ ($[\text{DAniF}]^- = N,N'\text{-di-}p\text{-anisylformamidinate}$), and the trigonal paddlewheel compound, $\text{Co}_2(\text{DAniF})_3$ have been reported

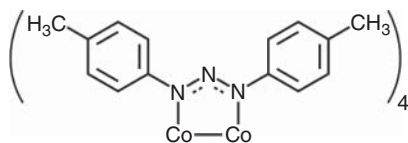
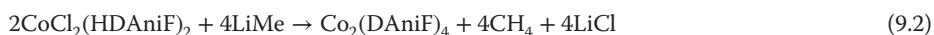
Figure 9.1 $\text{Co}_2(\text{NNN})_4$.

Table 9.1 Selected Co–Co bond lengths for dicobalt paddlewheel compounds.

Compound	Co–Co distance (Å)	References
Formamidine-type ligands		
$\text{Co}_2(\text{DPhF})_4$	2.3735(9)	[3]
$\text{Co}_2(\text{DAniF})_4$	2.3580(16)	[8]
$\text{Co}_2(\text{NNN})_4$	2.265(2)	[1]
$\text{Co}_2(\text{DPhBz})_4$	2.302(1)	[4]
$[\text{Co}_2(\text{DPhBz})_4][\text{PF}_6]$	2.322(2), 2.332(2)	[3]
$\text{Co}_2(\text{DPhF})_3$	2.385(1)	[5b]
$\text{Co}_2(\text{DAniF})_3$	2.3773(5)	[8]
$\text{Co}_2(\text{DPhBz})_3$	2.3201(9)	[5a]
$\text{Co}_2(\text{L}^{\text{Ph}})$	2.385(1)	[9]
$\text{Co}_2(\text{py}_3\text{tren})$	2.4986(4)	[10]
$\text{CoFe}(\text{py}_3\text{tren})$	2.491(3)	[10]
$\text{CoMn}(\text{py}_3\text{tren})$	2.5312(4)	[10]
$\text{Co}_2(\text{NN}^{\text{tBu}})_2$	2.1404(10)	[11]
$\text{Co}_2(\text{NN}^{\text{NCy}^2})_2$	2.1345(7)	[11]
Other compounds		
$\text{Co}_2(\text{MesNP}^i\text{Pr}_2)_2(\text{PMe}_3)_2$	2.5536(3)	[12]
$[\text{Co}_2(\text{MesNP}^i\text{Pr}_2)_2(\text{PMe}_3)(\text{THF})]^+$	2.4864(6)	[12]
$[\text{Co}_2(\mu\text{-NC}^t\text{Bu})_3(\text{NC}^t\text{Bu})_2]^-$	2.4097(7)	[13]
$\text{Co}_2(\text{HN}(\text{PPh}_2)_2)_2(\mu\text{-PPh}_2)_2$	2.3857(5)	[14]

$[\text{DPhF}]^-$ = diphenylformamidine.

[8]. The synthetic route to the tetragonal species involved the initial formation of the intermediate $\text{CoCl}_2(\text{HDAniF})_2$, by the reaction of CoCl_2 and HDAniF in toluene. Deprotonation of the intermediate by methyl lithium resulted in the formation of $\text{Co}_2(\text{DAniF})_4$ (Eqs. (9.1) and (9.2)), which is an air-sensitive diamagnetic compound. The reduction of the intermediate with NaEt_3BH , prior to the deprotonation with methyl lithium resulted in the formation of paramagnetic $\text{Co}_2(\text{DAniF})_3$. The Co–Co bond lengths for the tetragonal $\text{Co}_2(\text{DAniF})_4$ (2.3580(16) Å) and the trigonal $\text{Co}_2(\text{DAniF})_3$ (2.3773(5) Å) are compared to related species in Table 9.1. As yet, there is no clear explanation for the trend in Co–Co bond lengths found for dicobalt compounds with N-donor bridging ligands.



The tris(amidinato)amine ligand $[\text{L}^{\text{Ph}}]^{3-}$ has been used to isolate the dicobalt(I,II) compound $\text{Co}_2(\text{L}^{\text{Ph}})$ (Figure 9.2) [9]. It was generated in a stepwise synthesis, with the initial step involving the reaction of $\text{K}_3\text{L}^{\text{Ph}}$ with CoCl_2 to generate the mononuclear complex $\text{K}(\text{THF})[\text{Co}(\text{L}^{\text{Ph}})]$. The reaction of this species with KCl and CoBr_2 generated $\text{Co}_2(\text{L}^{\text{Ph}})$, which crystallizes in the trigonal $\bar{R}3$ space

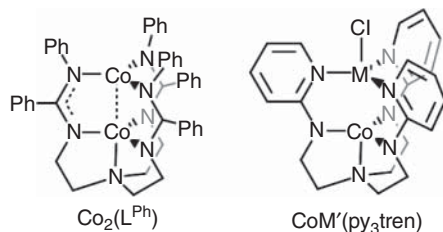


Figure 9.2 Structures of $\text{Co}_2(\text{L}^{\text{Ph}})$ and $\text{CoM}'(\text{py}_3\text{tren})$.

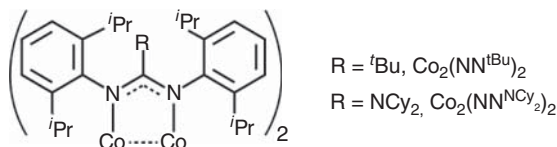


Figure 9.3 Structures of $\text{Co}_2(\text{NN}^{\text{tBu}})_2$ and $\text{Co}_2(\text{NN}^{\text{NCy}_2})_2$.

group, resulting in a dicobalt core that has perfect C_3 symmetry, and a Co–Co bond length of 2.385(1) Å. The magnetic properties of $\text{Co}_2(\text{L}^{\text{Ph}})$ were studied, with measurements on $\text{Co}_2(\text{DPhF})_3$ included for comparison (the authors also report a modified synthetic procedure for $\text{Co}_2(\text{DPhF})_3$, in which $\text{Co}_2(\text{DPhF})_4$ was reduced with KC_8) [9]. Variable temperature magnetic susceptibility and EPR measurements on $\text{Co}_2(\text{L}^{\text{Ph}})$ and $\text{Co}_2(\text{DPhF})_3$ showed that these compounds have an energetically isolated high-spin sextet ground state. Below 50 K, deviations from the high temperature limit are observed in the effective magnetic moment due to weak intermolecular antiferromagnetic interactions and small ($<10 \text{ cm}^{-1}$) zero-field splittings.

In a related study, the homo- and hetero-bimetallic compounds $\text{CoM}'\text{Cl}(\text{py}_3\text{tren})$, ($\text{M}' = \text{Co}$, Fe, Mn; Figure 9.2) were synthesized [10]. Their crystal structures revealed metal–metal bond distances of 2.4986(4) Å ($\text{M}' = \text{Co}$), 2.491(3) Å ($\text{M}' = \text{Fe}$) and 2.5312(4) Å ($\text{M}' = \text{Mn}$). The nature of the bonding in these systems was rationalized using CASSCF/CASPT2 calculations. The main electronic configuration of the dicobalt compound, accounting for 19% of the total wavefunction, predicts a formal single σ -bond between the cobalt atoms. However, the sum of all the configurations provides an effective bond order of only 0.22.

Amidinate and guanidinate ligands have been shown to stabilize exceptionally short Co–Co interactions in low coordinate $\text{Co}_2(\text{I,I})$ complexes. The compounds $\text{Co}_2(\text{NN}^{\text{tBu}})_2$ and $\text{Co}_2(\text{NN}^{\text{NCy}_2})_2$ (Figure 9.3) were generated by the reduction of the halide-bridged precursors $[\text{NN}^{\text{R}}\text{Co}(\mu\text{-X})]_2$ with potassium [11]. The solid-state structures revealed these compounds to be planar dimers, which have the shortest Co–Co bond lengths found to date of only 2.1404(10) and 2.1345(7) Å for the amidinate and guanidinate structures, respectively. Room temperature magnetic moments of 5.35 and $5.10 \mu_{\text{B}}$ indicated four unpaired electrons per dimer. The short Co–Co bond lengths suggest strong covalent bonding interactions in these systems, and CASPT2 calculations were employed to provide insight into the nature of the metal–metal bond. Difficulties were encountered, however, when optimizing the geometry of the model compounds used in the calculations; this combined with the highly multiconfigurational nature of bonding in these systems means that a formal Co–Co bond order could not be assigned.

Short dicobalt bonds have also been found in systems having two- or one-atom bridging ligands. For example, low-coordinate dicobalt complexes supported by phosphinoamide ligands have been synthesized. The $\text{Co}_2(\text{I,I})$ complex $\text{Co}_2(\text{MesNP}^i\text{Pr}_2)_2(\text{PMe}_3)_2$, Figure 9.4, has a symmetric arrangement of the ligands around the dicobalt core and a Co–Co bond length of 2.5536(3) Å [12]. One-electron oxidation of this species results in a structural rearrangement and the formation

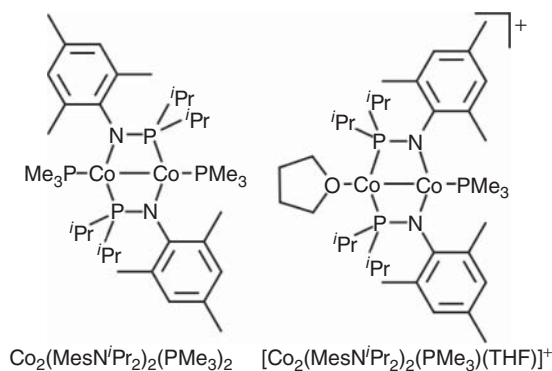


Figure 9.4 Structures of $\text{Co}_2(\text{MesN}^i\text{Pr}_2)_2(\text{PMe}_3)_2$ and $[\text{Co}_2(\text{MesN}^i\text{Pr}_2)_2(\text{PMe}_3)(\text{THF})]^+$.

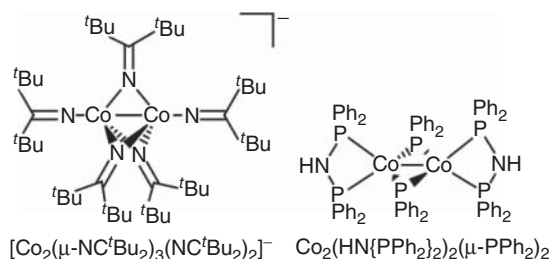


Figure 9.5 Structures of $[\text{Co}_2(\mu\text{-NC}^t\text{Bu}_2)_3(\text{NC}^t\text{Bu}_2)_2]^-$ and $\text{Co}_2(\text{HN}\{\text{PPh}_2\}_2)_2(\mu\text{-PPh}_2)_2$.

of an asymmetric species, $[\text{Co}_2(\text{MesNP}^i\text{Pr}_2)_2(\text{PMe}_3)(\text{THF})][\text{PF}_6]$ (Figure 9.4), which has a slightly shorter Co–Co bond length (2.4864(6) Å). DFT calculations indicate that σ -bonding interactions are responsible for the MM contacts in these systems.

The cobalt ketamide complex $[(^t\text{BuCN})\text{Co}(\mu\text{-NC}^t\text{Bu})_3\text{Co}(\text{NC}^t\text{Bu})]^-$ (Figure 9.5) was prepared by the reaction of the lithium ketamide with CoCl_2 [13]. The solid-state structure shows three bridging and two-terminal ketamide ligands, and a short Co–Co bond distance (2.4097(7) Å). Magnetic susceptibility measurements showed that this compound has a magnetic moment of $3.50 \mu_B$ in the solid-state at room temperature, which changes to $5.3 \mu_B$ in solution, indicating a structural change upon dissolution. The magnetic susceptibility decreased gradually from $3.50 \mu_B$ at 300 K to $0.68 \mu_B$ at 4 K indicating strong magnetic communication, although attempts to model this behavior were unsuccessful.

Also shown in Figure 9.5 is the structure for the phosphido-bridged compound $\text{Co}_2(\text{HN}\{\text{PPh}_2\}_2)_2(\mu\text{-PPh}_2)_2$, isolated from a redox reaction involving a phosphinohydrazine monocobalt complex in which the ligand undergoes P–N and N–N bond cleavage [14]. The short Co–Co bond length (2.387(5) Å) was rationalized with the aid of DFT calculations, which revealed a formal Co–Co double bond achieved by σ - and δ -bonding interactions.

9.1.3

Cobalt Extended Metal Chains

Extended metal-atom chains (EMACs), or metal string complexes consist of a linear chain of three or more metal atoms bridged by an organic ligand [15]. The ligand is typically a polypyridylamide derivative, and examples of these types of ligands that will be discussed in this section are shown in Figure 9.6.

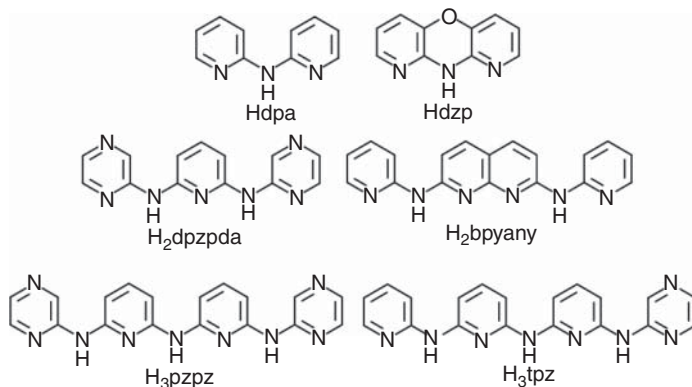


Figure 9.6 Typical polypyridylamide ligands used in the construction of cobalt EMACs.

The first reported EMAC incorporating cobalt was $\text{Co}_3(\text{dpa})_4\text{Cl}_2$ (Hdpa = bis(2-pyridyl)amine) [16], which was isolated in low yield. An improved synthetic route involving the reaction of Lidpa and CoCl_2 in refluxing THF was reported later [17]. The axial ligands can undergo a variety of exchange reactions to yield compounds of the type $\text{Co}_3(\text{dpa})_4\text{X}_2$ ($[\text{X}]^- = [\text{Br}]^-$ [18], $[\text{BF}_4]^-$ [19], $[\text{PF}_6]^-$ [20], $[\text{CN}]^-$ [21], $[\text{NCS}]^-$ [21]). The crystal structures of $\text{Co}_3(\text{dpa})_4\text{Cl}_2$ show either equal (symmetric) or unequal (asymmetric) Co–Co bond lengths, depending on the polymorph [22]. This fascinating behavior has resulted in numerous studies on the effects that polymorphism and temperature have on the Co–Co bonding in $\text{Co}_3(\text{dpa})_4\text{Cl}_2$ [23]. These studies were performed alongside variable temperature magnetic susceptibility measurements, which show equilibrium between low-spin ($S = 1/2$) and high-spin ($S = 3/2$ or $5/2$) states, with a temperature dependence that often reflects structural changes. DFT calculations show that the bonding in the symmetric tricobalt clusters can be thought of as “three-electron three-center” in nature, involving the bonding and non-bonding σ -orbitals [24].

The observance of symmetric and asymmetric forms of $\text{Co}_3(\text{dpa})_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) in different polymorphs and the relationship between molecular isomerism with magnetic properties were recently rationalized with the aid of DFT calculations [25]. The symmetric and asymmetric forms observed at high temperatures were found to be a result of the population of doublet ^2A or quartet ^4B states, respectively. At lower temperatures, spin-crossover to another, distinct, doublet ^2B symmetric state was found. These results showed that three distinct electronic states should be considered in order to account for the complex structural behavior in tricobalt EMACs.

Even weak intermolecular interactions have been shown to effect molecular isomerism in linear tricobalt chains. Crystal structures of $\text{Co}_3(\text{dpa})_4\text{Cl}_2 \cdot n\text{CH}_2\text{Cl}_2$ display a symmetrical Co_3^{6+} unit when $n = 1$, but it is unsymmetrical when $n = 2$. Hirshfeld surface analysis showed large differences in the strength of the intermolecular interactions involving one of the axial chloride ligands, which is significant enough to induce a change in the spin state and Co–Co bond lengths, resulting in molecular isomerism [26].

The two EMAC complexes $[\text{Co}_3(\text{mpepta})_2][\text{X}]_2$ ($[\text{X}]^- = [\text{Cl}]^-$, $[\text{BPh}_4]^-$, $\text{mpepta} = N,N'$ -bis[(6'-pyrid-2''-yl)aminopyrid-2'-yl]-bismethyl-2,6-diaminopyridinate) have been prepared, resulting in a tricobalt chain “cocooned” by two polypyridylamide ligands (Figure 9.7) [27]. The Co_3 core in both compounds is symmetrical with Co–Co bond lengths of ~ 2.3 Å. The electrochemical and magnetic behavior of these compounds is different from the analogous open-chain species, displaying only one reversible oxidation wave and large magnetic susceptibilities at room temperature corresponding to a spin state intermediate between $7/2$ and $5/2$.

Another trinuclear cobalt EMAC, $\text{Co}_3(\text{dzp})_4(\text{NCS})_2$ ($\text{Hdzp} = 1,9$ -diazaphenoxazine), also crystallized in the symmetric form [28]. This compound has smaller torsion angles and longer Co–Co bond

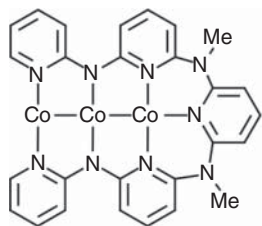


Figure 9.7 Drawing highlighting the binding mode of the “mpepteaa” ligand in $[\text{Co}_3(\text{mpepteaa})_2]^{2+}$.

lengths (~ 2.40 Å) than those found in the structures of the symmetric form of $\text{Co}_3(\text{dpa})_4\text{Cl}_2$ (~ 2.34 Å), thought to be a consequence of the increased rigidity associated with the dzp ligand. This also manifests itself in differences in the variable temperature magnetic behavior, as the structural changes enforced by the rigid dzp ligand result in a reduction of the gap between the doublet and quartet spin states.

The heterotrinnuclear EMAC $\text{NiCoRh}(\text{dpa})_4\text{Cl}_2$ was prepared by direct metal replacement upon treatment of $\text{CoCoRh}(\text{dpa})_4\text{Cl}_2$ with $\text{Ni}(\text{O}_2\text{CCH}_3)_2$ in refluxing naphthalene [29]. While structural disorder precluded accurate discussion of bond lengths associated with the central cobalt atom, nonetheless, it is the first structurally characterized example of a Co–Rh bond.

The length of the cobalt chain in EMACs has been extended to 5, 6, and 7 cobalt atoms in the compounds $\text{Co}_5(\text{dpzpd})_4\text{X}_2$ ($[\text{X}]^- = [\text{Cl}]^-$, $[\text{NCS}]^-$) [30], $[\text{Co}_6(\text{bpyany})_4(\text{NCS})_2][\text{X}]$ ($[\text{X}]^- = [\text{PF}_6]^-$, $[\text{OTf}]^-$) [31], and $\text{Co}_7(\text{L})_4\text{X}_2$ ($\text{L} = \text{pzpz}$ or tpz ; $[\text{X}]^- = [\text{Cl}]^-$, $[\text{NCS}]^-$) [32]; see Figure 9.6 for ligand structures). The pentanuclear species have short Co–Co bond distances that range from 2.2385(7) to 2.2888(15) Å, with the valence electrons delocalized along the metal chain through Co_5 σ -bonding orbitals. The LUMO in this system is a Co_5 σ^* -orbital, and there is a corresponding increase of the inner Co–Co bond distances by ~ 0.03 Å upon reduction by one electron. Infrared, Raman, and surface-enhanced Raman spectroscopy measurements on the pentanuclear string complex $\text{Co}_5(\text{tpda})_4\text{Cl}_2$ (tpda = tripyridyldiamido) showed only the symmetric form of the Co_5 chain present at 295 K [33].

The Co–Co bond distances in the hexanuclear EMACs $[\text{Co}_6(\text{bpyany})_4(\text{NCS})_2][\text{X}]$ ($[\text{X}]^- = [\text{PF}_6]^-$, $[\text{OTf}]^-$) range from 2.249(1) to 2.313(1) Å [31]. The Co_6^{11+} cores can be oxidized by one electron to give the corresponding Co_6^{12+} species, resulting in a spin-state change from $S = 1/2$ to $S = 1$. A qualitative molecular orbital diagram, generated using the extended Hückel molecular orbital method, indicates that the electron is removed from a σ^* -orbital, resulting in a Co_6^{12+} species with two unpaired electrons in δ^* and σ^* antibonding combinations. The removal of an electron from an antibonding MO increases the overall bond order, and for $[\text{X}]^- = [\text{PF}_6]^-$ the length of the cobalt chain is reduced from 11.429(1) Å (Co_6^{11+}) to 11.381 Å (Co_6^{12+}).

The heptanuclear $\text{Co}_7(\text{L})_4\text{X}_2$ ($\text{L} = \text{pzpz}$ or tpz ; $[\text{X}]^- = [\text{Cl}]^-$, $[\text{NCS}]^-$) complexes also have symmetric bond lengths in their Co_7^{14+} chains, with remarkably short inner Co–Co bond distances (2.194(1)–2.199(1) Å) [32]. Two reversible oxidations and one reversible reduction are observed in their cyclic voltammograms, which correspond to the removal of electrons from δ -type HOMOs, and the addition of an electron into a σ^* LUMO orbital.

The delocalization of the valence electrons through the extent of the cobalt chain in the symmetrical systems makes them attractive targets for the incorporation in molecular electronic devices. The single-molecule conductance of tri- and penta-nuclear cobalt EMACs with axial NCS ligands has been compared to their chromium and nickel analogs using STM break-junction experiments on gold substrates [34]. The order of conductance was found to be $\text{Cr} > \text{Co} > \text{Ni}$, which mirrors the overall metal–metal bond orders found in the chain (Cr chains have the highest overall bond order). DFT calculations on $\text{Co}_3(\text{dpa})_4(\text{NCS})$, sandwiched between two gold surfaces, indicate that the dominant electron transport pathway involves the non-bonding σ -orbital [35]. As the number of cobalt atoms in the chain increases, different MO combinations (σ , π , δ) are present in the frontier region. This affects the nature and efficiency of the dominant electron transport pathways [36].

9.2

Rhodium

9.2.1

Introduction

The synthesis and characterization of dirhodium tetraacetate in the 1960s introduced a new era for metal–metal bonded compounds due to their diverse array of applications as catalysts [37–39], photocatalysts [40–43], peptide-modifying agents and metalloproteinase catalysts [44–51], DNA and RNA nucleobase-modification catalysts [52], metallo-pharmaceuticals [53–56], photodynamic therapy agents [57], building blocks for the design of supramolecular architectures [58], and others. In this respect, many new $\text{Rh}_2(\text{II,II})$ systems displaying unique properties have been reported in recent years.

A comprehensive review on metal–metal bonded rhodium compounds by Chifotides *et al.* [59] was published in the book by Cotton *et al.* in 2005. In this chapter, more than 1800 dirhodium complexes were systematically categorized based on the types of bridging groups and the oxidation states of the metal centers, and the syntheses, the structural characteristics, and the applications of the complexes were discussed [59]. The catalytic applications of chiral dirhodium(II) complexes were covered in a separate chapter by Doyle *et al.* in the 2005 monograph [60a].

In this section, we highlight the chemistry of dirhodium compounds reported in the last 10 years, with a major emphasis on their widely known applications in catalysis. Dirhodium tetraacetate was characterized by X-ray crystallography [61], and was first used as a catalyst for the decomposition of diazo compounds in the 1970s [62]. At present, the ongoing interest in the synthesis of complex natural products and pharmaceuticals, catalyzed by dirhodium(II) compounds [63], has rapidly expanded the number of new highly active and efficient catalysts [39, 64]. In addition, dirhodium adducts with applications as photocatalysts [40–43], metalloproteinase catalysts [44–46], metal organic frameworks for gas-adsorption and heterogeneous catalysis [65–67], colorimetric sensors or inhibitors of small molecules such as CO [68] and NO [69, 70], nanoscale devices [71], building units for entities with planar or bowl-shaped polyarenes and nanotubes [72, 73], heterometallic chains, as well as other dirhodium complexes of interest are highlighted, although the present chapter is not intended to be comprehensive.

A simplified molecular orbital description of the dirhodium unit involves 14 electrons distributed in the four bonding σ , π , and δ orbitals and three antibonding π^* and δ^* orbitals ($\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$), resulting in a net Rh–Rh single bond (see Chapter 1) [59, 60b]. In general, paddlewheel dirhodium(II) compounds are supported by a diverse range of bridging ligands in the eight equatorial (eq) sites (Figure 9.8), with carboxylate, formamidinate, and amidinate being the most common ones [59]. Air-stable dirhodium tetracarboxylate complexes $\text{Rh}_2(\text{O}_2\text{CR})_4$ are readily synthesized from RhCl_3 , the carboxylic acid, and the sodium carboxylate in alcohols [74]. Ligand-exchange reactions of the acetate groups, in the presence of excess amount of other carboxylic acids, provide an easy route to

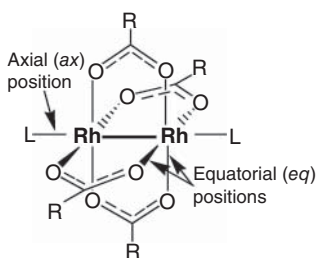


Figure 9.8 Schematic drawing of $\text{Rh}_2(\text{O}_2\text{CR})_4 \text{L}_2$.

access other dirhodium carboxylate derivatives [59], chemistry that has enhanced the widespread applications of dirhodium complexes as catalysts. A plethora of dirhodium complexes have been derived from the dirhodium tetraacetate by substituting the equatorial and the axial (ax) ligands on the dirhodium core [59]. Typically, two labile axial ligands L occupy the two sites *trans* to the metal–metal bond (Figure 9.8). The type of axial donor atoms has an important impact on the electronic spectra of the dirhodium complexes [59, 75], and the axial interactions are linked to their catalytic activity [76]. Although for 40 years the catalytic properties of dirhodium complexes have been altered by substituting the equatorial groups, which have been recognized as a critical factor in dirhodium catalysis [60a], recent efforts to tune the properties of the dirhodium centers have been directed at also modifying the axial groups [46, 76].

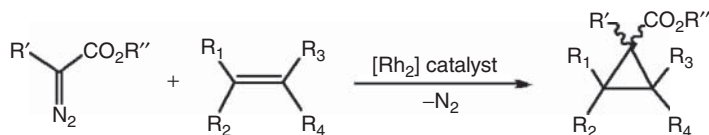
9.2.2

Catalysis

Dirhodium compounds have proved to be highly efficient and effective catalysts for diverse reactions, which has led to their reputation as being important players in synthetic organic chemistry. A wide range of synthetically useful transformations, such as cyclopropanation, cyclopropanation, insertion into C–H and heteroatom–H bonds, cycloadditions, ylide formation and rearrangement, and other processes are mediated by the catalytic formation of dirhodium(II) carbenes via diazocarbonyl compounds [77].

9.2.2.1 Cyclopropanation and Cyclopropanation

The C–C bond formation reactions are among the most important reactions in organic synthesis [78]. Cyclopropanation reactions are challenging as they involve the formation of highly strained three-membered rings. Cyclopropane rings can be synthesized from a diazo precursor in the presence of a metal catalyst under mild conditions (Scheme 9.1) [37]. Initially, commercially available ethyl diazoacetate was employed as the carbene source for cyclopropanation reactions, but subsequently, other diazo compounds were developed for various carbene-transfer reactions [79]. Extensive studies involving the use of dirhodium catalysts for cyclopropanation and cyclopropanation reactions have been reported by Doyle [80], Davies [81], and Fox *et al.* [82] with chiral dirhodium(II) tetracarboxylates and their derivatives being the most common [83]. A large number of chiral dirhodium(II) carboxamidate complexes have been developed, primarily by Doyle *et al.*, [60a] to perform asymmetric cyclopropanation [84] and cyclopropanation [85] reactions.

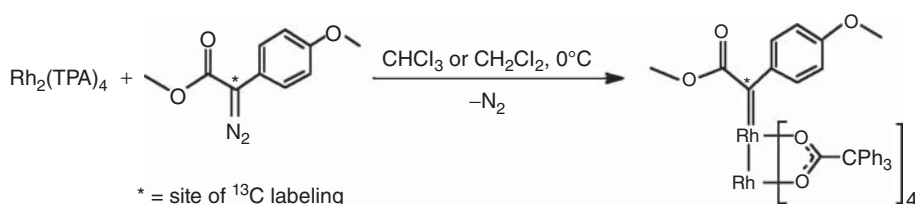


Scheme 9.1 Cyclopropanation of olefins by dirhodium catalysts.

Cyclopropanation reactions are presumed to proceed via a highly reactive, electrophilic dirhodium–carbene intermediate (see Chapter 1, Figure 1.8 [86], and the Review article by Berry and Ritter *et al.* [87a]). In the previous Review [87a], and a perspective article by Berry [87b], the importance of the three-centered/four electron (3c/4e) bonding motif for the carbene $[Rh-Rh]=CR_2$ intermediate is discussed. In particular, the 3c/4e bonding interactions result in weaker distances between the atoms as compared to the 2c/2e systems [87b]. Also, the excited states, derived from the 3c/4e bonding manifold are lower in energy than the 2c/2e bonding, resulting in a higher degree of reactivity for the 3c/4c bonding, and an unusual *super electrophilic* character of the $[Rh-Rh]=C(or N)$ intermediates. Dirhodium catalyzed reactions by means of metal carbenoids and

donor/acceptor functionalized carbenoids have become advantageous strategies for the synthesis of various natural products and pharmaceuticals [63, 87a, 88].

The previous highly reactive, electrophilic carbenoid $[\text{Rh}-\text{Rh}] = \text{C}$ intermediate, formed during these catalytic reactions, remained elusive until a recent seminal study by Berry and Davies *et al.* [89]. In this study, $\text{Rh}_2(\text{TPA})_4$ (**1**, TPA = triphenylacetate) was reacted with ^{13}C -labeled methyl 2-diazo-2-(4-methoxyphenyl)acetate, and a metastable $\text{Rh}_2(\text{TPA})_4$ -carbenoid intermediate, supported by a donor–acceptor carbene fragment, was generated (Scheme 9.2). The stability of the dirhodium–carbenoid intermediate in CHCl_3 at 0°C for ~ 20 h allowed for the determination of its physical and chemical properties for the first time. The characterization of the bonding within the $[\text{Rh}-\text{Rh}] = \text{C}$ framework by vibrational and ^{13}C NMR (^{13}C $\delta_{\text{carbene}} = 242$ ppm, $J_{\text{Rh}-\text{C}} = 27$ Hz) spectroscopies, and extended X-ray absorption fine structure analysis was supported by quantum chemical calculations [89]. The information obtained from this study has significant implications for the field of catalysis and in particular for C–H functionalization [63].



Scheme 9.2 Schematic representation of the dirhodium–carbenoid intermediate formation.

Table 9.2 Dirhodium catalysts used in cyclopropanation reactions.

Entry	Catalyst	Yield (%)	dr (%)	ee (%)	R' ^{a)}	R'' ^{a)}	References
1	$\text{Rh}_2(\text{TPA})_4$	80–100	95:5 ^{b)}	—	Et	Et	[92]
2	$\text{Rh}_2(\text{S-PTTL})_4$	>72–100	>95:5 ^{b)}	61–97	Bu	Et	[93]
3	$\text{Rh}_2(\text{S-DOSP})_4$	66–93	>95:5	87–90	<i>p</i> -(Y)Ph ^{c)}	Me	[94]
4	$\text{Rh}_2(\text{S-PTAD})_4$	93	>95:5	96	<i>p</i> -(Y)Ph ^{d)}	Me	[94]
5	$\text{Rh}_2(\text{S-PTAD})_4$	70	>95:5	94	3,4-(OMe) ₂ Ph	Me	[94]
6	$\text{Rh}_2(\text{R-BNP})_4$	93	>95:5	97	3,4-(OMe) ₂ Ph	Me	[94]
7	$\text{Rh}_2(\text{R-BNP})_4$	80–90	>95:5	80–90	<i>p</i> -(Y)Ph ^{e)}	Me	[94]
8	$\text{Rh}_2(\text{S-DOSP})_4$	59	>97:3	77	<i>p</i> -Tol	Me	[95a]
9	$\text{Rh}_2(\text{S-PTAD})_4$	70	>97:3	35	<i>p</i> -Tol	Me	[95a]
10	$\text{Rh}_2(\text{S-PTTL})_4$	68	>97:3	27	<i>p</i> -Tol	Me	[95a]
11	$\text{Rh}_2(\text{S-NTTL})_4$	69	>97:3	24	<i>p</i> -Tol	Me	[95a]
12	$\text{Rh}_2(\text{S-BPTV})_4$	65	>97:3	5	<i>p</i> -Tol	Me	[95a]
13	$\text{Rh}_2(\text{S-TCPTTL})_4$	71	>97:3	74	<i>p</i> -Tol	Me	[95a]
14	$\text{Rh}_2(\text{S-TCPTV})_4$	62	>97:3	65	<i>p</i> -Tol	Me	[95a]
16	$\text{Rh}_2(\text{S-TCPTAD})_4$	71	>97:3	84	<i>p</i> -Tol	Me	[95a]
17	$M\text{-Rh}_2(\text{O}_2\text{CCF}_3)_2^-$ [(4-BrC ₆ H ₃)P(4-BrC ₆ H ₄)Ph]- [(C ₆ H ₄)PPh ₂] $\cdot 2\text{CH}_3\text{CO}_2\text{H}$	>60	50:50	>83	H	Et	[96]

S-BPTV = *N*-benzene-fused-phthaloyl-(*S*)-valinate and TCPTTL = tetrachloro-PTTL.

a) R' and R'' are substituents of the diazo precursors (see Scheme 9.1).

b) At -78°C .

c) Y = CH₃, CF₃, OMe, Cl.

d) Y = OMe.

e) Y = CH₃, CF₃, OMe, Cl, NO₂.

Several of the most widely used chiral dirhodium adducts and their catalytic activities for cyclopropanation reactions are summarized in Table 9.2. Among the most notable ones are **1**, $\text{Rh}_2(\text{S-PTTL})_4$ (**2**; S-PTTL = tetrakis[*N*-phthaloyl-(*S*)-*tert*-leucinate]), $\text{Rh}_2(\text{S-DOSP})_4$ (**3**; DOSP = *N*-(dodecylphenylsulfonyl)-(S)-prolinate), $\text{Rh}_2(\text{BNP})_4$ (**4**; BNP = bi-naphthylphosphate), $\text{Rh}_2(\text{S-PTAD})_4$ (**5**; PTAD = (*S*)-(+)-(1-adamantyl)-(N-phthalimido)acetato), and $\text{Rh}_2(\text{S-TCPTAD})_4$ (**6**) (Figure 9.9) [90, 91].

The incorporation of *N*-phthaloyl amino acids into the dirhodium(II) platform afforded excellent asymmetric cyclopropanation catalysts [81b, 97]. In contrast to other phthaloyl catalysts [97], the X-ray crystal structure of $\text{Rh}_2(\text{S-PTTL})_4$ (**2**), reported by Fox *et al.* revealed that the four phthalimido groups are situated on one face of the catalyst in a ‘chiral crown structure’ (Figure 9.10) [93]. The four *t*Bu- groups are directed on the other face of the catalyst, and all C–*t*Bu bonds are parallel to the Rh–Rh bond. Compound **2** exhibits high diastereoselectivity and yields for cyclopropanation with α -alkyl- α -diazoesters (Table 9.2, entry 2). The enantiomeric excess (ee) increases with the α -alkyl diazoester substituent size, and the highest 99% ee and 95% yield were achieved in the reaction of styrene with ethyl-2-diazo-5-methylhexanoate [93].

Davies *et al.* carried out a comparative study on the catalytic activities of $\text{Rh}_2(\text{S-DOSP})_4$ (**3**), $\text{Rh}_2(\text{R-BNP})_4$ (**4**), and $\text{Rh}_2(\text{S-PTAD})_4$ (**5**) toward asymmetric cyclopropanation reactions (Table 9.2, entries 3–9) [94]. In general, $\text{Rh}_2(\text{S-DOSP})_4$ was found to be the most effective catalyst for asymmetric intermolecular cyclopropanation of methyl aryldiazoacetates with styrene. $\text{Rh}_2(\text{S-PTAD})_4$ exhibited lower levels of enantioinduction with 4-substituted aryldiazoacetates but it proved to be superior with the 4-methoxy substituted aryldiazoacetate (Table 9.2, entry 4, 96% ee) [94, 98]. $\text{Rh}_2(\text{R-BNP})_4$, however, functions as an extremely effective catalyst with all the aryldiazoacetates substituted with three methoxy groups (88–97% ee). The asymmetric inductions varied with the aryl groups on the aryl diazoacetate but the choice of olefin had no effect on the selectivity.

A range of catalysts were surveyed by Fox *et al.* for the cyclopropanation of alkenes with α -alkyl- α -diazoesters [92]. Catalyst **1** (Table 9.2, entry 1) exhibited better catalytic activity and selectivity

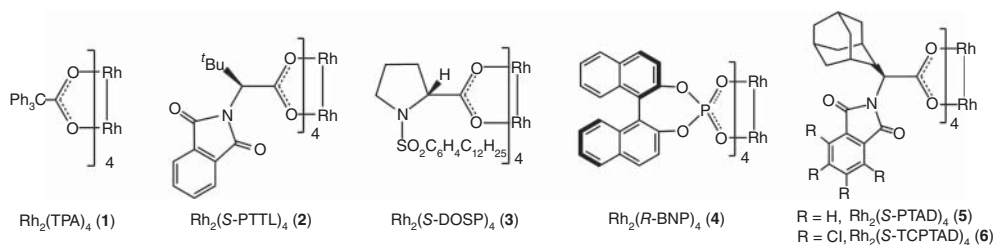


Figure 9.9 Common chiral dirhodium catalysts for cyclopropanation.

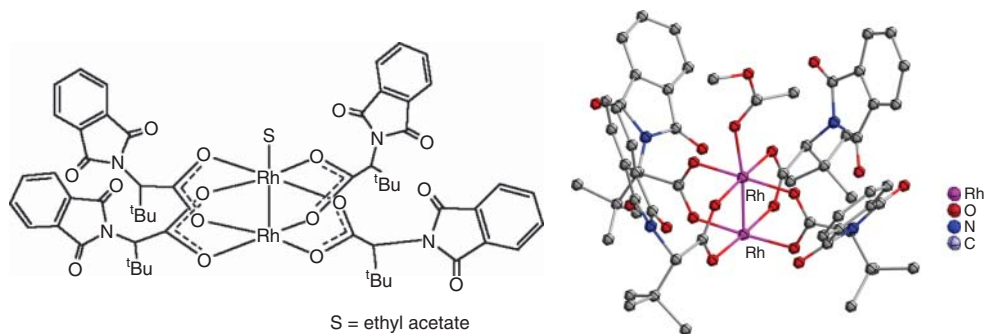
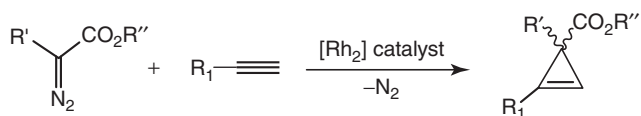


Figure 9.10 Schematic drawing and molecular structure of **2**.

as compared to $\text{Rh}_2(\text{Oct})_4$ (**7**; Oct = octanoate), $\text{Rh}_2(\text{Piv})_4$ (**8**; Piv = pivalate), and $\text{Rh}_2(\text{O}_2\text{CCMePh}_2)_4$ (**9**). A high yield of the cyclopropanation product, with excellent diastereoselectivity, was obtained with **1**. The bulky Ph_3C groups hinder the alternate β -hydride elimination reaction resulting in the absence of α,β -unsaturated alkene traces (at -78°C). The challenge of electron-deficient olefin cyclopropanation has been met by very few catalysts [63, 99, 100]. Systematic studies showed that the adamantylglycine derived adduct $\text{Rh}_2(\text{S-TCPTAD})_4$ (**6**, Figure 9.9) is superior to other catalysts such as $\text{Rh}_2(\text{S-BPTV})_4$ (**10**) and $\text{Rh}_2(\text{S-TCPTTL})_4$ (**11**) for these reactions (Table 9.2, entries 12–16) with high asymmetric inductions for a range of substrates (up to 98% ee) [95]; α,β -unsaturated olefins were efficiently converted to the desired products, and up to 99% ee yields were obtained.

Cyclopropanation, that is, the formation of highly strained three-membered rings from alkynes (Scheme 9.3), is a desirable reaction, and considerable efforts have been invested in developing methods for the synthesis of highly substituted cyclopropanes [101, 102]. The catalytic activities of the well-known catalysts $\text{Rh}_2(\text{S-PTTL})_4$ (**2**), $\text{Rh}_2(\text{S-DOSP})_4$ (**3**), $\text{Rh}_2(\text{S-PTTL})_3(\text{TPA})(\text{C}_2\text{H}_5\text{OH})_2$ (**12**; Figure 9.11), $\text{Rh}_2(\text{S-PTTL})_2(\text{TPA})_2$ (**13**), and $\text{Rh}_2(\text{S-TBPTTL})_4$ (**14**) toward cyclopropanation reactions are summarized in Table 9.3.



Scheme 9.3 Cyclopropanation of alkynes by dirhodium catalysts.

$\text{Rh}_2(\text{S-DOSP})_4$ (**3**) is an effective catalyst for cyclopropanation between terminal alkynes and arylvinyl diazoacetates, and affords enantioselective cyclopropanated products (Table 9.3, entry 1, up to 89% yields and 99% ee at -45°C ; Scheme 9.4) [103a]. A mixture of cyclopentadienes (major product) and vinyl cyclopropane (minor product), however, was obtained at room temperature, unless the reagents were refluxed in 2,2-dimethylbutane, which exclusively afforded the cyclopentadienes (Scheme 9.5); the high enantioselectivity was attributed to the directed approach of the alkyne to the carbenoid in the transition state. Recently, silica-immobilized $\text{Rh}_2(\text{S-DOSP})_4$ was

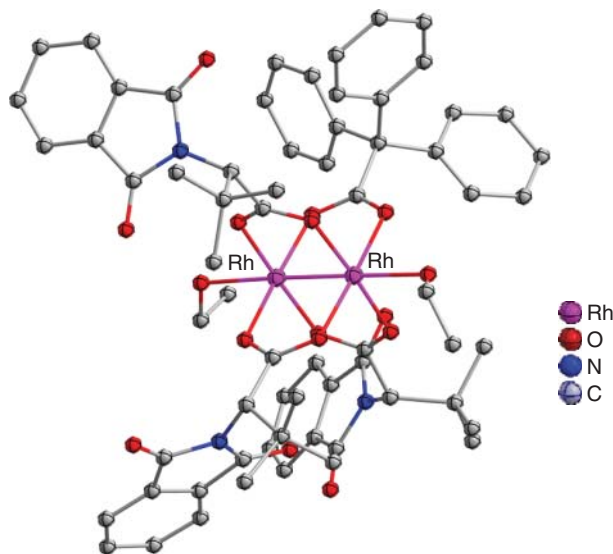


Figure 9.11 Molecular structure of $\text{Rh}_2(\text{S-PTTL})_3(\text{TPA})(\text{C}_2\text{H}_5\text{OH})_2$ (**12**).

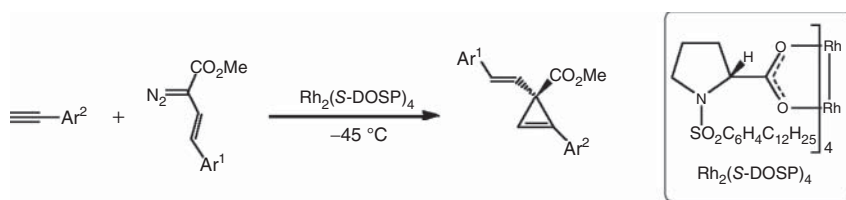
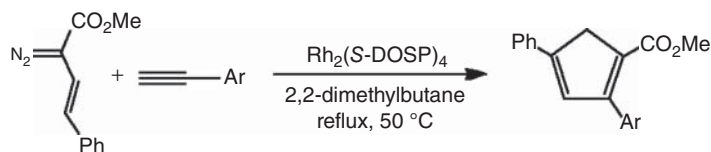
Table 9.3 Chiral dirhodium catalysts used in cyclopropenation reactions.

Entry	Catalyst	Yield (%)	ee (%)	R ^{a)}	R'' ^{a)}	References
1	Rh ₂ (S-DOSP) ₄	46–89	95–99 ^{b)}	PhCH=CH	Me	[103a]
2	Rh ₂ (S-PTTL) ₃ (TPA)	82	91	Et	Et	[104]
3	Rh ₂ (S-TBPTTL) ₄	90	95	Me	CH ⁱ Pr ₂	[105]
4	Rh ₂ (S-PTTL) ₄	86	46	Me	CH ⁱ Pr ₂	[105]
5	Rh ₂ (S-PTV) ₄	78	36	Me	CH ⁱ Pr ₂	[105]
6	Rh ₂ (S-PTA) ₄	91	38	Me	CH ⁱ Pr ₂	[105]
7	Rh ₂ (S-TFPTTL) ₄	80	35	Me	CH ⁱ Pr ₂	[105]
8	Rh ₂ (S-TCPTTL) ₄	89	72	Me	CH ⁱ Pr ₂	[105]

TBPTTL = tetrabromo-PTTL, PTV = *N*-phthaloylvalinate, PTA = *N*-phthaloylalaninate, and TFPTTL = tetrafluoro-PTTL.

a) R' and R'' are substituents of the diazo precursors (see Scheme 9.3).

b) At –45 °C.

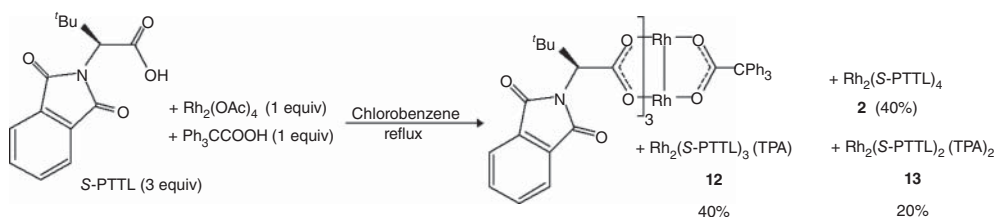
**Scheme 9.4** Cyclopropenation catalyzed by Rh₂(S-DOSP)₄ (3).**Scheme 9.5** Exclusive formation of cyclopentadiene catalyzed by Rh₂(S-DOSP)₄ (3).

used in enantioselective carbenoid transformations with comparable results to the homogeneous counterpart [103b].

The reaction of Rh₂(O₂CCH₃)₄ (1 equiv.) with *S*-PTTL (3 equiv.) and Ph₃CCO₂H (1 equiv.) afforded a mixture of the products **2**, **12**, and **13** (Scheme 9.6). The mixed-ligand complex **12** catalyzes the enantioselective cyclopropenation for a wide variety of substrates (aliphatic alkynes, silylacetylenes, α-olefins) with α-alkyl-α-diazoesters, exhibiting the highest yields (82%) and 90% ee for reactions between terminal alkynes and α-alkyl-α-diazoesters [104]. The achieved enantioselectivity for cyclopropenation reactions with **12** is comparable or superior to **2** (Table 9.3, entries 2 and 4).

The chiral dirhodium catalysts **14**–**18** (Figure 9.12), with phthaloyl-*tert*-leucinate based ligands on the dinuclear scaffold, were tested for asymmetric cyclopropenation reactions [105]. It was found that **14** exhibits the best catalytic activity for enantioselective cyclopropenation of 1-alkynes with 2,4-dimethyl-3-pentyl α-alkyl-α-diazoacetates, with high enantioselectivity (up to 99% ee). The high selectivity of **14** is attributed to the C₄-symmetry-like chiral crown conformation [105].

The enantioselective [2+1]-cycloaddition reactions of ethyl diazoacetate to terminal acetylenes was evaluated for a series of mixed-ligand complexes of the type Rh₂(O₂CCH₃)₃(DPTI)_{4–n} (DPTI: *R,R*-diphenyl-*N*-triflylimidazolidinone; *n* = 2 to 0) [38]. The fourteen possible isomers (**19**–**32**, Scheme 9.7) were synthesized except for the (4,0)-Rh₂(DPTI)₄ (**32**) derivative. The complexes



Scheme 9.6 Synthesis of $\text{Rh}_2(\text{S-PTTL})_3(\text{TPA})$ (**12**).

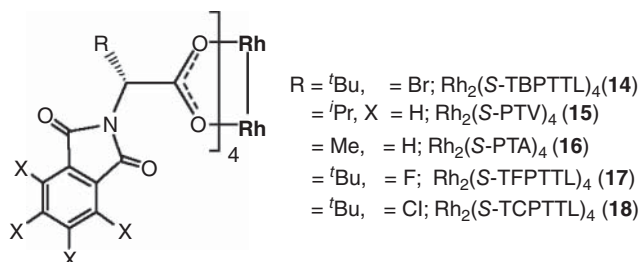
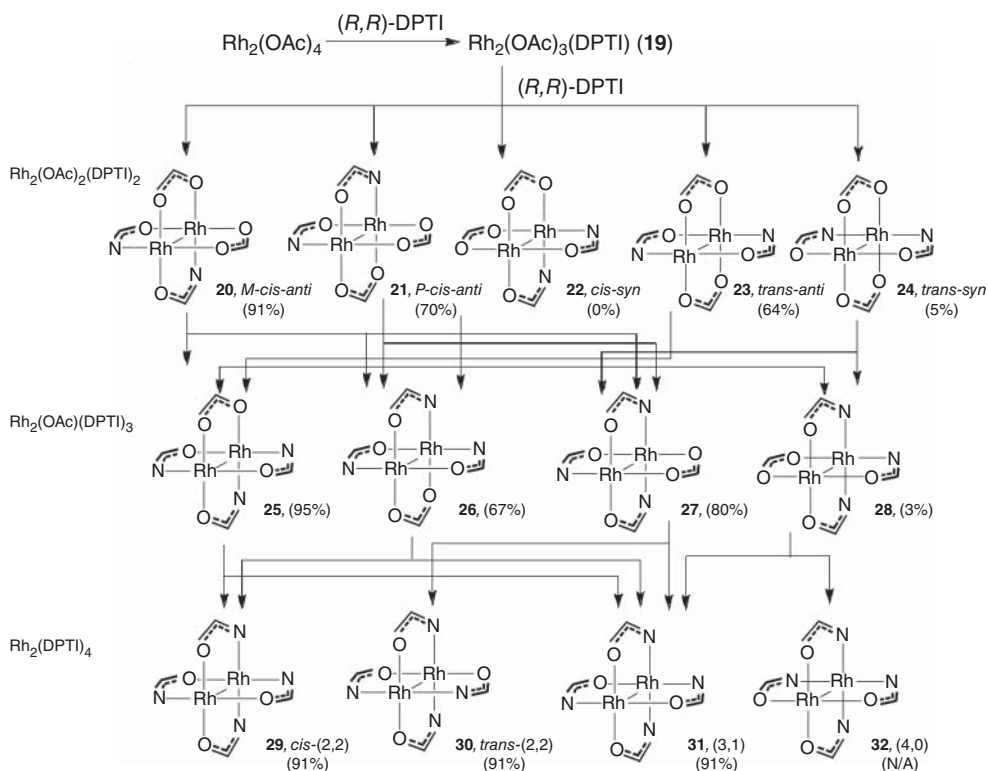


Figure 9.12 Schematic drawing of dirhodium catalysts containing phthaloyl-*tert*-leucinate based ligands.



Scheme 9.7 Sequential formation of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_n(\text{DPTI})_{4-n}$. Values in parentheses show ee amounts for the cycloaddition reaction of ethyl diazoacetate to 1-heptyne (in CH_2Cl_2 at 23 °C).

20 and **25** (Figure 9.13) exhibit the highest enantioselectivities in accord with the mechanistic model, in which one of the bridging ligands is cleaved in the Rh–carbene intermediate [38]. The *trans-anti*-Rh₂(O₂CCH₃)₂(DTBTI)₂ (**33**; Figure 9.13, DTBTI = (*R,R*)-di-4,5-di-*tert*-butyl-*N*-triflylimidazolidinone) afforded better enantioselectivity than the *trans-anti*-Rh₂(O₂CCH₃)₂(DPTI)₂ (**23**) due to the bulkier DTBTI ligand in **33** [38].

In recent studies, Petrukhina *et al.* adopted a synthetic strategy to graft dirhodium tetracarboxylates, namely [Rh₂(O₂CC₆H₄CO₂C₂H₅)₄] (**34**) and [Rh₂(O₂CC₆H₄CO₂C₂H₅)₄(OCMe₂)₂] (**35**) [66a] (Figure 9.14), with simple or functionalized bridging groups into the channels of mesoporous silica, while the dimers were also engaged in strong noncovalent axial N-anchor contacts [66b] or covalent interactions [66a]. These immobilized dirhodium paddlewheel complexes were recently evaluated as catalysts for the cyclopropanation reaction of styrene with methyl phenyldiazoacetate (de 88%, yield 86%). In addition to the similar or improved selectivity and reactivity profiles of the heterogeneous catalysts as compared to the homogeneous counterparts, this strategy offers the advantages of recyclable, reusable, and durable dirhodium-based catalysts [66].

In recent innovative studies by Ball *et al.*, a high-throughput ‘on bead’ (solid support) strategy to efficiently screen dirhodium metalloprotein catalysts (see Section 9.2.3.2) in asymmetric cyclopropanations was developed [48]. A later study, with a dirhodium adduct bearing a tridentate *eq–eq–ax* peptide ligand, generated more efficient and enantioselective catalysts for asymmetric cyclopropanation, and provided further insight in the development of immobilized homogeneous catalysts [47].

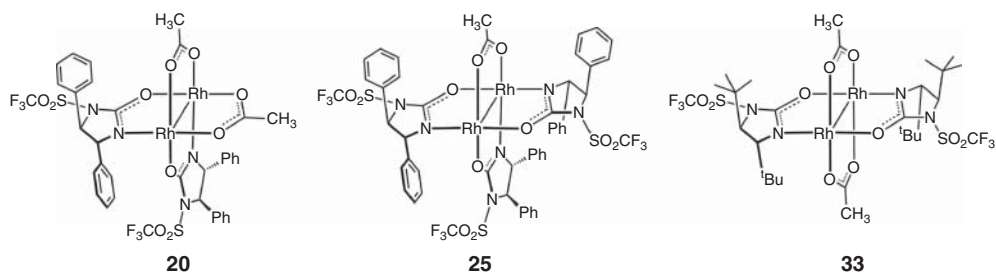


Figure 9.13 Schematic drawings of *cis-anti*-Rh₂(DPTI)₂(O₂CCH₃)₂ (**20**), Rh₂(DPTI)₃(O₂CCH₃) (**25**), and *trans-anti*-Rh₂(DTBTI)₂(O₂CCH₃)₂ (**33**).

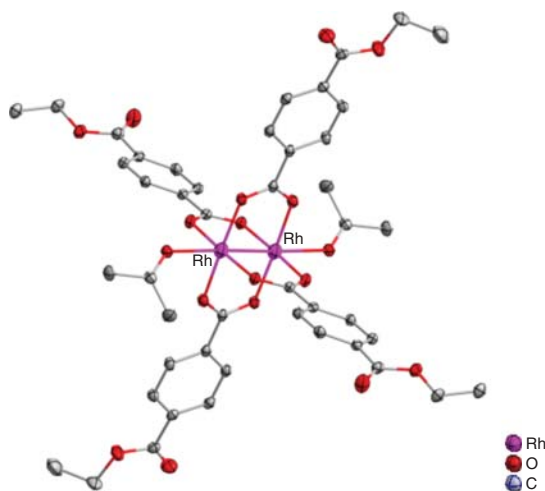
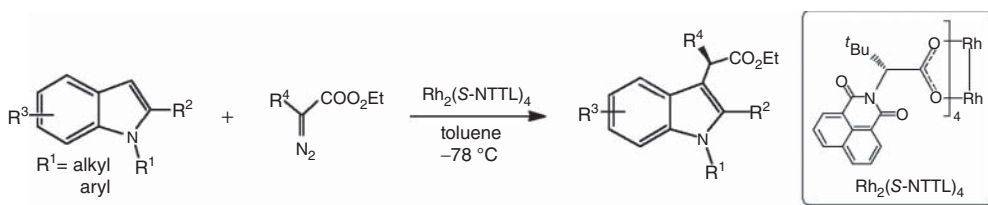


Figure 9.14 Molecular structure of [Rh₂(O₂CC₆H₄COOC₂H₅)₄(OCMe₂)₂] (**35**).

9.2.2.2 Functionalization of C–H Bonds

The selective functionalization of C–H bonds constitutes an important yet challenging transformation in organic synthesis [63, 106]. In this respect, dirhodium catalysts have exhibited great use and versatility in both intra- and inter-molecular C–H functionalizations from their early applications until present [37, 81b, 107]. A number of dirhodium catalysts have been successfully employed for these transformations with chiral carboxylate and carboxamidate derivatives being the most efficient [37, 108]. A recent theoretical study showed that the differences between the dirhodium catalysts with carboxylate, carboxamidate, and orthometalated arylphosphine bridging groups in catalytic carbene reactions are attributed to the different degrees of electron-donation of the bridging ligands to the dirhodium core; in this respect, the enhanced σ -donating ability of orthometalated arylphosphine groups results in a decreased carbene carbon electrophilicity, which is an important factor in catalytic reactions [76, 109]. This study was preceded by an analogous one in which Lahuerta *et al.* focused on the properties of dirhodium complexes with bridging orthometalated aryl groups and various Lewis bases in axial positions [110]. One of the conclusions from this study, which is supported by others for tetracarboxylates [111], is that the increase in the basicity or the π -donation ability of the axial group enhances the reactivity of the rhodium centers. A comprehensive review about metal carbene insertion reactions was recently reported by Doyle *et al.* [37].

Indole derivatives have versatile applications in the pharmaceutical industry [63, 81b, 112], and due to their importance, several methodologies have been developed to prepare highly functionalized indoles [81b, 113]. The enantioselective C–H functionalization of indoles at position C(3) by diazo compounds is depicted in Scheme 9.8 [114]. The putative Rh–carbene intermediate, generated from α -alkyl- α -diazoesters, in the presence of catalytic amounts of $\text{Rh}_2(\text{S-NTTL})_4$ (**36**; NTTL = tetrakis[*N*-(1,8-naphthaloyl)-(S)-*tert*-leucinate]), was reacted with indoles to afford α -alkyl- α -indolylacetates, in high yields (up to 95%) and excellent enantioselectivity (up to 97% ee), which is attributed to the indole approaching the *si*-face of the Rh–carbene. *N*-Aryl or *N*-alkyl substituted indoles were successfully functionalized in contrast to indoles bearing electron-withdrawing groups on the nitrogen (acetyl, Boc), which prevented their formation [114]. The asymmetric synthesis of 4-substituted indoles, which are particularly difficult to prepare by traditional methods, has also been achieved with *N*-phthaloyl- and *N*-naphthaloyl catalysts [81b, 104].



Scheme 9.8 C–H functionalization of the indole at position C(3) catalyzed by $\text{Rh}_2(\text{S-NTTL})_4$ (**36**).

It is notable that efforts have been directed in preparing durable, recoverable, and selective catalysts. In this respect, the effective chiral catalyst $\text{Rh}_2(\text{S-PTTL})_4$ (**2**), supported by phthaloyl *tert*-leucinate bridging ligands, and the mixed-ligand complex $\text{Rh}_2(\text{S-PTTL})(\text{S-TCPTTL})_3$ were recently immobilized by tethering one of the bridging groups to a polymer chain; their catalytic performance evaluation, in asymmetric intramolecular C–H insertion and enantioselective carbonyl ylide cycloaddition reactions, respectively, revealed comparable results to the respective homogeneous catalysts [115].

Recently, Francis *et al.* reported the selective modification of tryptophan indole side chains in several proteins with a diazo reagent catalyzed by dirhodium tetraacetate [44], and Ball *et al.* achieved remarkable rate accelerations for tryptophan modification ($>10^3$) using dirhodium metallopeptides (Section 9.3.2) [45].

Bera *et al.* also synthesized several dirhodium complexes to study the role of axial coordination in determining the selectivity of diazo insertion into C–H bonds. The reaction of 2-mesityl-1,8-naphthyridine (Mes-NP) with $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ afforded *trans*- $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{Mes-NP})_2][\text{BF}_4]_2$ (**37**) (Figure 9.15) [116a], whereas the systematic use of the dirhodium precursors $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$, $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$, and $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$, with the newly synthesized amide functionalized naphthyridine ligands **38** and **39** (Figure 9.16) [116b] produced the series of complexes **40–46** (Scheme 9.9) [117]. The authors observed a structural diversity among **40–46** with respect to the number, nature (neutral/anionic), and coordinating modes of the incorporated ligands depending upon the *ortho* substituent on the ligand, lability of the bridging carboxylates, and hydrogen bonding interactions between the amide hydrogen and carboxylate oxygen atoms. The efficiency of the dirhodium catalyst was modulated by the incorporation of hemilabile amide functionalities. Compound **46** (Figure 9.17), which exhibits hemilabile amide side arms at both the axial sites, attained higher catalytic activity for carbene insertion into the C–H bonds of substituted indoles with appropriate diazo compounds, whereas the other compounds remained far less reactive. Weak axial coordination by the amide groups plays an important role in differentiating between the diazo compounds and controlling the selective insertion of more nucleophilic donor/acceptor carbenoids into the C–H bond of indoles.

Structurally complex heterocycles were synthesized by a three-component reaction in one step [118]. Metal-catalyzed cycloadditions involving carbonyl ylides produce stereochemically complex molecules from three simple starting materials [119, 120]. Dirhodium tetrapivalate $\text{Rh}_2(\text{Piv})_4$ (**8**) catalyzes the reactions of aldehydes, α -alkyl- α -diazoesters, and dipolarophiles to afford highly functionalized dihydro- and tetrahydro-furan (Scheme 9.10) [121]. The presence of an alkyl group on the diazo precursor leads to highly reactive alkyl-substituted carbonyl ylides in cycloaddition reactions, and high selectivity. The high regio- and diastereo-selectivities are attributed to an asynchronous, *endo*-selective transition state. The diazo compound equipped with an aromatic group, however, failed to achieve such high selectivity [122].

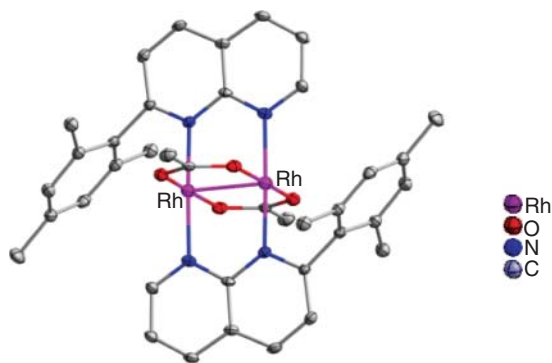


Figure 9.15 Molecular structure of the cationic unit in **37**.

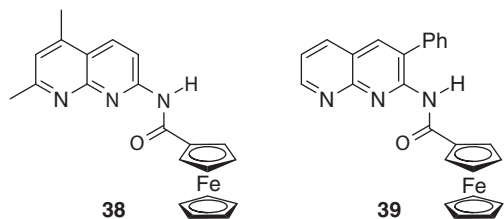
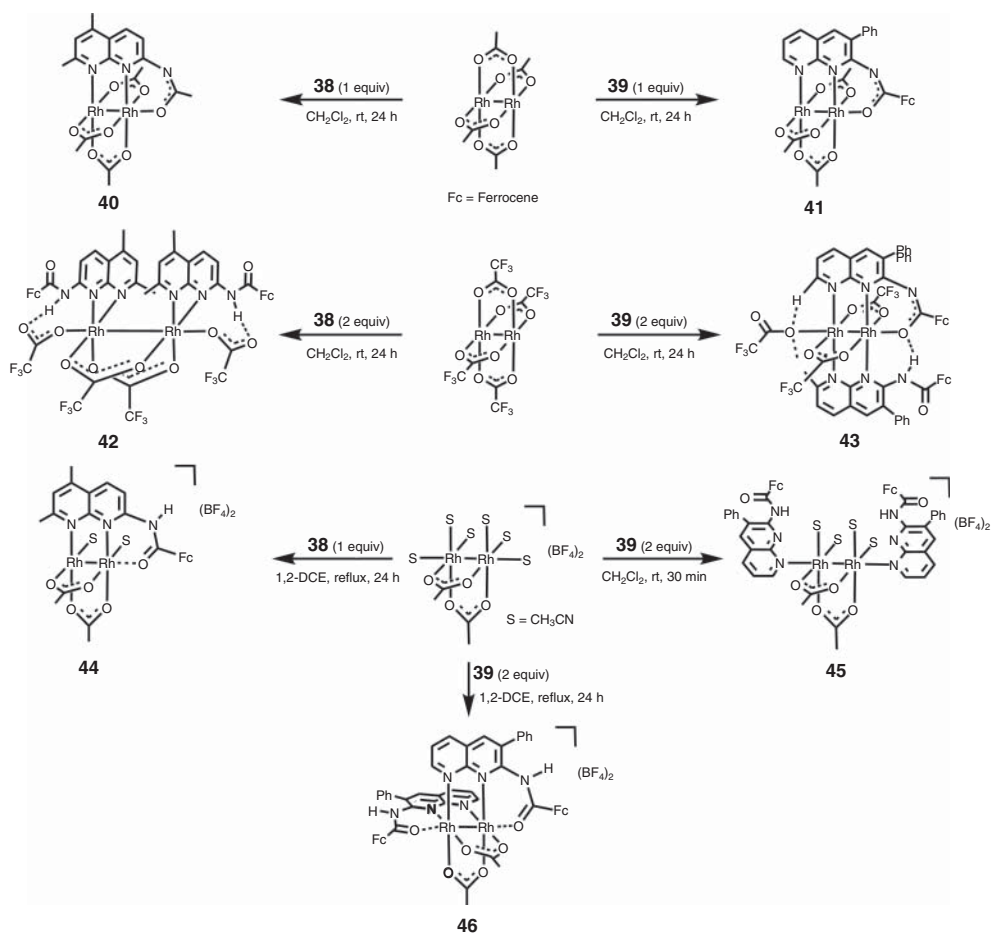


Figure 9.16 Schematic drawing of the ligands **38** and **39**.



Scheme 9.9 Syntheses of the dirhodium complexes 40–46.

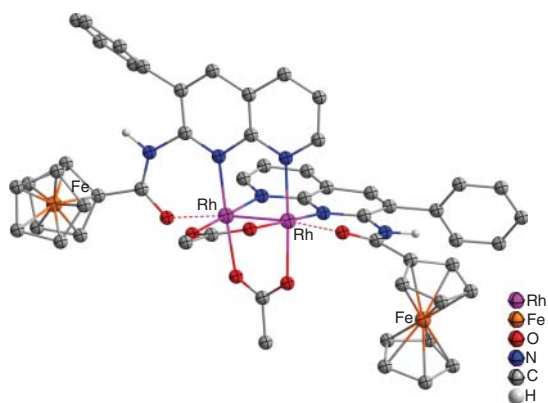
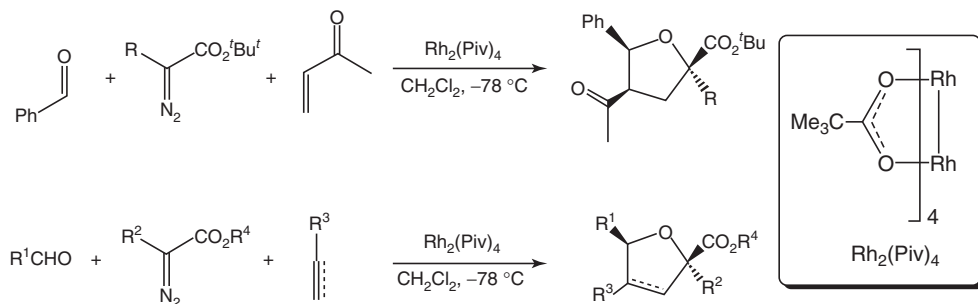


Figure 9.17 Molecular structure of the cationic unit in 46.

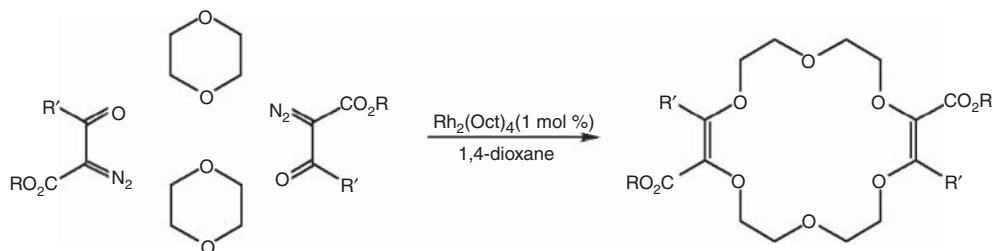


Scheme 9.10 Three-component cycloaddition catalyzed by $\text{Rh}_2(\text{Piv})_4$ (8).

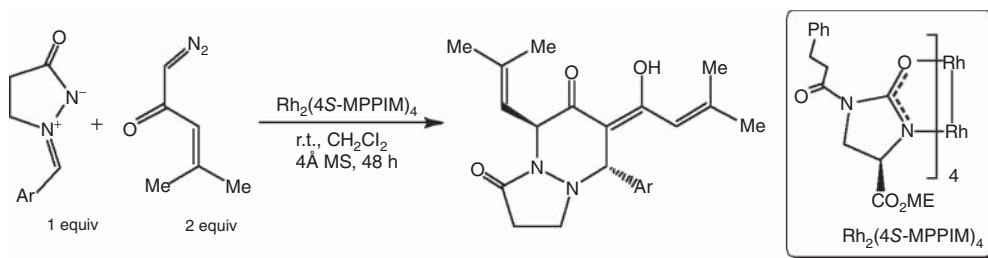
The synthesis of macrocycles is very important due to their versatile applications in medicinal and natural product chemistry [123]. The rhodium-catalyzed one-pot synthesis of functionalized polyether macrocycles, at high concentrations from four components, was achieved under mild conditions by Lacour *et al.*; the synthesis of 16- to 18-membered macrocycles by the regioselective condensation of two α -diazo- β -ketoesters, and two cyclic ethers, in the presence of $\text{Rh}_2(\text{Oct})_4$ is depicted in Scheme 9.11 [124]. Various diazo esters have been successfully employed as substrates with up to 75% yields.

Dipolar cycloaddition reactions with stable and easily prepared azomethine imines, for the synthesis of a diverse array of heterocycles, have attracted considerable attention [125]. The complex $\text{Rh}_2(4\text{S-MPPIM})_4$ (47) catalyzes the highly diastereoselective [3+2+1]-cycloaddition reaction between a diazo ketone and azomethine imines [126]. The final products are multi-functionalized bicyclic pyrazolidinone derivatives isolated in moderate to high yields (Scheme 9.12).

The synthesis of oxonium ylides by catalytic reactions of diazocarbonyl compounds with ethers has numerous applications in the preparation of natural products [127]. Two diastereomers of oxabicyclo[4.2.1]-nonane were obtained from ylide intermediates, which were produced from the

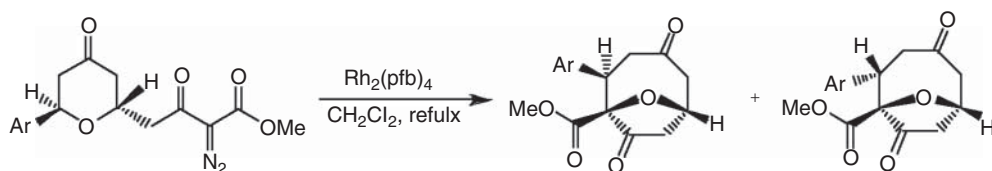


Scheme 9.11 Synthesis of macrocycles catalyzed by $\text{Rh}_2(\text{Oct})_4$ (7).



Scheme 9.12 Cycloaddition reaction catalyzed by $\text{Rh}_2(4\text{S-MPPIM})_4$ (47).

reactions of aryl-substituted tetrahydropyranone diazoacetates catalyzed by $\text{Rh}_2(\text{pfb})_4$ (**48**, pfb = perfluorobutyrate; Scheme 9.13). The selective production of a single diastereomer, however, was achieved by increasing the steric bulk of the aryl substituent [128].



Scheme 9.13 Synthesis of oxonium ylide catalyzed by $\text{Rh}_2(\text{pfb})_4$ (**48**).

Complexes of the general formulae $\text{Rh}_2(\text{O}_2\text{CR})_2(\text{PC})_2(\text{HO}_2\text{CCH}_3)_2$ or $\text{Rh}_2(\text{O}_2\text{CR})_3(\text{PC})(\text{HO}_2\text{CCH}_3)_2$ {PC = orthometalated aryl phosphine: $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)_2$ } were first characterized by Cotton *et al.* [59]. Due to the H–T arrangement of the orthometalated bridging PC ligands in $[\text{Rh}_2(\text{PC})_2]^{2+}$, these dirhodium units are chiral and are thus encountered in the *R*- or *S*-conformations; a secondary source of chirality arises from the twist pattern of each PC ligand designated as *P* or *M* [129a]. Dirhodium complexes with orthometalated PC groups and analogs with substituted PC groups have been developed by Lahuerta *et al.* as important catalysts for enantioselective C–H insertion reactions of α -diazo compounds via metalcarbene intermediates [129b]. The exchange of the acetate for trifluoroacetate groups in *cis*- $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{PMP})_2(\text{HO}_2\text{CCH}_3)_2$ (**49**, {PMPH = tris(*p*-methoxyphenyl)phosphine} afforded H–T *cis*- $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{PMP})_2(\text{H}_2\text{O})_2](\text{HO}_2\text{CCF}_3)_2$ (**50**; Figure 9.18a) [130]; the electron-withdrawing trifluoroacetate groups confer better catalytic properties to these complexes [131], but the number of PC ligands and the geometrical arrangement are important for the catalytic activity. The trifluoroacetate analogs of the chiral stereoisomers of H–T *cis*- $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(4\text{-BrC}_6\text{H}_3)\text{P}(4\text{-BrC}_6\text{H}_4)\text{Ph}][\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)_2]\cdot 2\text{CH}_3\text{CO}_2\text{H}$ (*M*-**51** and *P*-**52** [96]; Figure 9.18b) exhibit excellent catalytic activity in enantioselective cyclopropanation reactions (Table 9.2, entry 17); the highest 86% ee and 80% yields were achieved with these catalysts. Also, high enantio- and diastereo-selective controls were achieved in cyclopropanation reactions catalyzed by dirhodium complexes bearing bulky orthometalated aryl phosphines [132a], but not when the catalysts were immobilized on cross-linked polystyrene resins [132b]. Furthermore, the *R*-, *S*-building blocks *cis*- $[\text{Rh}_2\{\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)_2\}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ were used as corner pieces to build chiral molecular loops, triangles, and carceplex supramolecular structures; a few exhibit promising catalytic behavior in cyclopropanation reactions [58b, 129a].

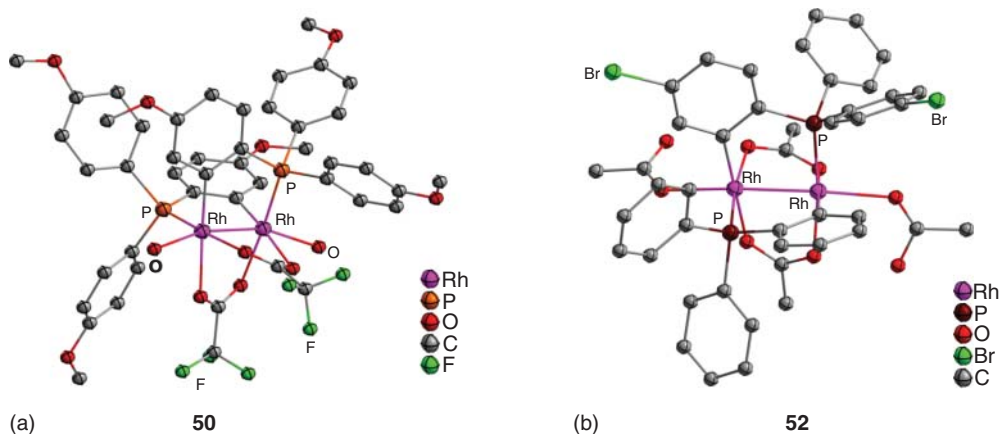
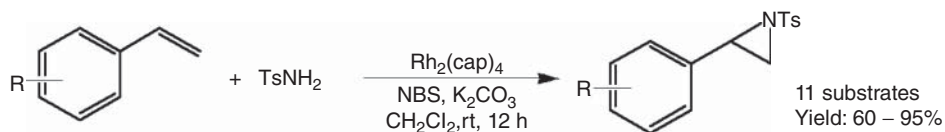


Figure 9.18 Molecular structures of the compounds (a) **50**, and (b) **52**.

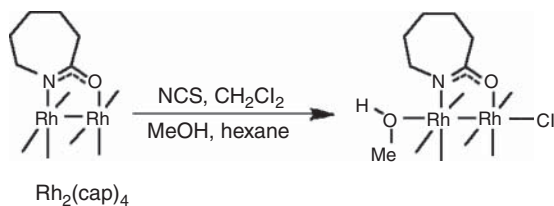
9.2.2.3 Formation of C–N Bonds

The formation of C–N bonds is an important process in organic synthesis to endow simple hydrocarbons with complex functionalities, and develop complex natural products and pharmaceutical agents [63, 133]. The C–N bond formation occurs via aziridination or C–H amination starting from readily available chemicals such as olefins [134], and dirhodium catalysts are critical for the outcome of these reactions. Doyle *et al.* [135], Berry [136], and Du Bois *et al.* [137] have explored the activity of dirhodium scaffolds in C–N bond formation reactions. Intermolecular C–H amination is a challenging transformation, whereas the intramolecular amination is accomplished with simple tetracarboxylate catalysts, for example, **1**, **7**, and **8**. In a recent pioneering study, Du Bois was able to capture, by using electrospray mass spectrometry, fleeting intermediate complexes in the C–H amination cycle catalyzed by a dirhodium tetracarboxylate complex [138]; in particular, the highly electrophilic short-lived nitrene complex $[\text{Rh}-\text{Rh}]=\text{N}$ (by analogy to the corresponding isoelectronic carbene $[\text{Rh}-\text{Rh}]=\text{C}$ [87]; see Section 9.2.2.1) was detected [138].

Dirhodium carboxamidates are effective catalysts for aziridination reactions most likely due to their low oxidation potentials, for example, dirhodium caprolactamate $\text{Rh}_2(\text{cap})_4$ (**53**) successfully catalyzes the aziridination of olefins. To this effect, the use of *p*-toluenesulfonamide (TsNH_2), *N*-bromosuccinimide (NBS), and potassium carbonate affords aziridines in high yields (95%), under extremely mild conditions (Scheme 9.14). It is postulated that the reaction proceeds via the mixed-valence dirhodium(II,III) complex $\text{Rh}_2(\text{cap})_4\text{Cl}(\text{OHCH}_3)$ (**54**), which was synthesized (Scheme 9.15; NCS = chlorosuccinimide) and characterized by X-ray crystallography (Figure 9.19) [139].



Scheme 9.14 Aziridination of olefins catalyzed by $\text{Rh}_2(\text{cap})_4$ (**53**).



Scheme 9.15 Synthetic scheme for $\text{Rh}_2(\text{cap})_4\text{Cl}(\text{OHCH}_3)$ (**54**).

The achiral dicarboxylate catalyst $\text{Rh}_2(\text{esp})_2$ (**55**; esp = α,α,α -tetramethyl-1,3-benzene dipropanoate), which has exhibited exemplary performance in a wide variety of intra- and intermolecular C–H amination reactions (e.g., Scheme 9.16) [137a], at low catalyst loadings, was introduced by Du Bois, who also investigated the mechanism of the later transformation [134]. The stability and robustness of **55** as compared to simple carboxylate catalysts, under the highly oxidizing conditions of C–H amination, is attributed to the chelating effect of the bridging dicarboxylic acid H_2esp [134]. To gain further insight in the C–H amination reaction mechanism, two new dirhodium adducts **56** and **57**, which are analogs of **55**, were synthesized by Berry *et al.* [140]. The redox-active 2-[3-(1-carboxy-1-methylethoxy)phenoxy]-2-methylpropanoic (**H2L1**) and (3-methoxycarbonyl-2,5-di-*tert*-butylphenoxy)ethanoic (**H2L2**) acids, which are structurally similar to esp, were treated with $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$ to afford the catalysts $[\text{Rh}_2(\text{L1})_2]$ (**56**) and $[\text{Rh}_2(\text{L2})_2]$ (**57**; Figure 9.20), which exhibit similar activities with **55** in C–H amination reactions. Cyclic voltammetric and controlled-potential electrolytic measurements pointed to plausible mechanisms for intermolecular C–H

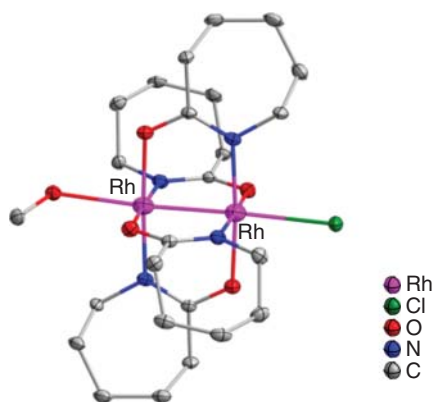


Figure 9.19 Molecular structure of 54.

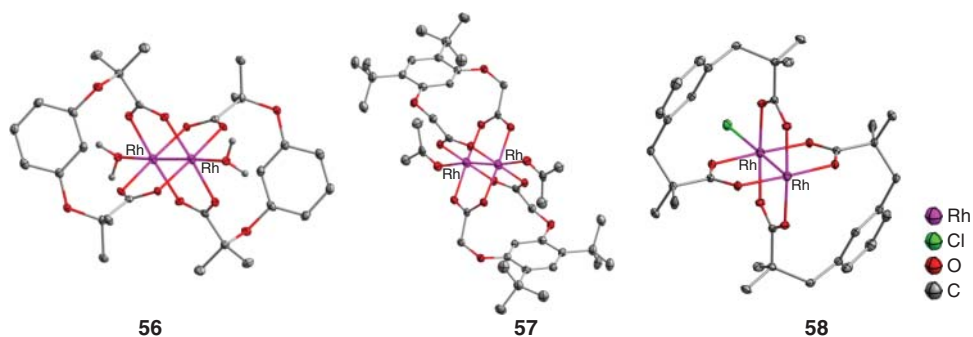
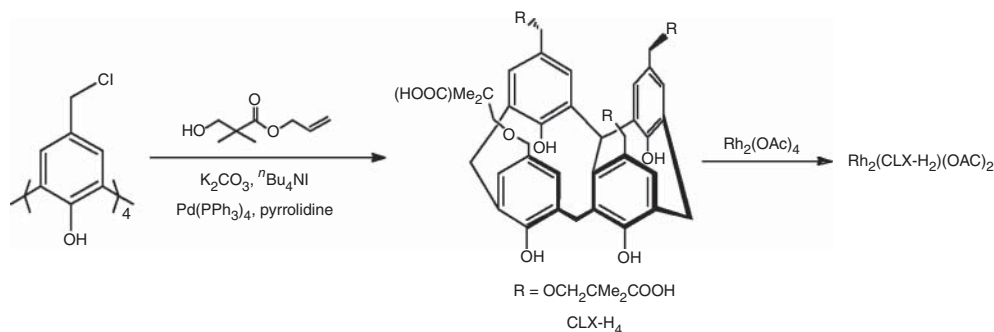
Scheme 9.16 Intermolecular C–H amination of ethyl benzene catalyzed by $\text{Rh}_2(\text{esp})_2$ (55).

Figure 9.20 Molecular structures of 56–58.

amination [141]. Furthermore, the new mixed-valence analog of 55, namely the $\text{Rh}_2(\text{II,III})$ dimer $[\text{Rh}_2(\text{espn})_2\text{Cl}]$ (58) ($\text{espn}^{2-} = \alpha,\alpha,\alpha,\alpha$ -tetramethyl-1,3-benzene dipropanamidate), which efficiently catalyzes the intramolecular C–H amination reaction with turn-over numbers greater than 1400, was synthesized and its structure was determined by X-ray crystallography (Figure 9.20) [142]. The intramolecular selectivity preferences displayed by catalyst 58, which are similar to those of 55, support the presence of a mixed-valence $\text{Rh}_2(\text{II,III})$ species under amination conditions, evidenced by the color change of the solution, an observation noted by Du Bois *et al.* [134d] which is also in agreement with relevant studies conducted by Doyle *et al.* with catalyst 53 [139b].

A strategy directed at exploiting another bimetallic framework with tethered carboxylate groups led to the isolation of an unusual dirhodium(II) tetracarboxylate catalyst with calix[4]arene (CLX), which was synthesized (Scheme 9.17) and used in C–H amination reactions [143]; the structures of



Scheme 9.17 Synthetic scheme for the dirhodium calixarene adduct **59**.

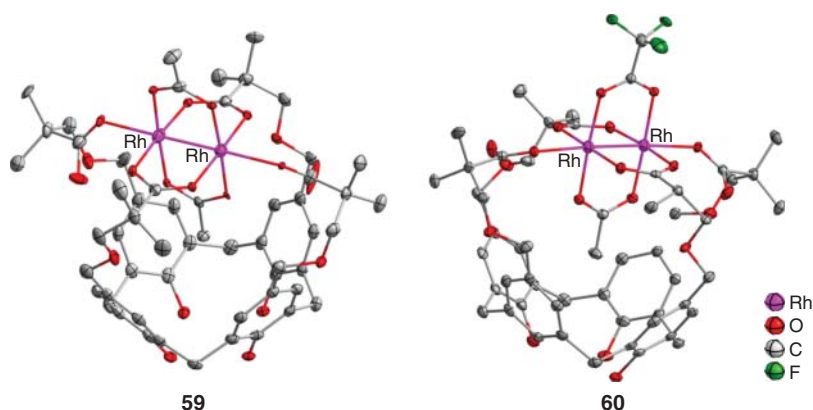
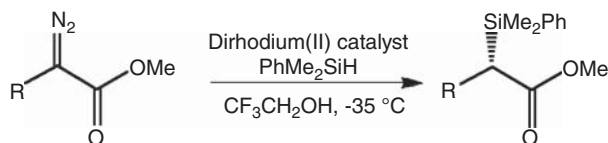


Figure 9.21 Molecular structures of the dirhodium calixarene complexes **59** and **60**.

$\text{Rh}_2(\text{CLX-H}_2)(\text{O}_2\text{CCH}_3)_2$ (**59**) and $\text{Rh}_2(\text{CLX-H}_2)(\text{O}_2\text{CCH}_3)(\text{O}_2\text{CCF}_3)$ (**60**) were determined by X-ray crystallography (Figure 9.21).

9.2.2.4 Functionalization of Si–H and S–H Bonds

As in the case of C–H insertion, Si–H bond functionalization in aryl- and vinyl-diazoacetates takes place in the presence of dirhodium catalysts, and chiral ones result in asymmetric induction [60a]. In pioneering studies by Doyle *et al.*, enantioselective Si–H bond insertion with chiral dirhodium catalysts was achieved [90]. Recently, Ball *et al.* reported innovative studies with bis-acetate dirhodium complexes, bearing chelating nona-peptides (see Section 9.2.3.2), which catalyzed the enantioselective carbenoid insertion into Si–H bonds (Scheme 9.18) [46]. The optimization of the peptide bound to the dirhodium unit or the presence of a phosphite additive significantly improved the enantioselectivity of the silane products [46].

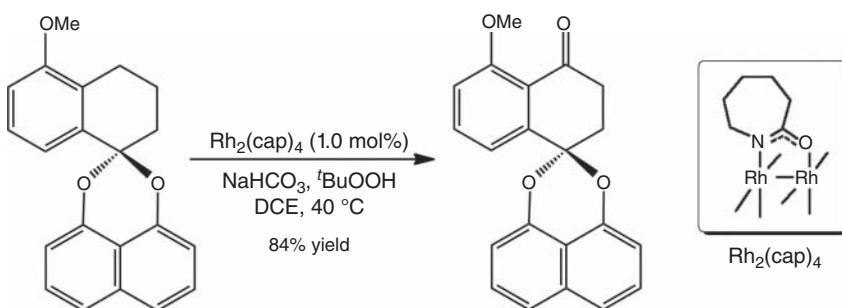


Scheme 9.18 Asymmetric insertion of diazoacetates into Si–H bonds.

The S–H insertion is also of great importance in light of many chiral sulfur-containing pharmaceuticals, and the presence of sulfur-containing amino acids in many proteins. In this vein, the first highly enantioselective S–H bond insertion reaction by cooperative catalysis of dirhodium(II) carboxylates, with high yields and excellent enantioselectivities (up to 99% ee), was recently reported [144]. Also, Ball *et al.* succeeded in selectively modifying the surface-exposed thiol groups of the cysteine residues in several biologically relevant peptides, with diazo reagents in the presence of dirhodium tetraacetate [49].

9.2.2.5 Allylic and Benzylic Oxidations by Dirhodium(II) Caprolactamate

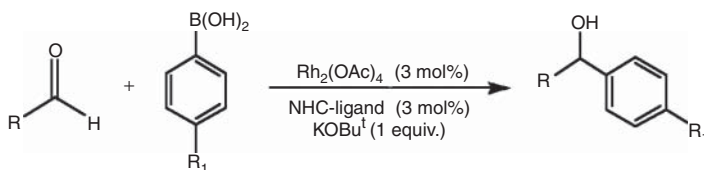
Bimetallic systems have been used as viable catalysts in various organic transformations [145]. The selective oxidation of hydrocarbons via the transition of metal catalysts has been sought after in the development of organic synthesis [146]. Recently, Doyle *et al.* reported that $\text{Rh}_2(\text{cap})_4$ (**53**) is an exceptional catalyst for allylic and benzylic oxidations in the presence of *t*-But-hydroperoxide (TBHP) under mild conditions, with sodium bicarbonate acting as a weak base, and carbonyl compounds as the final products (e.g., Scheme 9.19) [90b, 139a, 147]. In a similar fashion to aziridination reactions (see Section 9.2.2.3), the mixed-valence intermediate $\text{Rh}_2(\text{II,III})$ tetrakis caprolactamate **54** is readily generated from **53** during the reaction with TBHP, and is the active catalyst for the benzylic or allylic oxidations [139a, 147]. Studies of the reaction mechanism and spectroscopic evidence support the conversion of **54** to the $\text{Rh}_2(\text{II,III})$ *t*-But-peroxyether intermediate $\text{Rh}_2(\text{cap})_4(\text{OO}^t\text{Bu})$ (**61**) [87a, 139a].



Scheme 9.19 Benzylic oxidation catalyzed by $\text{Rh}_2(\text{cap})_4$ (**53**).

9.2.2.6 Other C–C Bond Formation Reactions

Gois *et al.* recently tuned the reactivity of dirhodium complexes by introducing one or two electron-donating σ -donor *N*-heterocyclic carbene (NHC) ligands at axial sites [148]. The axially coordinated adduct $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4\text{--NHC}$, in the presence of KO^tBu , exhibited excellent catalytic activity for the arylation of aldehydes (Scheme 9.20). The syntheses and the X-ray crystal structures of the axial–NHC adducts $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{IPr})$ (**62**) [76, 149] and $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{IPr})_2$ (**63**) (Figure 9.22; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) have been reported. Detailed investigations revealed that the mono-adduct is the active catalyst, and that the integrity of the bimetallic complex is maintained under the reaction conditions without disproportionation to $\text{Rh}(\text{I})$ and $\text{Rh}(\text{III})$ species.



Scheme 9.20 Arylation of aldehydes.

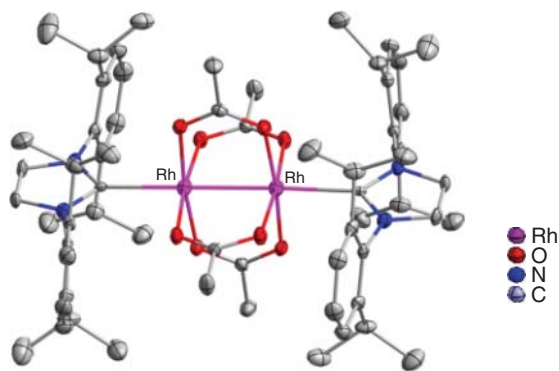


Figure 9.22 Molecular structure of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{IPr})_2$ (**63**).

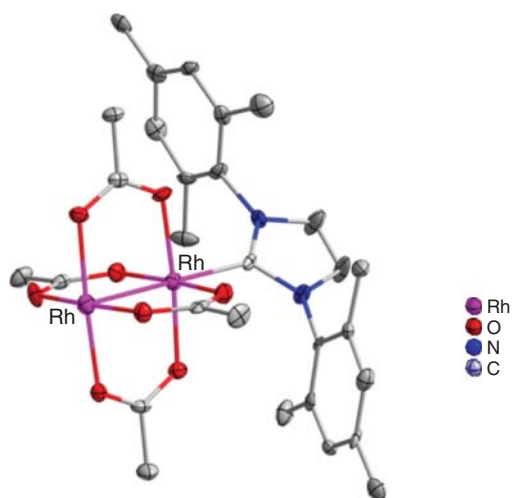
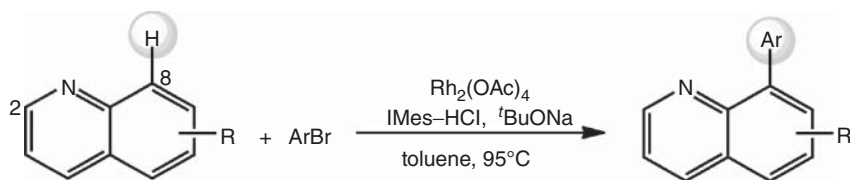


Figure 9.23 Molecular structure of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{IMes})$ (**64**).

The X-ray crystal structure of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{IMes})$ (**64**) (Figure 9.23; IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) was determined by Chang *et al.* [150]. Catalyst **64** was employed for the arylation at position 8 of quinoline (Scheme 9.21), which is a prominent structural entity in many natural products. The dirhodium tetracarboxylate itself failed to catalyze the reactions, but C–C bonded quinoline products were obtained in high yield with the dirhodium–NHC catalyst when quinoline and aryl bromide were reacted.



Scheme 9.21 Arylation of quinoline at position 8.

9.2.3

Dirhodium Complexes with Photochemical and Other Applications

9.2.3.1 Dirhodium Complexes as Photocatalytic Mediators for O₂ Reduction to H₂OPhotocatalytic H₂ Production, and Potential Mediators in Solar Energy Conversion

The challenging task of multielectron transfer reactions such as O₂ and H⁺ reductions, which are efficiently performed by many metalloenzymes, was explored in seminal studies by Gray *et al.* in photochemical reactions of dirhodium(I) isocyanide complexes: upon irradiation at 550 nm in aqueous HCl solutions, the Rh(I) isocyanide precursor Rh₂[CN(CH₂)₃NC]₄²⁺ forms H₂ and the dirhodium(II,II) salt [Rh₂[CN(CH₂)₃NC]₄Cl₂]₂ [151]. Further preminent studies by Nocera *et al.* [40] provided access to a suite of dirhodium-based photocatalysts that enable production of H₂ and O₂ reduction in HX (X = halide) solutions, as well as valuable insight into the corresponding photocycles (Scheme 9.22), which are currently actively explored along with the reactivity and further development of judiciously chosen dirhodium units [152].

Among the recent successful photocatalysts adept at O₂ reduction, which have been explored by Nocera *et al.*, are mixed-valence dirhodium units of the general formula Rh₂^{0,II}(tfepma)₂(L)₂Cl₂ with two bridging phosphazane groups, and a bulky monodentate capping ligand, for example, Rh₂^{0,II}(tfepma)₂(CN^tBu)₂Cl₂ (**65**, L = CN^tBu, Figure 9.24), which is furnished by the treatment of the Rh(I) complex [Rh(COD)Cl]₂ (COD = 1,5-cyclooctadiene) with tfepma (tfepma = CH₃N[P(OCH₂CF₃)₂]₂) in the presence of CN^tBu. The oxidation of **65** with PhICl₂ in toluene affords Rh₂^{II,II}(tfepma)₂(CN^tBu)₂Cl₄ (**66**), whereas reversible oxidative addition of HCl to **65** produces two isomeric hydrido-halide species Rh₂^{II}(tfepma)₂(CN^tBu)₂Cl₃H (**67**, Figure 9.24) in nearly quantitative yield [152b,c,d]. In the catalytic cycle depicted in Scheme 9.22a, in the presence of molecular oxygen and excess HCl, **67** is converted to **66** with the liberation of water; **65** is regenerated photochemically (by irradiation with λ > 313 nm), in the presence of a trap-Cl, to close an oxygen-to-water reduction photocycle.

Nocera *et al.* made important strides in developing HCl-splitting dirhodium photocatalysts due to the importance of HX splitting reactions (X = halide) as a route to solar-to-fuels energy conversion and substantial energy storage [152a,f,g,h]. The advantage of photocatalysis with HX-splitting, which stores substantial energy, similar to H₂O-splitting, is that only two proton/electron equivalents need to be managed for a complete photocycle as opposed to the four involved in H₂O-splitting.

In this context, the mixed-valence complex **65** splits HCl to generate H₂, which was demonstrated to derive from the HCl, in a photocatalytic cycle summarized in Scheme 9.22b [152a,f,g,h]. Despite the rapid H₂ production of **65**, the catalyst exhibits minimal turn over numbers (TON 2) due to degradation arising from the capping group CN^tBu; this is circumvented by substituting L = CN^tBu with adamantyl-isocyanide (CNAd), which enhances the photocatalytic performance of Rh₂^{0,II}(tfepma)₂(CNAd)₂Cl₂ to TON 7 [152g]. Further pioneering studies [152h,i] involving

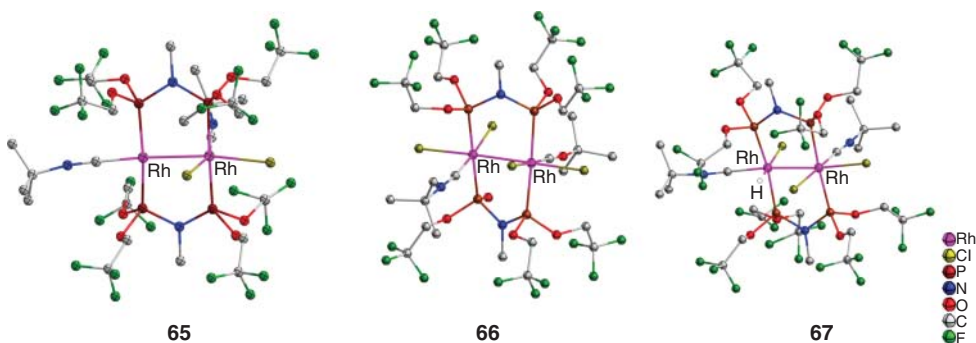
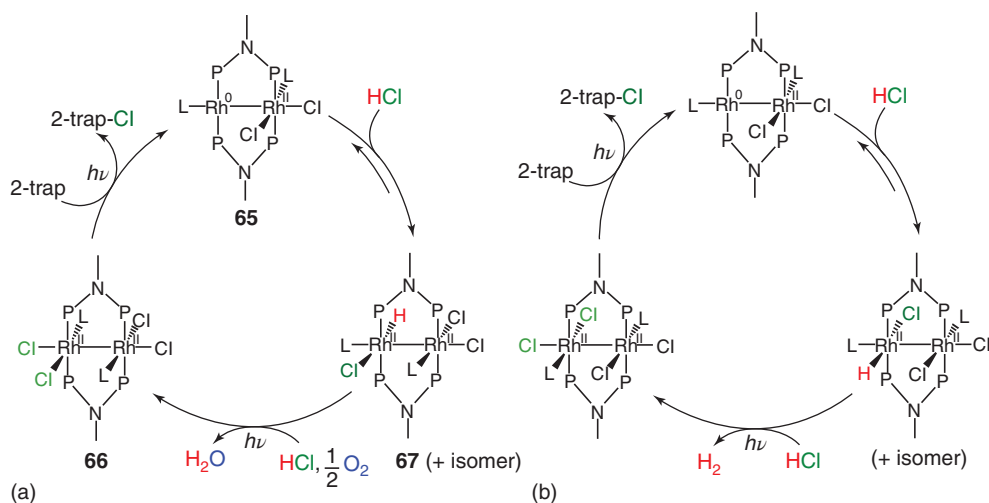


Figure 9.24 Molecular structures of **65**–**67**.



Scheme 9.22 Multi-electron transfer processes facilitated by mixed-valence dirhodium complexes of the type $\text{Rh}_2^{0,II}(\text{tfepma})_2(\text{L})_2\text{Cl}_2$. Photocatalytic cycles for (a) O_2 reduction, $\text{L} = \text{CN}^t\text{Bu}$, and (b) H_2 production, $\text{L} = \text{CN}^t\text{Bu}$ or CNAd .

nanosecond-resolved transient absorption spectroscopy, steady-state photocrystallography, and computational modeling have allowed direct observation of halide-bridged intermediates, which established binuclear reductive elimination as a viable pathway for metal-halide bond activation, and will thus lead to the development of new photocatalyst families.

Recently, Wang *et al.* showed the importance of the diimine groups in improving the photocatalytic H_2 production of dirhodium diimine complexes of the type $\text{cis-}[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{N-N})_2][\text{O}_2\text{CCH}_3]_2$, $\text{N-N} = \text{bpy}$ or phen [42], and Sakai *et al.* explored the photocatalytic H_2 production with a series of dirhodium tetra- or bis-carboxylate complexes in a multicomponent system in aqueous acetate buffer [41].

As part of their efforts to develop dirhodium complexes as sensitizers in solar cells, Dunbar and Turro *et al.* reported a series of new dirhodium complexes, namely $\text{cis-}[\text{Rh}_2(\text{DTolF})_2(\text{N-N})_2][\text{BF}_4]_2$ and $\text{cis-}[\text{Rh}_2(\mu\text{-F-form})_2(\text{N-N})_2][\text{BF}_4]_2$ ($[\text{DTolF}]^- = p\text{-ditolylformamidinate}$, $[\text{F-form}]^- = p\text{-difluorophenylformamidinate}$; $\text{N-N} =$ chelating diimine ligands dpq , dppz , and dppn ; Figure 9.25), and studied their excited-state photophysical properties [43]. These compounds are easily oxidized and exhibit directed ligand-to-ligand charge transfer (LLCT) excited states upon excitation from the formamidinate to the diimine ligands. Time-resolved studies showed that the LLCT states decay (lifetimes in the range 17–100 ps) to a longer-lived excited state. In the cases of the dpq and dppz complexes, the longer-lived excited state (lifetimes in the range 40–100 ns) was characterized as a metal-centered triplet (^3MC) arising from the $\text{Rh}_2(\pi^*) \rightarrow \text{Rh}_2(\sigma^*)$ transition. For the dppn complexes, the LLCT decays to the $3\pi\pi^*$ excited state (16–18 ps), which further decays to the ^3MC state with

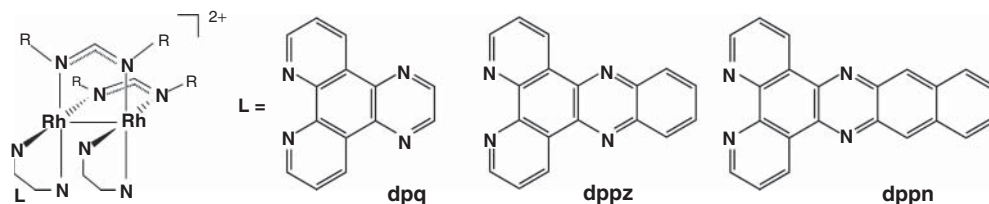


Figure 9.25 Schematic drawings of $\text{cis-}[\text{Rh}_2(\text{Formamidinate})_2(\text{N-N})_2]^{2+}$ complexes and the N-N ligands.

a long lifetime 2.4–3.0 μ s. The excited-state redox properties of the complexes render them very promising candidates as sensitizers in dye-sensitized solar cells [43].

9.2.3.2 Dirhodium Metallopeptides in Catalysis and Site-Selective Protein Modifications

In pioneering studies, Ball *et al.* designed, synthesized, and developed dirhodium enzyme-like catalysts (Figure 9.26a) [51b] that achieved site-specific protein modifications (e.g., Figure 9.26b) for a broad range of amino acids (Phe, Tyr, Asn, Gln, Asp, Glu, Trp, Arg, Ser, Lys, His), and medically relevant recognition motifs [45], enantioselective carbenoid insertion into Si–H and S–H bonds (Section 9.2.2.4) [46, 49], as well as asymmetric cyclopropanations [48]. Further studies revealed elegant ways to inhibit designed dirhodium metalloptides by histidine-containing inhibitors [50], as well as dirhodium peptides that block protein–protein interactions [51a]. The new dirhodium catalysts $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{L1})$, unlike the typical ones with four chiral centers, are bis-acetate complexes, bearing single chelating bis carboxylate natural nonapeptides L1 (Figure 9.26a), with carboxylate-containing residues (aspartate D or glutamate E) placed at judiciously chosen locations in the peptide [45]. Metal binding to appropriately spaced residues induces helical structures, which serve as molecular recognition elements for the substrates, whereas the rhodium centers are the modification catalysts, resulting in designed metallopeptide catalysts with remarkable selectivity [45].

9.2.3.3 Dirhodium Frameworks as Hosts for Gas-Adsorption

Flexible molecular framework hosts, with high stability and regularity of the pores, are of fundamental importance, and have many potential applications in gas storage, purification, and catalysis. In this context, inorganic frameworks $[\text{Rh}_2(\text{O}_2\text{CPh})_4(\text{Rpyrazine})]_n$ (**68a**, Figure 9.27, $\text{R}_1 = \text{R}_2 = \text{H}$; $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{Me}$; $\text{R}_1 = \text{R}_2 = \text{Me}$) have been investigated by Takamizawa *et al.*, as hosts to accommodate gas molecules of various sizes and properties, such as H_2 , O_2 , CO_2 , CH_4 , N_2 , NO , Xe , Ar , as well as

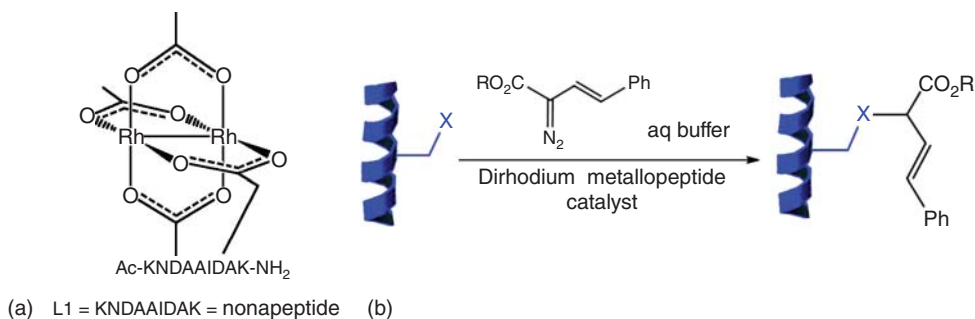


Figure 9.26 (a) $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{L1})$ bearing the nonapeptide L1, and (b) dirhodium complex catalyzing a protein site modification.

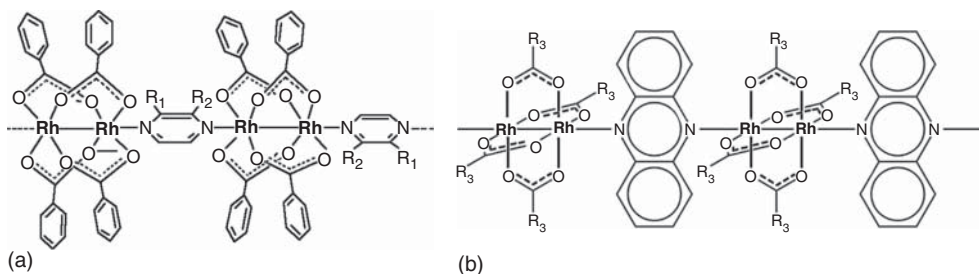


Figure 9.27 Schematic drawing of the infinite chains (a) $[\text{Rh}_2(\text{O}_2\text{CPh})_4(\text{Rpyrazine})]_n$ (**68a**), and (b) $[\text{Rh}_2(\text{R}_3\text{CO}_2)_4(\text{phz})]_n$ (**68b**), $\text{R}_3 = 4\text{-Cl-2-OMePh}$.

acetonitrile, and alcohol vapors, and corrosive gases such as NO_2 , SO_2 [65]. The structural transformations of the hosts, their correlations with the dynamic absorption behavior and the motion of the gases in the host channels, and the X-ray crystal structures of the aggregates were extensively investigated under various gas pressure and temperature conditions [65].

For example, in a series of experiments, the single-crystal adsorbents $[\text{Rh}_2(\text{O}_2\text{CPh})_4(\text{BL})]$ (BL = pyrazine, 2-methyl pyrazine, and 2,3-dimethyl pyrazine) were examined as gas adsorbates for N_2 , H_2 , O_2 , and CO_2 at 195 and 77 K [65]. Single-crystal X-ray analyses of all the host crystals, in the presence and absence of CO_2 , revealed large structural changes that occurred through CO_2 adsorption (Figure 9.28), to increase the inner space for the adsorbed gases, depending on the pyrazine ring substituents. A phase transition occurred during cooling under the CO_2 atmosphere, which resulted in 1-D channels incorporating CO_2 molecules. Similarly, O_2 inclusion studies were undertaken with the $[\text{Rh}_2(\text{O}_2\text{CPh})_4(\text{pyrazine})]_n$ host at 298, 90, and 10 K [65].

More recently, Miyasaka *et al.*, designed and synthesized the one-dimensional chain dirhodium compound $[\text{Rh}_2(4\text{-Cl-2-OMePhCO}_2)_4(\text{phz})]_n$ (**68b**, Figure 9.27b, $\text{R}_3 = 4\text{-Cl-2-OMePh}$) with 4-chloroanisate bridging groups and phenazine (phz) chain linkers. This porous compound exhibits flexible structural transformations induced by the selective trapping of reactive molecules in the pores, e.g., NO guest molecules [67a]. Trapping of NO by **68b** (Figure 9.28b) induces stepwise transformations with hysteresis adsorption/desorption behavior accompanied by gate-opening structural transitions [67a], which were monitored *in situ* by applying ac electric fields to pelletized samples [67b].

9.2.3.4 Dirhodium Adducts Exhibiting π -Polyarene Interactions

The elaboration of organometallic networks and supramolecular assemblies, assembled via directional dirhodium– π -arene interactions [72, 153], is important due to the relevance of alkene coordination to the dirhodium core in cyclopropanation reactions, and thus their applications in catalysis. Also, they are relevant to the issues of π -arene interactions encountered in fullerene and carbon nanotubes [154], in hydrogen storage and fuel cell technology.

The first dirhodium tetrakis(trifluoroacetate) olefin 1 : 2 complex with (–)-*trans*-caryophyllene was reported by Cotton *et al.* [155]. Later, Petrukhina *et al.* introduced the “solventless synthesis” gas-phase technique for the synthesis of a series of dirhodium adducts bridged by the Lewis acidic trifluoroacetate or trifluoromethyl substituted benzoate with axial π -ligands spanning the range from ethene, conjugated polyarenes to curved unsaturated π bowls, for example, corannulene, hemibuckminsterfullerene, and hemifullerene [72, 156]. The heterobimetallic Rh–Bi 1D polymeric structure $[\text{RhBi}(\text{O}_2\text{CCF}_3)_4(\text{C}_{16}\text{H}_{10})]_\infty$ with pyrene is discussed in Section 9.3.5 [157].

The previous studies by Petrukhina *et al.* were extended to non-planar aromatic ligands with two and three benzene rings, namely [2.2]- and [2.2.2] paracyclophanes, which also form 1D extended

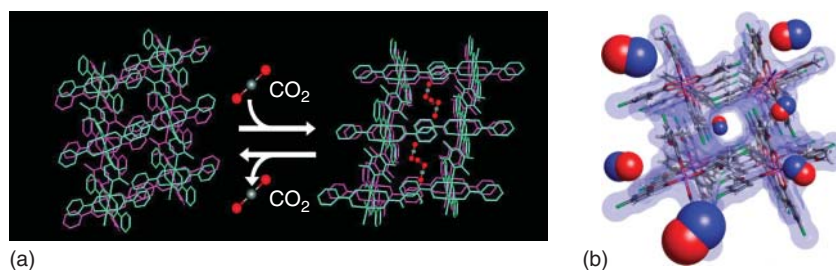


Figure 9.28 Schematic diagram of (a) the channel transformations in **68a** by the adsorption of CO_2 . (Adapted with permission from Ref. [65a]. Copyright (2010) American Chemical Society.) and

(b) Trapping of NO molecules by **68b** at 121K. (Adapted with permission from Ref. [67a]. Copyright (2013) American Chemical Society.)

organometallic networks, exhibiting η^2 -Rh $\cdots$ C interactions with the bound aromatic rings. The reaction of $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ with [2.2.2]-paracyclophane affords 1 : 2 and 3 : 2 Rh_2 :L complexes. The bis-adduct $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\eta^1\text{-C}_{24}\text{H}_{24})_2]$ (**69**, Figure 9.29) consists of a central dirhodium unit flanked by two η^1 -bound [2.2.2]-paracyclophane ligands, whereas the 3 : 2 adduct $[\{\text{Rh}_2(\text{O}_2\text{CCF}_3)_4\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{24}\text{H}_{24})_2]$ (**70**, Figure 9.30) exhibits a unique 2-D layered structure built on an unprecedented tridentate $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ coordination [158].

Doyle *et al.* also synthesized and investigated the structural and electrochemical properties of several Rh_2 (III,III) carboxamidate and caprolactamate adducts with axial aryl groups [159]. In this vein, Bear *et al.* also reported Rh_2 (II,III), Rh_2 (III,III) anilinopyridinate and *N,N*-diphenylformamidinate adducts with axial R groups, R = CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , or C_5H_{11} [160].

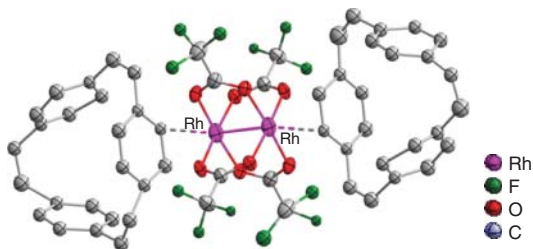


Figure 9.29 Molecular structure of $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\eta^1\text{-C}_{24}\text{H}_{24})_2]$ (**69**).

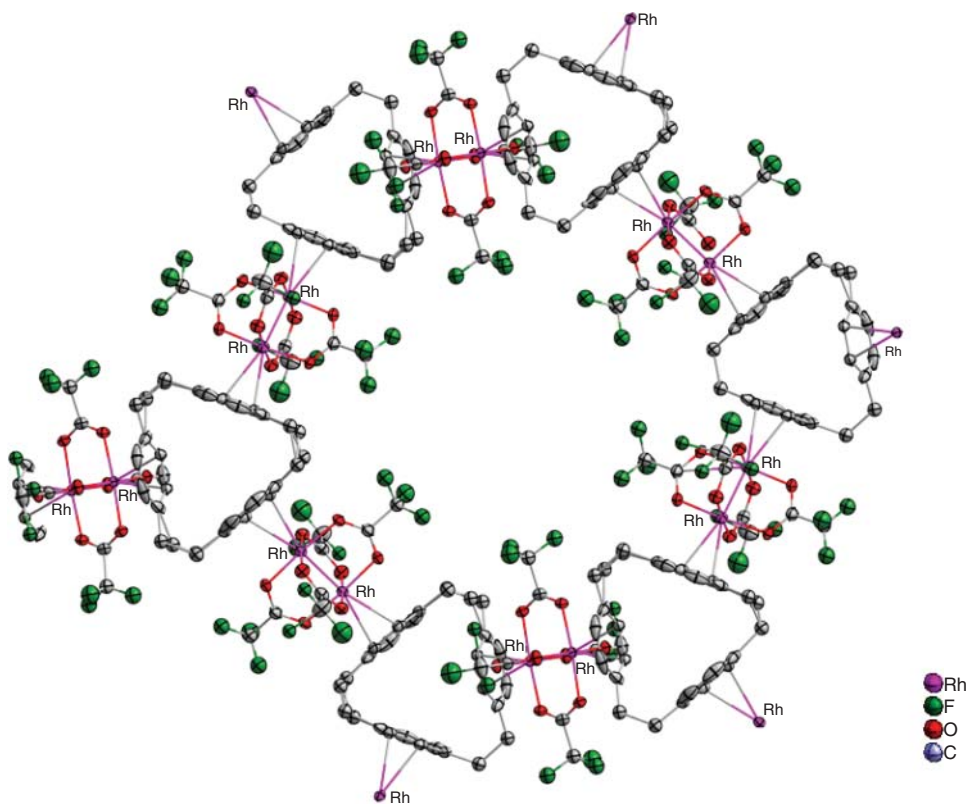


Figure 9.30 Molecular structure of $[\{\text{Rh}_2(\text{O}_2\text{CCF}_3)_4\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{24}\text{H}_{24})_2]$ (**70**).

9.2.3.5 Dirhodium Adducts Exhibiting π -Back Bonding

A series of orthometalated complexes $\text{H-T Rh}_2(\text{O}_2\text{CR})_2(\text{PC})_2\text{L}_2$, $\text{R} = \text{CH}_3$, CF_3 , $\text{C}(\text{CH}_3)_3$, and $\text{L} = \text{RCO}_2\text{H}$ or H_2O were recently reported to be selective and very sensitive chromogenic sensors for CO via axial coordination, both in solution and on silica beads [68]. The CO detection by these complexes is a result of effective π -backbonding between the dirhodium units and the CO molecules, which is enhanced by the σ -donating ability of the bridging phosphine groups on the dirhodium core. When the purple-colored complexes $\text{H-T Rh}_2(\text{O}_2\text{CR})_2(\text{PC})_2\text{L}_2$ were exposed to increasing CO concentrations, immediate color changes to pink-orange and yellow were observed, owing to the formation of the CO mono- and bis axial adducts, respectively (Figure 9.31) [68].

In another recent comprehensive investigation of partial paddlewheel complexes involving ligands with enhanced σ -donating and π -accepting abilities, Dunbar *et al.* synthesized a series of unprecedented dirhodium methyl isocyanide compounds, namely *cis*- $[\text{Rh}_2(\text{DTolF})_2\text{L}_6][\text{BF}_4]_2$ (**71a**) (Figure 9.32), *cis*- $[\text{Rh}_2(\text{F-form})_2\text{L}_6][\text{BF}_4]_2$ (**72a**), *cis*- $[\text{Rh}_2(\text{NNN})_2\text{L}_6][\text{BF}_4]_2$ (**73a**) ($[\text{NNN}]^- = p$ -ditolyl-triazenide), and *cis*- $[\text{Rh}_2[\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)]_2\text{L}_6][\text{BF}_4]_2$ (**74a**) (Figure 9.32) for $\text{L} = \text{CH}_3\text{NC}$, as well as their corresponding acetonitrile analogs **71b**–**74b** (for $\text{L} = \text{CH}_3\text{CN}$) [161]. The methyl isocyanide analogs **71a**–**74a** are a rarity in metal–metal bond chemistry due to the synthetic challenges of circumventing reduction of the metal centers. In this study, the corresponding findings from the structural, electronic, infrared, and electrochemical data, which are in excellent agreement with

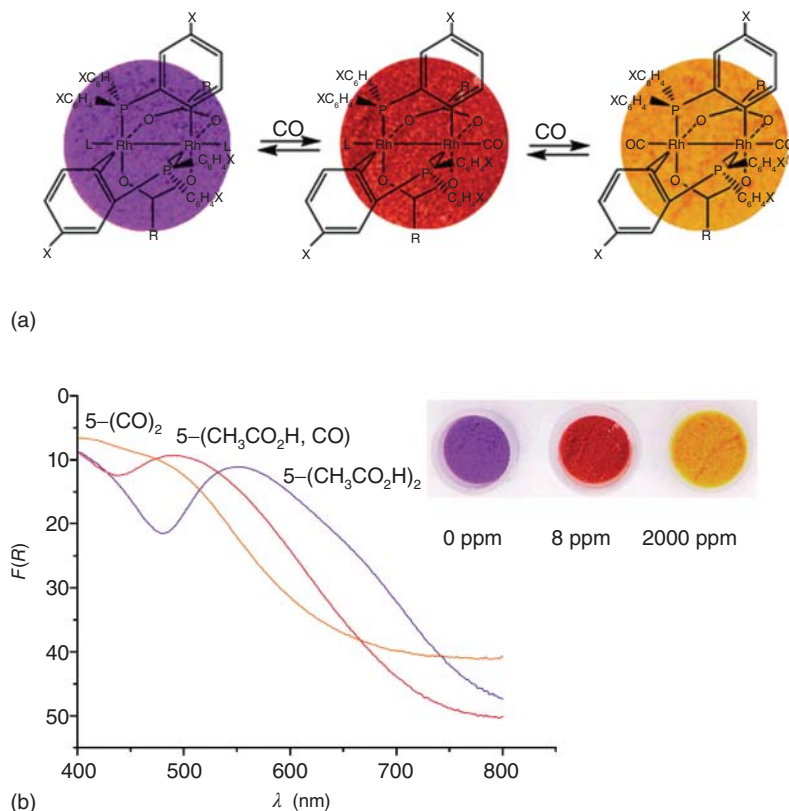


Figure 9.31 (a) Reaction of $\text{H-T Rh}_2(\text{O}_2\text{CR})_2(\text{PC})_2\text{L}_2$ $\text{P}(m\text{-CH}_3\text{C}_6\text{H}_4)_2(\text{O}_2\text{CCH}_3)_2\text{L}(\text{CH}_3\text{CO}_2\text{H})_2$ in the presence of 8–2000 ppm CO. (Adapted with permission from Ref. [68b]. Copyright (2011) American Chemical Society.)
 (b) Diffuse reflectance spectra of a silica mixture containing $\text{H-T Rh}_2\{(m\text{-CH}_3\text{C}_6\text{H}_3)\}$

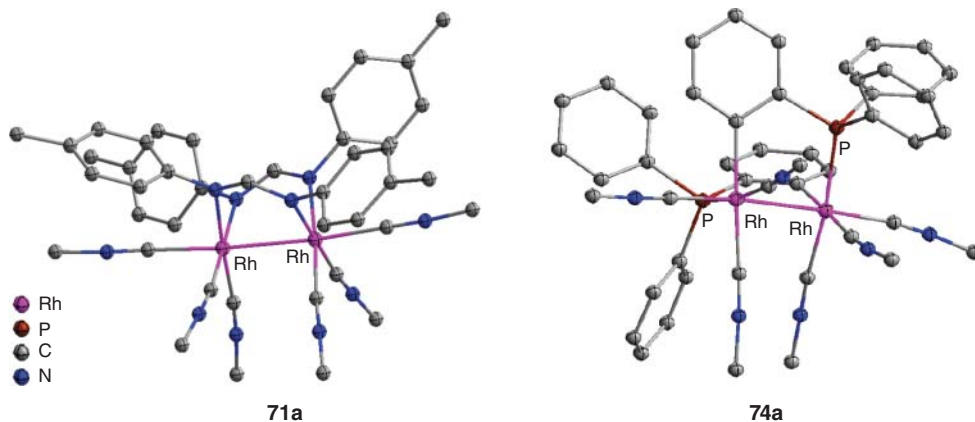


Figure 9.32 Molecular structures of the cationic units in **71a** and **74a**.

the TD-DFT calculations, were nicely correlated for the two series. The strong *trans* influence of the axial methyl isocyanide ligands in **71a–74a**, resulted in longer Rh–Rh distances as compared to **71b–74b**. Furthermore, the observed short Rh–C (isocyanide) distances in the X-ray crystal structures reflect the strong π -accepting ability of methyl isocyanide as compared to acetonitrile, whereas the short CN(isocyanide) distances and the higher $\nu(\text{CN})$ stretching bands are attributed to the significant σ -donation of the methyl isocyanide groups [161]. In accord with the enhanced π -backbonding and σ -donation of CH_3NC as compared to CH_3CN , it is more difficult to reduce and to oxidize **71a–74a** as compared to **71b–74b**, respectively. It is notable that **74a** exhibits longer Rh–Rh bonds ($\sim 2.76 \text{ \AA}$), and remarkably short axial Rh–C distances in the same range as the equatorial Rh–C bonds ($2.01\text{--}2.04 \text{ \AA}$). The computational studies showed that the π -backbonding stabilizes the $\text{Rh}_2(\pi^*)$ orbitals, and σ -donation from CH_3NC destabilizes the $\text{Rh}_2(\sigma)$ orbitals in **71a–74a** (Figure 9.33). The extreme case is that of **74a** (Figure 9.32) wherein, the $\text{Rh}_2(\sigma)$ actually

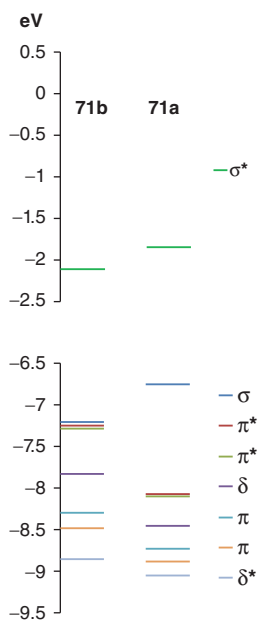


Figure 9.33 Energy levels of the MOs for **71b** and **71a** obtained by TD-DFT calculations. (Reproduced from Ref. [161] with permission from The Royal Society of Chemistry (RSC).)

becomes the HOMO; this fact accounts for the approximate 20-fold increase in the intensity of the HOMO $\text{Rh}_2(\sigma) \rightarrow \text{LUMO } \text{Rh}_2(\sigma^*)$ transition for **74a** [161].

9.2.3.6 Dimers with Rhodium in Multimetallic Assemblies

In pioneering studies by Dikarev *et al.*, heterobimetallic Rh–Bi tetracarboxylates, incorporating both main group and transition elements, were synthesized and determined by X-ray crystallography [162a,b]. In particular, the heterobimetallic complexes $[\text{RhBi}(\text{O}_2\text{CCF}_3)_4]$ (**75**, Rh–Bi distance 2.5493(3) Å; Figure 9.34a) [162a] and *cis*- $[\text{RhBi}(\text{O}_2\text{CCF}_3)_2(\text{O}_2\text{CBu}^t)_2]$ (**76**, Rh–Bi distance 2.5317(2) Å; Figure 9.34b) [162b] were prepared by the “solventless” gas-phase technique. These investigations aimed at obtaining less-expensive rhodium catalysts with novel bimetallic cooperativity [162c]. Although the heterobimetallic complex **76** exhibited comparable catalytic activity to the homometallic analog, the reactivity of the former was ~ 1600 times lower, a finding consistent with DFT calculations [162c]. In another study, the parent complex $[\text{RhBi}(\text{O}_2\text{CCF}_3)_4]$ (**75**) was further cosublimed with pyrene in a sealed ampoule to afford the 1D polymeric structure $[\text{RhBi}(\text{O}_2\text{CCF}_3)_4(\text{C}_{16}\text{H}_{10})]_\infty$ (**77**, Figure 9.35) with η^2 - and η^6 - π -arene interactions at the Rh and Bi open axial sites of the heterobimetallic core, respectively (average distances $\text{Rh}\cdots\text{C}$ 2.68–2.71 Å and $\text{Bi}\cdots\text{C}$ 3.36–3.61 Å) [157].

In an alternative effort to build supramolecular light-harvesting mixed-metal species, Hanan *et al.* reported several Rh_2/Re_4 assemblies such as **78** (Scheme 9.23, Figure 9.36), wherein dirhodium units bridged by benzamidinate, or functionalized benzamidinate ligands with appended pyridyl groups [163–165], were coupled with carboxyl-derived Ru(II) polypyridyl complexes to afford **79** (Scheme 9.24).

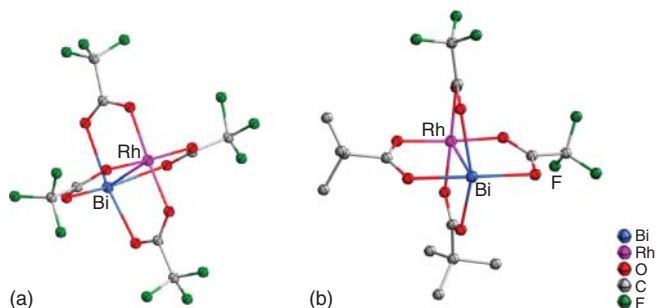


Figure 9.34 Molecular structures of (a) $[\text{RhBi}(\text{O}_2\text{CCF}_3)_4]$ (**75**) and (b) *cis*- $[\text{RhBi}(\text{O}_2\text{CCF}_3)_2(\text{O}_2\text{CBu}^t)_2]$ (**76**).

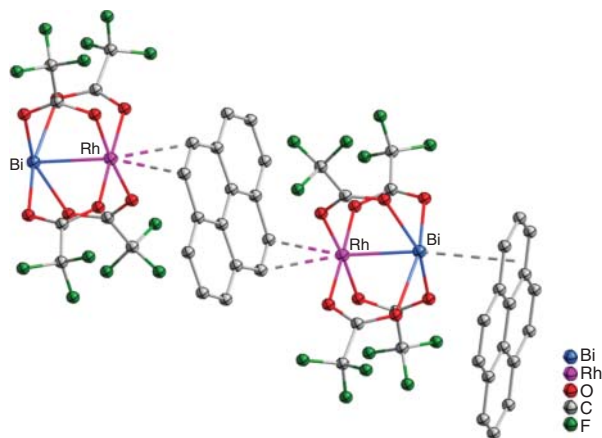
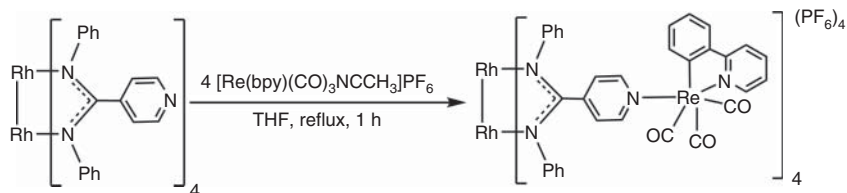


Figure 9.35 Molecular structure of the Rh–Bi polymeric chain $[\text{RhBi}(\text{O}_2\text{CCF}_3)_4(\text{C}_{16}\text{H}_{10})]_\infty$ (**77**).



Scheme 9.23 Synthesis of the mixed Rh_2/Re_4 assembly **78**.

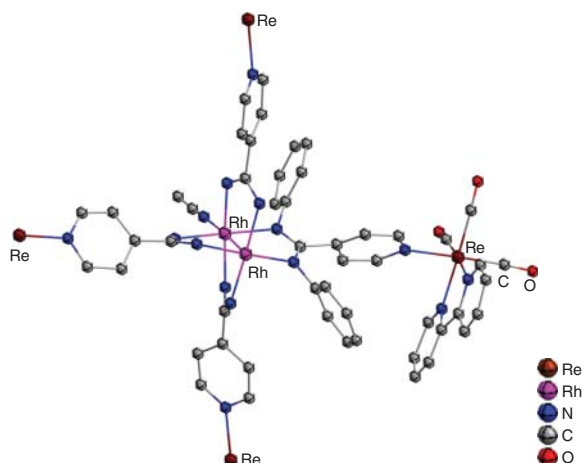
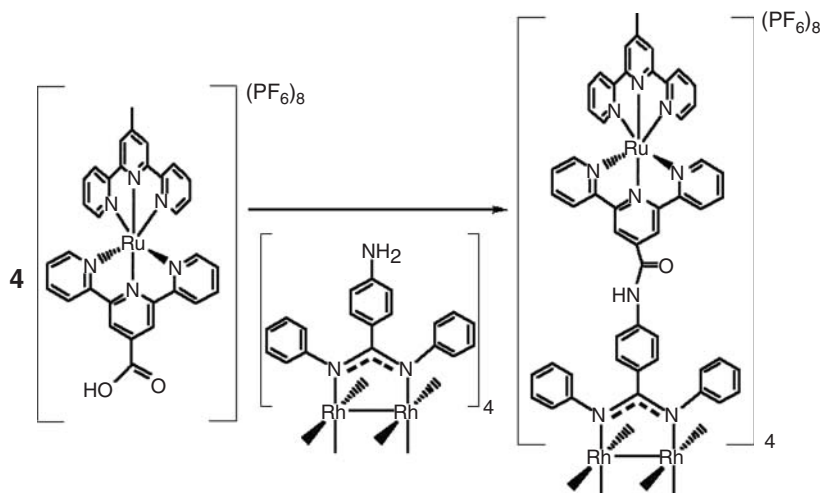


Figure 9.36 Molecular structure of the cation in **78**; the coordinated ligands to the three Re atoms and the amidinate substituents (except for one) have been omitted for clarity.



Scheme 9.24 Synthesis of the Rh_2/Ru_4 assembly **79**.

Similar Ru(II) polypyridine units were connected to dirhodium(II) tetracarboxylate platforms to form the supramolecular assemblies **80**–**82** (Figures 9.37 and 9.38) [166], exhibiting several metal-centered oxidation and ligand-centered reduction processes, and intense LC and MLCT bands centered on the Ru(II) units. Efficient energy transfer from $^3\text{MLCT}$ (Ru-based) to the lowest-energy

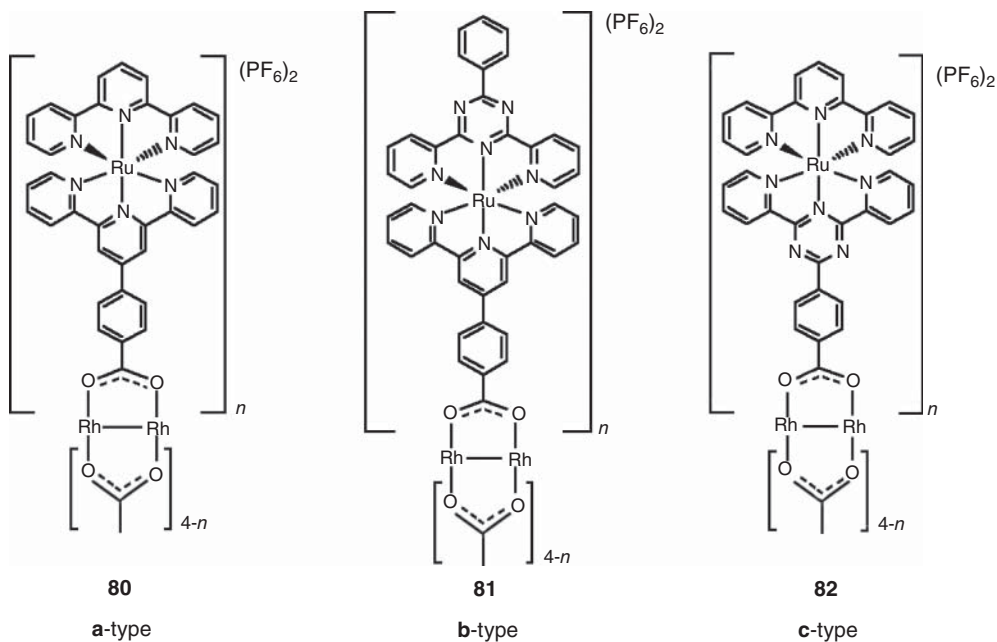


Figure 9.37 Ru(II) complexes assembled with the dirhodium core; $n = 1, 2, 3, 4$.

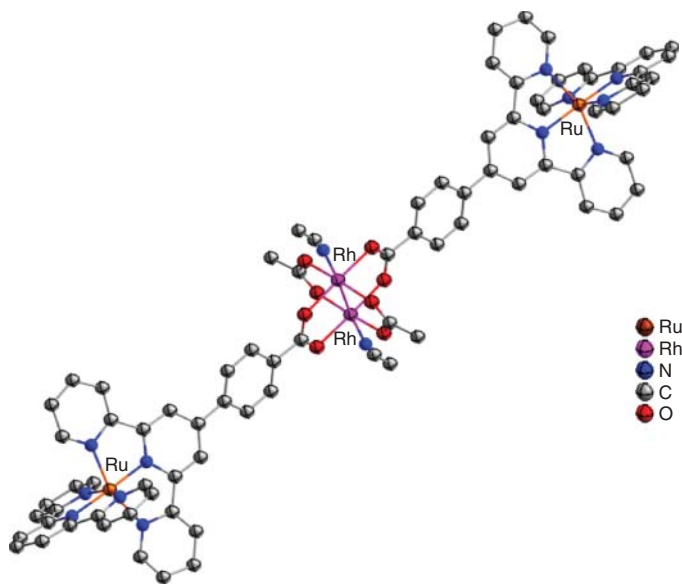
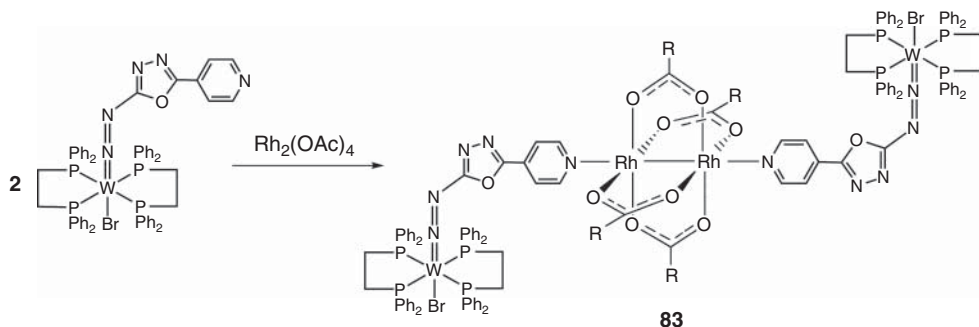


Figure 9.38 Molecular structure of **80**.

excited state of the dirhodium core occurred for the a-type compounds, whereas the b- and c-type species exhibited the typical MLCT emissions.

In another approach, the axial interactions of the $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$ unit were employed to furnish mixed-metal adducts, such as the tetranuclear W–Rh–Rh–W assembly **83** (Scheme 9.25), which was structurally characterized (Figure 9.39) [167]. In a similar fashion, the axial interactions of



Scheme 9.25 Synthesis of **83**.

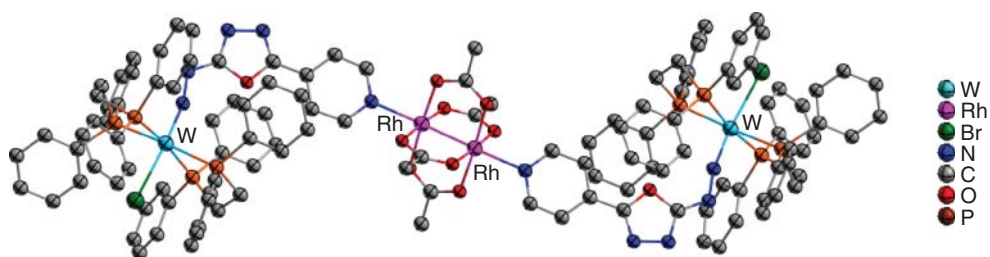


Figure 9.39 Molecular structure of the W–Rh₂–W assembly **83**.

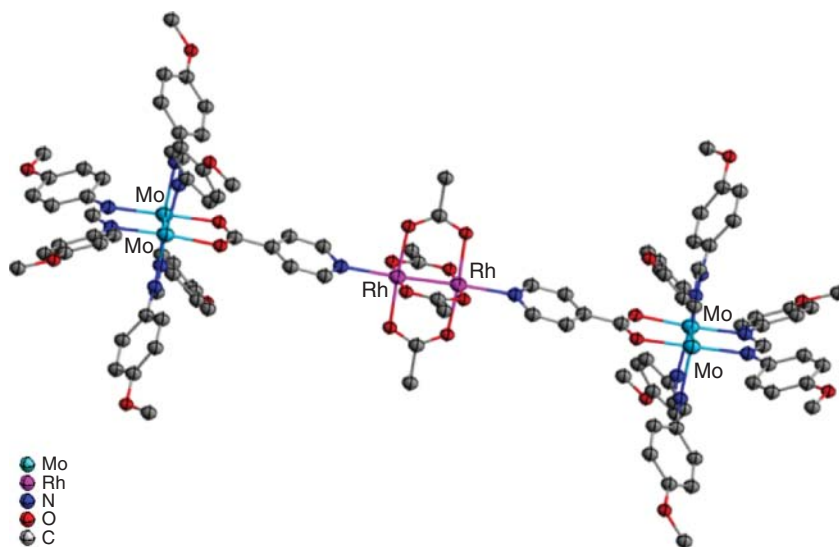
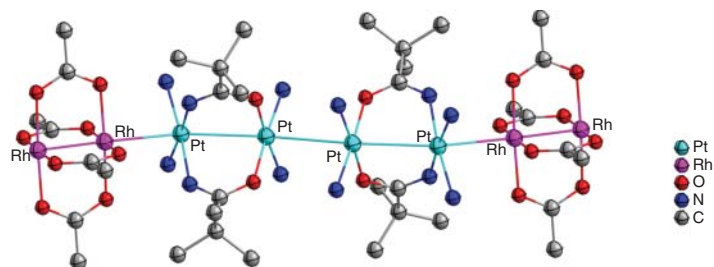
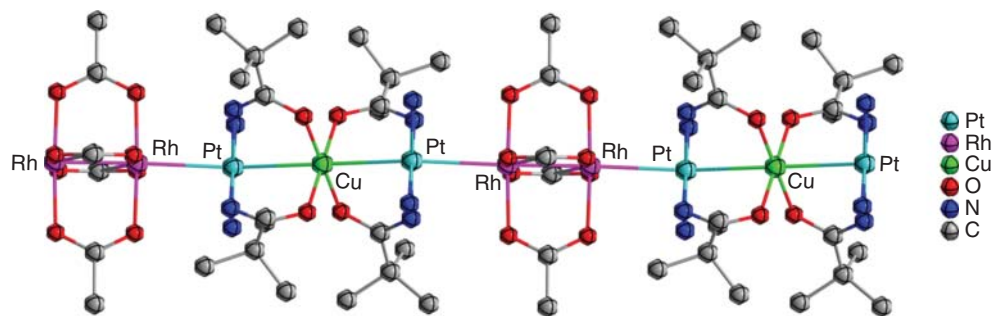


Figure 9.40 Molecular structure of **84**.

Figure 9.41 Molecular structure of **85**.Figure 9.42 Molecular structure of **86**.

the $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$ dimers with the pyridyl groups of the bridging isonicotinate ligands on Mo_2^{4+} units afforded the heterometallic supramolecules $[\text{Mo}_2(\text{DAniF})_3(\text{O}_2\text{CC}_5\text{H}_4\text{N})_2][\text{Rh}_2(\text{O}_2\text{CCH}_3)_4]$, (**84**; Figure 9.40, $[\text{DAniF}]^- = N,N'$ -di(*p*-anisyl)formamidinate) exhibiting perpendicular Rh_2^{4+} and Mo_2^{4+} dinuclear units [168].

In light of the interest in 1-D novel materials with unusual electrical and physical properties, Ebihara *et al.* prepared and characterized several heterometallic 1D chains comprised of two or three metallic species with direct metal–metal bonds [169]. The 1D heterometallic chains were assembled with dirhodium(II) building units, bearing acetate, trifluoroacetate or acetamidate bridging groups, and pivalamidate diplatinum units, via Rh–Pt interactions, for example, $-\{[\text{Rh}_2]-[\text{Pt}_2]-[\text{Pt}_2]\}_n-$ (**85**, Figure 9.41) [169a]. In an attempt to prepare 1D paramagnetic chains, the authors introduced Cu^{2+} ions, resulting in novel trimetallic $-\{[\text{Rh}_2]-[\text{Pt}(\text{II})-\text{Cu}(\text{II})-\text{Pt}(\text{II})]\}_n-$ chains (**86**, Figure 9.42) exhibiting axially symmetric EPR spectra [169a].

9.2.4

Perspective

From the studies highlighted herein, it is obvious that dirhodium chemistry has continued to blossom during the last decade. The synthetic possibilities of dirhodium complexes span many fields and their applications cover a wide range of possibilities with emphasis on their viability as highly effective and efficient catalysts, providing unique advantages in the synthesis of natural products and pharmaceutical targets. The field is expected to continue expanding rapidly in the future as new developments occur in the chemistry of dirhodium compounds and new pertinent reactions are explored.

9.3

Iridium

In this section, the properties and reactivities of diiridium compounds that have two square planar ML_4 units that come together to form M_2L_4 compounds and closely related analogs will be discussed. The MM bond can be supported, which generates paddlewheel-type compounds, or unsupported, which generates square-parallelepiped-type compounds. The Ir–Ir bond lengths for diiridium compounds supported by formamidinate ligands are typically by ~ 0.2 Å shorter than compounds with unsupported Ir–Ir bonds (~ 2.5 vs 2.7 Å) [7]. Similar to their dirhodium analogs, diiridium tetraformamidinate species have a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ electronic configuration and a single Ir–Ir σ -bond.

9.3.1

Synthesis and Characterization of Diiridium Compounds

The $Ir_2(II,II)$ complex $Ir_2(O_2CCH_3)_2Cl_2(CO)_2(py)_2$ undergoes a variety of axial and equatorial ligand exchange reactions [170]. The reaction with $AgSbF_6$ yields the cationic complexes $[Ir_2(O_2CCH_3)_2(CO)_3Cl(py)_2][SbF_6]$ and $[Ir_2(O_2CCH_3)_2(CO)_2Cl(py)_3][SbF_6]$, upon the addition of CO or pyridine (py) to the reaction mixture. Reaction with 1-hydroxyisoquinoline (Hhiq) at $150^\circ C$ in naphthalene results in substitution of the two acetate ligands to yield $Ir_2(hiq)_2(CO)_2Cl_2$, whereas reaction with neat 2-hydroxy-4-methylpyridine (Hmhp) at $160^\circ C$ yields the triply bridged complex $Ir_2(\mu\text{-mhp})_3(CO)_2Cl(Hmhp)$. The reaction of the oxyquinoline complex with PPh_3 or 4-methylpyridine results in the formation of their corresponding axial adducts. The Ir–Ir bond lengths in these compounds were found to range from $2.5512(4)$ Å in the triply bridged mhp compound, to $2.6359(8)$ Å in $Ir_2(hiq)_2(CO)_2Cl_2(PPh_3)_2$.

One-electron oxidation of $Ir_2(OPy)_2(CO)_4$ ($[OPy]^- = 2\text{-pyridonate}$) with iodine or $[FeCp_2][PF_6]$ results in the immediate formation of the symmetrical diamagnetic tetranuclear chains $[Ir_2(OPy)_2(CO)_4I]_2$ and $[Ir_2(OPy)_2(CO)_4(MeCN)_2]_2[PF_6]_2$ [171]. Both compounds have two supported and one unsupported Ir–Ir bonds, which are $2.6966(8)$ Å (supported) and $2.7772(10)$ Å (unsupported) in $[Ir_2(OPy)_2(CO)_4(MeCN)_2]_2^{2+}$ [171b]. Addition of potassium phenylacetylide to $[Ir_2(OPy)_2(CO)_4(MeCN)_2]_2^{2+}$ displaces the acetonitrile ligands, resulting in the formation of $[Ir_2(OPy)_2(CO)_4]_2(CCC_6H_5)[PF_6]$ (Figure 9.43), in which the acetylide and tetranuclear Ir core form a nearly linear chain, with Ir–Ir bond lengths of $2.6923(7)$ (Ir¹–Ir²), $2.7621(16)$ (Ir²–Ir³) and $2.7935(7)$ (Ir³–Ir⁴) Å. DFT calculations indicate that the HOMO of this compound is a ligand-centered π -orbital, while the LUMO and HOMO-1 are iridium-based σ^* - and σ -orbitals formed from overlap of Ir d_{z^2} atomic orbitals. On the other hand, the reaction of $[Ir_2(OPy)_2(CO)_4(MeCN)_2]_2^{2+}$ with 1,4-bis(ethynyl)benzene results in the formation of an octanuclear species, in which two tetranuclear iridium chains are bridged by the diacetylide. DFT calculations on the one-electron oxidized form of this compound show full delocalization of the spin density of the unpaired electron across the molecule in the Ir- σ and acetylide- π orbitals, suggesting that these types of compounds are promising candidates for incorporation into molecular wires.

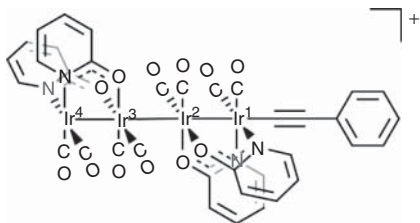


Figure 9.43 Structure of $[Ir_2(OPy)_2(CO)_4]_2(CCC_6H_5)^+$.

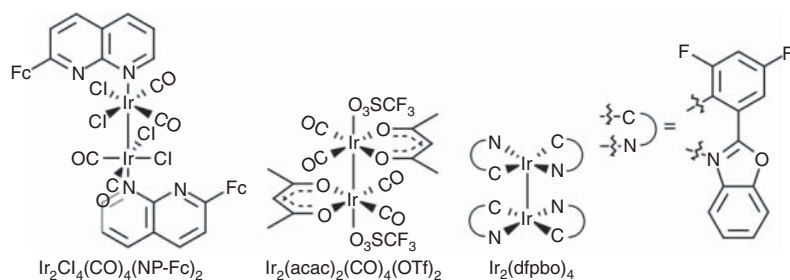


Figure 9.44 Structures of $\text{Ir}_2\text{Cl}_4(\text{CO})_4(\text{NP-Fc})_2$, $\text{Ir}_2(\text{acac})_2(\text{CO})_4(\text{OTf})_2$ and $\text{Ir}_2(\text{dfpbO})_4$.

Diiridium complexes with unsupported Ir–Ir bonds are scarce as compared to those containing supported bonds, although recently progress has been made in this area. For example, the reaction of $[\text{Ir}(\text{COD})(\eta^1\text{-NP-Fc})][\text{BF}_4]$ (NP-Fc = 2-ferrocenyl-1,8-naphthyridine) with CO in dichloromethane yields the purple iridium(II,II) dimer $\text{Ir}_2\text{Cl}_4(\text{CO})_4(\text{NP-Fc})_2$ (Figure 9.44) [172]. The reaction is thought to proceed via the formation of the diiridium(I,I) intermediates, with the solvent acting as the chloride source. The Ir–Ir bond length in this compound is 2.7121(8) Å, and DFT calculations support a $\sigma^2\pi^4\delta^2\pi^4$ electronic configuration.

The diamagnetic complex $\text{Ir}_2(\text{acac})_2(\text{CO})_4(\text{OTf})_2$ (Figure 9.44) was generated by the reaction of $\text{Ir}(\text{CO})_2(\text{acac})$ with AgOTf . It has a similar electronic structure to other diiridium compounds, but has the shortest unsupported Ir–Ir bond length known to date (2.6622(3) Å). The cyclometalated compound $\text{Ir}_2(\text{dfpbO})_4$ (dfpbO = 2-(3,5-difluorophenyl)benzooxalato-*N,C*^{2'}; Figure 9.44) also has an unsupported Ir–Ir bond (2.7357(10) Å) in the solid state [173]. In dichloromethane solutions at room temperature, however, the Ir–Ir bond is cleaved to generate the free radical $[\text{Ir}(\text{dfpbO})_2]^\bullet$, as evidenced by EPR spectroscopy.

9.3.2

Small Molecule and Bond Activation by Diiridium Compounds

As discussed in the rhodium Section 9.2.3.1, mixed-valence diphosphazine $\text{M}_2(0,\text{II})$ ($\text{M} = \text{Rh}, \text{Ir}$) compounds have rich addition and two-electron oxidation and reduction chemistries. Interest in these compounds arises in part because of the efficiency of bimetallic Group 9 complexes in the photocatalytic production of hydrogen from HX. The alkyl complexes $\text{Ir}_2\text{RBr}(\text{tfepma})_3$ (tfepma = $\text{MeN}[\text{P}(\text{OCH}_2\text{CF}_3)_2]_2$; $\text{R} = \text{CH}_3, \text{CH}_2\text{C}(\text{CH}_3)_3$; Figure 9.45) have been synthesized, and display relatively long Ir–Ir bonds of 2.82909(9) and 2.7910(8) Å for $\text{R} = \text{CH}_3$ and $\text{CH}_2\text{C}(\text{CH}_3)_3$, respectively [174]. Upon H_2 addition, the corresponding alkane is produced, with further H_2 addition yielding the diiridium(I,III) trihydride species $\text{Ir}_2(\text{H})_3\text{Br}(\text{tfepma})_3$. The trihydride has a relatively long Co–Co separation (2.8703(8) Å), and this interaction is considered being an $\text{Ir}^{\text{I}} \rightarrow \text{Ir}^{\text{III}}$ dative bond.

The closely related mixed-valence complex $\text{Ir}_2^{0,\text{II}}(\text{tfepma})_2(\text{CN}^t\text{Bu})_2\text{Cl}_2$ (Figure 9.45) reacts with HX ($[\text{X}]^- = [\text{Cl}]^-, [\text{OTs}]^-$) to generate $\text{Ir}_2^{\text{II,II}}(\text{tfepma})_2(\text{CN}^t\text{Bu})_2\text{Cl}_2\text{HX}$, and reacts reversibly with

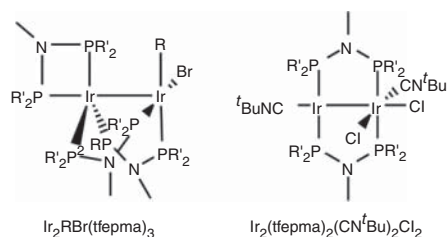


Figure 9.45 Structures of $\text{Ir}_2\text{RBr}(\text{tfepma})_3$ and $\text{Ir}_2(\text{tfepma})_2(\text{CN}^t\text{Bu})_2\text{Cl}_2$

dihydrogen to generate the *cis*-dihydride $\text{Ir}_2^{\text{II,II}}(\text{tfepma})_2(\text{CN}^t\text{Bu})_2(\text{H})_2\text{Cl}_2$. The substitution of tfepma with bis(diphenylphosphino)-methane (dppm) also results in the formation of $\text{Ir}_2^{\text{II,II}}$ hydride species, as one of the dppm ligands undergoes an intramolecular cyclometalation [175]. Thus, diiridium mixed-valence diphosphazine complexes can be used to generate a range of diiridium hydride complexes.

The diiridium compounds are convenient models for understanding the mechanistic details of O_2 reduction by the analogous dirhodium species, as shown earlier in Scheme 9.22 for dirhodium complexes, as it is possible to isolate and characterize plausible reaction intermediates with iridium. For example, $\text{Ir}_2(\text{tfepma})_2(\text{CN}^t\text{Bu})_2\text{Cl}_3\text{H}$ reacts cleanly with O_2 to generate the hydroperoxide complex $\text{Ir}_2(\text{tfepma})_2(\text{CN}^t\text{Bu})_2\text{Cl}_3(\text{OOH})$, and $\text{Ir}_2^{0,\text{II}}(\text{tfepma})_2(\text{CN}^t\text{Bu})_2\text{Cl}_2$ reacts with O_2 to form $\text{Ir}_2^{0,\text{II}}(\text{tfepma})_2(\text{CN}^t\text{Bu})_2\text{Cl}_2(\eta^2\text{-O}_2)$ [152c]. Both dioxygen reaction products were isolated as well as structurally and spectroscopically characterized. Kinetic [152c] and computational [176] studies demonstrate that these types of peroxide and hydroperoxide compounds are key intermediates in the reduction of O_2 to water using diiridium and dirhodium diphosphazine catalysts. Further evidence that these are plausible intermediates comes from acidolysis of $\text{Ir}_2(\text{tfepma})_2(\text{CN}^t\text{Bu})_2\text{Cl}_3(\text{OOH})$ with HCl, which induces cleavage of the O–O bond to release water [177].

Dinuclear iridium compounds can also perform C–H and C–F bond activation for a broad range of compounds [178]. For example, the activation of the C–F bond in trifluoroethylene is achieved selectively with $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\text{dppm})_2]$ [179], tandem C–F and C–H activation in fluoroolefins is promoted by $[\text{Ir}_2(\text{CO})_3(\mu\text{-H})(\text{depm})_2]^+$ (depm = bis(diethylphosphino)methane) [180], and intramolecular C–H bond activation is observed upon arylation of $\text{Ir}_2(\text{tfepma})_3\text{Cl}_2$ with $\text{C}_6\text{H}_5\text{MgBr}$ [181].

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10

Group 10 Metal–Metal Bonds

Erli Lu and Stephen T. Liddle

10.1

Introduction

This chapter focuses principally on bimetallic compounds (homo- and heterobimetallic), and the content is cataloged according to the metal atom incorporated into the metal–metal bond. Bimetallic compounds constitute the vast majority of reported group 10 metal–metal bonds, and are also the most thoroughly studied category both from structural and reactivity perspectives. The cluster compounds containing group 10 metals, although exhibiting fascinating structural and physical/chemical characters, are beyond the scope of this chapter. Useful reviews of these cluster compounds and the metal–metal interactions within them have been published elsewhere and are recommended to reader [1]. However, a brief introduction of sandwich compounds with a multimetallic group 10 metal atom sheet, which firstly emerged in 2006 and developed rapidly afterwards will be provided at the end of the chapter.

As the historic aspects of the chemistry of group 10 metal–metal bond have been excellently summarized in the textbook by Cotton *et al.* [2], major effort will be delivered on the latest developments in the last decade (2005–2014). Due to the fact that this 10 years witnessed an explosion of the field and an extremely large body of works has been reported in this time (a search of Cambridge Structural Database (CSD version 03/2014) with key word $M-M'$, where M and M' is an arbitrary group 10 metal, resulted in over 1000 hits published after 2005!), a comprehensive coverage of the literature is impracticable. Instead, representative synthesis, structural properties, reactivity, as well as applications in catalysis of these compounds will be focused on.

10.2

Bimetallic Compounds

This section discusses the group 10 homo- and heterobimetallic compounds with metal–metal bonds. The discussion for each metal follows the line of oxidation state, for example, dinickel(0), dinickel(I), and dinickel(II), while mixed-valent compounds are discussed in a section on their own for each metal. Heterobimetallic compounds with $M-M'$ bonds (M and M' are different group 10 metals) are discussed separately from the homobimetallic compounds. For the convenience of readers, values of $M-M'$ bond length are summarized in a table after each section.

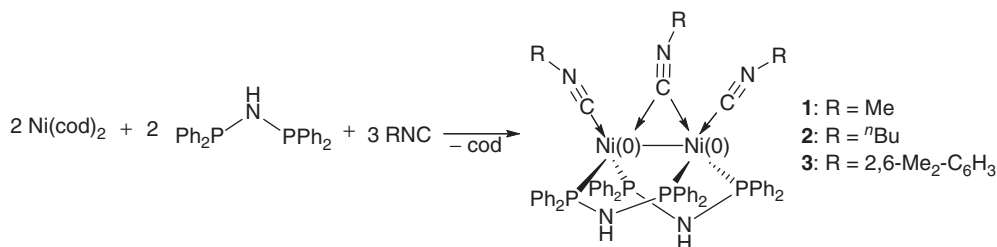
10.2.1

Dinickel Compounds

10.2.1.1 Dinickel(0) Compounds

Due to the potentially high occupancy of anti-bonding molecular orbitals (MOs) (δ^* , π^* , and σ^*) and the resulting destabilization effect, the electron-rich low-valent Ni(0)–Ni(0) compounds are less studied than their higher oxidation state counterparts. Olefin ligands, π -acids, for example, CO and its isoelectronic species, as well as monovalent group 13 ligands are prevalent in this category of chemistry.

A series of dinuclear Ni(0)–Ni(0) compounds with the general formula $[\text{Ni}_2(\mu\text{-dppa})_2(\mu\text{-CNR})(\text{CNR})_2]$ (dppa = bis(diphenylphosphine)amine, R = Me (**1**), $n\text{Bu}$ (**2**), 2,6- $\text{Me}_2\text{C}_6\text{H}_3$ (**3**)) were synthesized from reactions between Ni(0) precursor $[\text{Ni}(\text{cod})_2]$ (cod = cyclooctadiene), dppa, and corresponding isocyanide, in satisfactory yields (Scheme 10.1) [3]. Among them, **1** was structurally characterized by single-crystal X-ray diffraction. The Ni(0)–Ni(0) bond is bridged by two bidentate $\kappa^2\text{-P, P'}$ -dppa ligands and one monodentate $\mu\text{-C-MeNC}$ ligand. The Ni(0)–Ni(0) distance was reported as 2.5174(9) Å (Entry 1, Table 10.1), which is significantly shorter than the corresponding distance in its more flexible dppm (dppm = bis(diphenylphosphine)methane) counterpart $[\text{Ni}_2(\mu\text{-dppa})_2(\mu\text{-CNR})(\text{CNR})_2]$ (2.572(1) Å) [6]. It was found that the Ni(0)–Ni(0) moiety in **2** can undergo irreversible 1-electron reduction to produce a $[\text{Ni-Ni}]^-$ radical anion. If the reduction was carried out under CO_2 atmosphere, **2** can act as a catalyst for the electrochemical reduction of CO_2 into CO and CO_3^{2-} .



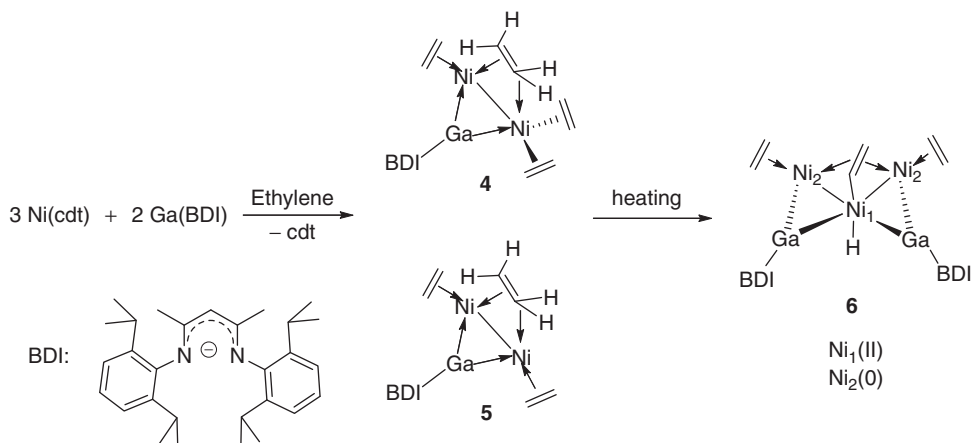
Scheme 10.1 Synthesis of $[\text{Ni}_2(\mu\text{-dppa})_2(\mu\text{-CNR})(\text{CNR})_2]$.

Monovalent group 13 ligands have been used to stabilize the Ni(0)–Ni(0) moiety. A Ga(I) β -diketiminato (BDI) compound $[\text{Ga}(\text{BDI})]$ was reported to react with $[\text{Ni}(\text{0})(\text{cdt})]$ (cdt = 1,5,9-cyclododecatriene) under an ethylene atmosphere, producing a trinuclear mixed-valent compound **6** via separable bimetallic Ni(0)–Ni(0) intermediates **4** and **5** (Scheme 10.2) [4]. The Ni(0)–Ni(0) bond lengths in **4** and **5** were reported as 2.5051(18) and 2.4830(14) Å (Entries 2 and 3, Table 10.1), respectively, and the agostic interaction between Ni(0) center and C–H bond of ethylene is notable. The mixed-valent Ni(0)–Ni(II)–Ni(0) compound **6** was produced by the oxidative addition of

Table 10.1 Ni(0)–Ni(0) bond lengths.

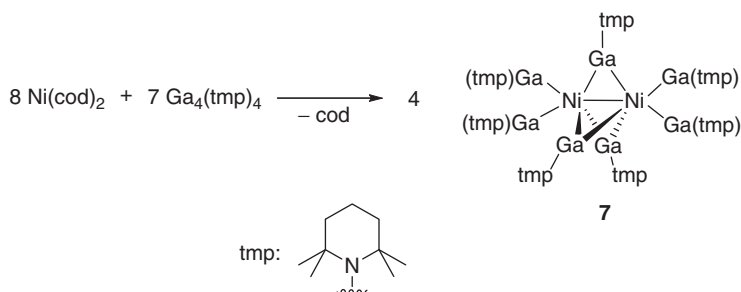
Entry	Compound	Ni(0)–Ni(0) bond lengths	References
1	1	2.5174(9) Å	[3]
2	4	2.5051(18) Å	[4]
3	5	2.4830(14) Å	[4]
4	7	2.522(1) Å	[5]

a C–H bond of coordinated ethylene toward the Ni(0) center under elevated temperature. The Ni(II)–Ni(0) bond length in **6** was determined to be 2.5531(5) Å.



Scheme 10.2 Synthesis of Ga(I)-ligand supported dinuclear Ni(0)–Ni(0) compounds (**4**, **5**) and trinuclear mixed-valent Ni(0)–Ni(II)–Ni(0) compound (**6**).

Another example of a Ga(I) ligand-bridging dinickel(0) compound was reported in 2008. The Ga(I) derivative [Ga₄(tmp)₄] (tmp = 2,2,6,6-tetramethylpiperidino) reacted with [Ni(cod)₂] to produce homoleptic [Ni₂{Ga(tmp)}₇] (**7**), via extrusion of the cod ligand (Scheme 10.3) [5]. Three of the [Ga(tmp)] ligands bridge the Ni₂ core, and the other four cap the two Ni centers as terminal ligands (two each). The Ni(0)–Ni(0) distance is reported to be 2.522(1) Å (Entry 4, Table 10.1).



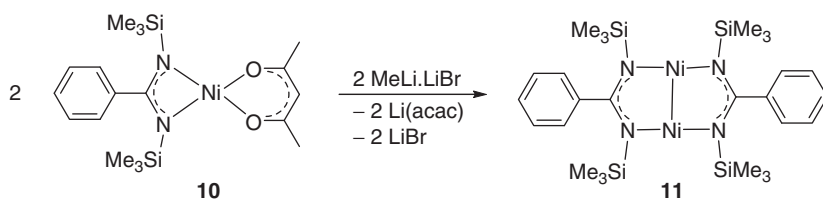
Scheme 10.3 Synthesis of [Ni₂{Ga(tmp)}₇].

Recently, a Ni(0)–Ga(I) adduct [Ni(cod)(GaAr')₂] (Ar' = 2,6-(2,6-*i*Pr₂-C₆H₃)₂-C₆H₃) (**8**) was reported to undergo addition toward one molecule of ethylene under mild conditions, giving the diamagnetic ethenylene bridging dinickel(0) compound [Ni₂(GaAr')₂(η¹:η¹-μ²-C₂H₄)] (**9**) as the product [7]. In **9**, the Ni–Ni distance was reported to be 2.437(5) Å, while the C–C distance within the bridging ethylene was consistent with a single bond (1.57(4) Å). These metric parameters indicate a reduction of ethylene to (H₂C–CH₂)²⁻. Generally speaking, Ni(0) compounds were widely used as 1- or 2-electron reductant, while the Ga(I) aryl dimer [Ar'Ga(I)–Ga(I)Ar'] had been reported to undergo oxidative addition/cyclometallation toward olefin/alkyne/dihydrogen/ammonia to produce [Ar'Ga(III)(R)(R')] (R, R' = alkane, alkene, hydride, amide) [8]. However, the oxidation state of Ni/Ga centers in **9** is open to debate.

10.2.1.2 Dinickel(I) Compounds

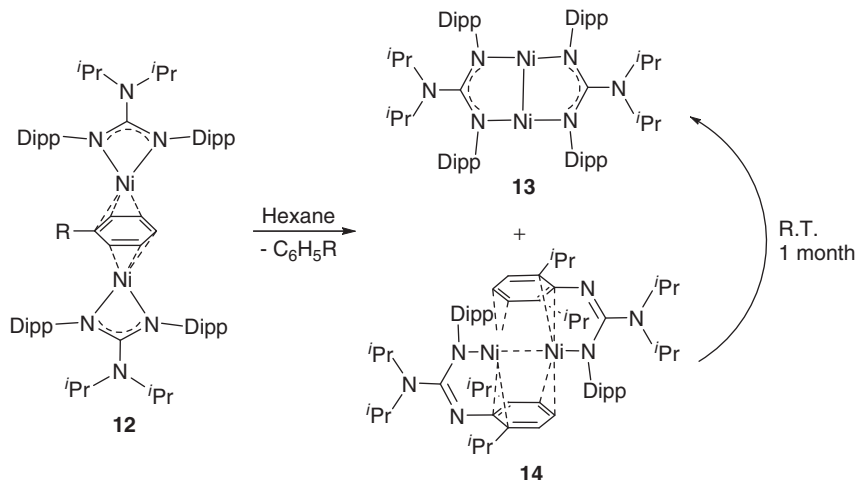
Compounds with Carboxylate, Amidinate, and Related Ligands Bisdentate monoanionic carboxylate and its nitrogen analogs (amidinate, guanidinate) are popular ligands for synthesizing paddlewheel compounds containing M–M bonds. For nickel, the higher oxidation state Ni(II) compounds are more prevalent, but still a few examples of dinickel(I) compounds with these ligands were presented in the last decade.

A bulky *N,N'*-trimethylsilyl-phenylamidinate ligand was used to support a series of Ni(II) compounds as a precatalyst for the polymerization/oligomerization of nonpolar olefin monomers as norbornene, ethylene, and propylene. Attempt to synthesize the corresponding Ni(II) alkyl from salt elimination between $[\text{PhC}(\text{NSiMe}_3)_2\text{Ni}(\text{II})(\text{acac})]$ (**10**) and MeLi, however, did not lead to the desired Ni(II) alkyl product, instead gave a reduced dinickel(I) dimer **11** (Scheme 10.4) [9]. In this reaction, the reductant is the alkyl lithium reagent MeLi. The Ni(I)–Ni(I) bond length in **11** is 2.2938(12) Å (Entry 1, Table 10.2), and sits at the lower boundary of Ni(I)–Ni(I) bond length. Complex **11** was found to be unstable at room temperature in solution, and undergoes a disproportionation into metallic nickel and corresponding bisamidinate Ni(II) compound $[(\text{PhC}(\text{NSiMe}_3)_2)_2\text{Ni}(\text{II})]$.



Scheme 10.4 Synthesis of $[\text{Ni}_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}N,N'\text{-PhC}(\text{NSiMe}_3)_2\}_2]$ (**11**).

Complex **13**, a bulky guanidinato analog of **11**, was produced from arene ligand elimination reaction of an dinickel(I) arene compound **12** in presence of alkane solvent, with its isomeric form **14** as co-product (Scheme 10.5) [10]. Compound **14** can be fully converted into **13** in hexane solution in 1 month at room temperature, thus **13** is the thermodynamic product while **14** is the kinetic



Scheme 10.5 Synthesis and interconversion of guanidinato-ligand supported dinuclear Ni(I)–Ni(I) compounds **13** and **14**.

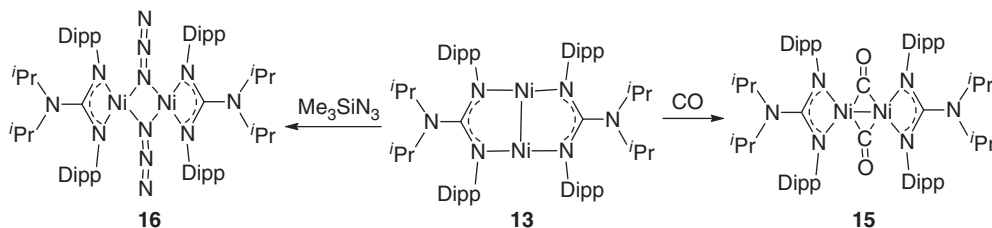
Table 10.2 Ni(I)–Ni(I) bond lengths.

Entry	Compounds	Ni(I)–Ni(I) (Å)	References
1	11	2.2938(12)	[9]
2	13	2.2908(11)	[10]
3	14	2.6338(9)	[10]
4	17	2.563(1)	[11]
5	19	2.4471(11)	[12]
6	20	2.3995(10)	[13a]
7	21	2.3918(8)	[13a]
8	22	2.4255(9)	[13a]
9	23	2.4015(3)	[13b]
10	24	2.4425(6)	[13b]
11	27	2.36580(16)	[14]
12	28	2.44266(19)	[14]
13	31	2.3201(2)	[15]
14	33	2.5248(3)	[16]
15	35	2.3510(3)	[17]
16	37	2.4238(4)	[17]
17	38	2.605(1)	[18]
18	40	2.2957(6)	[19]
19	44	2.3710(5)	[20]
20	48	2.3352(6)	[21]
21	50	2.515(1)	[22]
22	51	2.408(2)	[22]
23	54	2.5194(5)	[23]
24	55	2.5099(6)	[23]
25	57	2.314(1)	[24]
26	58	2.4354(9)	[25]
27	59	2.4152(6)	[26]
28	60	2.3259(2)	[27]

product. In **13**, the Ni(I)–Ni(I) bond length is 2.2908(11) Å (Entry 2, Table 10.2), which is one of the shortest Ni(I)–Ni(I) bond lengths [9], and suggests a very strong intermetallic interaction. In comparison, the Ni(I)–Ni(I) bond length in **14** is much longer (2.6338(9) Å) (Entry 3, Table 10.2) and indicates a weak intermetallic interaction. However, it should be noted that due to the diamagnetic nature of **14**, at least a weak Ni(I)–Ni(I) bond is present in this compound. In fact, an even longer Ni(I)–Ni(I) bond had been reported (2.693(2) Å) [28]. In contrast to the diamagnetism of **14**, **13** was proven to be paramagnetic. The room temperature solution magnetic moment of **13** ($2.10 \mu_{\text{B}}$ in d_{12} -cyclohexane) is smaller than the spin-only value for two uncoupled Ni(I) centers ($2.45 \mu_{\text{B}}$ for $S_1 = S_2 = 1/2$). Further magnetic studies revealed there was an antiferromagnetic coupling between the two Ni(I) centers within **13**. Theoretical studies identified a triplet ground state, as well as a triplet state and a singlet state being 3.6 and 3.9 kcal mol^{−1} higher in energy than the ground state respectively. The effective Ni(I)–Ni(I) bond order for the three states were determined as 0.62, 0.59, 0.62, respectively.

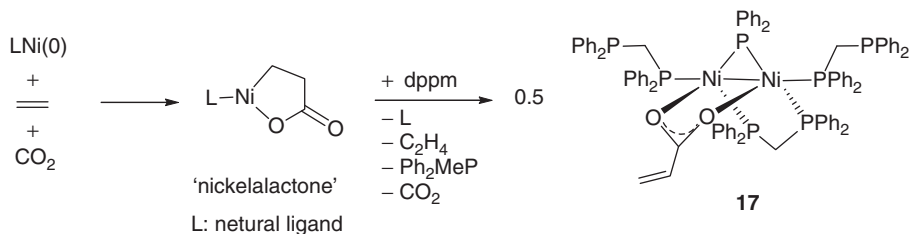
Reactivity studies of the dinickel(I) compound **13** were carried out (Scheme 10.6) [10]. The reaction between **13** and CO gas produces the dinickel(I) carbonyl compound **15**, with the Ni(I)–Ni(I) bond length elongated from 2.2908(11) in **13** to 2.437(1) Å in **15**. When **13** was treated with trimethylsilyl azide (Me_3SiN_3), a dinickel(II) azide **16** was obtained. The two Ni(II) centers

are separated from each other by a distance of 2.958(1) Å, which is too long for any intermetallic interaction.



Scheme 10.6 Reactivity studies of $[\text{Ni}_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}N,N'\text{-(}i\text{Pr}_2\text{N)C(NDipp)}_2\}_2]$ (**13**).

A dinickel(I) compound **17** was made from the reaction between metallacyclic Ni(II) carboxylate (“nickelalactone”) and bis(diphenylphosphino)methane (dppm) (Scheme 10.7) [11]. The Ni(I)–Ni(I) bond length in **17** is 2.563(1) Å (Entry 4, Table 10.2), and features three different bridging ligands (dppm, carboxylate, diphenylphosphido). The formation of **17** was proposed to proceed via the mechanism depicted in Scheme 10.8, and is remarkable because it acts as a model for the key step in the formation of acrylic acid from CO_2 and ethylene.

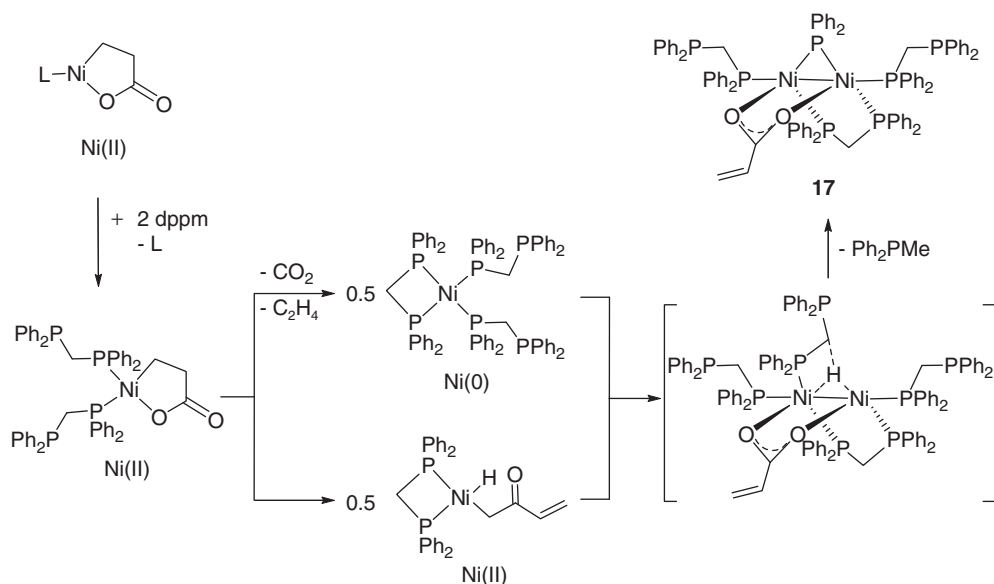


Scheme 10.7 Synthesis of $[\text{Ni}_2(\mu\text{-PPh}_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-O,O'-O}_2\text{CCH=CH}_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}\beta,\beta'\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]$ (**17**).

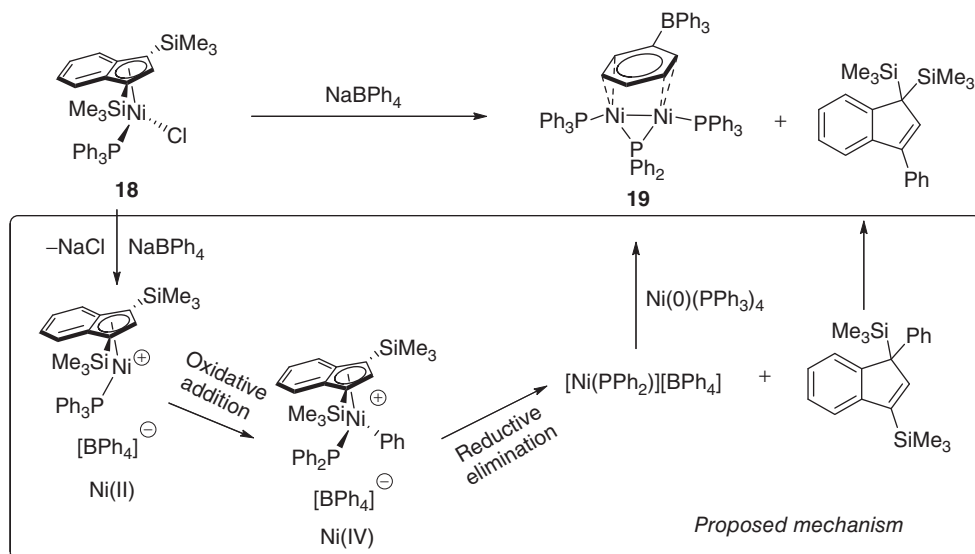
Compounds with Arene, Diene, and α -Diimine Ligands Arenes can act as effective neutral or anionic ligands in the organometallic chemistry of group 10 metals. The hapticity of these compounds is highly diverse and intriguing. Here, the dinickel(I) compounds with arene/diene/diimine bridging ligands in the last decade are highlighted, and in some instances their reactivity is summarized as well.

In 2005, the dinickel(I) zwitterion **19** was produced unexpectedly from reaction between nickel(II) indenyl chloride $[(1,3\text{-(SiMe}_3)_2\text{-ind)Ni(II)(PPh}_3\text{)(Cl)}]$ (**18**) and NaBPh_4 (Scheme 10.9) by Zagarian and coworkers [12]. The original target of the study was abstracting chloride from **18** to form a coordinative unsaturated and highly reactive Ni(II) cation species. However, **19** was formed as the major product, and the indenyl fragment was identified in the organic side-product 3-phenyl-1,3-bis(trimethylsilyl)indene. The elusive and remarkable $\text{syn-}\eta^2\text{:}\eta^2$ -bonding model of the phenyl ring in **19** was confirmed by X-ray crystallography, and the Ni(I)–Ni(I) bond length is 2.4471(11) Å (Entry 5, Table 10.2). The formation of **19** was suggested to occur via a Ni(IV) intermediate and following reductive elimination to extrude the indenyl ligand, and a comproportionation of Ni(II) and Ni(0) moiety to form **19** (Scheme 10.9).

After the pioneering work of Zagarian and coworkers, a handful of related $\text{syn-}\eta^2\text{:}\eta^2$ -coordinated arene-bridging dinickel(I) compounds were reported and are summarized in Scheme 10.10, and bond lengths of these Ni(I)–Ni(I) bond can be found both in Scheme 10.10 and Table 10.2 (Entries 6–10)

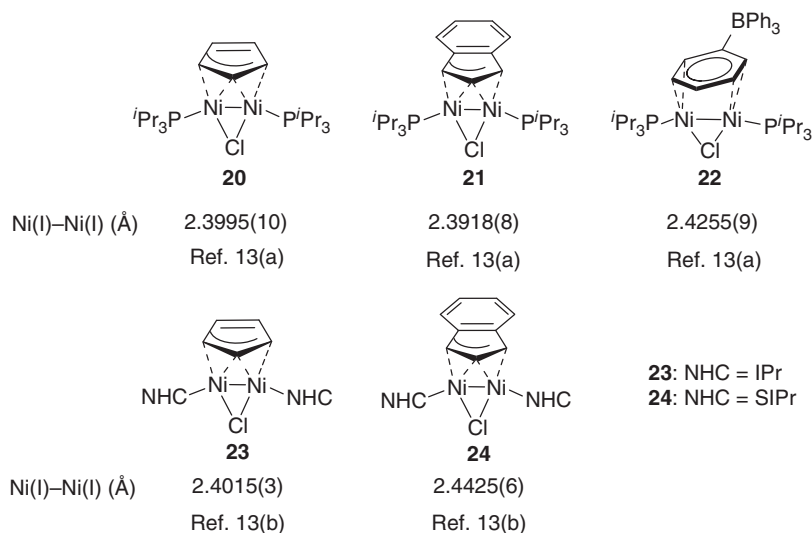


Scheme 10.8 Proposed mechanism for formation of dinickel(I) compound **17** from metallacyclic Ni(II) carboxylate “nickelalactone” and dppm.



Scheme 10.9 Synthesis of $[Ni_2(\mu-PPh_2)(\eta^1-PPh_3)_2\{(\mu-\eta^2:\eta^2-Ph)BPh_3\}]$ (**19**), and the postulated mechanism.

[13]. The methodology to synthesize these compounds can be salt elimination from Ni(I) precursor (for **20–22**) or comproportionation from Ni(II) and Ni(0) precursors (for **23, 24**).

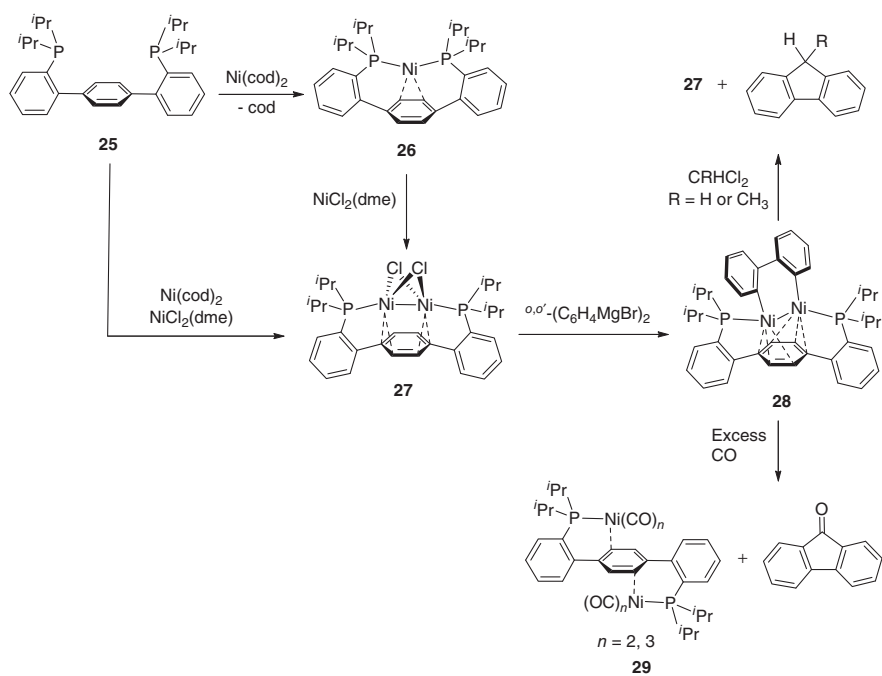


Scheme 10.10 $\text{syn-}\eta^2\text{:}\eta^2\text{-coordinated arene-bridged dinickel(I) compounds [13].$

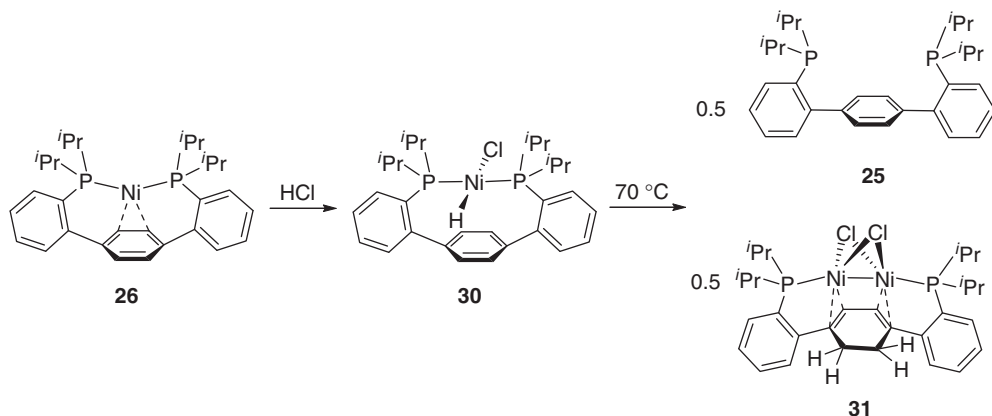
In 2010, an arene-tethered bis(phosphane) ligand (**25**) was used to stabilize a dinickel(I) compound (**27**) by Agapie and coworkers [14]. Compound **27** can be synthesized by comproportionation between a Ni(0) compound **26** and $[\text{NiCl}_2(\text{dme})]$, or by the reaction of ligand **25**, $[\text{Ni}(\text{cod})_2]$, and $[\text{NiCl}_2(\text{dme})]$ in a one-pot manner (Scheme 10.11). In **27**, the Ni(I)–Ni(I) core is bridged by two chlorides and one arene, and the Ni(I)–Ni(I) bond length is 2.36580(16) Å (Entry 11, Table 10.2). The metric parameters and the diamagnetism of **27** confirmed the existence of the Ni(I)–Ni(I) bond. Subsequent salt elimination of **27** in the presence of *o,o'*-bis(phenyldiyl) Grignard reagent led to a dinickel(I) bis(phenyldiyl) compound **28** (Scheme 10.11). In comparison with the parent compound **27**, the Ni(I)–Ni(I) bond in **28** is significantly elongated (2.36580(16) Å of **27** vs 2.44266(19) Å of **28**) (Entry 12, Table 10.2), and the bridging arene ring significantly deviates from planarity. Reactivity studies of **28** revealed the potential of the bimetallic compound to mediate fundamentally important C–C bond formation reactions. For example, **28** reacted with dichloroalkanes to produce fluorene derivatives with recovery of **27**; upon treating with CO, fluorenone was observed as product with concomitant formation of Ni(0) carbonyl **29**.

In the subsequent work, Agapie and coworkers demonstrated that the mononuclear Ni(0) compound **26** could be converted into a Ni(II) chloride hydride **30**, and subsequently transformed into a chloride- and diene-bridged dinickel(I) compound **31**, and free ligand **25**, upon heating via a nickel-to-arene H-migration (Scheme 10.12) [15]. In **31**, the Ni(I)–Ni(I) bond is rather short at 2.3201(2) Å (Entry 13, Table 10.2). The mechanism of the H migration was studied by isotopic labeling and a nickel-bound arenium species was invoked as an intermediate.

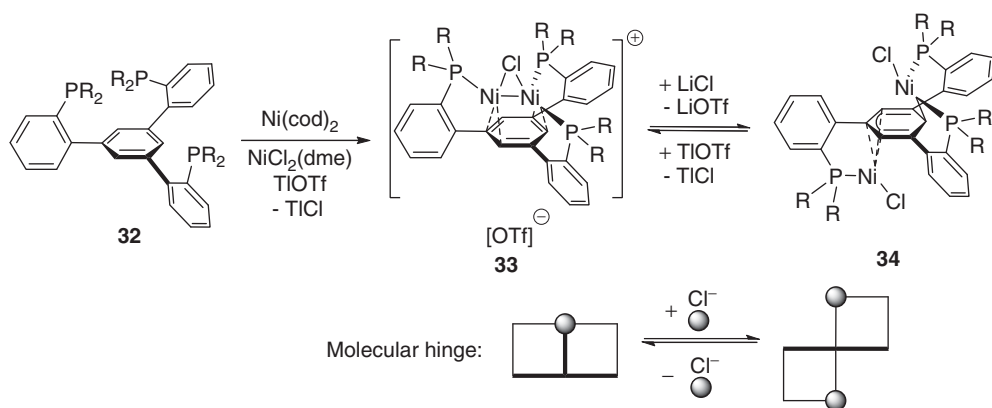
Based on their previous work, Agapie and coworkers extended the idea of using an arene-tethered multidentate phosphane ligand to construct a Ni–Ni bond and exploit their use in designing molecular device. A monochloride-bridging dinickel(I) compound (**33**) was synthesized based on an arene-tethered tri(phosphane) ligand (**32**) (Scheme 10.13) [16]. The Ni(I)–Ni(I) bond (2.5248(3) Å, Entry 14 in Table 10.2) in **33** undergoes a reversible halide-induced cleavage to form **34**, which is a dinickel(I) compound with a *trans*-conformation, thus constructing a molecular hinge (Scheme 10.13).



Scheme 10.11 Synthesis and reactivity of an arene-bridged dinickel(I) compounds **27** and **28**.



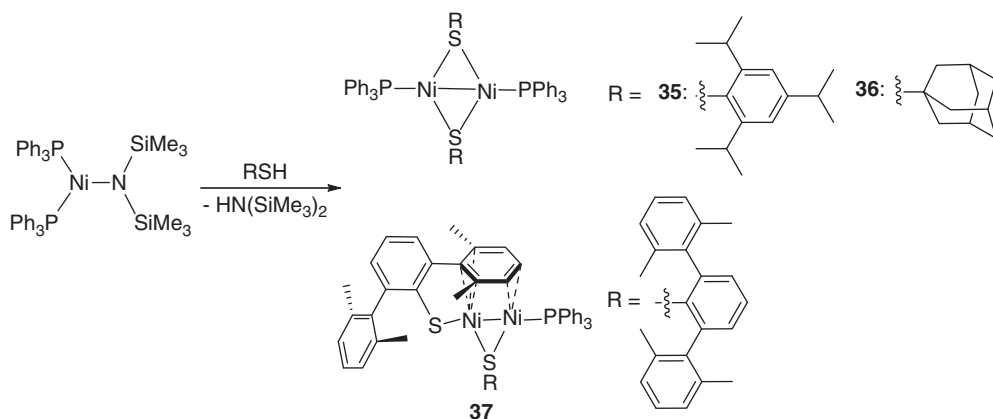
Scheme 10.12 Synthesis of an α -diene-bridged dinickel(I) compound (**31**) from dearomatization reaction.



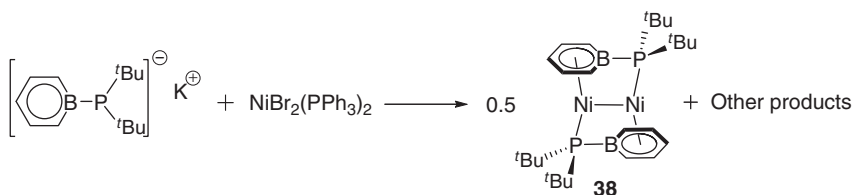
Scheme 10.13 Molecular hinge based on Ni(I)–Ni(I) bond.

Nickel(I) amide [Ni(N(SiMe₃)₂)(PPh₃)₂] was reported to react with thiols to produce dinickel(I) compounds with Ni(I)–Ni(I) bonds (Scheme 10.14) [17]. The structure of the dinickel(I) compounds depends on the substituents on the thiol: less sterically demanding thiols lead to S-bridged thiolate dimers **35** and **36**; thiols which are sterically bulky and with flanking aromatic substituents give the S- and arene-mixed-bridging thiolate dimer **37**. The Ni(I)–Ni(I) bond lengths in **35** and **37** are 2.3510(3) and 2.4238(4) Å, respectively (Entries 15 and 16 in Table 10.2).

Boratabenzene is a 6- π -electron isoelectronic analog of the cyclopentadienyl (Cp) anion. Recently, a new di-*tert*-butylphosphidoboratabenzene ligand was used to support a series of electronically unsaturated group 10 metal complexes [18]. Among them, the dinickel(I) compound **38** features a Ni(I)–Ni(I) bond, which is confirmed by X-ray crystallography (bond length: 2.605(1) Å) (Entry 17, Table 10.2) and the diamagnetism of the compound. The boratabenzene ring coordinates in a η^6 -mode. The synthesis started with a Ni(II) precursor [NiBr₂(PPh₃)₂] and **38** was produced in low yield (25%) (Scheme 10.15). These could be rationalized as the authors declared that there was an intermediate which cannot be isolated due to thermal instability, thus probably a disproportionation from Ni(II) to Ni(I) and higher oxidation state nickel species occurred.



Scheme 10.14 Synthesis of thiolate-bridged dinickel(I) compounds **35–37**.



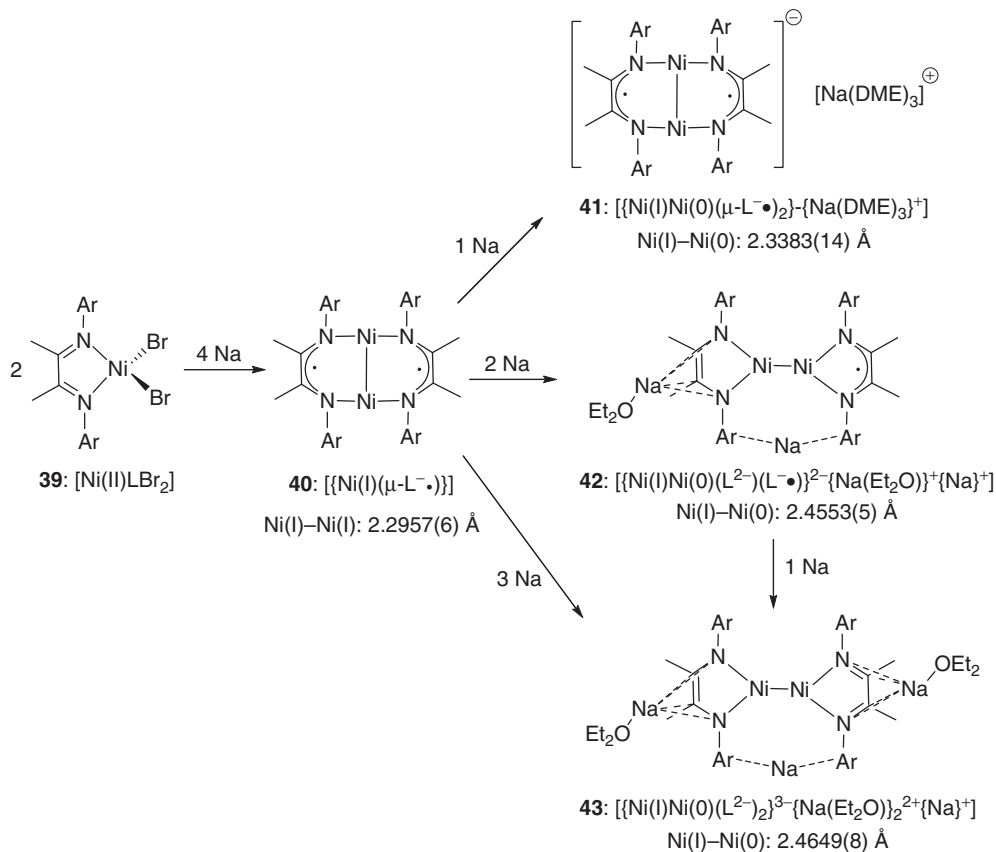
Scheme 10.15 Synthesis of $[\text{Ni}_2(\mu\text{-}\eta^1\text{-P-}\eta^6\text{-(C}_5\text{H}_5\text{)P}^t\text{Bu}_2)]$ (**38**).

α -Diimine is a type of important bidentate N,N-donor ligand, which was found to be crucial for the widely used DuPont's VersipolTM catalyst system [29]. Recently, α -diimine gathered increasing research interest due to its redox non-innocence character: in metal complexes it can be neutral, radical monoanionic, or dianionic. This character renders α -diimines to be ideal as an electron reservoir and versatile reactivities were realized based on that point.

In 2013, stepwise and controllable reductions of the α -diimine nickel(II) dibromide $[\text{LNiBr}_2]$ ($\text{L} = \{(2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3)\text{NC}(\text{CH}_3)_2\}_2$) (**39**) were studied and dinickel compounds **40–43** were obtained as products (Scheme 10.16) [19]. In the dinickel(I) compound **40**, the α -diimine ligand acts as radical monoanionic ligand ($\text{L}^{\cdot-}$). If further reductions were applied to **40**, both the Ni(I)–Ni(I) core and the radical monoanionic ligand ($\text{L}^{\cdot-}$) were found to be reducible, to produce a mixed-valent Ni(I)–Ni(0) core and L^{2-} dianionic ligand. The Ni–Ni bond lengths in compounds **40–43** increased gradually (Scheme 10.16). A DFT study was used to elucidate the σ -bond between two nickel centers and the role of different orbitals of nickel in Ni–Ni bonding. It was noteworthy that there are two coordinative modes for these dinickel compounds: perpendicular (**40**, **41**) and coaxial (**42**, **43**). For the coaxial compounds, an unsupported Ni–Ni bond was presented.

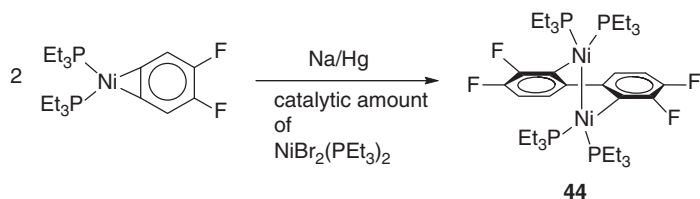
Compounds with Aryl and Aryne Ligands C–H and C–C bond activation/formation has become the most exciting field of research in recent decades. The dinickel(I) aryl and aryne compounds were usually studied as key intermediates in Ni(0) mediated C–H and C–C bond activation/formation on phenyl or other aromatic rings.

In 2006, it was found that $[\text{NiBr}_2(\text{PET}_3)]$ can act as catalyst for the transformation of a nickel aryne compound into the dinickel(I) biarylyl **44** in the presence of sodium amalgam (Scheme 10.17) [20]. A detailed study revealed that $[\text{NiBr}_2(\text{PET}_3)]$ was first reduced into $[\text{Ni}(0)(\text{PET}_3)_2]$, which subsequently formed a dinickel aryne complex and acted as the true catalyst. After oxidative



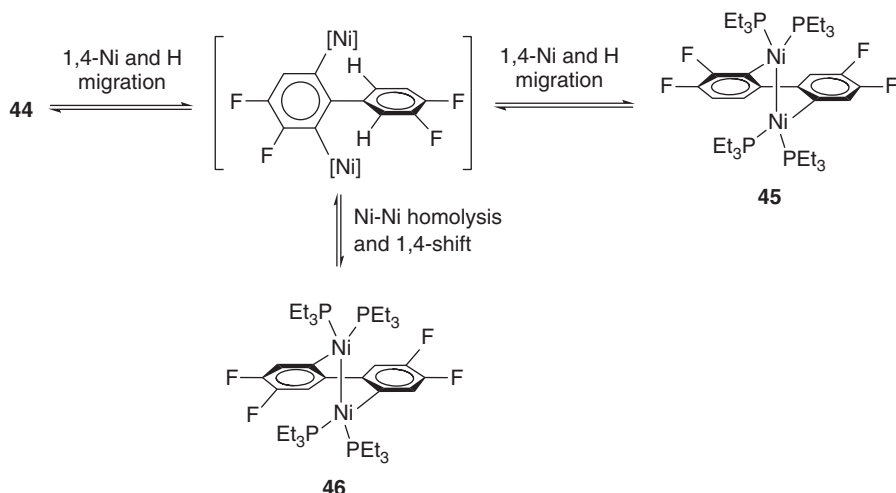
Scheme 10.16 Stepwise reduction of Ni(II) dibromide **39** to dinickel(I) and Ni(I)–Ni(0) compounds **40–43**.

addition, isomerization, and dimerization, the final product **44** was obtained. The presence of Ni(I)–Ni(I) bond (2.3710(5) Å) (Entry 19, Table 10.2) in **44** was confirmed by X-ray crystallography as well as multinuclear NMR. Further study demonstrated that the dinickel(I) compound **44** can undergo rearrangements and migrations to form two of its isomers **45** and **46** (Scheme 10.18) [30].



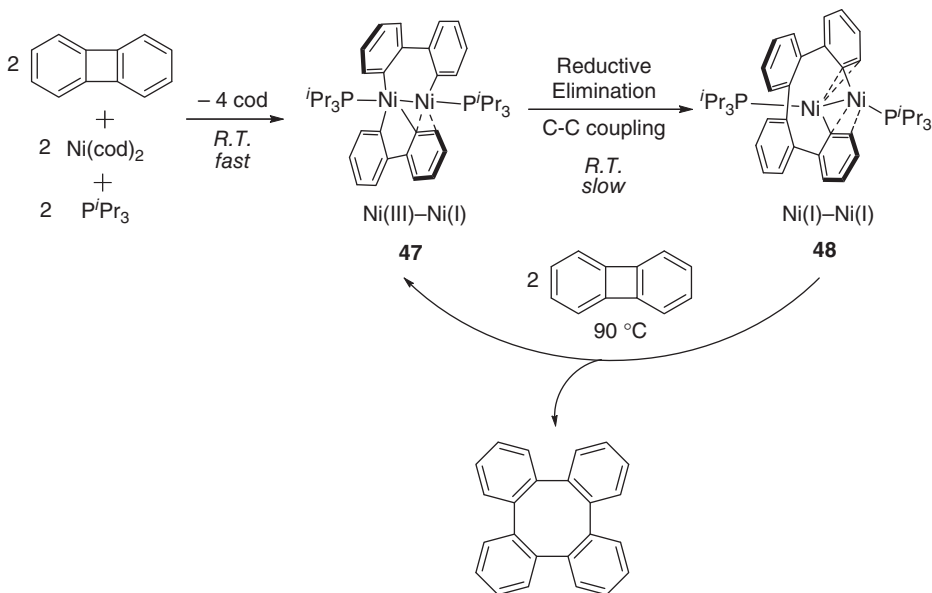
Scheme 10.17 NiBr₂(PEt₃)₂ catalyzed conversion of Ni(II) aryne compound into dinickel(I) biaryl compound **44**.

Ni(0) catalyzed ethyne cyclization to afford cyclooctatetraene (COT) and related biphenylene compounds, which involved a series of C–C bond couplings, were studied in the last decade, and dinickel(I) species were postulated as possible catalytic intermediates [31]. However, the mechanistic



Scheme 10.18 Isomerizations of the dinickel(II) biarylyl compound **44**.

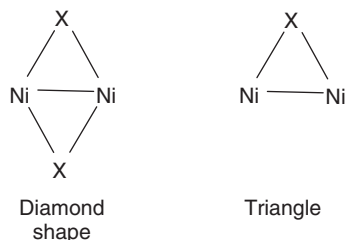
details of the catalytic process, especially for the C–C bond coupling step, are still ambiguous. In 2011, a novel Ni(I)–Ni(III) mixed-valent compound **47** was found to be key intermediate for the transformation [21]. Complex **47** was initially formed from the Ni(0) precursor $[\text{Ni}(\text{cod})_2]$, biphenylene, and phosphine ligand $[\text{P}^i\text{Pr}_3]$. Then, **47** was further converted into a Ni(I)–Ni(I) compound **48** via a reductive elimination at the Ni(III) center, which leads to C–C bond formation (Scheme 10.19). At elevated temperature, **48** reacted with 2 more equivalents of biphenylene to produce the cyclization product with recovery of **47**. The mechanism was further proven by an



Scheme 10.19 Dinickel(II) compound **48** acting as a key intermediate of C–C bond formation.

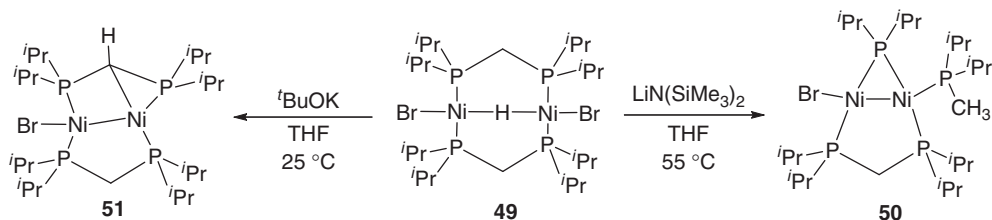
isotopic labeling experiment, to exclude the possible Ni(III)–Ni(I) bond cleavage in **47**. From a structural perspective, the Ni(III)–Ni(I) bond length in **47** is 2.3521(6) Å, while the Ni(I)–Ni(I) bond length in **48** is 2.3352(6) Å (Entry 20, Table 10.2).

Compounds with Other Ligands The Ni(I)–Ni(I) bond can be bridged by a monodentate anionic/neutral ligand to form a diamond-shape Ni_2X_2 core (X = monodentate anionic/neutral ligand) or a triangular Ni_2X core (Scheme 10.20).



Scheme 10.20 Diamond shape and triangle of monoatomic bridged Ni(I)–Ni(I) bond.

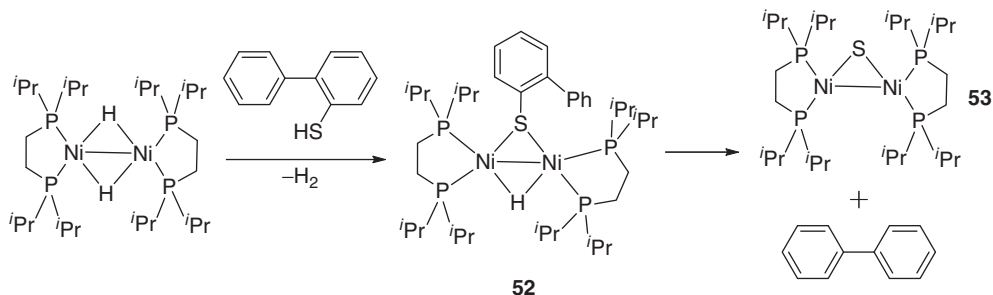
A mixed-valent dinickel monohydride **49** was found to react with bases ($^t\text{BuOK}$, $\text{LiN}(\text{SiMe}_3)_2$) to produce dinickel(I) compounds **50** and **51**, both of which feature a Ni(I)–Ni(I) bond (Scheme 10.21) [22]. Complex **50** features a triangular Ni_2P core with Ni(I)–Ni(I) bond length of 2.515(1) Å (Entry 21, Table 10.2); while **51** features a fused Ni_2PC and NiPC bicyclic core, with a significantly shorter Ni(I)–Ni(I) bond (2.408(2) Å) (Entry 22, Table 10.2) in comparison with that in **50**. These reactions involve sequences of deprotonation, C–H/C–P bond activation, and C–H bond formation, although the mechanism is still ambiguous.



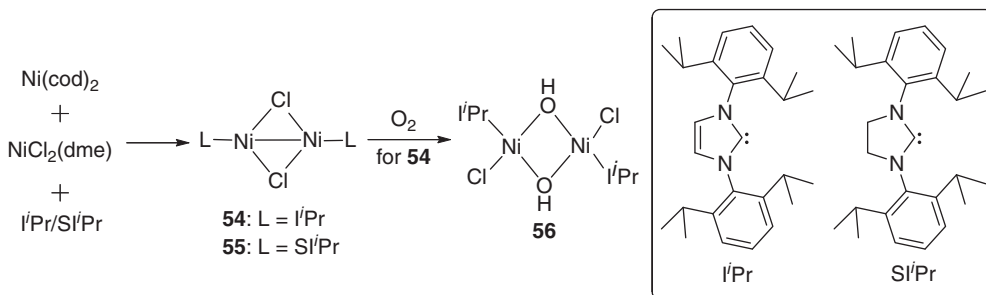
Scheme 10.21 Treatments of Ni(III)–Ni(I) hydride (**49**) with bases lead to dinickel(I) compounds (**50**, **51**).

Other bis(phosphane) ligands have found use in supporting this type of dinickel(I) compound. Starting from a known dinickel(I) dihydride $[\text{Ni}_2(\text{dippe})_2(\mu\text{-H})_2]$ [32], the dinickel(I) hydride thiolate compound $[\text{Ni}_2(\text{dippe})_2(\mu\text{-H})(\mu\text{-S-2-biphenyl})]$ (**52**) was separated as an intermediate of hydrodesulfurization of biphenyl-2-thiol [33], and was further converted into the dinickel(I) sulfido compound $[\text{Ni}_2(\text{dippe})_2(\mu\text{-S})]$ **53** (Scheme 10.22), with concomitant formation of biphenyl [34].

The *N*-heterocyclic carbene (NHC) ligand can play different roles in dinickel(I) compounds, either as a neutral $\kappa\text{-C}$ ligand, or, much more elusively, as an anionic ligand. Dinickel(I) μ -chloride compounds **54** and **55** were made from the comproportionation of Ni(0) and Ni(II) precursors in the presence of an NHC in good yield (Scheme 10.23) [23]. Both of the two compounds exhibited diamagnetic NMR spectra, and the Ni(I)–Ni(I) bond lengths in **54** and **55** are 2.5194(5) and 2.5099(6) Å, respectively (Entries 23 and 24, Table 10.2). NHCs here obviously act as neutral ligands. Further treatment of **54** with dioxygen produced a dinickel(II) μ -hydroxo chloride dimer **56**, with the cleavage of the Ni–Ni bond.

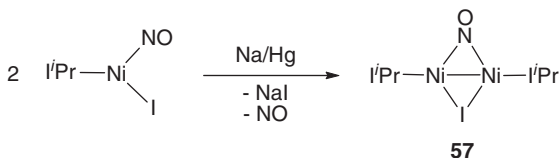


Scheme 10.22 Dinickel(I) compound mediated hydrodesulfurization.



Scheme 10.23 NHC-supported dinickel(I) compounds (**54**, **55**) and their oxidations by O₂.

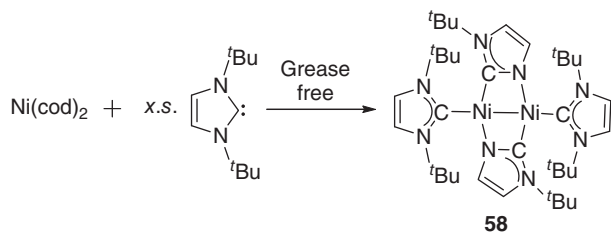
Another example of this type of neutral NHC-supported dinickel(I) compound is dinickel(I) μ -iodide μ -nitrosyl compound **57**, in which the two Ni(I) centers were bridged by an iodide and a nitrosyl, where the Ni(I)–Ni(I) bond length is 2.314(1) Å (Entry 25, Table 10.2). Complex **57** was made from the reduction of the Ni(II) nitrosyl iodide monomer [Ni(II)(*i*Pr)(NO)(I)] by sodium amalgam (Scheme 10.24) [24].



Scheme 10.24 Synthesis of [Ni₂(μ -I)(μ -N-NO)(*i*Pr)₂] (**57**).

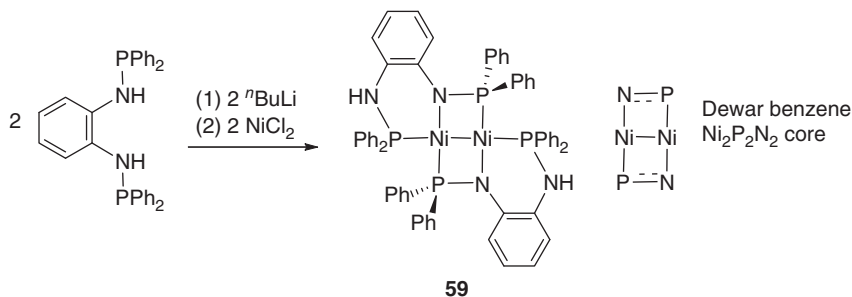
An elusive example of anionic NHC ligand in dinickel(I) chemistry can be found in Scheme 10.25 [25]. Compound **58** features both neutral and anionic NHC ligands, and the two nickel centers are bridged by two μ -*N,C* coordinated NHCs, with Ni(I)–Ni(I) bond length of 2.4354(9) Å (Entry 26, Table 10.2). Complex **58** was produced from the reaction between [Ni(cod)₂] and an excess amount of NHC in greaseless apparatus for a long period (14 days) with a relatively low but reproducible yield (~30%). Obviously, a N–C bond here is cleaved. It is noteworthy that with the presence of silicon grease, a Si=O bond-activated product was obtained.

Multidentate N,P-donor ligands were also used to support Ni(I)–Ni(I) bonds. A dinickel(I) compound **59** bearing a Dewar-benzene-type Ni₂P₂N₂ core was reported [26]. In this example, a



Scheme 10.25 Synthesis of a dinickel(I) compound (**58**) with bridging μ -N, C coordinated anionic NHC ligands.

bis-aminophosphine ligand was monodeprotonated and reacted with NiCl_2 to afford the dinickel(I) compound **59** (Scheme 10.26). The mechanism of reduction from Ni(II) to Ni(I) was ambiguous. In **59**, the Ni(I)–Ni(I) bond length is 2.4152(6) Å (Entry 27, Table 10.2). The Dewar benzene structure of the $\text{Ni}_2\text{P}_2\text{N}_2$ core was suggested by both metric parameters (P–N bond length = 1.640(2) Å) and a DFT calculation.



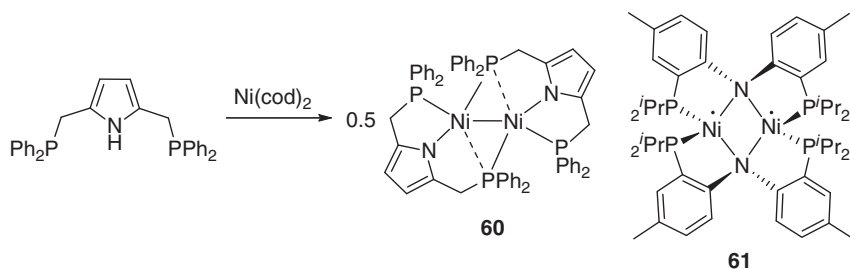
Scheme 10.26 Synthesis of **59** and the Dewar benzene $\text{Ni}_2\text{P}_2\text{N}_2$ core.

Recently, a novel monoanionic pyrrole-based PNP pincer ligand was synthesized and used to support a dinickel(I) compound **60**, which was prepared from the reaction between the ligand precursor and $[\text{Ni}(\text{cod})_2]$ (Scheme 10.27) [27]. Complex **60** can also be obtained from the corresponding mononuclear Ni(II) iodide upon treatment with reductant (LiEt_3BH). Compound **60** features a Ni(I)–Ni(I) bond length of 2.3259(2) Å (Entry 28, Table 10.2). It is intriguing to make a comparison of the magnetism of **60** and the related dinickel(I) compound **61**, which also bears a monoanionic pincer PNP ligand (Scheme 10.27) [35]. Although the Ni(I)–Ni(I) distance in **61** resembles that of **60** (**60**: 2.3259(2); **61**: 2.3288(7) Å), the existence of a Ni(I)–Ni(I) bond in **60** is confirmed by the diamagnetic behavior of the compound, while **61** is a paramagnetic diradical compound.

10.2.1.3 Dinickel(II) Compounds

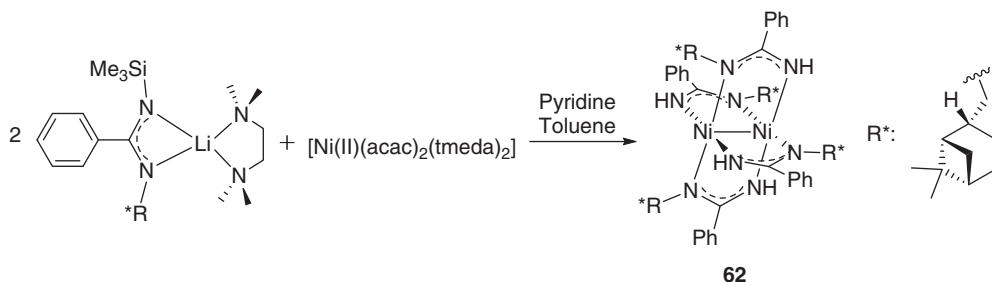
The +2 oxidation state of nickel (and also for Pd and Pt) gives rise to a stable closed-shell d^8 electronic configuration, thus it is the most prevalent for nickel in general inorganic chemistry. However, where metal–metal bonds are concerned, and from a MO perspective, the dinickel(II) Ni_2^{4+} moiety has an electronic configuration of $\sigma^2\pi^4\delta^2\delta^*\pi^4\sigma^*\pi^4$ which leads to a net bond order of 0 which will clearly be unfavorable for metal–metal bonding.

In the last decade, a few of dinickel(II) compounds with a Ni(II)–Ni(II) bond were reported, although they are not that prevalent compared to their dinickel(I) analogs. In the following section, a summary of these advances will be presented.



Scheme 10.27 Pyrrole-based PNP-pincer ligand precursor, its dinickel(I) compound **60**, and a related dinickel(I) diradical compound **61**.

A paddlewheel dinickel(II) compound **62** with a chiral and steric demanding benzamidinate ligand was synthesized in 2005 (Scheme 10.28) [36]. In **62**, the two Ni(II) centers adopt slightly distorted square pyramidal geometry, and the Ni(II)–Ni(II) bond length is 2.4484(13) Å (Entry 1, Table 10.3), which is significantly longer than its *N*-silyl-benzamidinate dinickel(I) analog (2.2990(12) Å) [9]. It is noteworthy that the *N*-trimethylsilyl group of ligand precursor was replaced by a proton, which was explained by a sequence of pyridine-induced proton abstraction from (acac)[−] and SiMe₃ abstraction.



Scheme 10.28 Synthesis of an amidinate ligand-supported paddlewheel dinickel(II) compound **62**.

A related paddlewheel dinickel(II) compound **63** with dtp ligand (dtp = dithiopropionate) was synthesized and characterized as a one-dimensional chain with moderate inter-dimer interaction (Figure 10.1) [37]. The intra-dimer Ni(II)–Ni(II) bond length is 2.5267(10) Å (Entry 2, Table 10.3), while the inter-dimer Ni(II)–Ni(II) distance is 3.644(2) Å. Although the inter-dimer metal–metal distance is longer than twice the van der Waals radius of nickel, some inter-dimer charge-transfer transitions were observed on diffuse reflectance spectra. The origin of the transition is the orbital interaction between two adjacent Ni(II)–Ni(II) σ^* orbitals.

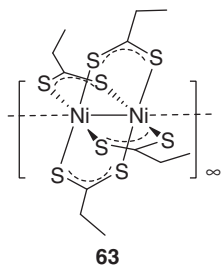
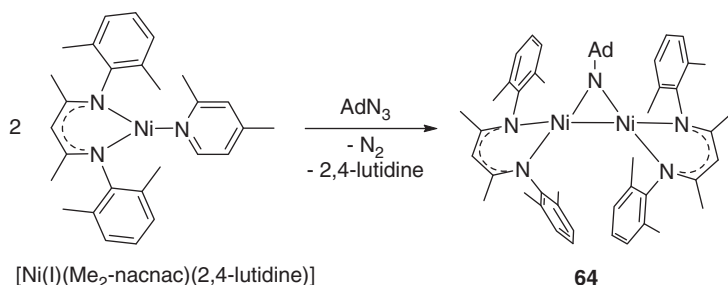


Figure 10.1 Dithiopropionate (dtp) ligand-supported paddlewheel dinickel(II) compound **63** with intermolecular Ni···Ni interaction.

Table 10.3 Ni(II)–Ni(II) bond lengths.

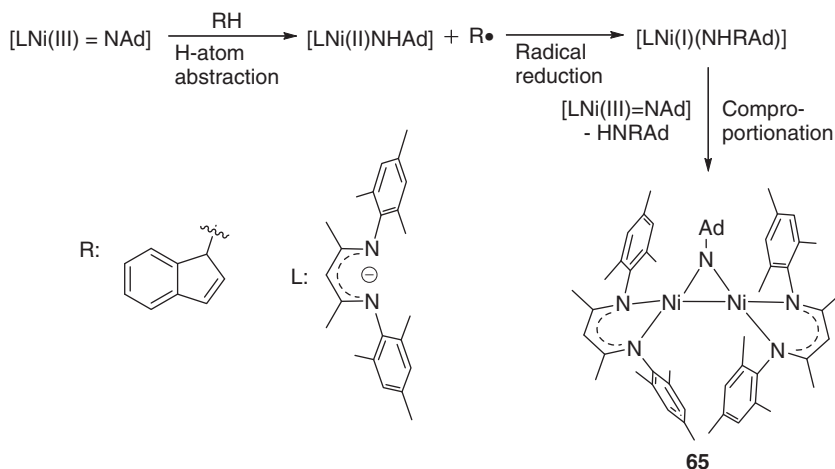
Entry	Compounds	Ni(II)–Ni(II) (Å)	References
1	62	2.4484(13)	[36]
2	63	2.5267(10)	[37]
3	64	2.506(1)	[38]
4	65	2.4872(7)	[39]
5	66	2.5767(15)	[40]
6	67	2.2911(8)	[40]
7	69	2.4312(10)	[41]
8	70	2.4385(9)	[41]
9	71	2.3158(10)	[42]

An imide (AdN^{2-}) bridging dinickel(II) compound **64** was produced upon the oxidation of mononuclear $[\text{Ni}(\text{Me}_2\text{-nacnac})(2,4\text{-lutidine})]$ ($\text{Me}_2\text{-nacnac} = \{(2,6\text{-Me}_2\text{-C}_6\text{H}_3)\text{NC}(\text{Me})_2\text{CH}\}$) by 1-azidoadamantane (Scheme 10.29) [38]. The Ni(II)–Ni(II) bond length is 2.506(1) Å (Entry 3, Table 10.3). Exceptionally, as a dinickel(II) d^8 compound, **64** was reported to be paramagnetic and exhibited a low solution magnetic moment at room temperature ($\mu_{\text{eff}} = 0.95 \mu\text{B}$ in C_6D_6 solution). This was proposed as a result of possible weak antiferromagnetic coupling.

**Scheme 10.29** Synthesis of $[\text{Ni}_2(\mu\text{-Nad})(\text{Me}_2\text{-nacnac})_2]$ (**64**).

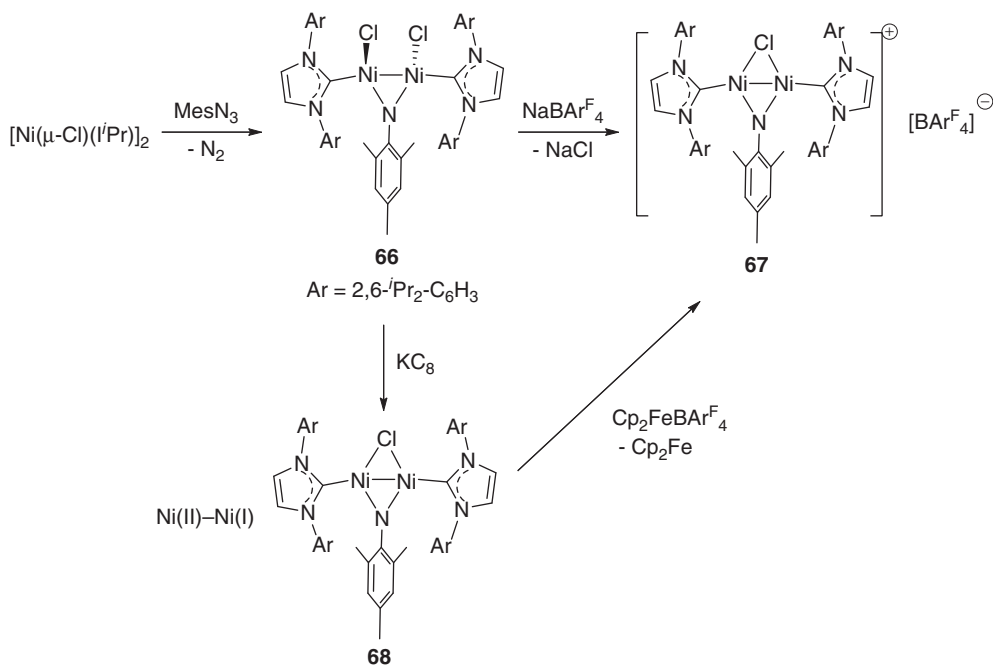
In a following report, another dinickel(II) bridging imide (**65**), the structure of which is nearly identical with **64** but with a slightly different ligand, was synthesized, but from an entirely different pathway (Scheme 10.30) [39]. Here, a Ni(III) terminal imide $[\text{LNi}(\text{III})=\text{NAd}]$ underwent H-atom abstraction and reduction to form the Ni(II) amide ($[\text{LNi}(\text{II})\text{NHAd}]$) and a free radical. The free radical further reduced the Ni(II) amide into a Ni(I) amine-adduct ($[\text{LNi}(\text{I})(\text{NHRad})]$), and the $[\text{LNi}(\text{I})(\text{NHRad})]$ underwent comproportionation with $[\text{LNi}(\text{III})=\text{NAd}]$ to form the dinickel(II) compound **65**, and the amine HNRAAd was separated as an organic side product. The Ni(II)–Ni(II) bond length in **65** is 2.4872(7) Å (Entry 4, Table 10.3).

Related dinickel(II) $\mu\text{-N}^{\text{imide}}$ bridging compounds with NHC ligands were reported by Hillhouse *et al.* in 2009 (Scheme 10.31) [40]. $[\text{Ni}(\text{I})(\mu\text{-Cl})(\text{I}^i\text{Pr})]_2$ underwent one-electron oxidation by MesN_3 to afford a dinickel(II) bridging imide $[\{\text{Ni}(\text{II})(\text{I}^i\text{Pr})(\text{Cl})\}_2(\mu\text{-NMes})]$ **66**, in which one of the chlorides can be abstracted by $\text{NaBAR}_4^{\text{F}}$ to produce the dinickel(II) ion pair compound **67**. The Ni(II)–Ni(II) bond lengths in **66** and **67** are 2.5767(15) and 2.2911(8) Å, respectively (Entries 5 and 6, Table 10.3). Complex **66** can also undergo one-electron reduction of the $[\{\text{Ni}(\text{II})\text{Cl}\}_2(\mu\text{-NMes})]$ core, to afford a mixed-valent Ni(I)–Ni(II) compound **68**, which upon treating with a one-electron oxidant gives **67** as the product. It is noteworthy that **67** and **68** bear similar core structures, but the Ni–Ni bond



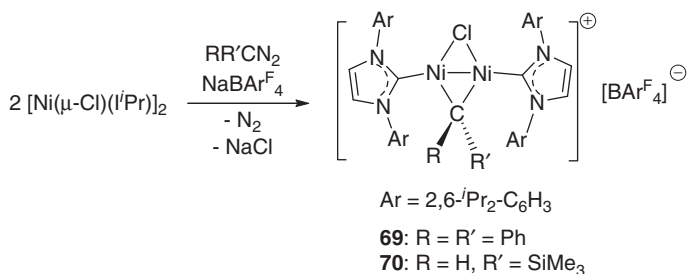
Scheme 10.30 Formation of a dinickel(II) compound **65** from H-atom abstraction, reduction, and comproportionation.

length in **68** is longer (2.3284(5) for **68**, 2.2911(8) Å for **67**), which is probably the result of one more anti-bonding orbital-occupying electron in **68**. The imido group in **66** can be transferred onto CO and PMe_3 to produce the corresponding isocyanate and phosphinimine, and **67** can act as a catalyst for isocyanate formation from MesN_3 and CO under ambient temperature with catalyst loading of 10 mol%.



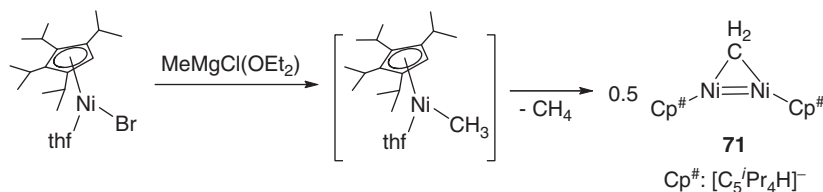
Scheme 10.31 Formation and interconversion of dinickel(II) compounds **66** and **67**, via a mixed-valent Ni(I)–Ni(II) compound **68**.

Beside imide, a carbene ligand ($RR'C^{2-}$) can also bridge two Ni(II) centers to form a Ni(II)–Ni(II) bond. Reaction between NHC-supported dinickel(I) dichloride dimers with diazoalkanes and $NaBAR^F_4$ produced carbene-bridged dinickel(II) compounds $\{[iPrNi(II)]_2(\mu-Cl)(\mu-CRR')\}[BAR^F_4]$ (**69**: $R=R'=Ph$; **70**: $R=H$, $R'=SiMe_3$) (Scheme 10.32) [41]. The Ni(II)–Ni(II) bond length is 2.4312(10) (**69**) or 2.4385(9) Å (**70**) (Entries 7 and 8, Table 10.3). Carbene group transfer reactions of **69** toward mesityl azide, CO, and *t*-butyl isocyanide were studied. For the reaction between **69** and 3 equiv. of CO, $Ph_2C=C=O$ and μ -chloride dinickel(I) carbonyl $\{[iPrNi(CO)]_2(\mu-Cl)\}[BAR^F_4]$ were obtained as products.



Scheme 10.32 Synthesis of carbene-bridged dinickel(II) compounds **69** and **70**.

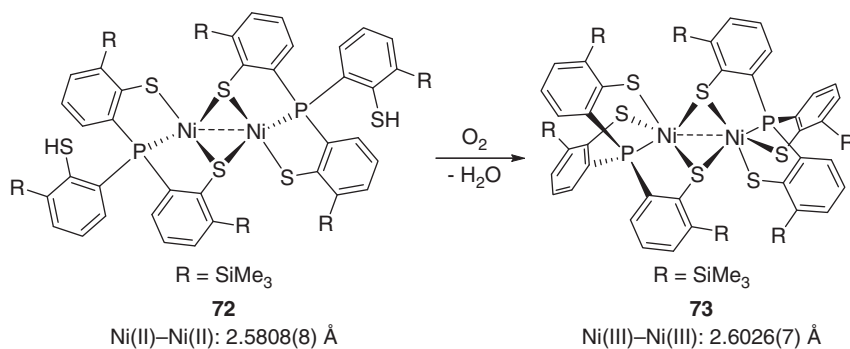
A dinickel(II) μ -methylene compound **71** supported by a bulky Cp derivative was reported in 2011 (Scheme 10.33) [42]. The formation of **71** was postulated to be as a result of α -H abstraction of a Ni(II) methyl compound and following intermolecular proton abstraction. Complex **71** is a diamagnetic compound. The valence-electron counting requires a Ni(II)=Ni(II) double bond, and the bond length is 2.3158(10) Å (Entry 9, Table 10.3).



Scheme 10.33 Synthesis of a methylene-bridged dinickel(II) compound **71**.

10.2.1.4 Dinickel(III) Compounds

In comparison with the abovementioned dinickel(0), dinickel(I), and dinickel(II) compounds, dinickel(III) compounds with metal–metal bonds are much more elusive. At the time of writing, only one example of this type of compound has been reported so far, which is supported by a phosphine-tethered multi-thiolate ligand. Upon treatment with dioxygen (O_2), dinickel(II) precursor **72** was oxidized into a dinickel(III) compound **73** (Scheme 10.34) [43]. **73** was confirmed as a diamagnetic compound by NMR, EPR, and magnetic measurements, thus the electronic structure of the compound can be best described as two antiferromagnetically coupled d^7 Ni(III) centers, both with $S = 1/2$ spin. The Ni(III)–Ni(III) bond length in **73** is 2.6026(7) Å (Entry 1, Table 10.4), which is slightly longer than Ni(II)–Ni(II) bond length (2.5808(8) Å) within its parent dinickel(II) compound **72**, but the difference in steric profile should be taken into account.



Scheme 10.34 Synthesis of a dinickel(III) compound **73**.

Table 10.4 Ni(III)–Ni(III) bond lengths.

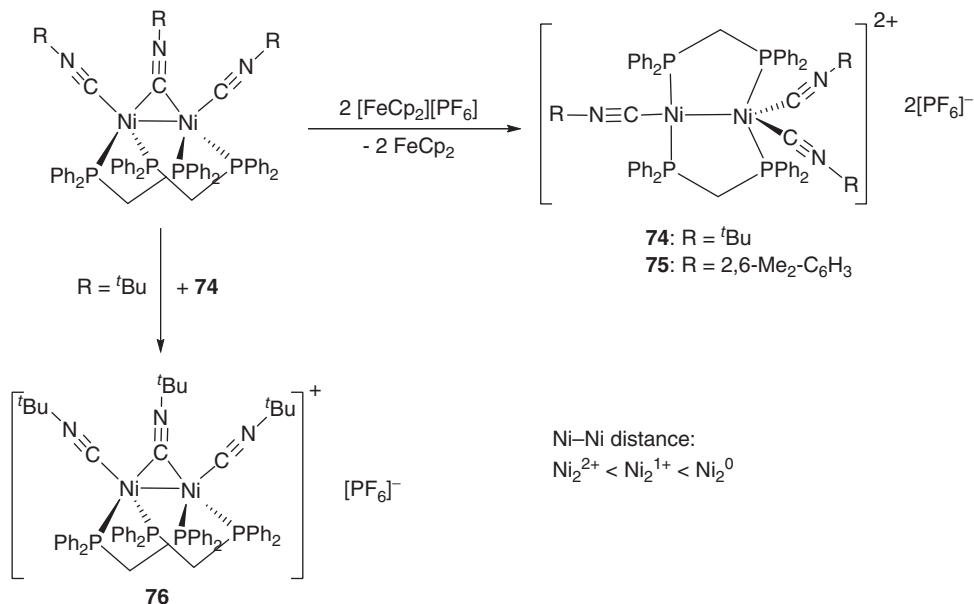
Entry	Compounds	Ni(III)–Ni(III) (Å)	Reference
1	73	2.6026(7)	[43]

10.2.1.5 Mixed-Valent Dinickel Compounds

In this section, advancements on mixed-valent dinickel compounds which were made in the last decade are summarized. For this type of compound, sometimes $\text{Ni}_2^{(n+m)+}$ is a better description rather than a discrete $\text{Ni}^{n+}\text{--Ni}^{m+}$, and fractional oxidation states are usually invoked.

Two-electron oxidation of a dppm- and isocyanide-supported dinickel(0) compound led to Ni_2^{2+} compounds **74** and **75**, and comproportionation of **74** and the dinickel(0) compound led to Ni_2^{1+} compound **76** (Scheme 10.35) [44]. In **74** and **75**, two nickel centers have different geometries, named square planar and tetrahedral, which is in support of a $\text{Ni(II)}\text{--Ni(0)}$ structure. While in **76**, the two nickel centers are equivalent with each other, which suggests a $\text{Ni(+0.5)}\text{--Ni(+0.5)}$ structure that is further supported by spectroscopic and electrochemical data. A comparison of the Ni–Ni distance between the Ni_2^0 precursor, Ni_2^{2+} , and Ni_2^{1+} species can be revealing: oxidation of the dinickel core leads to the contraction of Ni–Ni distance. The bond length in the Ni_2^0 precursor is 2.5555(10) (for $\text{R} = t\text{-Bu}$) or 2.6194(5) Å (for $\text{R} = 2,6\text{-Me}_2\text{-C}_6\text{H}_3$), while that for the Ni_2^{1+} compound **76** is 2.5879(8) Å, and that for the Ni_2^{2+} compounds is much shorter (2.3931(13) for **74**, 2.4813(10) Å for **75**) (Entries 1–3, Table 10.5).

Two dinickel(II) paddlewheel compounds with amidinate (**77**) or guanidinate (**78**) ligands were synthesized and their one-electron oxidation was studied (Scheme 10.36) [45]. In the Ni_2^{5+} compounds **79** and **80**, the Ni–Ni distance was found to be ~ 0.1 Å shorter than the corresponding dinickel(II) precursor (2.476(1) Å [77] vs 2.3703(4) Å [79]; 2.4280(5) Å [78] vs 2.3298(6) Å [80]) (Entries 4 and 5, Table 10.5). Based on this observation, it was proposed that upon oxidation one electron was removed from a metal-based σ^* orbital to give an overall Ni–Ni bond order of 1/2 in the Ni_2^{5+} species. Furthermore, a single-point calculation with no simplified solid-state structure of **79** suggested that the unpaired electron in the Ni_2^{5+} species is in a metal-based σ^* orbital, and this was also verified by a solution EPR spectrum.

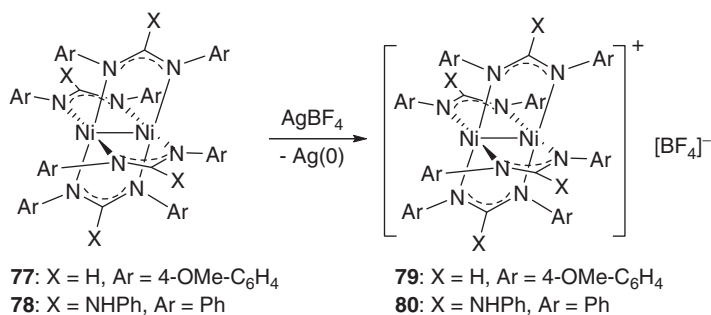


Scheme 10.35 Ni(II)–Ni(0) compounds **74** and **75**, Ni(0.5)–Ni(0.5) compound **76**.

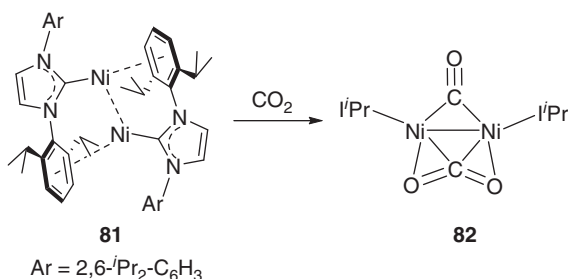
Table 10.5 Ni–Ni bond lengths in mixed-valent dinickel compounds.

Entry	Compounds	Ni–Ni (Å)	References
1	74	Ni(II)–Ni(0) 2.3931(13)	[44]
2	75	Ni(II)–Ni(0) 2.4813(10)	[44]
3	76	Ni(0.5)–Ni(0.5) 2.5879(8)	[44]
4	79	Ni(2.5)–Ni(2.5) 2.3703(4)	[45]
5	80	Ni(2.5)–Ni(2.5) 2.3298(6)	[45]
6	82	Ni(2.5)–Ni(2.5) 2.3374(4)	[46]

A NHC-coordinated dinickel(0) compound **81** was found to react with CO₂, giving a dinickel compound **82** with a doubly bridging CO₂ ligand and deoxygenation of CO₂ (Scheme 10.37) [46]. The novel coordinative mode of the CO₂ ligand is noteworthy, while all other related precedent with C atom coordinated to one metal center, the C atom in **82** acts as a μ²-bridge. In **82**, the CO₂ ligand is bent with a O–C–O angle of 133.43(15)°, and the C–O bond lengths are 1.2552(19) and 1.257(2) Å. These C–O bond lengths are significantly longer than that in free CO₂ (1.16 Å), but still are much shorter in comparison with a typical C–O covalent single bond (1.43 Å) [47]. The C–O distance in the carbonyl ligand of **82** is comparable with other nickel carbonyl compounds, and the Ni–Ni distance is 2.3374(4) Å (Entry 6, Table 10.5). The oxidation state of the dinickel core is still open to debate.



Scheme 10.36 Ni(II)–Ni(0) compounds **74** and **75**, Ni(0.5)–Ni(0.5) compound **76**.



Scheme 10.37 Synthesis of a mixed-valent dinickel compound **82** with bridging CO₂ and CO.

10.2.2

Dipalladium Compounds

Palladium catalyzed organic transformations (couplings, C–H and C–X bond activations, and much more) are cornerstones of modern organic chemistry. Thus, it is of the utmost importance to understand fundamental palladium organometallic chemistry, not only for the purpose of the organometallic chemistry itself but also for the development and design of catalysts for new, desirable organic transformations. The last decade witnessed the explosion of organopalladium compounds with Pd–Pd bonds, which was relatively less developed historically [2, 48]. These developments have not only extended the frontier of fundamental palladium organometallic chemistry but also inspired the emergence of new palladium catalysts for important organic transformation (such as C–H bond oxidation catalyzed by dipalladium(III) compounds, which will be further discussed in following section).

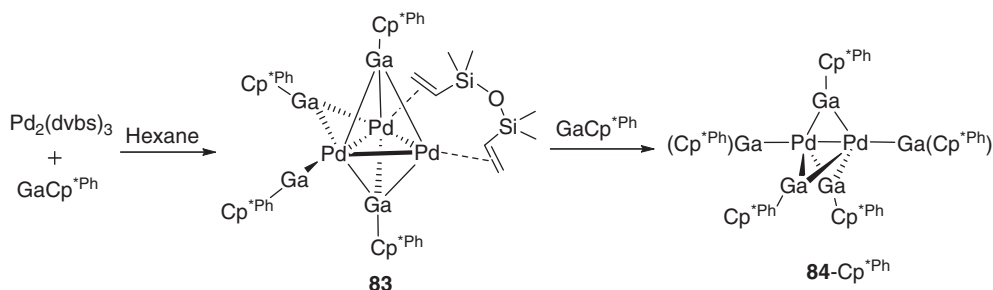
10.2.2.1 Dipalladium(0) Compounds

The d¹⁰–d¹⁰ Pd(0)–Pd(0) bond within dipalladium(0) compounds is expected to have no σ-bonding interaction, although some short Pd(0)–Pd(0) distances were reported (2.7–3.0 Å) [48, 49]. The bonding interaction was called “closed-shell attraction” and has been discussed in full theoretical detail [50].

As it was demonstrated earlier in the section for the Ni(0)–Ni(0) compounds, monovalent group 13 ligands can also stabilize dipalladium(0) compounds with Pd(0)–Pd(0) bond.

A steric bulky Ga(I) ligand [GaCp^{*Ph}] (Cp^{*Ph} = C₅Me₄Ph) was found to react with the Pd(0) precursor [Pd₂(dvds)₃] (dvds = tetramethyldivinylsiloxane) to produce tripalladium(0) cluster **83**, which can further react with the [GaCp^{*Ph}] to afford dipalladium(0) compound **84**–Cp^{*Ph} (Scheme 10.38)

[51]. Complex **84**-Cp^{*Ph} bears a similar structure to its dinickel(0) analog **7** [7], and is almost isostructural with its Cp^{*} analog [Pd₂(GaCp^{*})₃] (**84**-Cp^{*}) [52]. The bond lengths of the three Pd(0)–Pd(0) bonds in **83** vary from 2.591(1) to 2.841(1) Å (Entry 1, Table 10.6), which is dependent on the specific coordinative environment around the Pd(0) centers concerned. The Pd(0)–Pd(0) bond lengths in dipalladium(0) compounds **84**-Cp^{*Ph} and **84**-Cp^{*} are 2.572(10) and 2.609(1) Å, respectively (Entries 2 and 3, Table 10.6).



Scheme 10.38 Synthesis of tripalladium(0) (**83**) and dipalladium(0) (**84**) compounds that are supported by Ga(I) ligands.

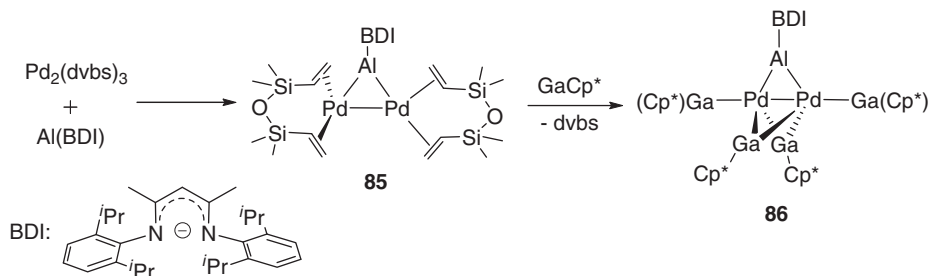
Complex **86**, an aluminum(I) analog of **84**, in which one of the bridging Ga(I) ligands was replaced by an Al(I) ligand, was obtained using [Pd₂(dvbs)₃] as the Pd(0) precursor (Scheme 10.39) [53]. A mono-Al(I) bridging dipalladium(0) dvbs compound **85** was separated as an intermediate of the conversion. The Pd(0)–Pd(0) bond lengths in **85** and **86** are 2.8589(7) and 2.5824(15) Å, respectively (Entries 4 and 5, Table 10.6).

Beside Ga(I) and Al(I) ligands, their lighter analog borylene ligand was also incorporated into a dipalladium(0) compound. Reaction between μ -borylene dimanganese(I) compound and [Pd(PCy₃)₂] gave the Pd(0)–Pd(0)–Mn(I) trimetallic compound **87** and [Cp'Mn(CO)₂(PCy₃)] (Cp' = C₅H₄Me) as products (Scheme 10.40) [54]. Complex **87** features a MnPd₂ triangle (bond lengths: Pd–Pd 2.8423(7), Mn–Pd 2.6458(10)/2.6426(10) Å) (Entry 6, Table 10.6), which is capped by μ^3 -coordinated borylene ligand.

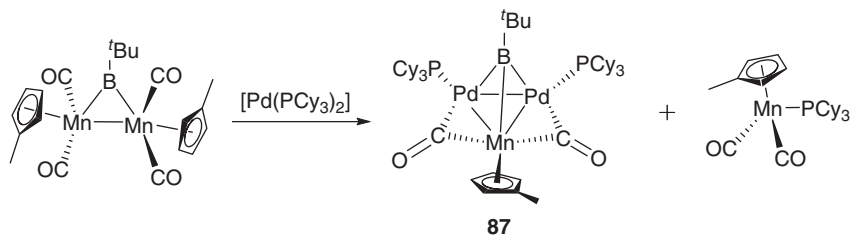
Dipalladium(0) compounds with μ -P, P'-coordinated diphosphane ligands [R₂P(CH₂)_nPR₂] have been known for long time [49a] and have been studied for their potential to activate organic halides and hydrosilanes [49, 56]. Recently, another example of this type of compound was reported from the reduction of Pd(II) dichloride with ⁿBuLi (Scheme 10.41). The dipalladium(0) compound **88** features a Pd(0)–Pd(0) bond (2.8560(6) Å) (Entry 7, Table 10.6), and can react with dichloromethane to produce dipalladium(II) compound [55].

Table 10.6 Pd(0)–Pd(0) bond lengths.

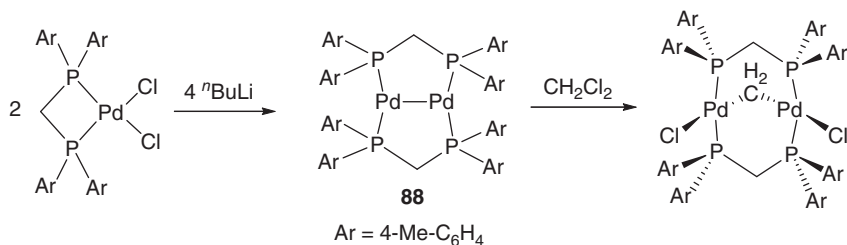
Entry	Compounds	Pd(0)–Pd(0) (Å)	References
1	83	2.591(1)	[51]
2	84 -Cp ^{*Ph}	2.572(10)	[51]
3	84 -Cp [*]	2.609(1)	[52]
4	85	2.8589(7)	[53]
5	86	2.5824(15)	[53]
6	87	2.8423(7)	[54]
7	88	2.8560(6)	[55]



Scheme 10.39 Synthesis of dipalladium(0) compounds (**85**, **86**) with bridging Al(I) ligand.



Scheme 10.40 Synthesis of Pd(0)–Pd(0)–Mn(I) cluster compound **87** with borylene fragment.



Scheme 10.41 Synthesis and reactivity of dipalladium(0) compound [Pd₂{μ-η¹:η¹-P, P'-(4-Me-C₆H₄)₂PCH₂P(4-Me-C₆H₄)₂}] (**88**).

10.2.2.2 Dipalladium(I) Compounds

In consideration of electronic configuration, the Pd(I)–Pd(I) compound should have a Pd–Pd σ-bond. From a perspective of structure, there are two extreme geometries of the dipalladium(I) compounds: ‘corner-sharing’ and ‘edge-sharing’ (Figure 10.2). The former bears an unsupported Pd(I)–Pd(I) bond, while the latter features a bridging neutral or anionic ligand, and there are some other geometries in between these two extremes. The early examples of these compounds were comprehensively covered in an earlier review [48]. In the following section, advancements in the last decade are summarized and cataloged according to type of geometry as well as the bridging ligand incorporated.

Compounds with Unsupported Pd(I)–Pd(I) Bond – ‘Corner-Sharing’ Geometry This type of Pd(I)–Pd(I) compound has a long history and is fundamentally important in understanding the nature of the Pd(I)–Pd(I) bond, in homogeneous catalytic reactions, and as model complex for cluster and for metallic surfaces [57]. The two four-coordinate square planar Pd(I) centers are connected by an unsupported Pd(I)–Pd(I) bond, with the bond length usually less than 2.6 Å,

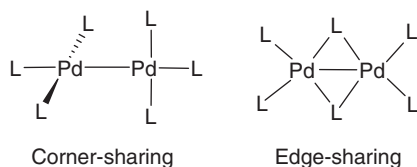
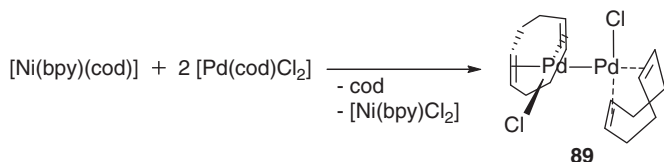


Figure 10.2 Two extreme geometries of dipalladium(I) compound: ‘corner-sharing’ and ‘edge-sharing’.

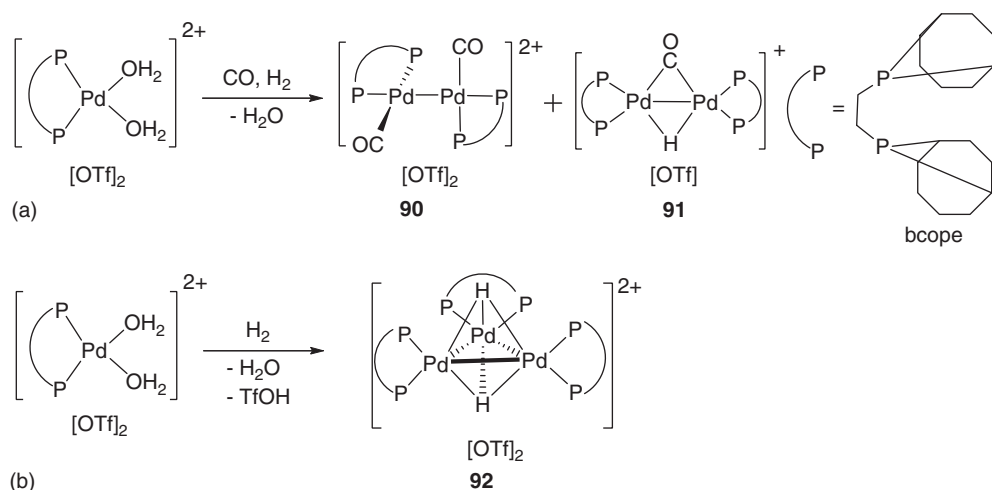
which is generally shorter than that of the bridging Pd(I)–Pd(I) bond. But it needs to be borne in mind that the Pd(I)–Pd(I) bond length is strongly dependent on the ligand steric profile, thus comparisons of bond strength based only on bond length is a dangerous extrapolation and can be misleading.

A dipalladium(I) dichloride **89** was synthesized from the reduction of a Pd(II) precursor using Ni(0) reductant in 2006 (Scheme 10.42) [58]. The Pd(I)–Pd(I) bond length in **89** is 2.5379(4) Å (Entry 1, Table 10.7), with both of the Pd center in a square planar environment.



Scheme 10.42 Synthesis of dipalladium(I) compound **89** with unsupported Pd(I)–Pd(I) bond.

Hydroformylation, known as an oxo process, which converts alkene, H₂, and CO into higher value organic carbonyl compounds, is fundamentally important for modern chemical industry [88]. To understand the mechanism of the palladium catalyzed oxo process, the reaction of the Pd(II) compound [Pd(bcope)(H₂O)₂(OTf)₂] with CO/H₂ was studied (Scheme 10.43a) [59]. The [Pd(bcope)(H₂O)₂(OTf)₂] was reduced by H₂ to produce two dipalladium(I) products **90** and **91**, among them **90** was characterized by X-ray crystallography. The Pd(I)–Pd(I) bond length in **90**



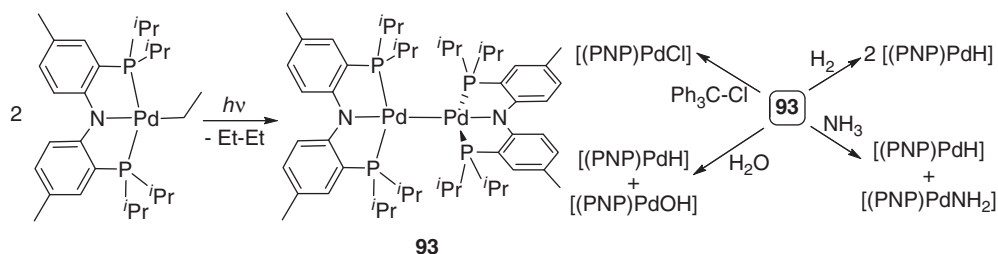
Scheme 10.43 Reactions of Pd(II) precursor with H₂/CO.

Table 10.7 Pd(I)–Pd(I) bond lengths.

Entry	Compounds	Pd(I)–Pd(I) (Å)	References
1	89	2.5379(4)	[58]
2	90	2.6085(4)	[59]
3	93	2.5758(4)	[60]
4	93-F	2.7167(2)	[61]
5	95	2.530(1)	[62]
6	96	2.752(1)	[63]
7	97	2.6704(9)	[64]
8	98	2.429(4)	[65]
9	99	2.4309(3)	[66]
10	100	2.4202(3)	[66]
11	101	2.4158(4)	[66]
12	102	2.5824(3)	[67]
13	103	2.5459(8)	[68]
14	104	2.3952(8)	[69]
15	105	2.5898(3)	[70]
16	106	2.637(2)	[71]
17	107	2.6186(12)	[72]
18	108	2.5309(9)	[73]
19	109	2.5755(7)	[73]
20	110	2.6182(5)	[74]
21	111	2.5649(5)	[75]
22	112	2.5627(8)	[76]
23	113	2.7037(3)	[77]
24	114	2.7265(4)	[78]
25	115	2.558(6)	[79]
26	116	2.5892(7)	[80a]
27	117-H	2.4783(9)	[80b]
28	117-Me	2.4800(6)	[80b]
29	118	2.5683(3)	[80b]
30	119	2.9400(5)	[81]
31	120	2.770(1)	[81]
32	121-Cy	2.5971(8)	[82]
33	121-Ph	2.6031(6)	[82]
34	123-H	2.7112(4)	[83]
35	123-Me	2.6920(5)	[83]
36	124-PMe₃	2.6386(5)	[83]
37	124-PPh₃	2.6267(3)	[83]
38	125	2.5489(7)	[84]
39	126	2.5230(4)	[84]
40	127	2.5470(5)	[85]
41	128	2.7530(4)	[86]
42	129	2.4565(3)	[87]

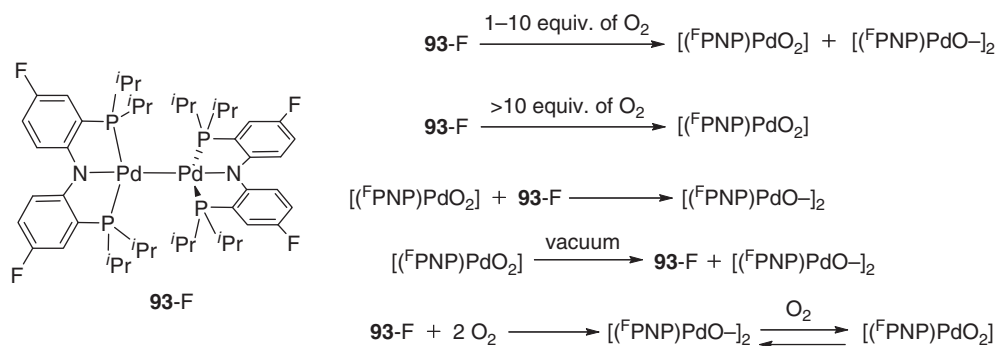
is 2.6085(4) Å (Entry 2, Table 10.7), and the square planar geometry of the two Pd(I) centers are orthogonal to each other along the Pd(I)–Pd(I) bond. If the reduction of [Pd(bcope)(H₂O)₂(OTf)₂] was carried out solely with H₂, a mixed-valent tripalladium Pd₃⁴⁺ compound **92** was obtained as the product (Scheme 10.43b). The Pd₃⁴⁺ triangle is perfectly equilateral and the Pd–Pd distance is 2.8280(12) Å.

A ‘corner sharing’ dipalladium(I) compound with PNP-pincer ligand (**93**) was synthesized by Ozerov and coworkers from photolysis of a Pd(II) alkyl precursor (Scheme 10.44), in which the Pd(I)–Pd(I) bond length was reported as 2.5758(4) Å (Entry 3, Table 10.7) and was validated as a Pd(I)–Pd(I) single σ-bond [60]. The Pd(I)–Pd(I) bond in the compound was proven to have versatile reactivity toward organic small molecules. A reactivity study revealed that C–X, H–H, and H–E (E=O, N) bonds can add across the Pd(I)–Pd(I) bond to afford the corresponding Pd(II) compounds, which represents a new pathway of activation of H₂, H₂O, and NH₃.



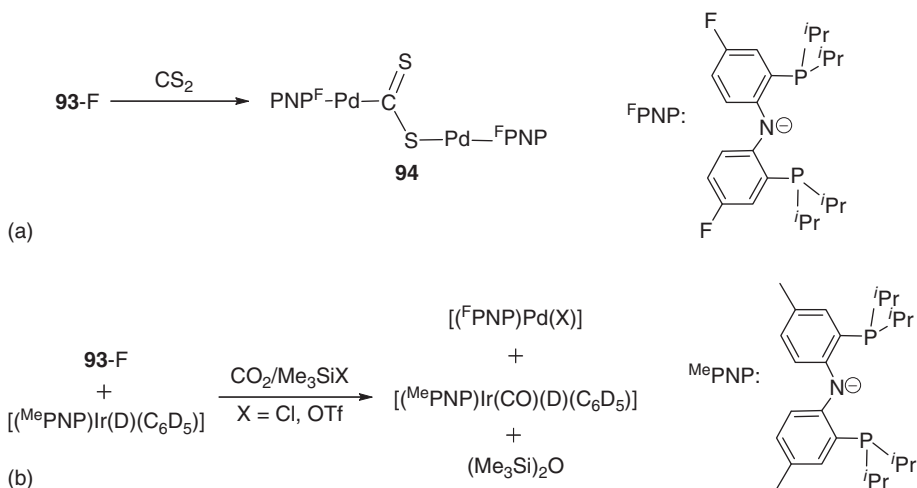
Scheme 10.44 Dipalladium(I) compound **93** and the addition reactions across the Pd(I)–Pd(I) bond.

In their following work, an F-substituted analog of **93** (**93-F**) was found to reversibly react with O₂, to produce Pd(II) superoxide [(^FPNP)PdO₂] or peroxide [(^FPNP)PdO–]₂ (Scheme 10.45) [89].



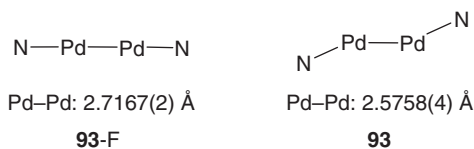
Scheme 10.45 Dipalladium(I) compound **93-F** and its reactivity toward O₂.

After the O₂ activation, reactions between **93-F** and CO₂ or CS₂ were examined very recently (Scheme 10.46) [90]. For CS₂, the C=S bond inserted into the unsupported Pd(I)–Pd(I) bond to form a dinuclear Pd(II) compound [(^FPNP)Pd(II)–C(S)–S–Pd(II)(^FPNP)] (**94**) (Scheme 10.46a). CO₂, on the other hand, was found to be inactive toward **93-F** by itself. However, it was found that with presence of [Me₃SiCl] and an iridium CO-trapping reagent, CO₂ can be reduced into CO by **93-F** (Scheme 10.46b).



Scheme 10.46 Reactivity of Pd(I)–Pd(I) bond toward CO₂/CS₂.

From a structural perspective, making a comparison between the Pd(I)–Pd(I) bond lengths in **93** and **93-F** is intriguing. In their comprehensive work, Ozerov and coworkers demonstrated that the substituent at the *para*-position on the PNP phenyl ring plays an important role on the structure. There are two distinctive structure motifs: A highly symmetric molecule (**93-F**) with long Pd(I)–Pd(I) bond (2.7167(2) Å) (Entry 4, Table 10.7), and a highly distorted molecule (**93**) with a short Pd(I)–Pd(I) bond (2.5758(4) Å) (Entry 3, Table 10.7) (Scheme 10.47) [61]. A comprehensive computational study indicated the variation of structure and Pd(I)–Pd(I) bond length arises from steric interaction between the PNP ligand scaffold and the innate preferences of the Pd(I)–Pd(I) bond.



Scheme 10.47 Highly symmetric (**93-F**) and highly distorted (**93**) structure and corresponding Pd(I)–Pd(I) bond length.

In 2008, a dipalladium(I) compound **95** with Pd(I)–Pd(I) bond length of 2.530(1) Å (Entry 5, Table 10.7) was synthesized and characterized. Complex **95** is supported by a PSB ligand and features a μ -Cl between palladium and boron (Figure 10.3) [62].

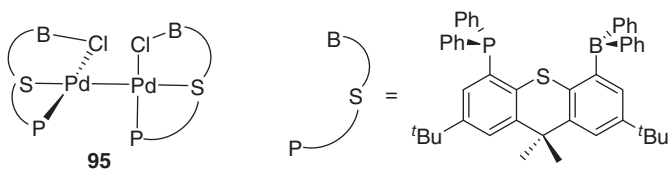
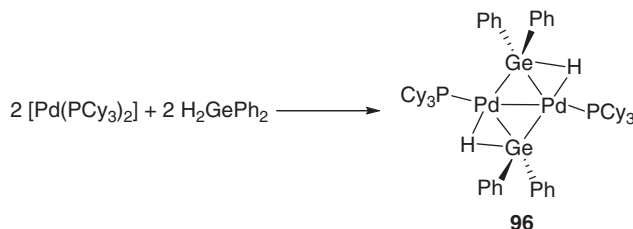


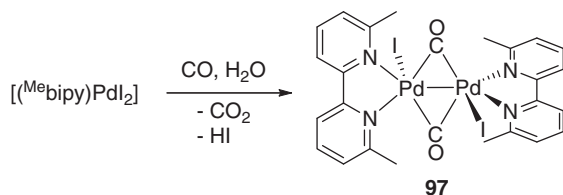
Figure 10.3 Dipalladium(I) compound **95** with a P-S-B pincer ligand.

Compounds with Mono-Bridging-Atom Ligand – ‘Edge-Sharing’ Geometry A low-valent Pd(0) compound was found to be able to activate a Si–H bond in silane to form a dipalladium(I) compound with a Pd(I)–Pd(I) bond and μ -silyl ligand [91]. This reaction was proposed to proceed via an initially formed mononuclear Pd(II) hydride silyl intermediate, which then converted into a dipalladium(I) product with the formation of H₂. In 2006, this type of chemistry was extended into germane (Ph₂GeH₂) and a dipalladium(I) germyl compound **96** was reported (Scheme 10.48) [63]. As for its silyl counterpart, the germyl compound **96** [$\{\text{Pd}(\text{PCy}_3)\}_2(\mu\text{-HGePh}_2)_2$] features a Pd–Ge σ -bond and Pd–H–Ge 3-center–2-electron bond. The Pd(I)–Pd(I) bond length in **96** is 2.752(1) Å (Entry 6, Table 10.7), which is significantly longer than one of its silyl counterparts ($\{\text{Pd}(\text{PCy}_3)\}_2(\mu\text{-HSiPh}_2)_2$): 2.691(1) Å [91a].



Scheme 10.48 Synthesis of dipalladium(I) compound **96** with bridging germyl ligand.

In 2011, a CO-bridged dipalladium(I) iodide **97** was isolated as an intermediate in palladium-catalyzed conversion of CO and H₂O into CO₂ (Scheme 10.49) [64]. The Pd(I)–Pd(I) bond length in **97** is 2.6704(9) Å (Entry 7, Table 10.7).

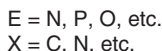


Scheme 10.49 Synthesis of $[\text{Pd}_2(\mu\text{-CO})_2\text{I}_2(6,6'\text{-dimethyl-2,2'-bipyridine})_2]$ (**97**).

Dipalladium(I) Paddlewheel Compounds Several examples of dipalladium(I) paddlewheel compounds supported by bidentate EXE type ligand were reported in the last decade. The general character of the EXE type ligand is two-donor atoms (E: anionic and/or neutral) tethered by one bridging atom (X) (Scheme 10.50). Representations of this type of ligand include amidinate, guanidinate, carboxylate, 2-aminopyridine, and diphosphine.

In 2006, a short Pd(I)–Pd(I) bond (2.429(4) Å) (Entry 8, Table 10.7) was reported in a dipalladium(I) compound **98** (Scheme 10.51) [65], which is one of the shortest Pd(I)–Pd(I) bonds reported. The presence of a Pd(I)–Pd(I) σ -bonding interaction was definitively indicated by scalar relativistic DFT calculations.

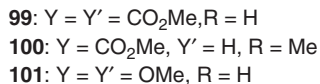
Triazenido ligands (R–NH=N=N–R') are isoelectronic with the widespread amidinate [92]. In 2007, a series of novel triazenido ligand were synthesized and used to support paddlewheel dipalladium(I) compounds (Scheme 10.52) [66]. The synthesis started from a Pd(II) precursor with satisfactory yields (50–80%). The resultant dipalladium(I) compounds **99–101** were reported to be diamagnetic, and to have very short Pd(I)–Pd(I) bonds (2.41–2.43 Å) (Entries 9–11, Table 10.7).



Scheme 10.50 Bidentate EXE type ligand and the corresponding bridging M–M bond.



Scheme 10.51 Synthesis of a dipalladium(I) compound **98** with amidopyridine ligand.



Scheme 10.52 Synthesis of a dipalladium(I) compounds **99–101** with triazenido ligands.

In 2009, a dipalladium(I) amidinate compound **102** was reported with a Pd(I)–Pd(I) bond length of 2.5824(3) Å (Entry 12, Table 10.7) (Figure 10.4) [67]. Complex **102** has two parallel isocyanide ligands, and can catalyze transformation of *t*BuNC and alkynes into pyrroles.

In 2010, an indolyl-phosphine ligand was used in the synthesis of a dipalladium(I) compound with Pd(I)–Pd(I) bond. The reaction between [Pd(OAc)₂] and a ligand precursor in acetonitrile afforded dipalladium(I) compound **103** as product with low yield (30%) (Scheme 10.53) [68]. If the reaction

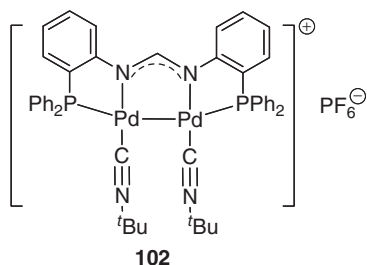
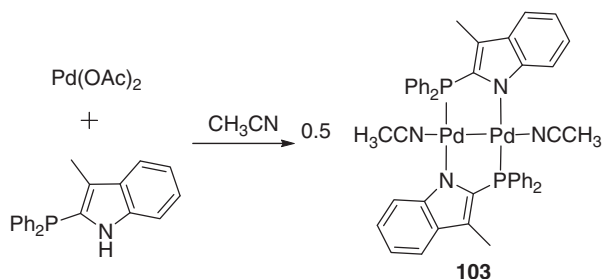


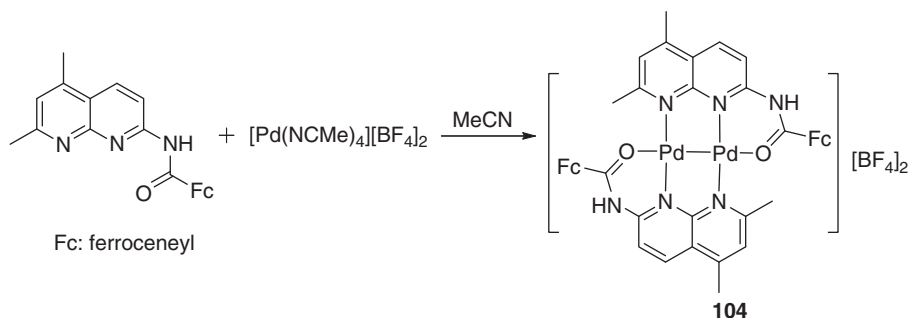
Figure 10.4 Dipalladium(I) compound **102** with bridging amidinate ligand and terminal isocyanide ligands.

was carried out with toluene as solvent, a dipalladium(II) compound was obtained as product, but without a Pd–Pd bond.



Scheme 10.53 Synthesis of dipalladium(I) compound **103** with bridging indolyl-phosphine ligand.

A tridentate ligand based on 1,8-naphthyridine (NP), which bears a ferrocenyl amide pendant arm, was synthesized and used to support dipalladium(I) and diruthenium(I) compounds [69]. The synthesis of the dipalladium(I) compound **104** started with a Pd(II) precursor, but the detail of the redox reaction was not discussed in the original article (Scheme 10.54). Complex **104** is diamagnetic and the Pd(I)–Pd(I) bond is short at 2.3952(8) Å (Entry 14, Table 10.7). Compound **104** was proven to be an active catalyst for Suzuki and Heck coupling, and a bimetallic-synergy mechanism was proposed for the pivotal oxidative addition/reductive elimination steps.



Scheme 10.54 Synthesis of dipalladium(I) compound **104** with 1,8-naphthyridine derived ligand.

A series of Pd(I)–Pd(I) compounds (**105–111**) bearing bidentate P-, P- or P, N-donor ligand were synthesized and characterized recently, of which the Pd(I)–Pd(I) bond length and references are listed

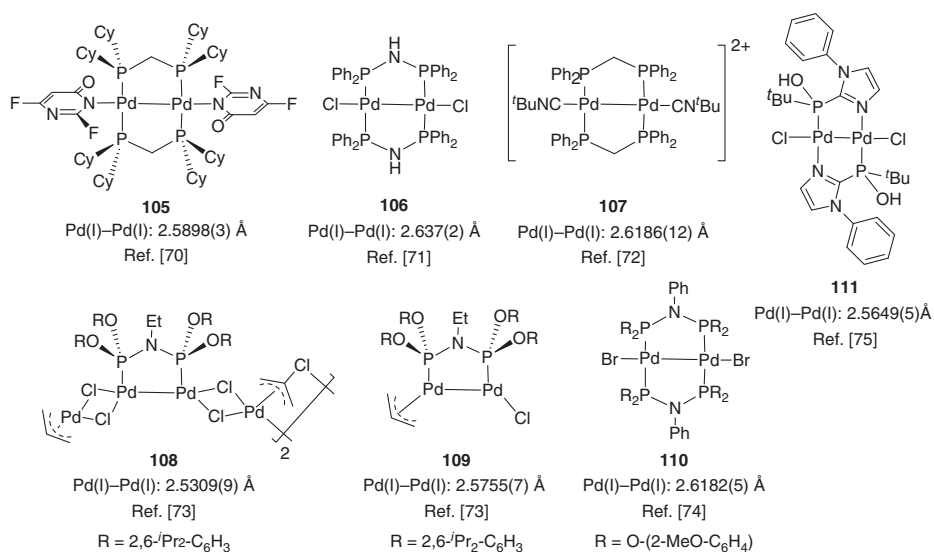
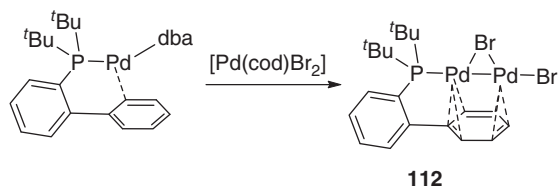


Figure 10.5 Dipalladium(I) compounds 105–111 with bidentate P, N- or P, P- ligands [70–75].

in Figure 10.5. All these compounds are diamagnetic and a Pd(I)–Pd(I) bond is present. It is noteworthy that **108** is a Pd(II)/Pd(I) mixed-valent compound with a Pd(I)–Pd(I) bond, while the chloro allyl ligand is the product of a nucleophilic substitution of chloride toward allyl [70–75].

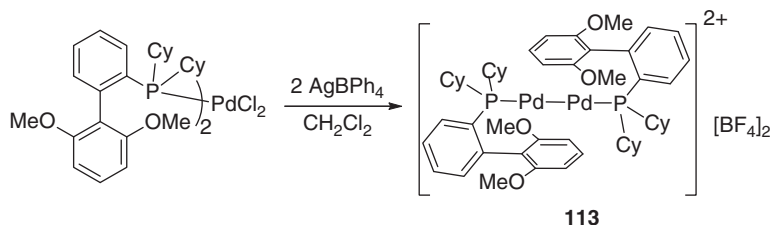
Dipalladium(I) Compounds with Arene, Allyl, and Related Ligand Neutral arene, anionic allyl, or cyclopentadiene ligands, and their derivatives, can act as bridging ligands for the Pd(I)–Pd(I) bond. Some of these compounds can play fundamentally important roles in catalysis by acting as catalysts for important organic transformations, for example, activating CO₂ [93]. In the following section, achievements in the last decade in this field are summarized, mainly from an organometallic perspective.

The dipalladium(I) compound **112** with a neutral arene bridging a Pd(I)–Pd(I) bond was synthesized from comproportionation from Pd(0) and Pd(II) precursors, and using a sterically demanding phosphine ligand (Scheme 10.55) [76]. In the compound, the phenyl ring is in a $\mu^2-\eta^3:\eta^3$ hapticity, and the Pd(I)–Pd(I) bond length is 2.5627(8) Å (Entry 22, Table 10.7). Complex **112** was reported to be an active catalyst for amination of aryl halides.



Scheme 10.55 Synthesis of an arene-bridged dipalladium(I) compound **112**.

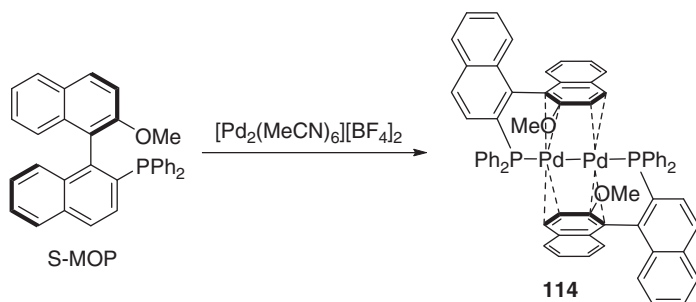
Two years after the report of **112**, a related dipalladium(I) compound **113** was synthesized with a similar ligand framework (Scheme 10.56) [77]. From X-ray crystallography, the two Pd–phenyl interactions are seemingly identical, however, the presentation is deceiving and the true picture is revealed by NMR and theoretical electron topographical analyses to be two kinds of different interactions. One is classified as an arenium-like complex, while the other is a novel π -interaction. The Pd(I)–Pd(I) bond length in **113** is 2.7037(3) Å (Entry 23, Table 10.7), which is significantly longer than that in **112**.



Scheme 10.56 Synthesis of an arene-bridged dipalladium(I) compound **113** with two kinds of Pd(I)–arene interactions.

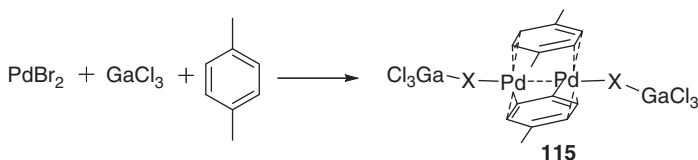
A chiral ligand with binaphthyl backbone *S*-MOP ((*S*)-2-diarylphosphino-1,1'-binaphthyl) was reported to react with $\{[\text{Pd}_2(\text{MeCN})_6][\text{BF}_4]_2\}$ to form a dipalladium(I) compound **114** (Scheme 10.57) [78]. The Pd(I)–Pd(I) bond is bridged by two phenyl rings both in $\mu^2-\eta^2:\eta^2$ hapticity, and the bonding mode was confirmed by ¹³C NMR to be present in solution. Here, the Pd(I)–Pd(I) bond length is 2.7265(4) Å (Entry 24, Table 10.7).

Recently, gallium(III) halide was used to reduce Pd(II) and Pt(II) precursor in the presence of an arene, to afford arene-bridged dipalladium(I) or diplatinum(I) compounds (Scheme 10.58) [79]. For



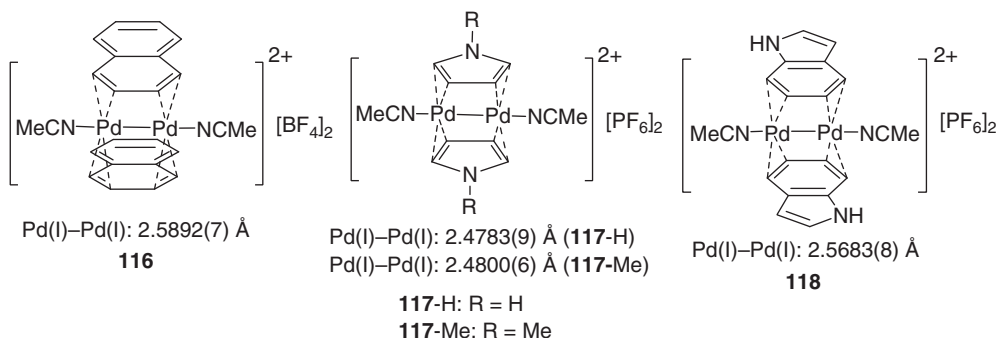
Scheme 10.57 Synthesis of dipalladium(I) compound **114** with chiral binaphthyl backbone.

the dipalladium(I) compound **115**, the Pd(I)–Pd(I) bond length is 2.558(6) Å (Entry 25, Table 10.7). Further conversion of **115** into a mixed-valent Pd₂³⁺ compound can occur.



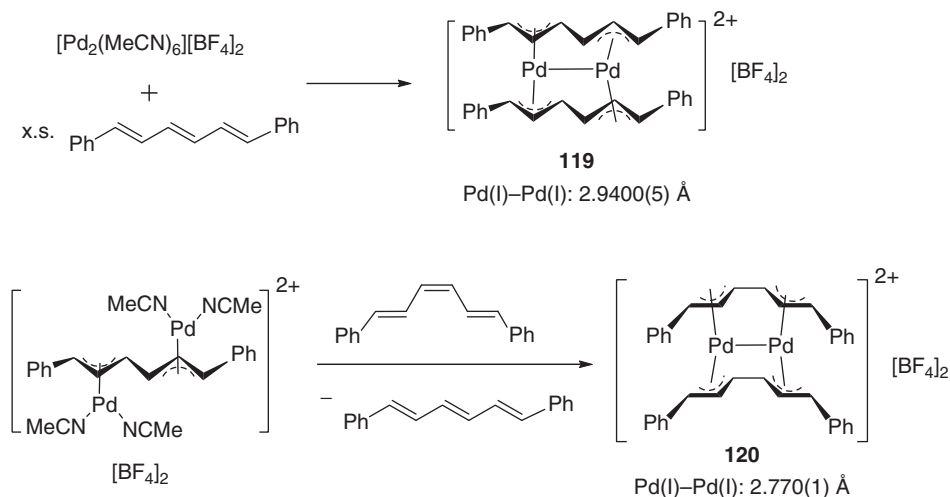
Scheme 10.58 Synthesis of dipalladium(I) compound **115** from reduction of Pd(II) by Ga(III).

Examples of dipalladium(I) compounds with π -coordinated bridging neutral naphthalene, pyrrole, and indole were reported very recently [80]. These syntheses started with [Pd₂(MeCN)₆][X]₂ (X = BF₄ or PF₆) and naphthalene, pyrrole, or indole, while **116**–**118** were obtained as products (Scheme 10.59).



Scheme 10.59 Neutral arene-bridged dipalladium(I) compounds **116**–**118**.

In 2006, Murahashi and coworkers comprehensively studied the reaction between {[Pd₂(MeCN)₆][BF₄]₂} and triene, and a series of sandwich dipalladium(I) compounds with conjugated olefin ligands were obtained (Scheme 10.60) [81]. The dipalladium(I) oxidation state in **119** and **120** was confirmed by not only X-ray crystallography but also NMR spectroscopy, and the triene ligand in these compounds act as neutral ligands. The triene ligand in **119** and **120** is in *E, E, E*- and *E, Z, E*-configuration, respectively; as a result, the Pd(I)–Pd(I) bond in **119** is significantly longer than that in **120** (Entries 30 and 31, Table 10.7).



Scheme 10.60 Synthesis of triene-bridging dipalladium(I) sandwich compounds.

$\mu\text{-}\eta^3$ -Indenyl bridging dipalladium(I) compounds were reported in 2006 (Figure 10.6), as product from a proposed comproportionation from Pd(II) and Pd(0) precursors. The Pd(I)–Pd(I) bond length of **121-Cy** and **121-Ph** is 2.5971(8) and 2.6031(6) Å, respectively (Entries 32 and 33, Table 10.7), and both of the two compounds are diamagnetic [82].

A series of dipalladium(I) compound with bridging anionic allylic ligands were synthesized as intermediates or catalysts for pivotal organic transformations, for example, allylic substitution (**122**) (Figure 10.7) [94], or functionalization of CO₂ (**123–124**) (Scheme 10.61) [83].

Dipalladium(I) Compounds with Other Ligand In 2009, two NPN-tridentate ligands with oxazoline pendant arms were reported to react with $\{[\text{Pd}_2(\text{MeCN})_6][\text{BF}_4]_2\}$ to afford dipalladium(I) compounds

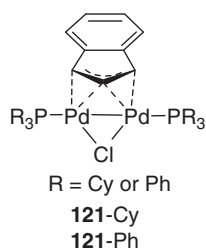


Figure 10.6 $\mu\text{-}\eta^3$ -Indenyl-bridged dipalladium(I) compounds **121-Cy** and **121-Ph**.

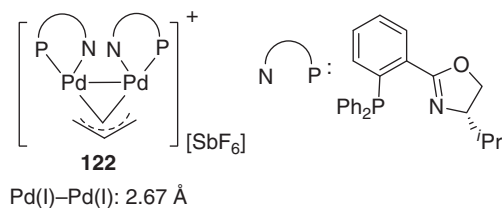
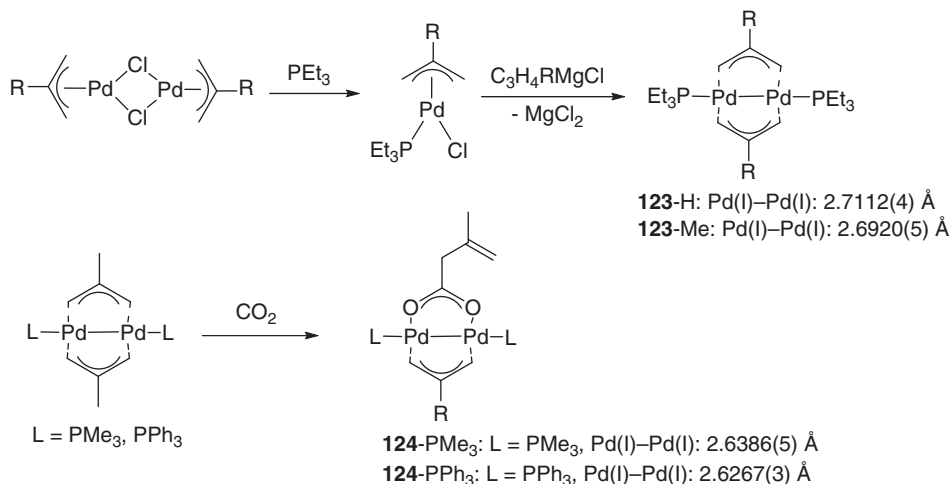
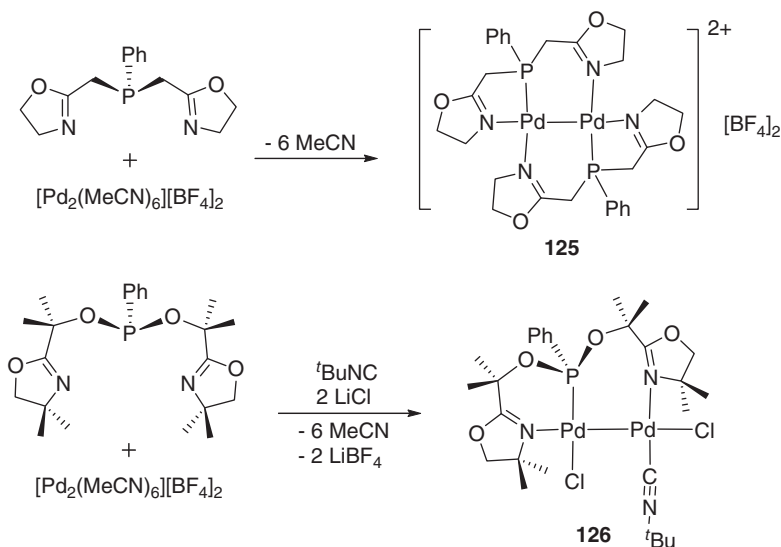


Figure 10.7 Anionic allylic ligand-bridged dipalladium(I) compound **122**.



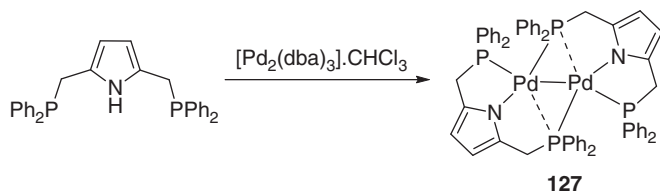
Scheme 10.61 Allyl bridging dipalladium(I) compounds and insertion of CO₂.

125 and **126** as products (Scheme 10.62) [84]. It was demonstrated that the N-site is more preferential than the O-site in the oxazoline pendant arm to coordinate to the palladium centers. The Pd(I)–Pd(I) bond lengths in **125** and **126** are 2.5489(7) and 2.5230(4) Å (Entries 38 and 39, Table 10.7), respectively.



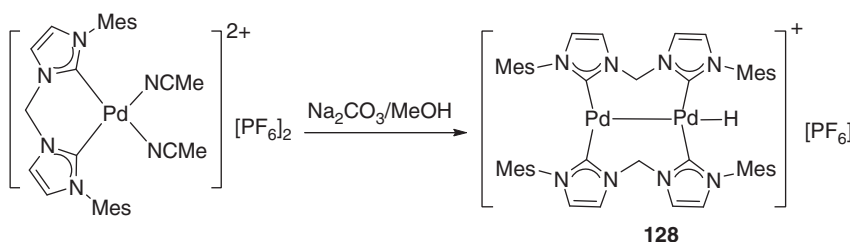
Scheme 10.62 Oxazoline-functionalized NPN-tridentate ligands-supported dipalladium(I) compounds **125** and **126**.

As for the dinickel(I) compound [35], the pyrrole-based PNP pincer ligand is also applicable for the dipalladium(I) compound (Scheme 10.63) [85]. The structure of the dipalladium(I) compound **127** closely resembles its dinickel(I) counterpart [35], and the Pd(I)–Pd(I) bond length is 2.5470(5) Å (Entry 40, Table 10.7).



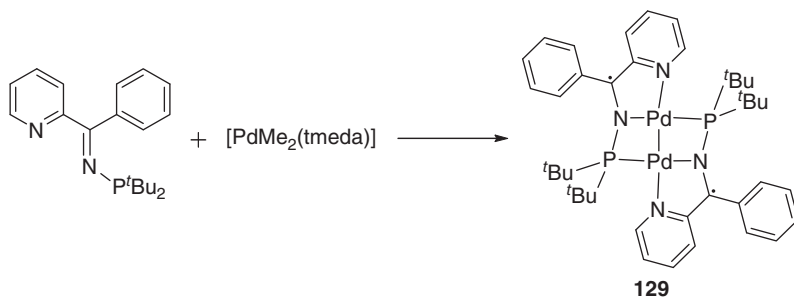
Scheme 10.63 Pyrrole-based PNP pincer ligand-supported dipalladium(I) compound **127**.

In 2010, a Pd(II) compound with a bis-NHC ligand was reduced to give the dipalladium(I) terminal hydride **128** (Scheme 10.64) [86]. Complex **128** was claimed as the first Pd(I) NHC complex as well as the first, and so far unique, structurally characterized Pd_2H^+ species with a Pd–Pd bond. The location of the hydride was determined by neutron diffraction, and the Pd(I)–Pd(I) bond length was reported to be 2.7530(4) Å (Entry 41, Table 10.7), which suggests a rather weak intermetallic interaction.



Scheme 10.64 Bis-NHC ligand-supported dipalladium(I) terminal hydride **128**.

Redox non-innocent ligands are widespread in the biochemistry of metalloproteins and enzymes [95], as well as in organometallic chemistry for their diverse and unique magnetic and electrochemical properties [96]. However, the incorporation of the redox non-innocent ligands into palladium organometallic chemistry is still generally elusive [97]. In 2010, it was found that upon treating with dimethyl palladium(II) $[\text{PdMe}_2(\text{tmeda})]$, the ligand precursor was reduced to form a dipalladium(I) compound with a monoanionic free-radical ligand (**129**) (Scheme 10.65) [87]. The structure of **129** was extensively characterized by X-ray crystallography, solid state EPR, and magnetism studies. The rather short Pd(I)–Pd(I) bond (2.4565(3) Å) (Entry 42, Table 10.7) was suggested by EHT (extended Hückel theory)/DFT theoretical study to be comprised of two 15-electron T-shaped $[\text{PdL}_3]^+$ fragments linked by a single Pd(I)–Pd(I) bond.



Scheme 10.65 Redox non-innocent ligand-supported dipalladium(I) compound **129**.

10.2.2.3 Dipalladium(II) Compounds

As mentioned at the very start of the chapter, +2 is the most common oxidation state for Group 10 metals due to the d^8 electron configuration. For palladium, Pd(II) species have played a pivotal role in elementary reactions in palladium-catalysis, for example, oxidative addition/reductive elimination, and thus have received extensive research interest historically. In the following section, the advancements of dipalladium(II) compounds with Pd(II)–Pd(II) bonds in the last decade will be summarized.

A major body of the family of dipalladium(II) compound were obtained during the studies of palladium-mediated C–H bond activation and functionalization, and can be treated as intermediates/catalysts in/of important catalytic process. A selection of structurally characterized dipalladium(II) compounds as catalytic intermediates are listed in Figure 10.8, along with their Pd(II)–Pd(II) bond lengths as well as references. Among them, **130** and **131** are intermediates for C–H bond arylation/alkylation via Suzuki coupling [98], **132** is an intermediate of C–H bond functionalization with strained alkenes [99], **133** are intermediates of C–H bond carbonylation using CO and alcohol [100], while **134** is an intermediate of aryl C–C bond coupling [101].

The bonding nature of the Pd(II)–Pd(II) bond was studied comprehensively with a combination of experimental and computational methods, using a series of dipalladium(II) compounds with the 2-arylpalladium ligand as model compound (Figure 10.9) [102]. The coordination geometry around the Pd(II) centers deviated from the expected approximate D_{2h} symmetry, but was found to be a slightly open “clamshell” conformation. The d^8 – d^8 Pd(II)–Pd(II) bonding interaction was proven by DFT and atoms in molecules theoretical analyses, and the highest occupied orbital was located as a d_{z^2} σ^* Pd–Pd antibonding orbital. Comparison between the Pd(II)–Pd(II) bond and other d^8 – d^8 M–M bonds (M=Rh, Ir, Pt) was made and the Pd(II)–Pd(II) bond was found to be quite different from the rest of these M–M bonds, for example, Pd(II)–Pd(II) compounds do not exhibit the distinctive

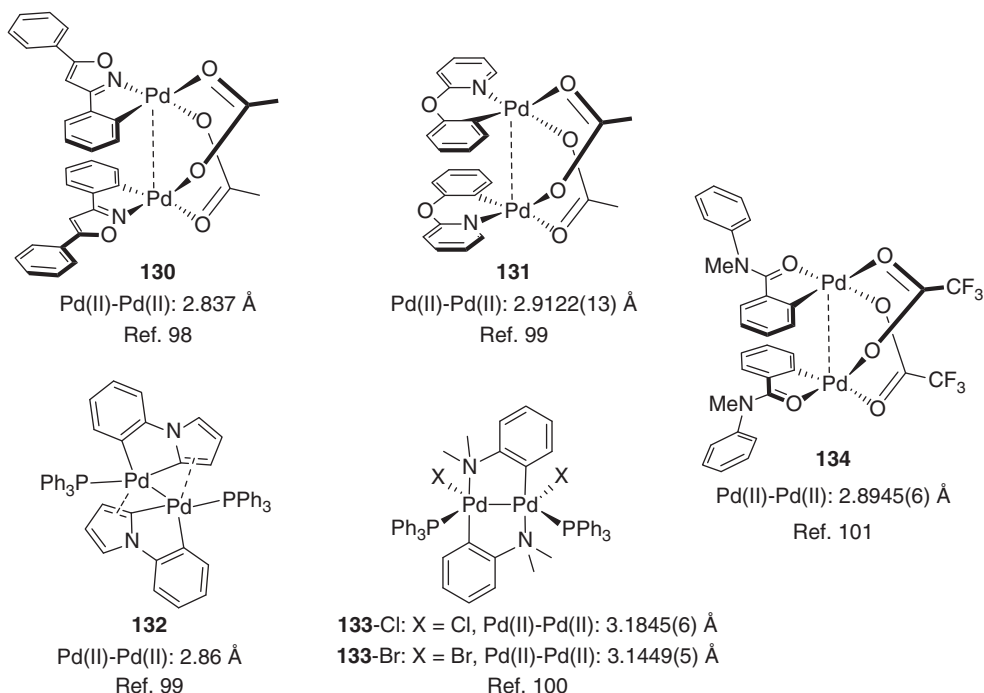


Figure 10.8 Dipalladium(II) intermediate of catalytic functionalization of C–H bond [98–101].

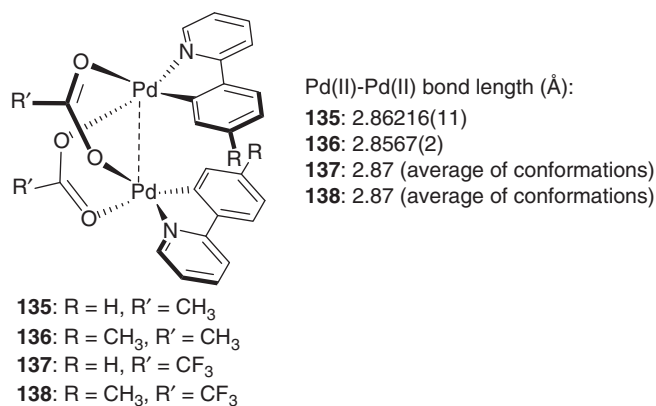
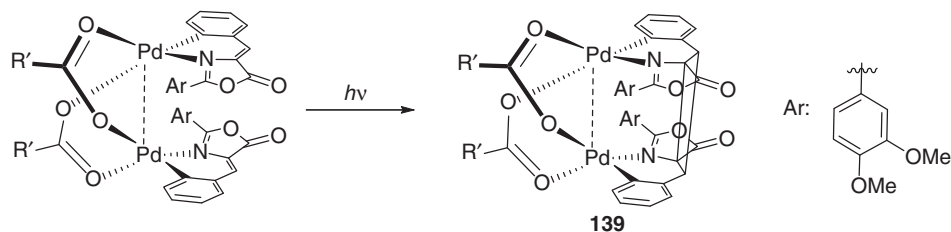


Figure 10.9 Dipalladium(II) compounds **135**–**138** were used as models for studying bonding nature of the Pd(II)–Pd(II) bond.

photophysical properties as for the others (M=Rh, Ir, Pt). The difference in bonding and properties has its roots in the unusually large energy gap between 4d and 5p orbitals in Pd.

In 2009, the dipalladium(II) compound **139** was found to be formed via an intramolecular [2+2] cycloaddition involving the benzyldenic C=C double bond (Scheme 10.66). The Pd(II)–Pd(II) bond length in **139** is rather short at 2.7815(7) Å (Entry 11, Table 10.8) [103].



Scheme 10.66 Formation of a dipalladium(II) compound **139** via intramolecular [2+2] photocycloaddition.

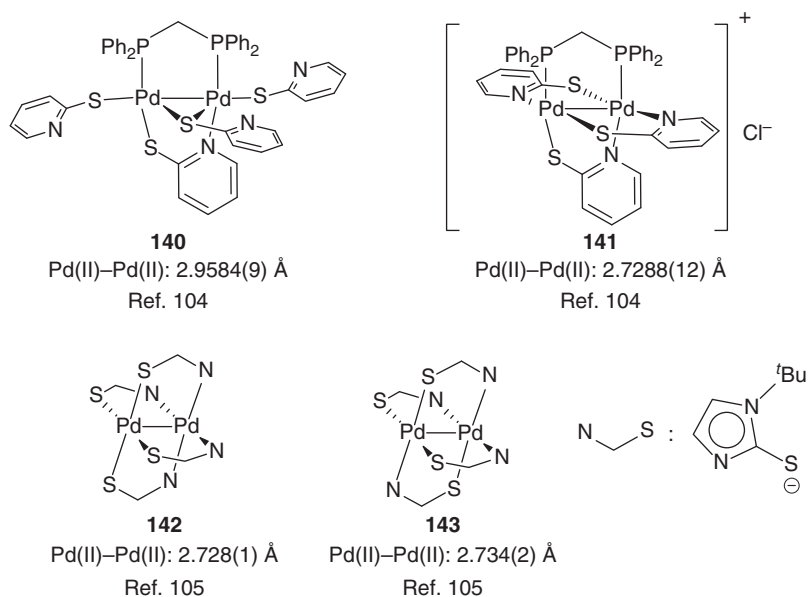
A handful of dipalladium(II) paddlewheel compounds with bidentate ligands were synthesized in the last decade and representations of them are listed in Figure 10.10. [104, 105] The Pd(II)–Pd(II) bond length interestingly varies from 2.72 to 2.95 Å in compounds **140**–**143** (Entries 12–15, Table 10.8).

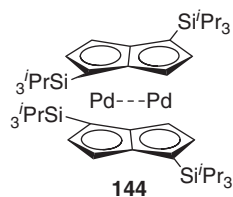
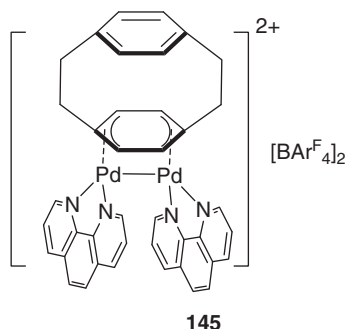
A dipalladium(II) bis(pentalene) compound [Pd₂(pent*)₂] (**144**) (pent* = 1,4-bis(triisopropylsilyl) pentalene) was made from salt metathesis between [K₂pent*] and 2 equiv. of [PdCl₂(cod)] (Figure 10.11) [106]. The low quality of crystallographic data (R1 = 10.9%) prevented the determination of reliable bond distances in the bis(pentalene) ligand, thus the coordination mode between Pd centers and ligand is ambiguous. However, the metal–metal distance is reliable at 2.786(2) Å (Entry 16, Table 10.8). The distance is comparable with other Pd(II)–Pd(II) bonds in this section. Formal electron counting indicates in excess of 18 per metal center (20-electron for a η⁵ cyclopentadiene-like hapticity), and antibonding metal–ligand interactions were suggested by DFT calculations.

As it has been discussed in Section 10.2.2.2.4, a dipalladium(I) precursor {[Pd₂(MeCN)₆][BF₄]₂} can react with neutral arene to produce a dipalladium(I) compound with Pd(I)–Pd(I) bond bridged by a neutral arene ligand [80a]. A systematic study revealed that the outcome of the reaction was dependent on the arene/conjugated alkene involved: small arenes (benzene, anthracene) afford the Pd(I)–Pd(I) compound, while cyclophane gives the oxidative addition of Pd(I)–Pd(I) toward

Table 10.8 Pd(II)–Pd(II) bond lengths.

Entry	Compounds	Pd(II)–Pd(II) (Å)	References
1	130	2.837(1)	[98]
2	131	2.9122(13)	[99]
3	132	2.861(2)	[99]
4	133 -Cl	3.1845(6)	[100]
5	133 -Br	3.1449(5)	[100]
6	134	2.8945(6)	[101]
7	135	2.86216(11)	[102]
8	136	2.8567(2)	[102]
9	137	~ 2.87	[102]
10	138	~ 2.87	[102]
11	139	2.7815(7)	[103]
12	140	2.9584(9)	[104]
13	141	2.7288(12)	[104]
14	142	2.728(1)	[105]
15	143	2.734(2)	[105]
16	144	2.786(2)	[106]
17	145	2.7889(6)	[80a]

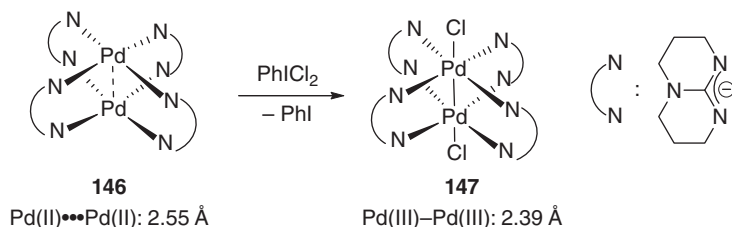
**Figure 10.10** Dipalladium(II) paddlewheel compounds [104, 105].

**Figure 10.11** Dipalladium(II) bis(pentalene) compound **144**.**Figure 10.12** Cyclophane-supported dipalladium(II) compound **145**.

arene, affording the Pd(II)–Pd(II) bis-(monoanionic-allyl) compound **145** (Figure 10.12) [80a]. The Pd(II)–Pd(II) bond length in **145** is 2.7889(6) Å (Entry 17, Table 10.8). It was also reported that larger polyacenes (tetracene, pentacene) also exhibited the oxidative addition reactivity, however, the Pd(II)–Pd(II) distance in the resulting dipalladium(II) allyl compounds were found to be too large for metal–metal bond (>3.2 Å) [80a].

10.2.2.4 Dipalladium(III) Compounds

Until very recently, +3 was an “overlooked” oxidation state for fundamental palladium organometallic chemistry. Dipalladium(III) compounds were elusive, while the only report of Pd(III)–Pd(III) bond before 2005 was made by Cotton and coworkers (**147** in Scheme 10.67) [107]. Significant distance contraction (0.16 Å) upon oxidation from dipalladium(II) **146** to dipalladium(III) **147** was observed which was attributed to the result of removing two electrons from an antibonding Pd–Pd σ^* orbital.

**Scheme 10.67** The first dipalladium(III) compound **147**.

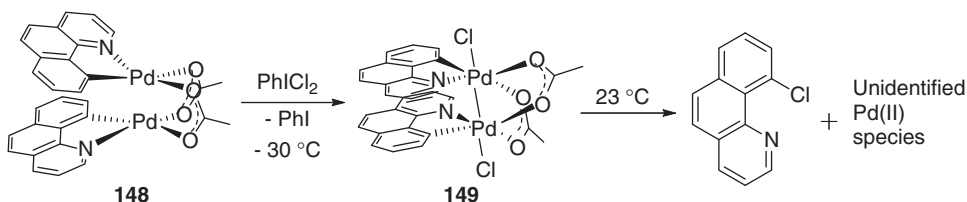
The milestone discovery by Cotton and coworkers opened a new horizon not only for fundamental palladium organometallic chemistry but also for palladium catalysis. As the cornerstone of modern organic synthesis, palladium catalysis was widely accepted to be based on Pd(II)/Pd(IV) monosite two-electron redox process. The two-electron oxidation of dipalladium(II) **146** into dipalladium(III)

Table 10.9 Pd(III)–Pd(III) bond lengths.

Entry	Compounds	Pd(III)–Pd(III) (Å)	References
1	149	~ 2.57	[108]
2	151	2.5548(5)	[109]
3	152	~ 2.40	[110]
4	155 -CF ₃	2.5434(4)	[111]
5	155 -CMe ₃	2.5241(9)	[111]
6	155 -Me	2.5294(17)	[112]
7	156	2.5411(9)	[112]

147 raised the possibility of intermetallic synergistic redox pair Pd(II)–Pd(II)/Pd(III)–Pd(III) to challenge the traditional Pd(II)/Pd(IV) mechanism of palladium catalysis.

In 2009, this possibility was realized by Ritter and coworkers. The two-electron oxidation of dipalladium(II) compound **148** at low temperature (–30 °C) afforded the dipalladium(III) compound **149** with significant Pd–Pd distance contraction from 2.84 Å in **148** to 2.57 Å in **149** (Entry 1, Table 10.9) (Scheme 10.68) [108]. The existence of a Pd(III)–Pd(III) bond was further proven by the diamagnetism of **149**, which was the result of spin pairing of two d⁷ Pd(III) centers. Warming **149** to ambient temperature led to bimetallic reductive elimination to form a C–Cl bond, along with unidentified Pd(II) species. This was the first clearly defined example of carbon-heteroatom reductive elimination from a binuclear transition metal complex, and created a new horizon of palladium organometallic chemistry based on synergetic Pd(III)–Pd(III) bond [113].

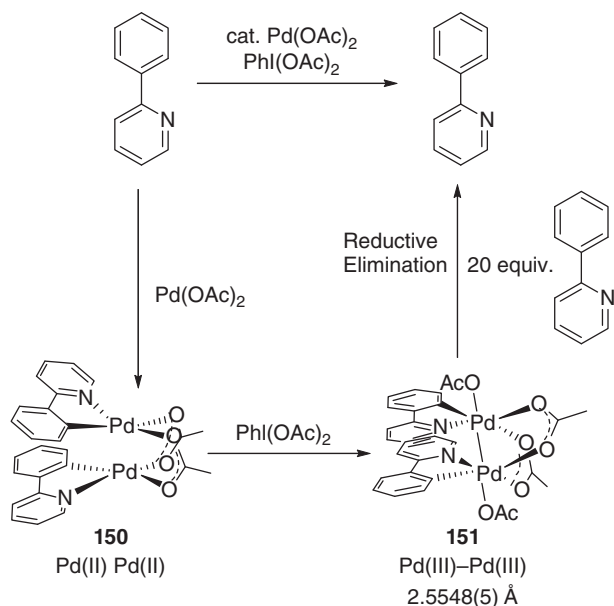


Scheme 10.68 Formation of dipalladium(III) compound **149**, and its bimetallic reductive elimination to form C–Cl bond.

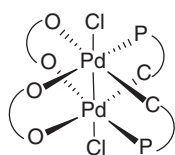
In their subsequent work, Pd(III)–Pd(III) compound **151** was observed as an intermediate in [Pd(OAc)₂] catalytic C–H bond acetoxylation, and bimetallic synergy was proven to be the key step in the catalytic process (Scheme 10.69) [109]. The mechanism of reactions in Schemes 10.68 and 10.69 were comprehensively studied, and the bimetallic synergy between two Pd(III) centers was experimentally and theoretically proven to be crucial for the catalysis [114].

The concept and methodology was extended to C–H bond hydroxylation with O₂, using dipalladium(II) compound **146** as catalyst [110]. A dipalladium(III) compound **152** was individually prepared and suggested by UV–vis spectroscopy as a possible model for the Pd(III) intermediate of the catalysis (Scheme 10.70).

It is noteworthy that **154**, although not structurally authenticated, was proposed as a Pd(III)–Pd(III) intermediate for a Pd(II) (**148**) to Pd(IV) (**153**) oxidation using an electrophilic trifluoromethylating reagent (“CF₃⁺”) [115]. The existence of **154** as intermediate was proven by comprehensive kinetic study and computational investigations, and a heterolytic Pd(III)–Pd(III) bond cleavage was suggested (Scheme 10.71) [116].



Scheme 10.69 Dipalladium(III) compound **151** as key intermediate in catalytic C–H bond acetoxylation.

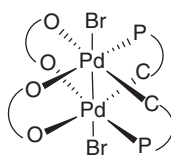


155–CF₃: R = CF₃, Pd(III)–Pd(III) = 2.5434(4) Å

155–CMe₃: R = CMe₃, Pd(III)–Pd(III) = 2.5241(9) Å

155–CH₃: R = CH₃, Pd(III)–Pd(III) = 2.5294(17) Å

Refs [111, 112]



156 Pd(III)–Pd(III) = 2.5411(9) Å

Ref. [112]

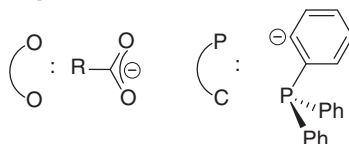
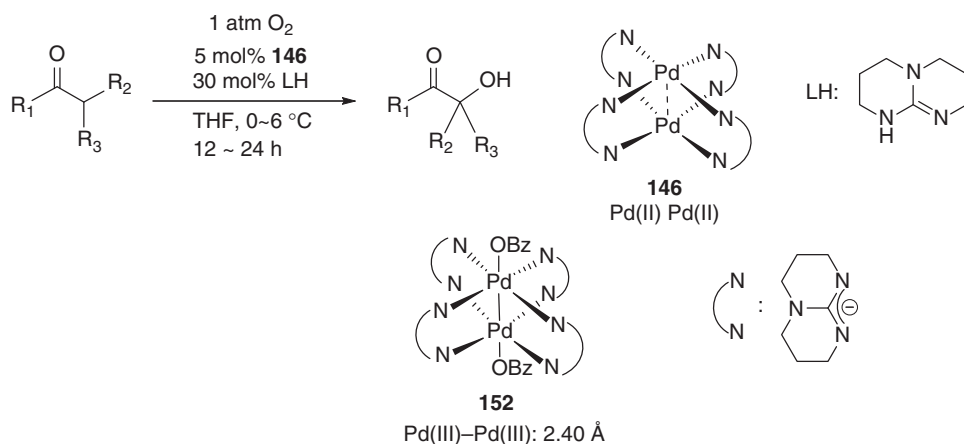


Figure 10.13 Dipalladium(III) paddlewheel compounds **155** and **156** [111, 112].

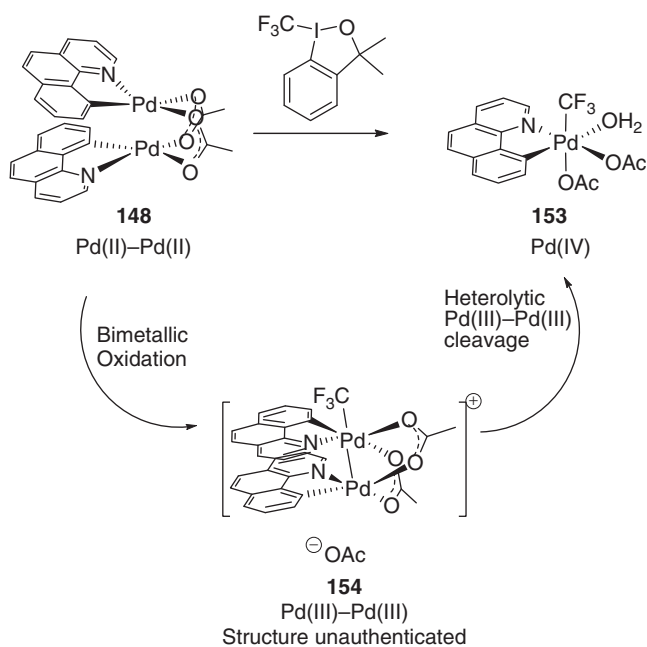
Other dipalladium(III) compounds (**155**–**156**) were made and structurally characterized (Figure 10.13) [111, 112]. All of the compounds were made from the oxidation of dipalladium(II) precursor, and significant contract of intermetallic distance upon oxidation were observed for all reactions.

10.2.2.5 Mixed-Valent Dipalladium Compounds

A few examples of mixed-valent dipalladium compounds with Pd–Pd bond interactions were reported in the last decade.



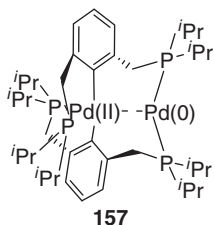
Scheme 10.70 Dipalladium(II) compound **146** catalyzed C–H bond hydroxylation with O₂, and the possible Pd(III) intermediate **152**.



Scheme 10.71 Pd(III)–Pd(III) species as intermediate for Pd(II)/Pd(IV) oxidation.

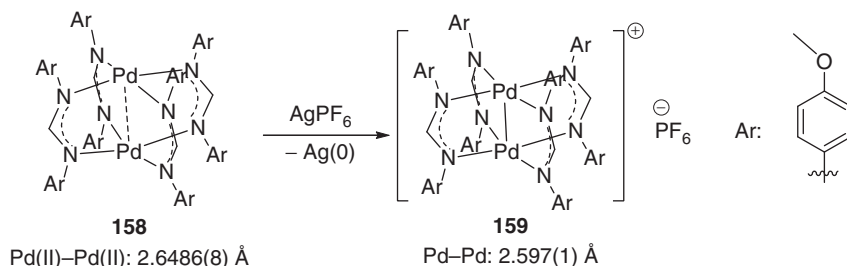
Table 10.10 Pd–Pd bond lengths in mixed-valent dipalladium compounds.

Entry	Compounds	Pd–Pd (Å)	References
1	157	Pd(II)–Pd(0) 3.0389(11)	[117]
2	159	Pd(+2.5)–Pd(+2.5) 2.597(1)	[118]

**Figure 10.14** A mixed-valent Pd(II)–Pd(0) compound **157**.

A Pd(II)–Pd(0) interaction was reported in compound **157** with a Pd(II)–Pd(0) distance at 3.0389(11) Å (Entry 1, Table 10.10) (Figure 10.14) [117]. It represents a very rare example of a nonplanar diamagnetic Pd(II) moiety, and the Pd(0) center slightly deviates from linearity and points toward the Pd(II) center. Complex **157** was made from the reduction of [LPdX] (L = PCP pincer ligand, X = Cl or CF₃CO₂) using sodium metal as reductant.

A paddlewheel dipalladium(II) compound **158** was oxidized by [AgPF₆] to form the Pd₂⁵⁺ moiety **159** (Scheme 10.72) [118]. There was only one precedent [119] of a structurally characterized Pd₂⁵⁺ compound before the preparation of **159**. After the oxidation, the Pd–Pd distance contracted by 0.052 Å. Comprehensive UV–vis spectroscopy, electrochemistry, and multifrequency EPR study of **159**, in combination with X-ray crystallography and DFT calculations, demonstrated that one-electron oxidation to be based on the metal–metal bond, and the Pd–Pd bond order in **159** was 1/2.

**Scheme 10.72** Pd₂⁵⁺ compound **159**.

10.2.3

Diplatinum Compounds

Historically, Pt–Pt bonds were the most prevalent amongst all group 10 metal–metal bonding. As mentioned earlier, here a higher oxidation state is favorable for a metal–metal bond, as removing electrons from antibonding orbitals stabilizes the bond. Since a higher oxidation state is generally more favorable for heavier elements within the same group in periodic table, it is reasonable to expect

Pt–Pt bonds to be more prevalent than Ni–Ni or Pd–Pd bonds. Actually, a search in the Cambridge Structural Database (CSD version 03.2014) for Pt–Pt bonds gives 1173 hits, while searches for Pd–Pd and Ni–Ni bonds gives 857 and 732 hits, respectively.

Among all possible oxidation states, diplatinum(III) (Pt_2^{6+}) compounds represents the vast majority and the quantity of compounds is second only to dirhodium(II) compounds among all metal–metal bonded moieties. In a comprehensive textbook chapter in 2005, the structure and chemistry of Pt–Pt bonded compounds were nicely reviewed by Murillo, which the reader is recommended to consult [2]. Therefore, an encyclopedic coverage of the literature is not the aim of the following section, and a representative selection of highlights made since 2005 will be introduced.

10.2.3.1 Diplatinum(0) Compounds

Only a few compounds with Pt(0)–Pt(0) bonds were reported since 2005, due to the fact that this low-valent metal–metal bond with highly occupied antibonding orbitals is thermodynamically unfavorable. Thus, sterically demanding ligands are necessary to provide kinetical stabilization.

In 2005, low-valent group 13 ligands were used to stabilize a series of Group 10 bimetallic and multimetallic compounds [120]. The diplatinum(0) compounds **160**–**163** and the Pt(0)–Pt(0) bond lengths are listed in Figure 10.15. The structures of **160**–**163** were found to be fluxional in solution, and ligand exchange reactions were demonstrated to be viable.

In the following work, monovalent Group 13 compound with β -diketiminato scaffold (BDI) were reacted with M(0) precursor, where M is Pd or Pt [121]. For platinum, a series of diplatinum(0) compounds were obtained and characterized (Figure 10.16) (Table 10.11).

10.2.3.2 Diplatinum(I) Compounds

In the last decades, major efforts toward preparing diplatinum(I) compounds with Pd(I)–Pd(I) bonds were made with phosphorus-containing ligands, for example, phosphine, phosphide, phosphinito, phosphinidene, and relatives.

A phosphide-bridged diplatinum(I) bis-ethylene compound **166** (Scheme 10.73) was made by a ligand exchange reaction from ethylene and a diplatinum(I) carbonyl precursor [122]. The Pt(I)–Pt(I)

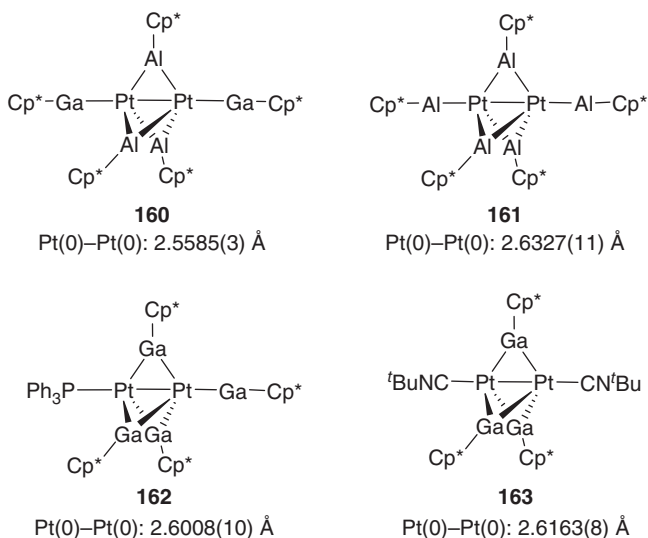


Figure 10.15 Ga(I) and Al(I) ligand-bridged diplatinum(0) compounds **160**–**163**.

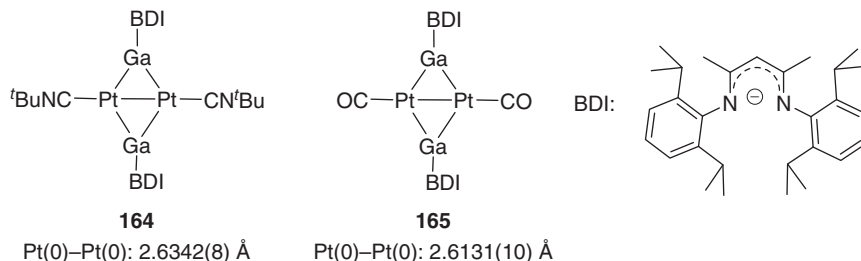
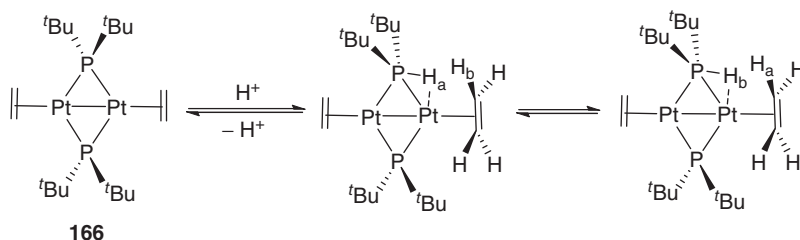


Figure 10.16 Ga(I) ligand-bridged diplatinum(0) compounds **164** and **165**.

Table 10.11 Pt(0)–Pt(0) bond lengths

Entry	Compounds	Pt(0)–Pt(0) (Å)	References
1	160	2.5585(3)	[120]
2	161	2.6327(11)	[120]
3	162	2.6008(10)	[120]
4	163	2.6163(8)	[120]
5	164	2.6342(8)	[121]
6	165	2.6131(10)	[121]

bond length in **166** is 2.6230(8) Å (Entry 1, Table 10.12), and the C=C bond length in ethylene is 1.41(2) Å, which is significantly longer than that in free ethylene (1.337 Å). Although it was not structurally authenticated, an elusive example of P–H–M agostic interaction and rapid H exchange via C(sp²)–H bond activation was observed in solution by multinuclear kinetic NMR experiment (Scheme 10.73).



Scheme 10.73 A phosphide-bridged diplatinum(II) compound **166**, and the proton exchange/C–H bond activation upon protonation.

In a related work, phosphido bridging diplatinum(I) dicarbonyl compound **167** was made from the reaction of known $[\text{Pt}_2(\mu\text{-P}^t\text{Bu}_2)_2(\text{P}^t\text{Bu}_2\text{H})(\text{CO})]$ [131] and CO (80 psi) [123]. Ligand exchange of **167** with corresponding phosphines afforded **168**-Me and **168**-Ph. **168**-Ph was protonated by Brønsted acid $\text{CF}_3\text{SO}_3\text{H}$ yielding diplatinum(I) hydride **169** (Figure 10.17). The Pt(I)–Pt(I) bond lengths vary from 2.60 to 2.64 Å (Entries 3–5, Table 10.12).

Pt(I)–Pt(I) compound **171** was produced by an unprecedented bimetallic reversible reductive formation of C(sp¹)–P bond of a diplatinum(II) compound **170** (Scheme 10.74) [124]. The intermetallic distance in diplatinum(II) precursor **170** is too long to be considered bonded (>3.5 Å), while the Pt(I)–Pt(I) bond length in **171** is 2.6282(2) Å (Entry 6, Table 10.12). Upon treatment by a bromide

Table 10.12 Pt(I)–Pt(I) bond lengths

Entry	Compounds	Pt(I)–Pt(I) (Å)	References
1	166	2.6230(8)	[122]
2	167	2.5999(8)	[123]
3	168 -Me	2.6053(4)	[123]
4	168 -Ph	2.6126(2)	[123]
5	169	2.6349(3)	[123]
6	171	2.6282(2)	[124]
7	173	2.6490(13)	[125]
8	175	2.7144(5)	[126]
9	176	2.7396(9)	[127]
10	177	2.5737(16)	[128a]
11	178	2.8502(6)	[128b]
12	179	2.8778(15)	[128b]
13	180	2.6355(8)	[72]
14	181	2.6453(3)	[72]
15	183	2.6069(2)	[129]
16	184	2.7032(6)	[130a]
17	185	2.7268(2)	[130a]
18	186	2.6951(7)	[130b]
19	187	2.708(1)	[130b]
20	188 -Et ₂	2.7011(3)	[130c]
21	188 -Hex ₂	2.6988(6)	[130c]
22	188 -Me	2.6982(3)	[130c]
23	188 -Ph ₂	2.6985(3)	[130c]
24	189	2.7614(5)	[130d]

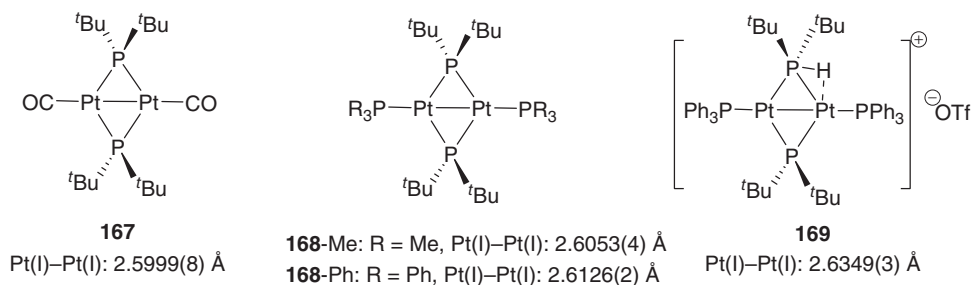
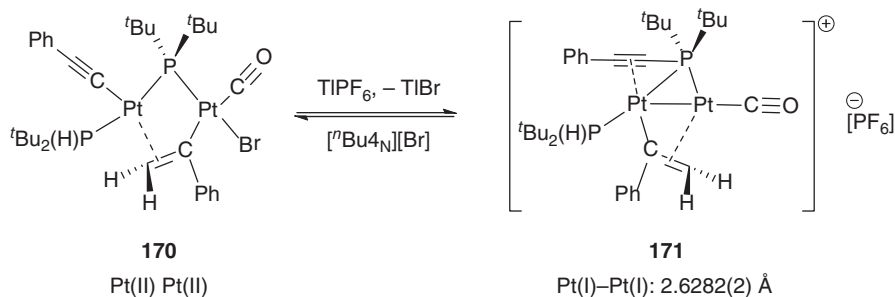


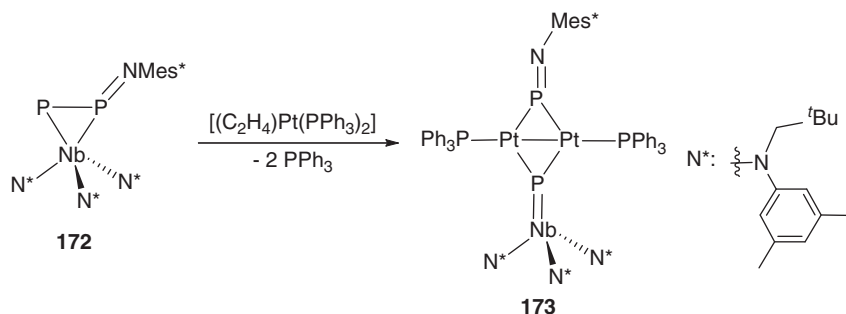
Figure 10.17 Phosphide-bridged diplatinum(I) compounds 167–169.

source {[ⁿBuN][Br]}, **171** was easily and cleanly converted back into **170** via a bimetallic P–C bond oxidative addition.

As a part of their quest for P₂ species and its organometallic synthon, Cummins and coworker reported that ethylenebis(triphenylphosphine) platinum(0) [(C₂H₄)Pt(PPh₃)₂] can act as effective probe for niobium-mediated diphosphorus chemistry [125]. Upon treatment by 2 equiv. of [(C₂H₄)Pt(PPh₃)₂], niobium diphosphaazide compound **172** was converted into heteromultimetallic compound **173** which bears a Pt(I)–Pt(I) bond (Scheme 10.75). The Pt₂P₂ diamond-shape core of **173** is in planarity, and the Pt(I)–Pt(I) bond length is 2.6490(13) Å (Entry 7, Table 10.12).

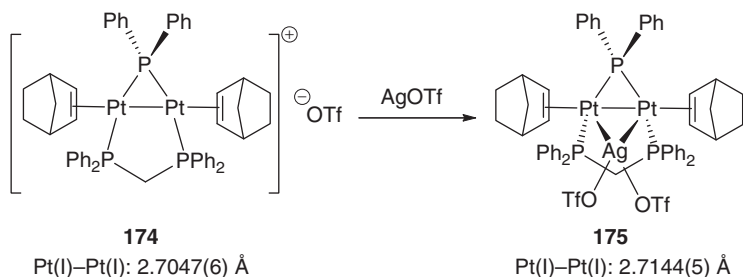


Scheme 10.74 Formation of a diplatinum(I) compound **171** via reductive C–P bond coupling.



Scheme 10.75 Formation of a diplatinum(I) compound **173** via oxidative cleavage of a P–P bond.

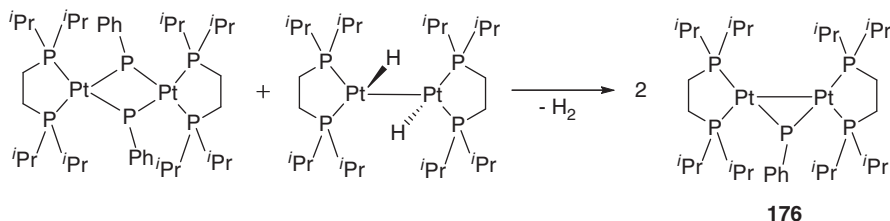
The reaction between a known phosphido bridging diplatinum(I) compound **174** [132] and [AgOTf] produced a Lewis acid adduct at the Pt(I)–Pt(I) bond (**175**) (Scheme 10.76) [126]. The coordination of Lewis acid has only minor influence on the Pt–Pt–P core.



Scheme 10.76 Addition of a Lewis acid (AgOTf) toward Pt(I)–Pt(I) bond.

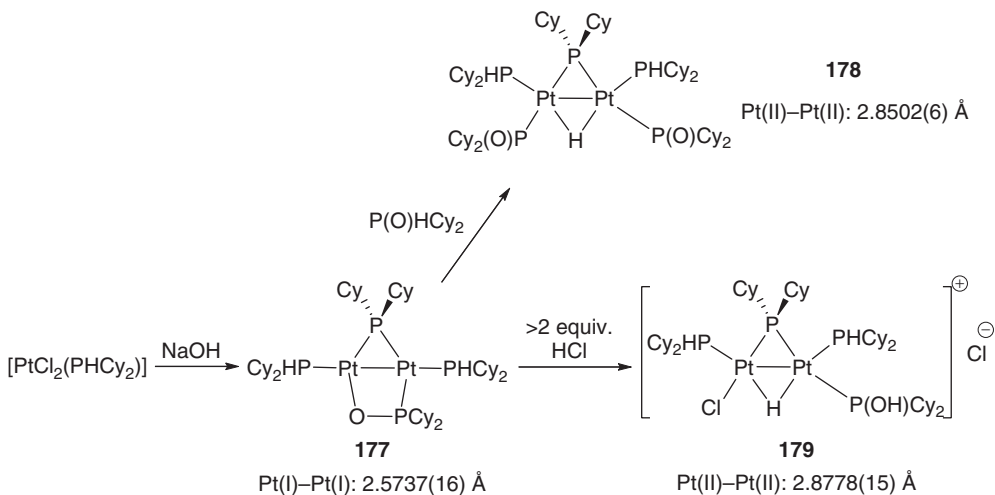
Recently, a comproportionation reaction between a diplatinum(II) compound and a Pt(0) source $\{[Pt(H)dippe]\}_2$ [133] was reported to yield a phosphinidene-bridged diplatinum(I) compound **176** (Scheme 10.77) [127]. The Pt(I)–Pt(I) bond in **176** is rather long (2.7396(9) Å) (Entry 9, Table 10.12).

A phosphinito (R_2PO^-) bridging diplatinum(I) compound **177** and its protonation reactions were reported recently. Complex **177** was protonated by a variety of proton sources (HCl, HBr, HBF_4 , $P(O)HCy_2$) to produce a series of phosphido hydride bridged diplatinum(II) compounds, while two of the protonations are presented in Scheme 10.78 [128]. It was found that the protonation preferentially



Scheme 10.77 Synthesis of diplatinum(I) compound $[\text{Pt}_2(\mu\text{-PPh})(^i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2]$ (**176**).

takes place at the Pt site coordinated by an O atom, and a combined NMR and DFT mechanistic study was conducted [128c].



Scheme 10.78 Synthesis and reactivity of phosphinito ligand-bridged diplatinum(I) compound **177**.

Two diphosphane bridging diplatinum(I) compounds **180**, **181** (Figure 10.18) were synthesized along with their dipalladium(I) counterpart (**107**, Section 10.2.2.2) [72]. They were demonstrated to exist as polymers or oligomers in the solid state, and the luminescence properties of these compounds were studied [72].

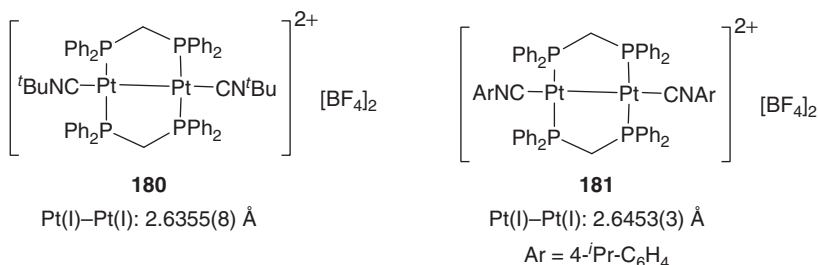
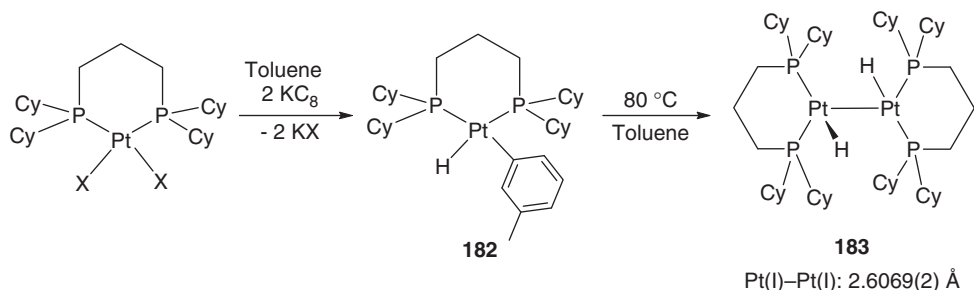


Figure 10.18 Diphosphane-bridged diplatinum(I) compounds **180** and **181**.

A diplatinum(I) hydride with unsupported Pt(I)–Pt(I) bond was reported recently, from a C–H bond activation of toluene (Scheme 10.79) [129]. The Pt(I)–Pt(I) bond length in diplatinum(I) compound **183** is 2.6069(2) Å (Entry 15, Table 10.12), while the two hydrides were found to be both terminal.



Scheme 10.79 Synthesis of diplatinum(I) hydride [Pt₂H₂{Cy₂P(CH₂)₃PCy₂}₂] (**183**) with unsupported Pt(I)–Pt(I) bond.

The reaction between Pt(0) or Pt(II) hydride precursors and silane or germanes with E–H bonds (E = Si, Ge) can provide a variety of E–H bond activated products, for example, a series of silyl or germyl bridging diplatinum(I) compounds (Figure 10.19) [130]. Further conversion of these compounds was possible including E–E bond coupling as well as the formation of Pt(II) silyl/germyl hydride.

10.2.3.3 Diplatinum(II) Compounds

Several examples of diplatinum(II) compounds with Pt(II)–Pt(II) bonds have been reported since 2005, which was historically underdeveloped in contrast with the prevalent diplatinum(III) compounds. Some examples of weak intermolecular metal–metal interactions were reported in the past few years [134]. But the intermolecular interaction, although it is intriguing from a structural perspective and has exhibited interesting physical properties, is outside the scope of the following section.

A series of compounds containing unsupported M(II)–M(II) d⁸–d⁸ bonds (M = Pd, Pt) were reported in 2012 using the macrocyclic N₂S₂ ligand (Figure 10.20) [135]. The M(II)–M(II) distances (for Pt(II)–Pt(II): Entry 1, Table 10.13) are significantly longer than the corresponding unsupported M(I)–M(I) bond length (e.g., **183**, see Scheme 10.79 and Ref. [130]), but shorter than the sum of van der Waals radii for both Pd and Pt (Pd: 3.26; Pt: 3.50 Å). The existence of a M(II)–M(II) bond was further confirmed by DFT, and the bond orders for **190** (Pt(II)–Pt(II)) and **191** (Pd(II)–Pd(II)) were found to be 0.24 and 0.19, respectively.

Two hydride- and acetylide-bridging diplatinum(II) compounds (**192**, **193**) were characterized as products of reactions between Pt(II) and Pt(0) precursors via C–H bond activation and/or rearrangement (Scheme 10.80) [136].

As stated in Section 10.2.3.2, the reaction between low-valent platinum (Pt(0)) compounds with silane or germane can provide silyl/germyl bis-Pt(I) compounds; it can also produce bis-Pt(II) compounds with bridging dianionic R₂E^{2–} ligands (E = Si, Ge). One example (**194**) is presented in Scheme 10.81 [137]. The reaction forming **194** involves cleavage of Si–Ge, Ge–Ge, and Ge–H bonds, and the Pt(II)–Pt(II) bond length is 2.7211(6) Å (Entry 4, Table 10.13).

Diplatinum(II) compounds (**195**, **196**) with both intramolecular Pt(II)–Pt(II) bond and intermolecular Pt(II)–Pt(II) interactions were reported in the last decade (Figure 10.21) [138]. The diplatinum(II) paddlewheel monomer assembles into 1-D infinite chains through weak intermolecular Pt(II)–Pt(II) interactions, which were studied by a combination of spectroscopic and

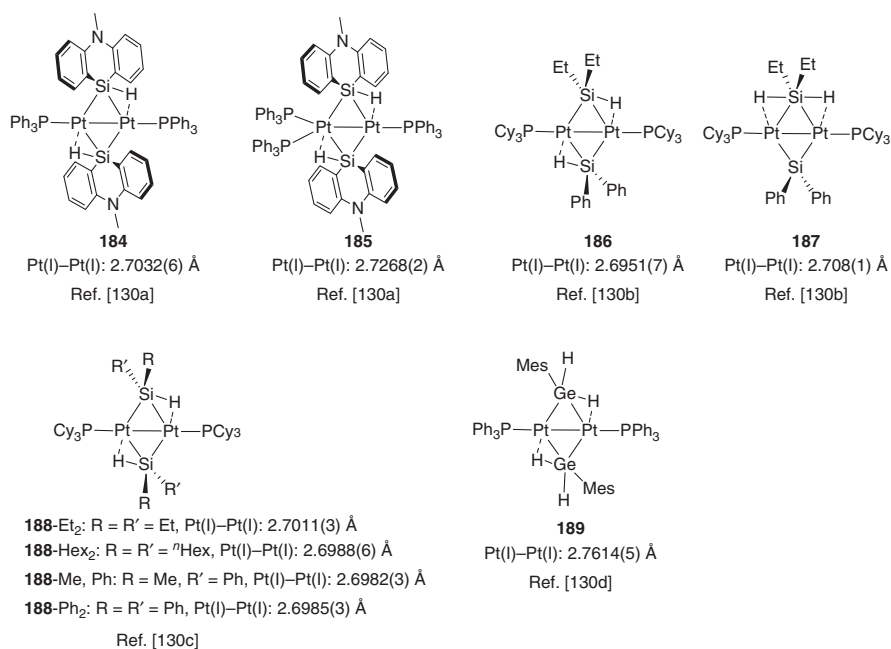


Figure 10.19 Silyl/germyl ligand-bridged diplatinum(I) compounds **184–189** [130].

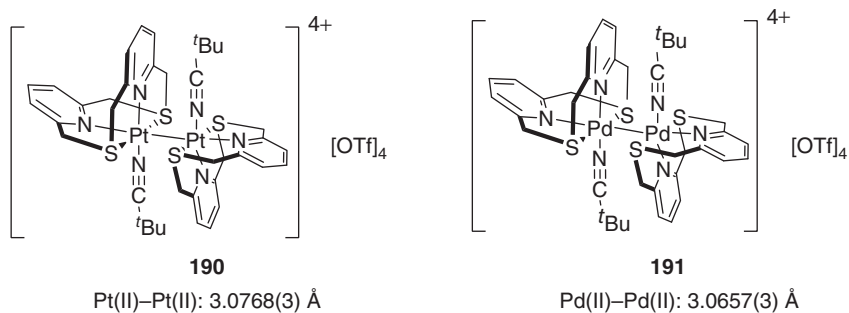
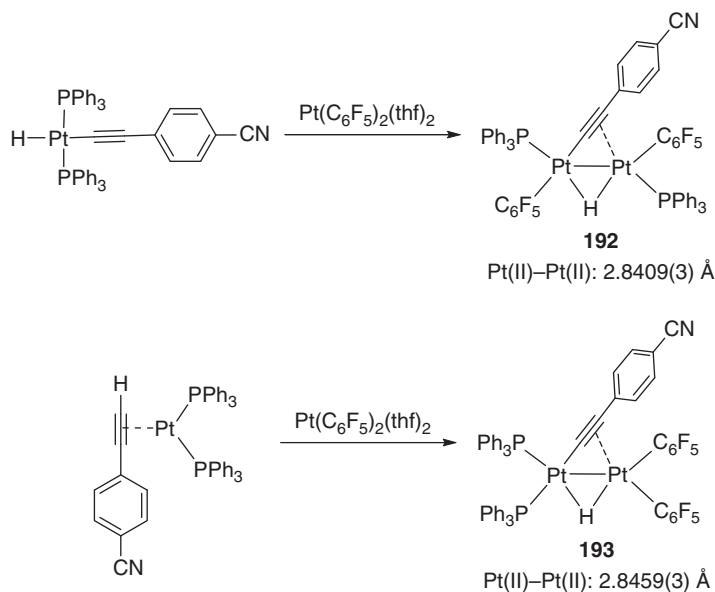


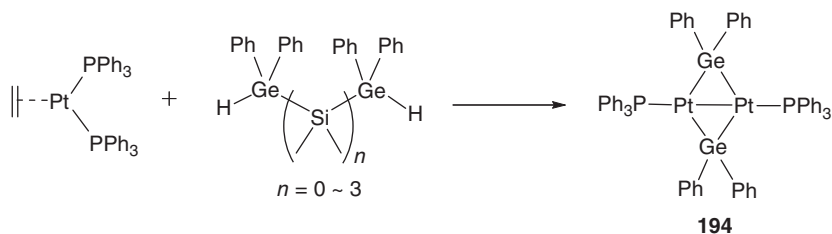
Figure 10.20 Diplatinum(II) compounds **190** and **191** with unsupported Pt(II)–Pt(II) bond.

Table 10.13 Pt(II)–Pt(II) bond lengths.

Entry	Compounds	Pt(II)–Pt(II) (Å)	References
1	190	3.0768(3)	[135]
2	192	2.8409(3)	[136]
3	193	2.8459(3)	[136]
4	194	2.7211(6)	[137]
5	195	2.711(1)	[138a]
6	196 - ⁿ Bu	2.7366(4)	[138b]
7	196 - ⁱ Bu	2.7619(12)	[138b]
8	197	2.8324(1)	[139]



Scheme 10.80 Synthesis of diplatinum(II) compounds **192** and **193** via C–H activation/rearrangement.



Scheme 10.81 Synthesis of diplatinum(II) compound $[\text{Pt}_2(\mu\text{-GePh}_2)_2(\text{PPh}_3)_2]$ (**194**).

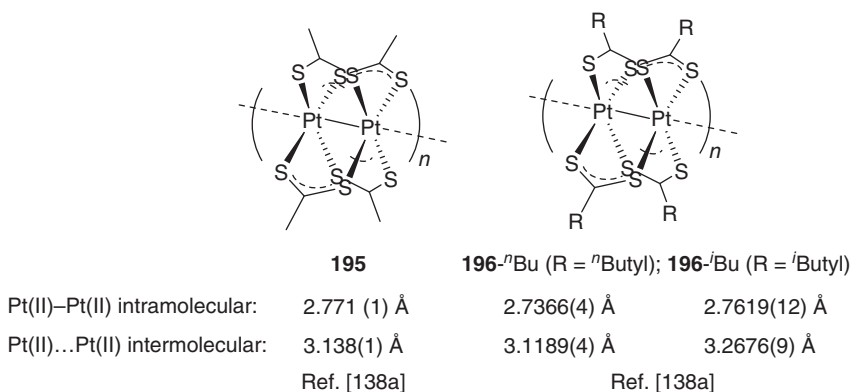
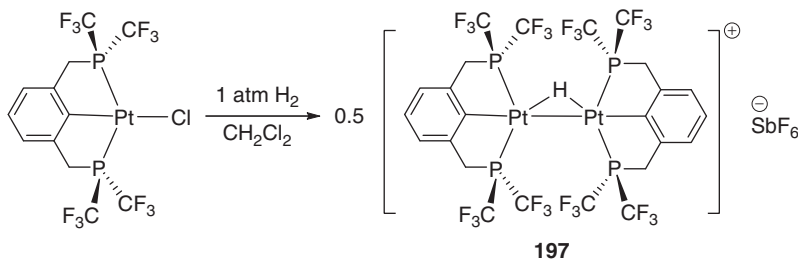


Figure 10.21 Paddlewheel diplatinum(II) compounds **195** and **196** with weak intermolecular Pt(II)···Pt(II) interaction.

computational methods. These compounds were found to behave as semiconductors and the conductivity value directly correlates with the Pt(II)–Pt(II) distance.

A hydride bridged Pt(II)–Pt(II) bond was reported in compound **197**, with a Pt–Pt bond length of 2.8324(1) Å (Entry 8, Table 10.13). Complex **197** was a product of hydrogenolysis of a Pt(II) chloride with pincer-type ligand (Scheme 10.82) [139].



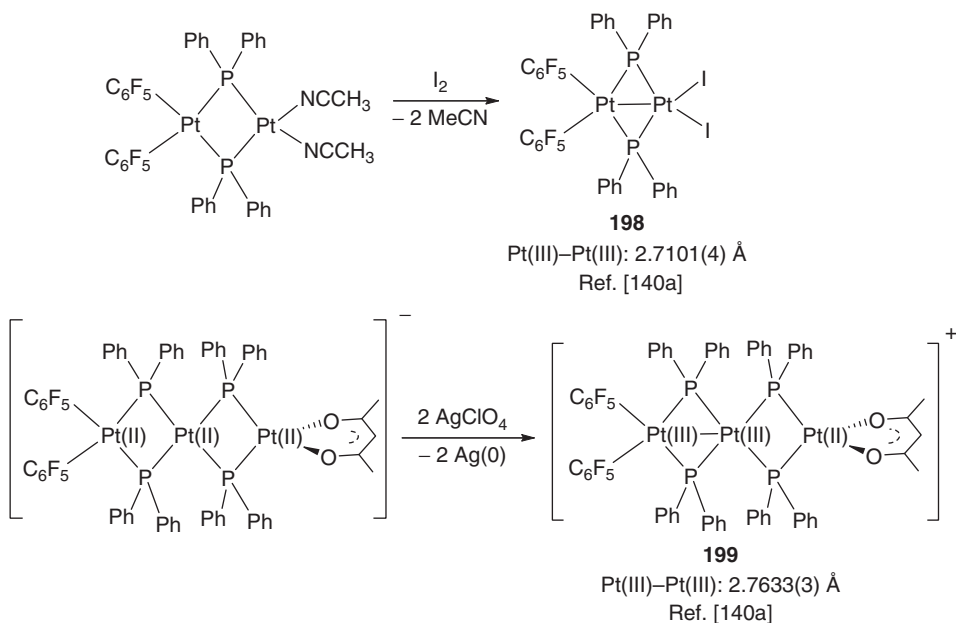
Scheme 10.82 Synthesis of a hydride-bridged diplatinum(II) compound **197**.

10.2.3.4 Diplatinum(III) Compounds

As was stated at the start of Section 10.2.3, the Pt(III)–Pt(III) single bond is one of the most prevalent metal–metal bonds in the whole periodic table. As a research field with historical prosperity but relatively slow in development recently, some of the latest advances of diplatinum(III) compounds,

to some extent spurred by the recently significant breakthrough of Pd(III)–Pd(III) chemistry, were made in the last decade and will be summarized in the following section.

As for the Pd(III)–Pd(III) moiety, 2-electron oxidation of diplatinum(II) compounds was proven to be a viable synthetic route toward Pt(III)–Pt(III) bonds. A series of phosphido bridged diplatinum(II) compounds were oxidized to form Pt(III)–Pt(III) compounds **198** and **199** (Scheme 10.83) [140]. Complex **198** can further undergo reductive coupling to produce $[C_6F_5PPh_2]$ and Pt(II) species under mild conditions. It is noteworthy that Pd(II) compounds with identical ligand profiles were also tested for the same reaction condition, but no corresponding Pd(III)–Pd(III) moieties were obtained.



Scheme 10.83 Oxidative formation of Pt(III)–Pt(III) bond from Pt(II) precursors [140a].

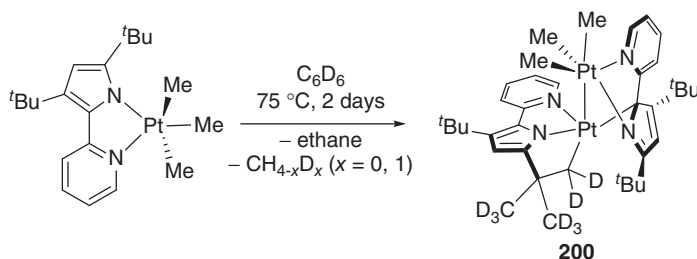
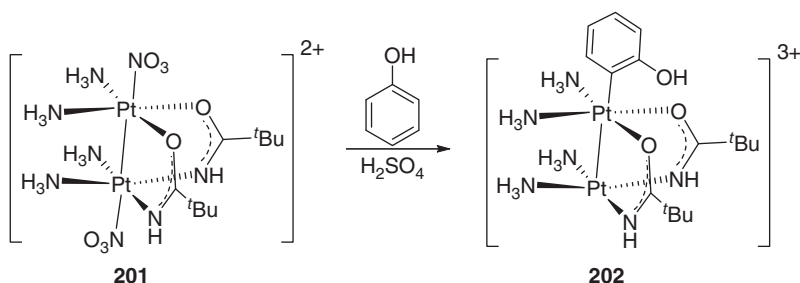
Beside oxidation, the reduction of Pt(IV) compounds is a less common but still a viable pathway to construct Pt(III)–Pt(III) bonds. The novel compound **200** with a Pt(III)–Pt(III) bond (2.7688(6) Å) (Entry 3, Table 10.14) was obtained as the major Pt-containing product in a reasonable yield from pyrolysis of a Pt(IV) trimethyl compound in C_6D_6 solution (Scheme 10.84) [141]. The Pt(III)–Pt(III) oxidation state of **200** is consistent with the spectral data, and a plausible mechanism for its formation was proposed by the authors, including the deuteration of ligand's t Bu substituent.

A diplatinum(III) compound **201** was produced from the oxidation of Pt-blue, which is a Pt_4^{9+} compound with formula of $[HH-\{Pt_4(NH_3)_8(tBuCONH)_4\}\{NO_3\}_5]$ (HH : head–head), with $Na_2S_2O_8$ in 0.1 M H_2SO_4 solution [146]. Historically, **201** was found to be reactive toward alkenes, alkynes, and dienes [147]. In 2005, it was reported **201** can activate the *ortho*-C–H bond of phenol to form **202**, in which the Pt(III)–Pt(III) bond length is 2.6836(17) Å (Entry 4, Table 10.14) (Scheme 10.85) [142].

A handful of diplatinum(III) aryl compounds with Pt(III)–Pt(III) bonds were made from oxidative C–H bond activation mediated by Pt(II) precursors (**203**–**205**, Figure 10.22) [143]. These compounds were studied as platinum models of Pd-catalyzed C–H bond functionalization (**203**) [143a], for their unique physical properties, for example, as a liquid crystal material (**204**) [143b] or a chiroptical material (**205**) [143c].

Table 10.14 Pt(III)–Pt(III) bond lengths.

Entry	Compounds	Pt(III)–Pt(III) (Å)	References
1	198	2.7101(4)	[140a]
2	199	2.7633(3)	[140b]
3	200	2.7688(6)	[141]
4	202	2.6836(17)	[142]
5	203	2.5647(2)	[143a]
6	204	2.5730(3)	[143b]
7	205	2.5952(6)	[143c]
8	206	2.9947(2)	[144a]
9	207	2.8394(3)	[144b]
10	208	2.527(2) or 2.533(2)	[145a]
11	209	2.4748(6)	[145b]
12	210-Cl	2.6896(2)	[145c]
13	210-Br	2.7526(3)	[145c]
14	210-I	2.7929(7)	[145c]

**Scheme 10.84** Reductive formation of Pt(III)–Pt(III) bond from Pt(IV) precursor.**Scheme 10.85** Diplatinum(III) compound **201** mediated C–H bond activation.

As for diplatinum(I) and diplatinum(II) compounds, the activation of E–H bonds (E = Si or Ge) can produce diplatinum(III) compounds. Compounds **206** and **207** were reported individually from reaction between a Pt(II) precursor and E–H bonds (Figure 10.23) [144]. It is noteworthy that in **207**, the bridging $\text{Ph}_2\text{Ge}^{2-}$ ligand is unsymmetrically coordinated to the two Pt(III) centers (Pt– μ -Ge: 2.5322(4) and 2.3800(3) Å), and the asymmetry was explained by a MO calculation [144a].

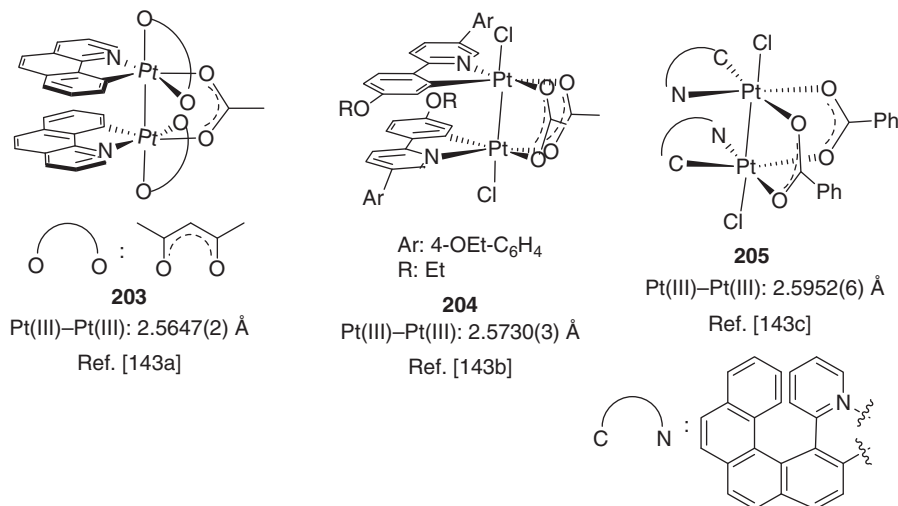


Figure 10.22 Diplatinum(III) compounds **203**–**205**, which are made from oxidative C–H bond activation mediated by Pt(II) precursors [143].

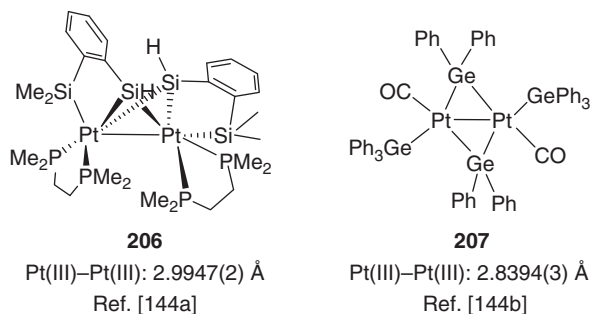


Figure 10.23 Diplatinum(III) compounds **206** and **207**, which are made from oxidative activation of Si–H/Ge–H bond mediated by Pt(II) precursors [144].

A few paddlewheel diplatinum(III) compounds were reported in the last decade, and some representative examples are presented in Figure 10.24 [145]. It was revealed that the Pt(III)–Pt(III) bond lengths of compounds **210**–Cl/Br/I (Entries 12–14, Table 10.14) were influenced by the axial ligands as well as intermolecular lattice packing effects, and these compounds exhibited unprecedented near-infrared emission at room temperature [145c].

10.2.3.5 Mixed-Valent Diplatinum Compounds

In 2009, a synergistic 2-center oxidation of a C–I bond toward a Pt(II) precursor was reported to form the diplatinum compound **211** (Scheme 10.86) [148]. Although the Pt–Pt bond length in **211** is 2.7639(4) Å (Entry 1, Table 10.15), which is within the range of Pt(III)–Pt(III) bond lengths (2.52–2.79 Å, see Table 10.14 in Section 10.2.3.4), detailed inspection of multinuclear NMR spectra and X-ray crystallographic data suggests a fluxional Pt(III)–Pt(III) ↔ Pt(IV)–Pt(II) formulation. The octahedral Pt^I has significant Pt(IV) character, while the quasi-square pyramidal Pt² plays the Pt(II) part.

A Pt(I)–Pt(III) compound **212** was prepared along with its Pt(I)–Pt(I) and Pt(III)–Pt(III) congeners, **213** and **214**, respectively (Figure 10.25) [149]. These compounds were studied as

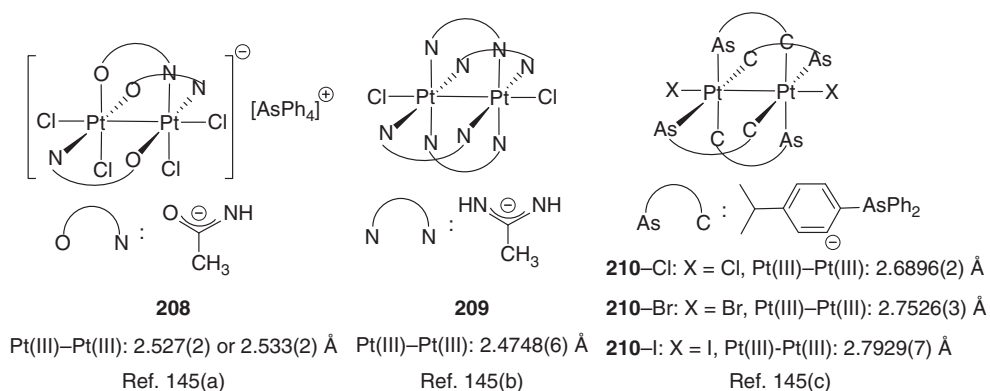
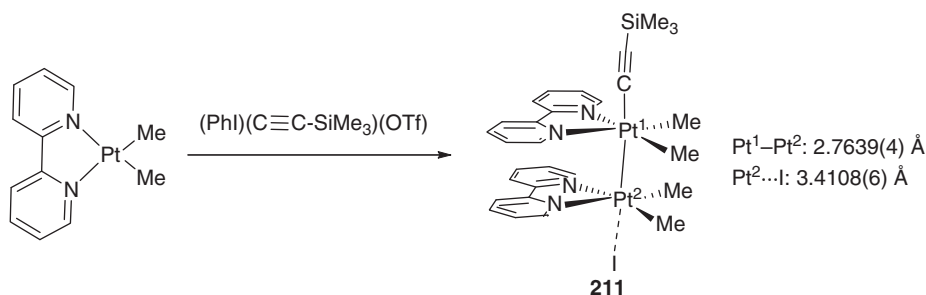


Figure 10.24 Paddlewheel diplatinum(III) compounds **208**–**210** [145].



Scheme 10.86 Synthesis of a mixed-valent Pt(IV)–Pt(II) diplatinum compound **211**.

Table 10.15 Pt–Pt bond lengths in mixed-valent diplatinum compounds.

Entry	Compounds	Pt–Pt (Å)	References
1	211	Pt(IV)–Pt(II) 2.7639(4)	[148]
2	212	Pt(I)–Pt(III) 2.6187(7)	[149]
3	215	Pt(I)–Pt(III) 2.6985(4)	[150]

high-quantum yield and halogen-trap-free photocatalysis system for HX photosplitting. From a structural perspective, a comparison of Pt–Pt bond lengths in different oxidation states but similar ligand environment is intriguing, as the Pt(I)–Pt(I), Pt(I)–Pt(III), and Pt(III)–Pt(III) bond lengths are 2.6187(6), 2.6187(7), and 2.7037(3) Å, respectively.

A triplatinum compound **215**, which has a Pt(I)–Pt(III) bond (2.6985(4) Å) (Entry 3, Table 10.15) was synthesized from a formal intramolecular disproportionation from a triplatinum(II) precursor (Scheme 10.87) [150]. The assignment of oxidation states of the three Pt centers and existence of the Pt(I)–Pt(III) d⁷–d⁹ bond was supported by a combination of computational techniques

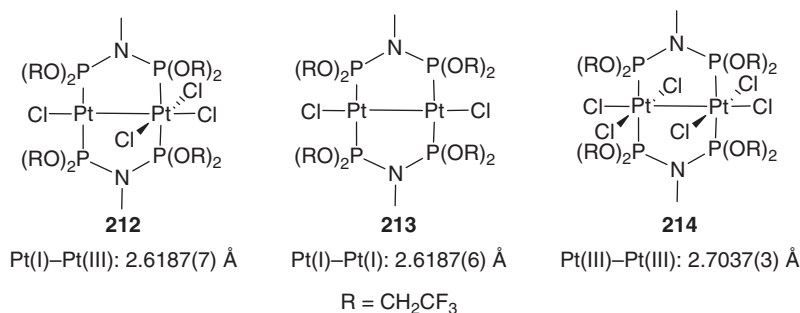
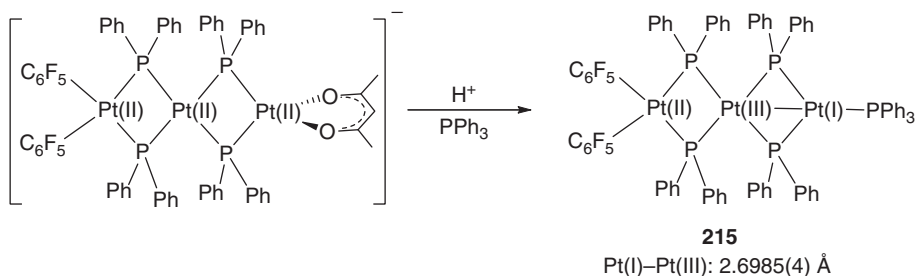


Figure 10.25 Mixed-valent Pt(I)–Pt(III) compound **212**, and its diplatinum(I) (**213**) and diplatinum(III) (**214**) congeners.

(natural bond order analysis, the Laplacian of the electron density, localized orbital locator profiles).



Scheme 10.87 Synthesis of a trinuclear compound **215** with a Pt(I)–Pt(III) bond.

10.2.4

Heterobimetallic Compounds

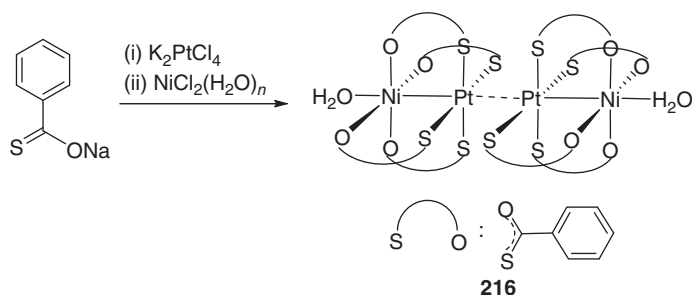
In contrast to homobimetallic compounds, heterobimetallic compounds with M–M' bonds (where M and M' are different group 10 metals) are far less developed. In the last decade, a few of these compounds were synthesized and representatives are summarized in the following section.

A Pt(II)–Ni(II) compound **216** was synthesized via straightforward salt metathesis reaction (Scheme 10.88) [151]. The Pt(II)–Ni(II) bond length in **216** is 2.570(1) Å (Entry 1, Table 10.16), and a weak intermolecular Pt–Pt interaction was found to be responsible for the formation of a head-to-tail dimer structure of **216**. A magnetism study revealed **216** to be one of the first examples of antiferromagnetic coupling through an unbridged Pt–Pt interaction.

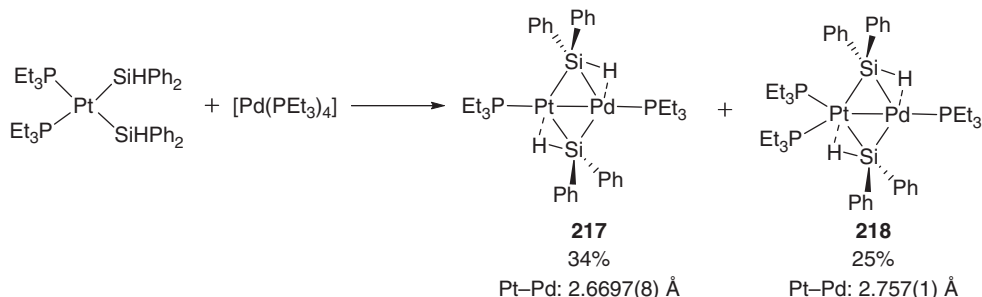
Pt–Pd compounds represent the vast majority of the family of Group 10 heterobimetallic compounds with metal–metal bonds.

The reaction between Pt(II) disilyl and [Pd(PEt₃)₄] produce Pt–Pd heterobimetallic compounds **217** and **218** as products in low yield (Scheme 10.89) [152]. Further reaction of **218** with isocyanate, via Pt–Pd bond cleavage and insertion of the C≡N bond into Si–H or M–Si bonds, produced a novel Pt(II) compound with a Pt–Si–C–N–Si five-membered ring.

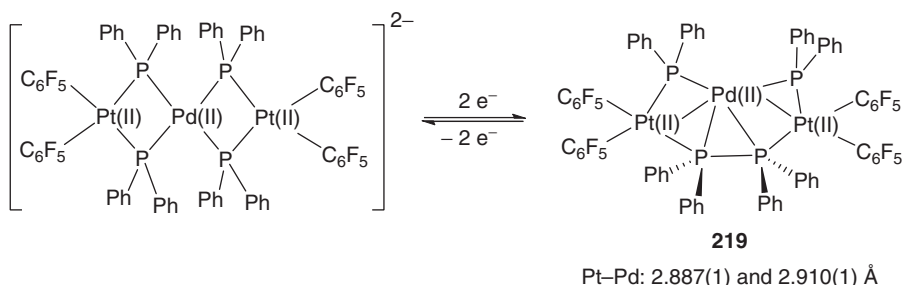
A series of heterobi- or multi-metallic Pt–Pd compounds with bridging phosphido ligands were reported by Forníés and coworkers in the last decade. In 2005, a reversible transformation of two Ph₂P[–] monoanionic ligands into the neutral diphosphine (Ph₂P–PPh₂) were reported (Scheme 10.90)



Scheme 10.88 Synthesis of heterobimetallic Ni(II)–Pt(II) compound **216**.



Scheme 10.89 Synthesis of heterobimetallic compounds (**217**, **218**) with Pd–Pt bonds.



Scheme 10.90 Reversible formation/cleavage of Pd(II)–Pt(II) bonds by two-electron reduction/oxidation.

[153]. The formation of a P–P bond and two Pt–Pd intermetallic bonds are presumably via a Pd(III) intermediate. Further conversions of **219** were achieved by reacting with pyridine, CO, and PPh₃ (Scheme 10.91). The production of **220–222** features the cleavage of one of the Pt–Pd bond while retaining the other [154].

Treatment of the phosphido bridged Pt(II)/Pd(II) heterobimetallic compound with [Ag(ClO₄)PPh₃] led to the formation of Pt–Pd and Pd–Ag bonds in **223** (Scheme 10.92) [155]. The oxidation states of the Pt and Pd centers do not change during the reaction.

A Pt(0)–Pd(0) bond was reported within the gallium(I) ligand-bridged heterobimetallic compound **224** (Figure 10.26), where the bond length was found to be 2.5888(10) Å (Entry 10, Table 10.16), which is rather short for a low-valent Group 10 metal–metal bond [52].

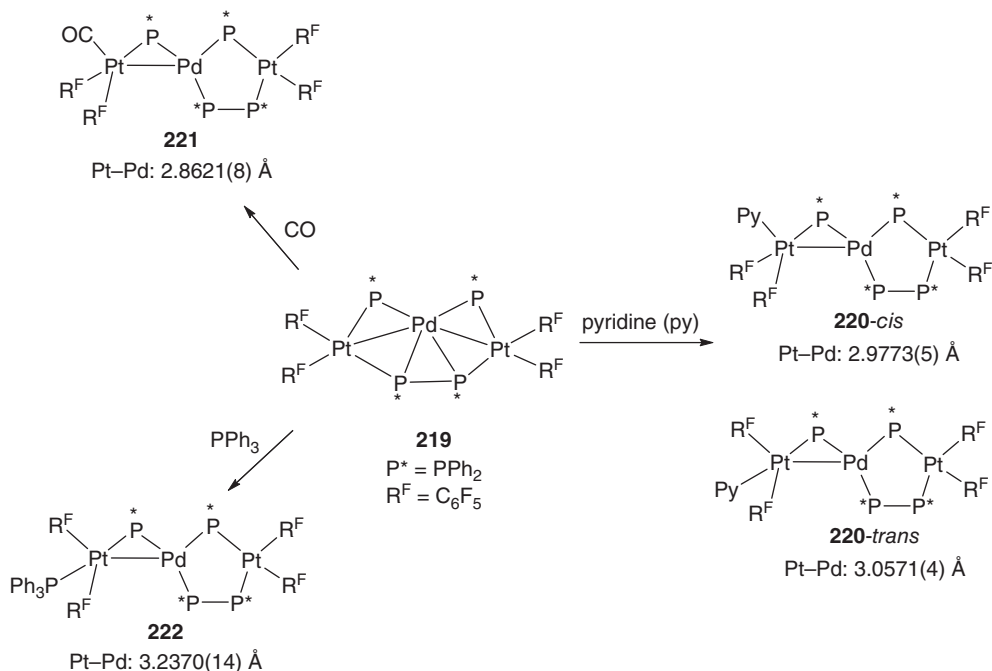
Table 10.16 M–M' bond lengths in Group 10 heterobimetallic compounds.

Entry	Compounds	M–M' (Å)	References
1	216	Pt(II)–Ni(II) 2.570(1)	[151]
2	217	Pd(I)–Pt(I) 2.6697(8)	[152]
3	218	Pd(I)–Pt(I) 2.757(1)	[152]
4	219	Pd(II)–Pt(II) 2.887(1) or 2.910(1)	[153]
5	220-cis	Pd(II)–Pt(II) 2.9773(5)	[154]
6	220-trans	Pd(II)–Pt(II) 3.0571(4)	[154]
7	221	Pd(II)–Pt(II) 2.8621(8)	[154]
8	222	Pd(II)–Pt(II) 3.2370(14)	[154]
9	223	Pd(II)–Pt(II) 2.6760(4)	[155]
10	224	Pd(0)–Pt(0) 2.5888(10)	[52]
11	225	Pd(I)–Pt(I) 2.7851(9)	[156]
12	226	Pd(I)–Pt(I) 2.649(4)	[157a]
13	227	Pd(I)–Pt(I) 2.691(1)	[157a]
14	228	Pd(I)–Pt(I) 2.571(1)	[157b]
15	229	Pd(I)–Pt(I) 2.9084(4)	[158]
16	230	Pd(I)–Pt(I) 2.9767(5)	[158]

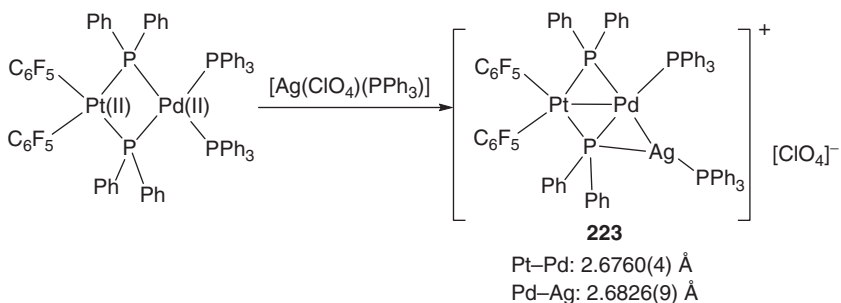
Since it was demonstrated that a bulky tertiary phosphine such as PPh_3 can act as neutral bridging ligand [159], much effort was focused on using this strategy to construct di- and polynuclear compounds of potentially great interest in catalysis, bioinorganic chemistry, and material sciences [160]. In 2005, a sterically demanding phosphine ligand with coordinative pendant arm was applied to synthesize a Pd–Pt compound **225** (Scheme 10.93) [156]. The Pd–Pt– P_2 core adopts a diamond shape and the Pd–Pt bond length is 2.7851(9) Å (Entry 11, Table 10.16). Based on the metric parameters as well as NMR data, the oxidation states of metal centers were proposed to be Pd(I)–Pt(I).

Other Pt(I)–Pd(I) compounds with bridging diphosphane and related ligands were reported and representations are listed in Figure 10.27 [157].

Very recently, two Pd–Pt heterobimetallic compounds (**229**, **230**) with 2,2'-bipyridine and pyridine-2-thiolate ligands were synthesized and characterized (Figure 10.28a) [158]. It was found that the Pt center in **229** and **230** can form intermolecular Pt–Pt interactions, which result in the formation of a phase named “dimer-of-dimer” (Figure 10.28b). The vapor and mechanically induced chromic behavior of these compounds was studied, and the weak Pt–Pt



Scheme 10.91 Reactivity of a heterotrimetallic compound 219.



Scheme 10.92 Synthesis of a heterotrimetallic Pd–Pt–Ag compound 223.

interaction along with the “dimer-of-dimer” phase was found to be responsible for these chromic behavior.

10.3

Multimetallic Sandwich Compounds – a Brief Introduction

As the most prevalent structure in organometallic chemistry, sandwich compounds, defined as two cyclic aromatic hydrocarbon ligands flanking one metal center, has played a central role on the stage of organometallic chemistry and catalysis ever since the seminal structure of ferrocene (Cp₂Fe) was elucidated in 1952 [161]. However, this chemistry had never been extended into compound mono-layers of multiple metal atoms in place of the one metal center as the “filling” of the “sandwich” until

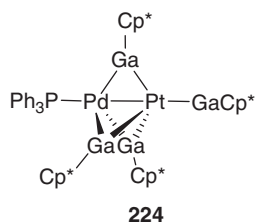
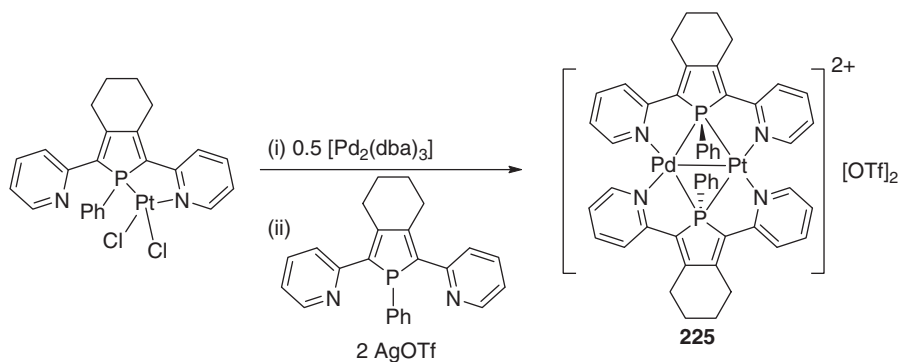


Figure 10.26 A Ga(I) ligand-supported Pd(0)–Pt(0) compound **224** with rather short Pd(0)–Pt(0) bond length.



Scheme 10.93 Synthesis of sterically demanding phosphine ligand-supported Pd(II)–Pt(II) heterobimetallic compound **225**.

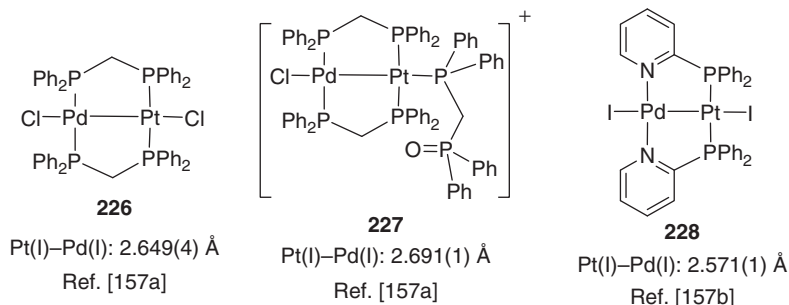


Figure 10.27 Diphosphane and the related ligands-bridged Pt(II)–Pd(II) compounds **226**–**228** [157].

2006. In that year, with the background of their previous work on a perylene–tetrapalladium compounds [162], tripalladium and pentapalladium monolayer sandwich compounds **231** and **232**, with the formula of $[\text{Pd}_3(\text{C}_7\text{H}_7)_2\text{Cl}_3][\text{PPh}_4]$ and $[\text{Pd}_5(\text{naphthalene})(\text{toluene})][\text{B}(\text{3,5-(CF}_3)_2\text{C}_6\text{H}_3)]$ respectively, were reported by Murahashi and coworkers (Scheme 10.94) [163]. The preparation of **231** started from a Pd(0) precursor $[\text{Pd}_2(\text{dba})_3]$, while the preparation of **232** started from a Pd(I) precursor $[\text{Pd}_2(\text{MeCN})_6][\text{BF}_4]_2$ with an unsupported Pd(I)–Pd(I) bond.

Complexes **231** and **232** have impressive structural features [163]. In **231**, the tripalladium core was sandwiched by two cationic cycloheptatrienyl ligands, and the Pd–Pd bond lengths within the Pd_3 triangle (2.745–2.789 Å) fall within the range of other Pd–Pd bonds. DFT calculations suggested that the interaction between $[\text{Pd}_3\text{Cl}_3]^{3-}$ and $[\text{C}_7\text{H}_7]^+$ is primarily comprised of backdonation of $d\sigma$ – $d\sigma$ antibonding orbital of $[\text{Pd}_3\text{Cl}_3]^{3-}$ to $[\text{C}_7\text{H}_7]^+$, along with a smaller contribution from backdonation of $d\pi$ – $d\pi$ bonding orbitals of $[\text{Pd}_3\text{Cl}_3]^{3-}$ to $[\text{C}_7\text{H}_7]^+$, and π orbitals of $[\text{C}_7\text{H}_7]^+$ to acceptor orbitals of

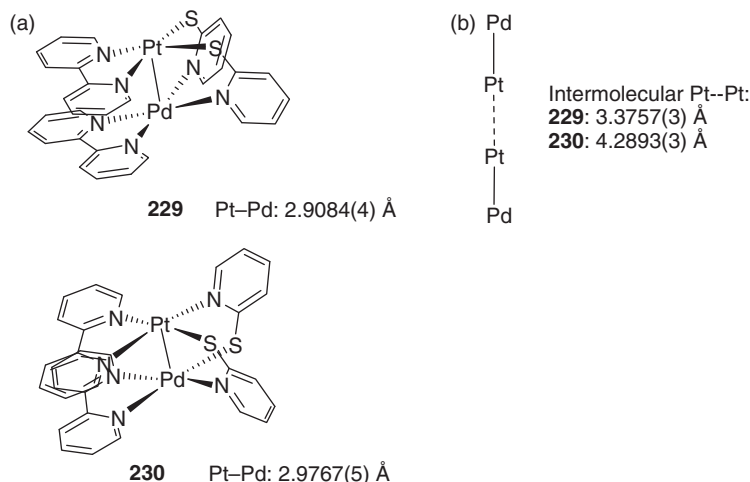
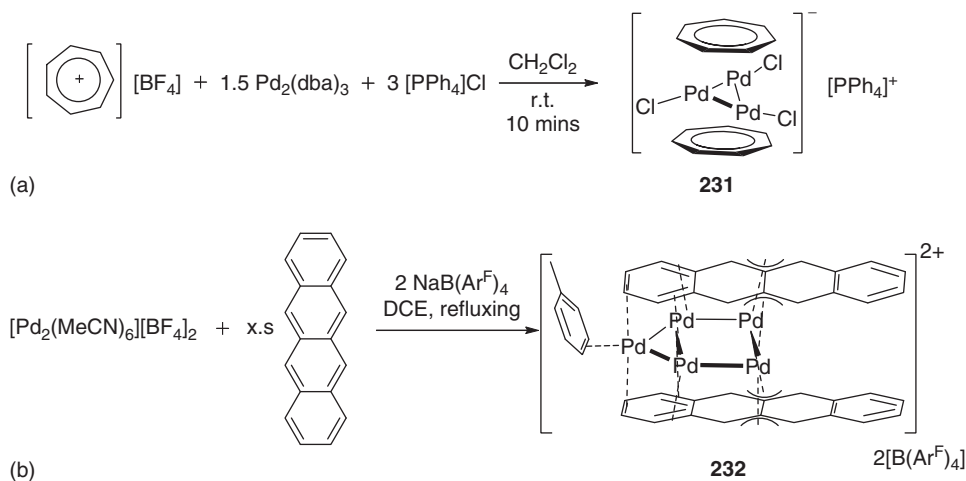


Figure 10.28 Pd–Pt heterobimetallic paddlewheel compounds (**229**, **230**), and (b) the intermolecular Pt–Pt interaction.



Scheme 10.94 Synthesis of (a) tripalladium (**231**) and (b) pentapalladium (**232**) monolayer sandwich compounds.

$[\text{Pd}_3\text{Cl}_3]^{3-}$. The Wiberg bond order of the Pd–Pd bonds in **231** was evaluated as 0.282, 0.282, and 0.258. In **232**, the pentapalladium sheet was sandwiched by two naphthalene ligands, and the five Pd centers were nearly coplanar. The bonding interactions in the $[\text{Pd}_5(\text{naphthalene})_2]^{2+}$ was quite complicated, and the Wiberg bond orders of the Pd–Pd bonds in **232** varied from ~ 0 to 0.198, indicating a weaker Pd–Pd bond in comparison with that in **231**.

After the seminal discovery of multimetallic sandwich compounds **231** and **232**, several palladium [164], platinum [165], and Pd/Pt heterometallic [166] sandwich compounds belonging to the new and burgeoning family were synthesized and characterized. Furthermore, it was found that the assembly of the multimetallic core can be tuned intermolecularly [167] or intramolecularly [168] by redox reactions. It can be foreseen that this novel and unique family of compounds will flourish in the near future and find its own position in catalysis.

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11

Group 11 Metal–Metal Bonds*Thomas G. Gray and Joseph P. Sadighi*

11.1

Introduction

Copper, silver, and gold form a wide variety of metal–metal bonds. In their $d^{10}s^1$ valence configurations, the elements form highly delocalized bonds in bulk metals and in nanoparticles. Diatomic metal(0) complexes, with a localized M–M bond arising from the interaction of the valence s^1 subshells, have been isolated only for gold, but those of silver and copper have been studied under transient conditions as well as theoretically. In their +1 oxidation state, all three elements form complexes with weak but substantial attractive interactions between d^{10} metal centers, despite the absence of a formal bond. In the +2 oxidation state, these elements might again be expected to form localized covalent bonds between d^9 metal centers, each with one unpaired electron. Generally, only gold does so, but certain metalloproteins contain mixed-valent copper centers with metal–metal covalency. The +3 oxidation state is known for all three elements, but close approaches between these d^8 metal centers are uncommon, and the nature of the metal–metal interactions has been ambiguous. Complexes of these metals in their extremely rare oxidation states of +4 ($[\text{CuF}_6]^{2-}$) and +5 (AuF_5 and salts of $[\text{AuF}_6]^-$) are mononuclear.

This chapter presents selected complexes in which interactions among a few individual metal centers illustrate key concepts of bonding. The vast and rapidly expanding nanoparticle literature thus lies outside its scope. Beginning with formally noncovalent attractions, the different types of metal–metal interactions will be discussed in order of increasing bond strength.

11.2

Formally Noncovalent Metal–Metal Interactions

The best known and most extensively studied interactions between d^{10} metal centers are those observed in gold(I) complexes. In the 1978 book, “The Chemistry of Gold,” Puddephatt pointed out that the X-ray crystal structures of a broad range of gold(I) complexes revealed a notable proximity between metal centers, sometimes requiring surprising geometric distortions [1]. In 1988, Schmidbaur coined the term “aurophilicity” to describe the general phenomenon in which two or more gold(I) centers lie between 2.7 and 3.2 Å apart in the solid state [2, 3]. These distances, significantly shorter than twice the van der Waals radius of 1.66 Å [4], suggested an attractive interaction between formally closed shell $5d^{10}$ metal centers, an interaction not explained by standard rules of valence bonding. The strength of the $\text{Au(I)} \cdots \text{Au(I)}$ interaction has been variously calculated and measured [5], and ranges from 20 to 60 kJ mol^{-1} [3a].

Theoretical discussions of aurophilicity have been reviewed [6]. Recent calculations find a decisive role for electron correlation effects [7], as attractions are found only with addition of explicit correlation between electrons of opposite spin. There is a general consensus that relativity augments closed-shell attractions [8]. Relativistic effects are less important for silver, and far less important for

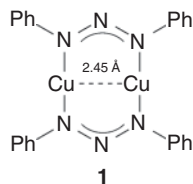


Figure 11.1 Solid state geometry of (1,3-diphenyltriazenido)copper(I).

copper, than for gold; interactions between gold(I) centers are the most numerous, and the concepts of argentophilicity and cuprophilicity have been more controversial [9]. Nonetheless, many copper(I) and silver(I) complexes display short intermetallic distances consistent with weak but nonnegligible metal–metal bonding [10]. Among congeneric assemblies of coinage metals, moreover, occasional examples appear in which argentophilic interactions seem to exceed those between gold atoms [11].

11.2.1

Copper(I)–Copper(I) Interactions

11.2.1.1 Early Identification of Close Approaches

In 1961, Brown and Dunitz obtained the X-ray crystal structure of 1,3-(diphenyltriazenido)copper(I) (Figure 11.1) [12]. In the solid state, this complex exists as a planar dimer with linear copper centers linked by bridging triazenido ligands, and a separation of 2.45 Å between copper centers. Structures of complexes such as $[(\text{H}_3\text{N})\text{CuCN}]$ [13] and $[(\text{PhCC})\text{Cu}(\text{PPh}_3)]$ [14] likewise displayed intermetallic separations notably shorter than twice the van der Waals radius of 1.40 Å [4].

The structures of many σ -organocopper(I) complexes reveal remarkably short metal–metal interactions, resulting from the bridging of adjacent metal centers by carbanions. In tetrakis [(trimethylsilyl)-methylcopper], (Figure 11.2), the Cu–Cu distances are 2.42 Å. The authors proposed that each alkyl was bound through a three-center, two-electron interaction, and that direct copper–copper bonding was unimportant [15]. In the arylcopper tetramer (4-methyl-2-cupriobenzyl)-dimethylamine, the Cu–Cu distances are as short as 2.38 Å [16].

An interesting analog of the (triazenido)copper(I) dimer appeared in 1985, when Beck and Strähle reported a (pentazadienido)-copper(I) trimer (Figure 11.3) [17]. On the striking copper–copper distances of 2.348(2) and 2.358(2) Å, far shorter than the 2.56 Å separation in copper metal, the authors commented, “It is still not fully clear whether such short Cu–Cu distances can be explained in terms of bonding interactions.” This study, at the time featuring the closest approach between copper centers in an isolated complex, sparked renewed interest in the nature of d^{10} – d^{10} interactions.

11.2.1.2 Theoretical Studies

Seeking to understand the interactions between metal centers in complexes such as $[(\text{Me}_3\text{Si})\text{CH}_2\text{Cu}]_4$, Mehrotra and Hoffmann carried out extended Hückel calculations on the fragments $[\text{Cu}_2]^{2+}$, $[\text{Cu}_3]^{3+}$, and $[\text{Cu}_4]^{4+}$, and examined the effects of bridging ligands on the resulting molecular orbitals [18].

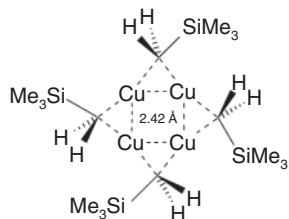


Figure 11.2 Tetrameric (trimethylsilyl)methyl copper.

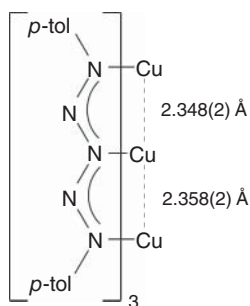


Figure 11.3 Copper(I) [1,5-di(*p*-tolyl)-1,4-pentazadienide].

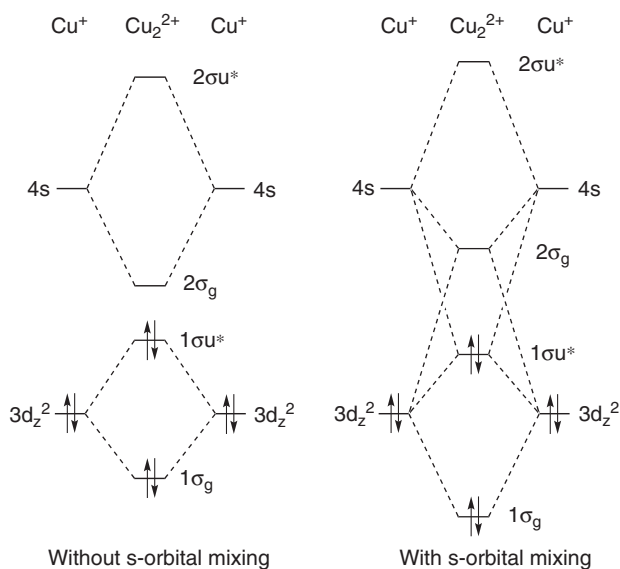


Figure 11.4 σ -Interactions of d_{z^2} in $[\text{Cu}_2]^{2+}$, without and with s-orbital mixing. Energy scale is qualitative; $4p_z$ mixing not shown.

The subject was later revisited and expanded on in the context of the (pentazadienido)copper(I) trimer [19]. These studies found that a pure $d^{10}–d^{10}$ interaction is repulsive for copper. Relative to the free d-orbitals, the antibonding combinations are slightly more destabilized than the bonding combinations are stabilized. Symmetry-allowed mixing of 4s and 4p orbital combinations reverses the situation: The occupied antibonding orbitals are less destabilized than the bonding orbitals are stabilized, and a net bond order results. A simplified subset of these interactions is depicted in Figure 11.4. In concluding their study Mehrotra and Hoffmann wrote that “it will be difficult to distinguish the effects of direct Cu–Cu interaction and the stereochemical demands of the ligand set around the copper atoms.” In a contemporaneous study, Avdeef and Fackler studied orbital interactions in a $[\text{Cu}_8(\text{SR})_{12}]^{4-}$ cluster using a modified self-consistent charge and configuration method, and found no net copper–copper bonding interaction at the observed intermetallic distance of 2.8 Å [20].

In an *ab initio* investigation of the (pentazadienido)copper(I) trimer, using coupled pair functional calculations, Kölmel and Alrichs ascribed the extremely short copper–copper distances to dispersive interactions between the d^{10} centers, rather than to substantial metal–metal bonding [21]. Cotton and coworkers examined this and related complexes using density-functional theory, and likewise concluded that its copper–copper distances could be explained satisfactorily without

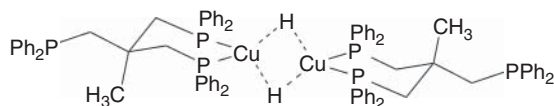


Figure 11.5 A (κ^2 -trisphosphine)copper μ -hydride dimer.

invoking copper–copper bonding [22]. Instead, both studies found, strong copper–nitrogen bonding combined with the rigid geometric constraints of the bridging ligand to force the copper centers into remarkable proximity. In contrast, Schwerdtfeger and coworkers studied complexes of the form $[(H_3C)CuL]_2$ using MP2 calculations, and determined that the closed-shell copper–copper attraction could be worth up to 17 kJ mol^{-1} [23]. The *ab initio* study revealed significant copper–copper bonding in a special case of ligand bridging: $Cu_2(\mu-H)_2$. The intermetallic distance in this complex, which does not have a covalent metal–metal bond, is calculated at $2.155\text{ \AA}$, compared to $2.22\text{ \AA}$ for gaseous Cu–Cu, which does! In the bridging hydride, the metal–metal bonding occurs not directly, but through strong three-center, two-electron interactions [24, 25].

11.2.1.3 Three-Center, Two-Electron Bonding in Copper(I) Complexes

The hydrogenolysis of copper(I) *tert*-butoxide in the presence of phosphine ligands leads to the formation of copper(I) hydride clusters [26]. Remarkably, when a tripodal phosphine was used, the product was not a monomeric copper hydride of the form L_3CuH , but a dinuclear, hydride-bridged structure $[L_2Cu(\mu-H)]_2$, with a pendant phosphine from each ligand (Figure 11.5) [27]. Even more than the very short copper–copper distance of $2.371(2)\text{ \AA}$, the formation of hydride bridges rather than additional Cu–P bonds reflects the strength of the Cu–H–Cu interactions. The change in enthalpy for the dissociation of $[(H_3P)_2Cu(\mu-H)]_2$ to two $[(H_3P)_2CuH]$ fragments was later calculated at $+132\text{ kJ mol}^{-1}$ [28]. Stronger donors such as the *N*-heterocyclic carbene (NHC) or, more recently, the cyclic alkylamino carbene (CAAC), support three-coordinate copper(I) hydride dimers of the form $[LCu(\mu-H)]_2$ [29], with copper–copper distances as short as $2.295(1)\text{ \AA}$.

Consistent with early studies of carbanion-bridged systems [15, 16], aryl ligands such as 2,4,6-trimethylphenyl (mesityl) [30] and bulkier 2,6-terphenyls [31] give rise to oligomeric copper(I) complexes with short copper–copper distances, on the order of $2.4\text{ \AA}$ and in some cases slightly shorter. Like an aryl anion, a free NHC bears an occupied sp^2 -hybridized orbital on carbon and can act as a bridging σ -donor, although this binding mode is quite rare for copper(I). Thus, a bis(phosphinoferrocenylethyl)-substituted NHC reacts with $(Ph_3P)CuI$ to form a dinuclear complex bridged by both iodide and NHC ligands (Figure 11.6a), with a Cu–Cu distance of $2.3561(13)\text{ \AA}$ [32]. For comparison, low-dimensional CuI crystals composed of Cu_8I_8 unit cells have been prepared within single-walled carbon nanotubes. The Cu–Cu distances of $2.42\text{--}2.72\text{ \AA}$ (compared to $4.28\text{ \AA}$ in bulk CuI) were analyzed computationally and interpreted as cuprophilic interactions, that is, as attractive interactions between closed-shell copper centers [33].

Because of strong π -donation from the two nitrogen atoms to the nominally empty carbon p-orbital, NHCs are very weak π -acceptors [34]. The much more electrophilic diphenylmethylene gives rise to a reactive carbene-bridged dicopper complex (Figure 11.6b) that cyclopropanates styrene. The bonding in the diphenylmethylene complex includes *two* three-center interactions (Figure 11.6c): one between an in-phase combination of σ -symmetric orbital hybrids and the carbene lone pair; the other between an in-phase $d\pi$ -orbital combination, occupied, and the vacant carbene p-orbital [35]. Although the differences in supporting ligands and coordination numbers must be kept in mind, it is worth noting that the complex with a strongly π -accepting carbene features shorter Cu–C_{carbene} bonds and a longer Cu–Cu distance than does the NHC-bridged complex.

As noted earlier, rigid bridging ligands with small bite angles can impose a short intermetallic separation, without necessarily resulting in a significant bonding interaction [22]. The two phenomena are not mutually exclusive, and are sometimes synergistic. Davenport and Tilley synthesized a series of (naphthyridine)dicopper(I) dications bearing a single σ -donor as a bridging ligand [36]. The series,

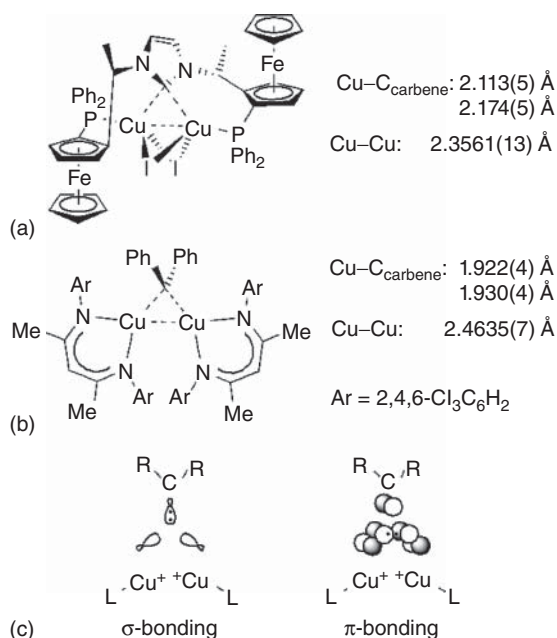


Figure 11.6 Dicopper complexes bridged by (a) nucleophilic and (b) electrophilic carbenes. (c) Bonding interactions between singlet carbene orbitals and (LCu)₂²⁺ combinations.

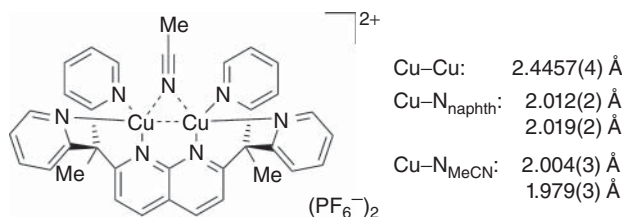


Figure 11.7 σ -Bridging acetonitrile and a cuprophilic interaction.

including a highly unusual σ -bridging acetonitrile complex (Figure 11.7), was studied structurally and by density-functional theory. The authors invoke a three-center, two-electron bonding interaction among the copper centers and bridging acetonitrile: Despite the rigidity of the bridging naphthyridine, the Cu–Cu distance in the absence of acetonitrile was calculated to be nearly 0.2 Å longer. Further analysis, using the quantum theory of atoms in molecules [37], indicated the presence of a bond critical point between the copper atoms, described as a weak, attractive closed-shell interaction. The atoms in molecules analysis has been applied to a range of dinuclear copper(I) complexes, and the resulting bond critical points discussed in the context of closed-shell attractive interactions [38].

A dicopper(I) μ -hydrido cation isolates the three-center, two-electron σ -bonding arrangement from the geometric constraints imposed by additional bridging ligands. The hydrogen 1s-orbital is spherically symmetric, and in principle the [Cu–H–Cu]⁺ linkage can adopt an angle up to 180°. In fact, although dinuclear monohydrides of many metals are bent [39], predictions for the closed-shell [Cu₂H]⁺ include a linear geometry in which steric and electrostatic repulsions are minimized [40]. The crystal structure of {[(IDipp)Cu]₂(μ -H)}⁺ BF₄[−] (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, also called IPr) reveals a Cu–H–C angle of 122(3)° [41]. The copper–copper distances

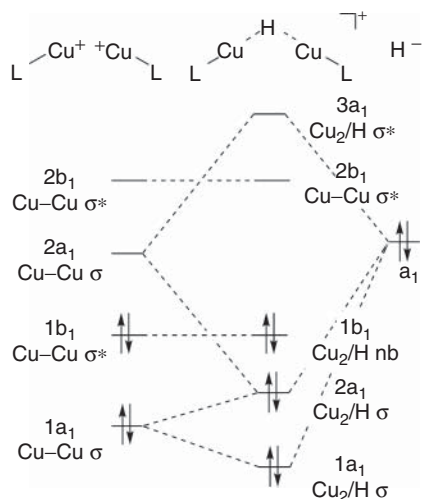


Figure 11.8 Simplified frontier orbital diagram for $[(\text{LCu})_2(\mu\text{-H})]^+$ ($\text{L} = 1,3\text{-dimethylimidazol-2-ylidene}$) in C_{2v} symmetry. Cu–Cu distance (calculated): 2.509 Å.

(two molecules are present in the asymmetric unit) of 2.5331(15) and 2.5354(15) Å are longer than in neutral $\{[(\text{IDipp})\text{Cu}]_2(\mu\text{-H})_2\}$ [29a]. Analysis of a simplified model complex using density-functional theory shows that the $[\text{Cu}_2\text{H}]$ bonding is more complex than a three-orbital, two-electron interaction (Figure 11.8). Extensive mixing of filled 3d-orbital combinations with empty 4s/4p combinations results in two occupied molecular orbitals that are bonding in character across the three centers; the highest occupied molecular orbital (HOMO) is antibonding between coppers and nonbonding with respect to hydrogen. Natural population analysis indicates a considerable copper–copper bond order (the Wiberg bond order [42] in the Löwdin basis is 0.386), but the atoms in molecules [37] analysis show no bond-critical point between the metal centers. The copper–copper bonding apparently occurs through the hydride rather than directly, an example of the “open” three-center interaction [43].

11.2.1.4 Unsupported Copper(I)–Copper(I) Interactions

Some copper(I) complexes display short intermetallic distances even without a bridging ligand. The copper–copper separation in $[\text{L}_2\text{Cu}]^+[\text{CuCl}_2]^-$ [$\text{L}_2 = 1,1'\text{-bis}(2\text{-pyridyl})\text{ferrocene}$] is 2.810(2) Å [44], although the attraction in this case may be largely electrostatic [9d]. The reaction of $[\text{Cu}(\text{NCCH}_3)_4]^+ \text{PF}_6^-$ with the anion of 2-[3(5)-pyrazolyl]pyridine leads to the formation of a cyclic trimer (Figure 11.9), which crystallizes in closely associated pairs [45]. The association between monomers appears to occur through two copper–copper interactions. The authors point out that neither crystal packing forces nor π -interactions between the ligands explain the relative orientation of two monomers, or the difference in intermetallic distances between this complex and its silver analog.

The solid-state structure of lithium (*tert*-butyl)cyanocuprate reveals a network of cyanocuprates complexed to solvated lithium ions through the cyanide nitrogen atoms (Figure 11.10) [46]. Pairs of cyanocuprate ions adopt a nearly perpendicular arrangement about a Cu–Cu axis, with an intermetallic distance of 2.713(1) Å. The C–Cu–C geometries are nearly linear at 168.0(3)° and 170.0(3)°, but this modest bending places the copper centers closer together than would a strictly linear geometry.

Other unsupported copper(I)–copper(I) interactions include those in $(\text{H}_3\text{N})\text{CuX}$ ($\text{X} = \text{Cl}, \text{Br}$) [47], in the pyridine adduct of (pentafluorophenyl)copper [48], and in the surprising approach of

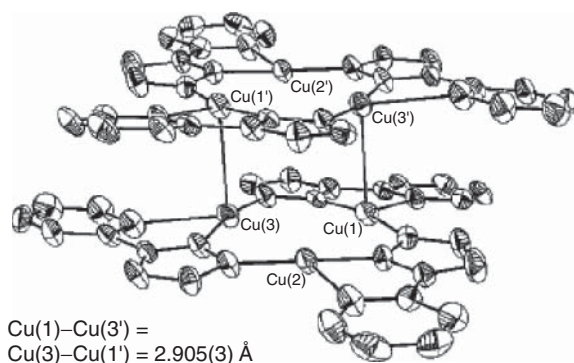


Figure 11.9 Intermolecular attractions between Cu centers in a (pyridylpyrazolato)copper(II) trimer. (Structure reprinted with permission from Ref. [45]. Copyright 1997, American Chemical Society.)

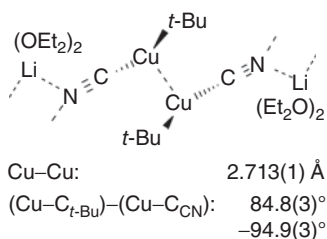


Figure 11.10 Structural representation of $\text{Li}[(t\text{-Bu})\text{CuCN}]$.

two $[\text{CuCl}_2]^-$ ions in a complex cocrystal of amidinium chlorocuprates(I) [49]. Finally, hydrogen bonding to a (phenolato)bis-(hydroxyphenyl)ethane anion allows a close approach between pairs of $[(\text{H}_3\text{N})\text{Cu}(\text{NH}_3)]^+$ cations within a supramolecular framework [50]. For many unsupported $\text{Cu(I)}\text{--Cu(I)}$ interactions, the intermetallic distances are slightly longer than the sum of two van der Waals radii, and not in themselves suggestive of bonding interactions. In their theoretical study [23], however, Schwerdtfeger and coworkers found that the energetic potential of the closed-shell attraction should be very shallow for copper–copper distances between roughly 2.5 and 3.5 Å. The interpretation of such contacts as cuprophilic in nature is therefore plausible.

11.2.2

Silver(I)–Silver(I) Interactions

Many of the observations and controversies of copper(I)–copper(I) interactions are echoed in studies of silver(I) coordination chemistry. Close approaches of d^{10} silver centers in ligand-bridged species are well known; notable examples include a (2-pyridyl)alkylsilver dimer with an Ag–Ag distance of 2.654(1) Å (Figure 11.11) [51], and the (1,3-diphenyltriazenido)silver(I) dimer, with an Ag–Ag distance of 2.669(1) Å [52]. These distances are much shorter than twice the van der Waals radius of 1.72 Å [4], shorter even than the interatomic distance of 2.889 Å in silver metal [53]. Cotton and coworkers characterized a (1,3-diarylformamidinato)silver(I) dimer and found a very short silver–silver interaction of 2.705(1) Å. In light of molecular orbital calculations for a model formamidinate complex, however, they argued that metal–metal bonding in all these complexes is negligible even at such short distances, since the empty silver 5s and 5p orbitals participate in metal–ligand bonding but do not mix sufficiently with the filled d-orbital combinations to produce

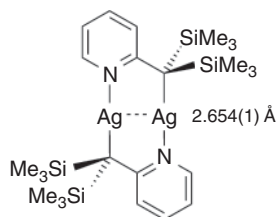


Figure 11.11 A remarkably close approach of Ag(I) centers.

a substantial net bond [54]. On the other hand, the Ag–Ag interactions of 2.794(4)–2.809(3) Å in silver(I) acetate have been studied using density-functional theory, and the atoms in molecules analysis [37] finds Ag–Ag bond critical points within acetate-bridged silver dimers; a peak in the Raman spectrum at 81 cm^{−1} is consistent with a calculated Ag–Ag stretching frequency [55]. These findings are interpreted, like similar findings in copper(I) chemistry, in terms of noncovalent attractive interactions between d¹⁰ metal centers. The structures of the wide array of clusters prepared from silver(I) acetylenediides and other silver salts, with Ag–Ag distances between 2.7 and 3.4 Å, provide additional evidence for such an effect [56].

Silver(I) centers bridged by monodentate σ -donors tend to form short silver–silver contacts. A diselenophosphate ligand supports the {Ag₈(μ_4 -H)[Se₂P(OR)₂]₆}⁺ cluster, in which each selenium atom bridges two silver(I) centers. The hydride ligand sits at the center of a tetracapped tetrahedron of silver(I) centers. The Ag–Ag distances, ranging from just under 3.0 to 3.2 Å, are in the range typically described as argentophilic [57]. This cluster represented the first where hydrogen was bound only to silver [58]. In {[dppm]₃Ag₃(μ_3 -H)(μ_3 -Cl)}⁺ [dppm = bis(diphenylphosphino)methane], short Ag–Ag contacts of 2.8988(2) Å are likewise consistent with argentophilic interactions [59], but also with multicenter, electron-deficient bonding involving the bridging hydride. In the dinuclear complex {(SIDipp)Ag₂(μ -H)}⁺ CF₃SO₃[−] (SIDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene, also called SIPr), hydride is the sole bridging ligand. The solid state structure shows a bent Ag–H–Ag core with an intermetallic distance of 2.8087(4) Å; the ¹⁰⁹Ag NMR spectrum reveals strong, well-resolved coupling of ¹⁰⁹Ag both to hydrogen and, in the mixed isotopologue, to ¹⁰⁷Ag. In the precursor complex {[{(SIDipp)Ag]₂[μ -(Ot-Bu)]}⁺ CF₃SO₃[−], with a three-center, four-electron interaction for which no metal–metal bonding is reasonably invoked, the Ag–Ag distance is much longer at 3.6409(5) Å, and no dipolar coupling between silver nuclei is observed by ¹⁰⁹Ag NMR spectroscopy (Figure 11.12). The bond distances and the spectroscopic observations in the μ -H complex are consistent with strong three-center, two-electron bonding in the [Ag₂H]⁺ core [60].

Examples in which the bridging ligand is an sp²-hybridized carbanion include 2,4,6-trimethylphenylsilver (Figure 11.13) [61], (dimethylaminomethyl)ferrocenylsilver [62], a perfluorovinylsilver [63], and (dimethylaminomethyl)phenylsilver [64]. All of these crystallize as tetramers in a square arrangement of silver centers, with roughly linear coordination to two bridging carbanions; the silver–silver distances range from 2.7 to 2.8 Å. Each Ag–C–Ag moiety may be viewed as having a three-center, two-electron interaction, in which unoccupied orbitals from both silver atoms participate in the bonding combination. This arrangement is analogous to that of the (trimethylsilyl)methylcopper(I) tetramer [15].

Neutral NHC ligands can take the place of carbanions as bridging donors in oligomeric silver(I) clusters. The first structural characterization of the C-bridging mode for an NHC was in the silver complex of a bis-NHC-linked cyclophane, in which a rhomboidal [Ag₄]⁴⁺ core exhibits close Ag–Ag contacts both along the edges (as short as 2.7680(9) Å) and across the ring (2.9712(11) Å) [65]. Subsequently, a 2-pyridylmethyl-substituted NHC ligand was shown to support a trimeric cluster (Figure 11.14), with Ag–Ag distances down to 2.7249(10) Å [66]. This and related complexes [67] are strongly photoluminescent; calculations using relativistic density-functional theory suggest significant net bonding in the [Ag₃]³⁺ core, with the luminescent behavior arising from metal–ligand to ligand charge transfer transitions [68].

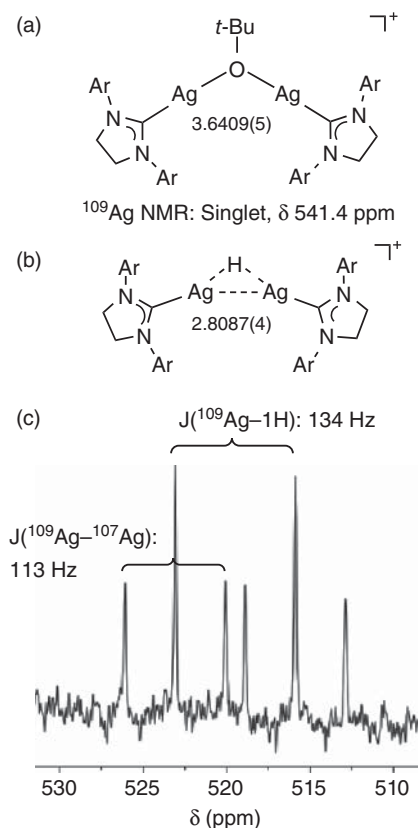


Figure 11.12 (a) Intermetallic distance and ^{109}Ag NMR findings for a three-center, four-electron interaction; (b) intermetallic distance and (c) ^{109}Ag NMR spectrum for a three-center, two-electron interaction.

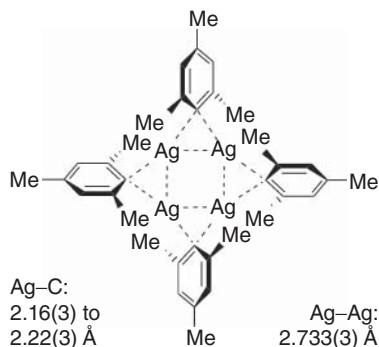


Figure 11.13 Tetrameric (2,4,6-trimethylphenyl)silver.

More frequently, the NHC ligand binds to a single silver(I) center. A number of halide complexes of the form $(\text{NHC})\text{AgX}$ exist in equilibrium with their ionic isomers $[(\text{NHC})_2\text{Ag}]^+[\text{AgX}_2]^-$. Such a salt was characterized in the first report on the extremely useful metallation of imidazolium salts using silver(I) oxide [69]. The crystal structure, represented in Figure 11.15, shows two linear ions staggered about the $\text{Ag}-\text{Ag}$ axis at an angle of 84.6° . The intermetallic distance of $2.954(4) \text{ \AA}$ is near

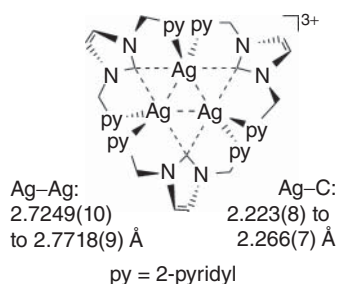


Figure 11.14 A trinuclear Ag(I) cluster with bridging NHC ligands.

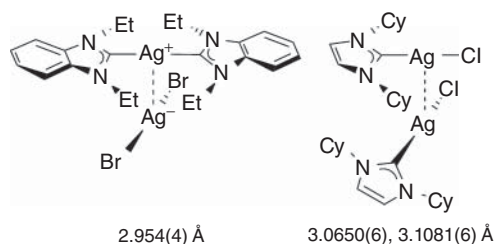


Figure 11.15 Short metal–metal separations in (NHC)silver(I) halide systems. Two distinct dimers are present in the asymmetric unit of (ICy)AgCl.

the short end of the range for ligand-unsupported Ag–Ag interactions [70]. The attraction between these ions may well be largely electrostatic, in analogy with some copper(I) ion pairs [9d]. The structures of some neutral (NHC)silver(I) halides, however, show a similar orientation of linear vectors, with intermetallic separations as small as 3.0650(6) Å (Figure 11.15) [71].

Finally, unsupported Ag–Ag interactions have been used to advantage in supramolecular chemistry [72], as in the spontaneous resolution of helical silver-based coordination polymers [73] and in the construction of homochiral chains [74]. Such interactions have also been used to assemble a three-dimensional porous network of polyoxometallate clusters [75]. In this network, dimeric $\{[(\text{H}_3\text{CCN})_2\text{Ag}]_2\}^{2+}$ cations serve as bridging units for $[\text{H}_3\text{W}_{12}\text{O}_{40}]^{5-}$ anions, with $[(\text{H}_3\text{CCN})_4\text{Ag}]^+$ cations providing charge balance. Argentophilic interactions are invoked not only because of the close Ag–Ag contacts (2.9075(2) Å) within the dimers, but because of an absorption in the UV–visible spectrum at $\lambda = 270$ nm, described as a characteristic feature of close Ag(I)–Ag(I) interactions in other dinuclear systems [76].

11.2.3

Supported and Semi-Supported Gold(I)–Gold(I) Interactions

Attractive interactions between closed-shell gold cations have a decade-long history that has been meticulously reviewed [3c, 77–81]. Interactions between gold(I) centers are the most common. Here, the participants are closed-shell d^{10} ions. All possible bonding combinations are offset by filled antibonding counterparts, and formal Au(I)–Au(I) bond orders are 0.

Schmidbaur and Schier [3a] distinguish semi-supported, supported, and unsupported interactions, Figure 11.16. Supported interactions are not limited to two-coordinate gold, but tri-bridged cases with three-coordinate gold are rare. Recent activity in dinuclear gold chemistry is animated by potential applications in catalysis, film deposition, and luminescence. Selected developments of broad interest are considered here.

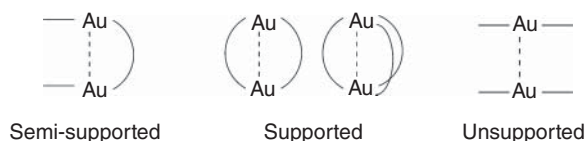


Figure 11.16 Classes of aurophilic interaction. (Reference [3a].)

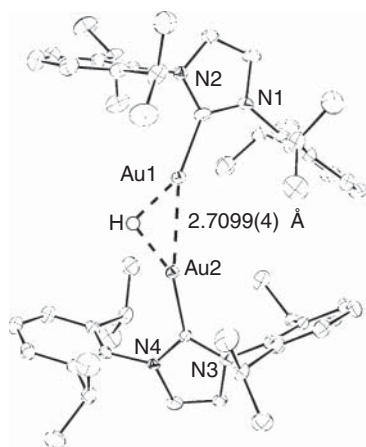


Figure 11.17 A hydride bridged di-gold cation. Hydrogen not located; CF_3SO_3^- anion not shown. Unlabeled atoms are carbon.

11.2.3.1 Diauration at Hydrogen

The isolobal analogy continues to shape molecular gold chemistry [82, 83]. The (phosphine) and (NHC)gold(I) cations are isolobal with H^+ . Yet, the chemistry of gold(I) hydrides remained narrow until 2008, with the report of the first isolable, mononuclear gold(I) terminal hydride [84]. The same work reports a dinuclear μ -hydride cation that is isolobal with H_3^+ . The gold–gold separation is 2.7099(4) Å, and this complex is semi-supported by virtue of the hydride bridge. This structure (Figure 11.17) proves that the NHC IDipp, although bulky, accommodates geminal diauration and close contact between gold atoms. The mononuclearity of (IDipp)AuH cannot be ascribed solely to the girth of the carbene ligand.

In simultaneous reports, Ito, Le Floch, and their respective coworkers [85, 86] described di-gold μ -hydride complexes supported by wide-bite angle diphosphines. The complex of Le Floch and coworkers is crystallographically characterized; the supporting ligand is a xanthene–phosphole, Figure 11.18. The gold–gold separation reveals a tight aurophilic interaction. Density-functional theory calculations find that the gold(I) cation and the hydride interact in a three-center, four-electron bond.

11.2.3.2 Geminal Auration at Carbon

1,1-Diaurated organic compounds were first reported in the 1970s [87]. They have gained renewed interest as possible participants in catalytic reactions. Occurrences of geminally diaurated species as off-cycle catalyst–resting states have been reviewed [88, 89]. Efforts to measure the stability of geminal diaurates have been reported [90]. Recent results are encapsulated here.

Gray and coworkers [91] have published a selective synthesis of geminally diaurated aryls. Reaction of arylboronic acids with (triphenylphosphine)gold(I) triflimidate results in gold-for-boron transmetalation to yield the geminally diaurated products. Upon crystallization, the geminal diaurates are isolated exclusively. The crystal structure of a typical compound appears in Figure 11.19, for which the

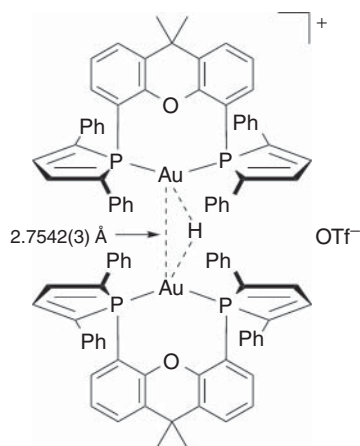


Figure 11.18 A phosphine-substituted di-gold(I) μ -hydride.

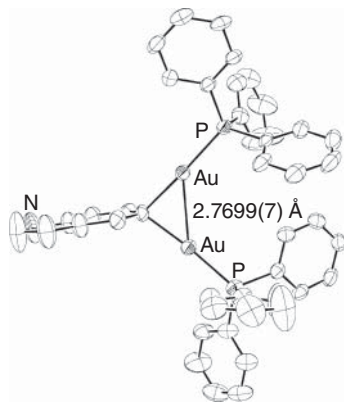


Figure 11.19 Crystal structure (50% ellipsoids) of a cationic 5,5-diaurated indole. NTf_2^- anion and H atoms omitted for clarity. Unlabeled atoms are carbon.

metal–metal separation is 2.7699(7) Å. This separation indicates aurophilic contact. Geminally diaurated aryls exhibit structured luminescence at room temperature in organic solvents. The emission spectrum of $[(\text{Ph}_3\text{PAu})_2(1\text{-naphthyl})]\text{NTf}_2$ ($\text{NTf}_2^- = \text{N}(\text{SO}_2\text{CF}_3)_2$) in dichloromethane is red shifted from that of the monoaurated analog. Density-functional theory calculations of 5-diaurated indole return frontier orbitals dominated by the heterocyclic fragment, with contributions from gold to the lowest unoccupied molecular orbital (LUMO). There is little evidence, either in crystal structures or in optimized geometries for disruption of the aromatic π -cloud.

Nolan and coworkers [92] subsequently reported that geminally diaurated IDipp complexes are accessible from reaction of the mono-gold complexes with $(\text{IDipp})\text{AuNTf}_2$, or by reaction of boronic acids with the pre-formed $\{[\text{Au}(\text{IDipp})]_2(\mu\text{-OH})\}\text{BF}_4$. The bridging hydroxo complex is structurally characterized, but with gold–gold separations that indicate a lack of aurophilic interaction, at least in the crystalline state [93]. Calculations based on second-order perturbation theory suggest interactions between gold atoms with Mayer bond orders indicating partial bonding [94].

Gagné and collaborators have reported equilibrium percentages of di- and monoaurated gold aryls with varying anions, and rates of protodeauration with acetic acid. Among seven anions, triflimidate was best at upholding geminal di-gold structures [95].

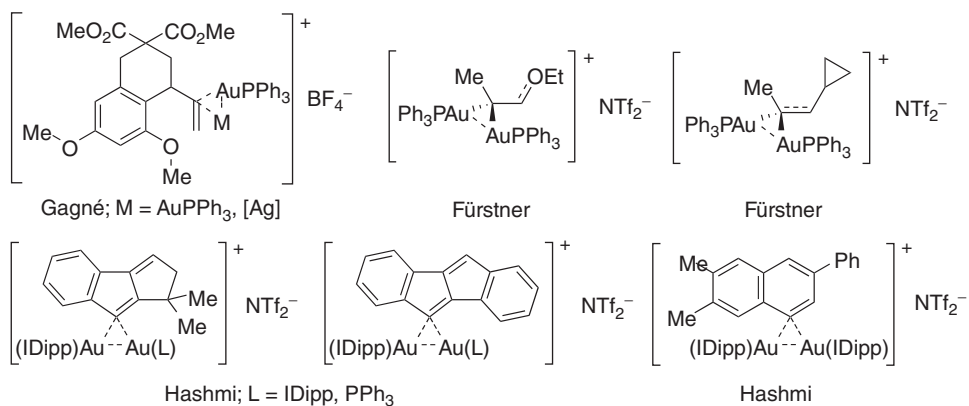


Figure 11.20 Geminally diaurated entities encountered in catalytic studies.

Geminally diaurated complexes have been retrieved from organic reaction mixtures where gold reagents have been added in catalytic amounts. Recent structurally characterized examples are considered here in Figure 11.20. Gagné and coworkers report the occurrence of geminal di-gold vinyls in catalyzed cyclization reactions of allenes. A bimetallic gold–silver complex was described but not structurally characterized. Such mixed-metal species were held to be responsible in part for silver effects in gold(I) catalysis [96]. Fürstner and coworkers [97] characterized geminal di-gold vinyls proximate to an oxygen atom and (separately) to a cyclopropyl group. Gold–gold distances are similar. The structures indicate loss of olefinic character and formation of a partial carbon–oxygen double bond in the ester complex, whereas the cyclopropyl-substituted alkene retains carbon–carbon double bonding. These geminal diaurates are prepared by reaction of (Ph₃P)AuNTf₂ with boronate esters. Cesium carbonate was added to the reaction mixture. Its role is unclear given that geminal diauration of arylboronic acids proceeds without a supporting base [91].

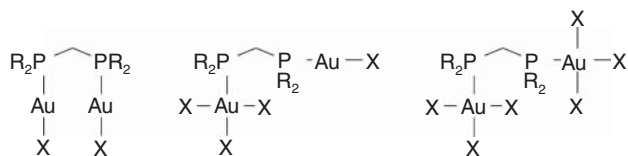
Hashmi and coworkers [98] isolated geminally diaurated species from gold-catalyzed cyclization reactions of 1,2-benzenediynes. One of the alkynyl groups is a terminal $\text{C}\equiv\text{CH}$, and so is easily transformed into a gold(I) alkynyl. A dimetallated benzofulvene is isolated with IDipp capping ligands. A rare example of a geminal diaurate with two different terminal ligands, IDipp and PPh₃, was structurally characterized. This complex was prepared by reaction of a normal gold(I) benzofulvenyl with (Ph₃P)AuNTf₂. Reports of similar compounds followed from the same laboratory [99]. Naphthalene derivatives were prepared in cyclization–arylation reactions with benzyne where gold, delivered as (IDipp)AuNTf₂, both catalyzes the reaction and activates the substrate by carbon–gold σ -bond formation. A geminal diaurate was isolated. Crystallographic characterization yielded a gold–gold distance of 2.7607(3) Å [100].

Very recently, a geminal di-gold isochromen-4-yl complex was characterized and found to be “inactive in catalysis but in equilibrium with the monogold complex and the LAu⁺ catalyst.” A crystal structure shows a gold–gold distance of 2.7315(9) Å. The complex is accessible from the reaction of the mono-gold analog with (Ph₃P)AuNTf₂ [101]. As with Fürstner’s diaurates, bond length changes in the isocoumarin ring are stated to reflect positive charge delocalization onto oxygen.

11.2.3.3 Redox Reactions with Bimetallic Cooperation

Di-gold(I) species supported or semi-supported by ditopic bridging ligands are legion. Chronicled here are some attractive developments of the last 5 years.

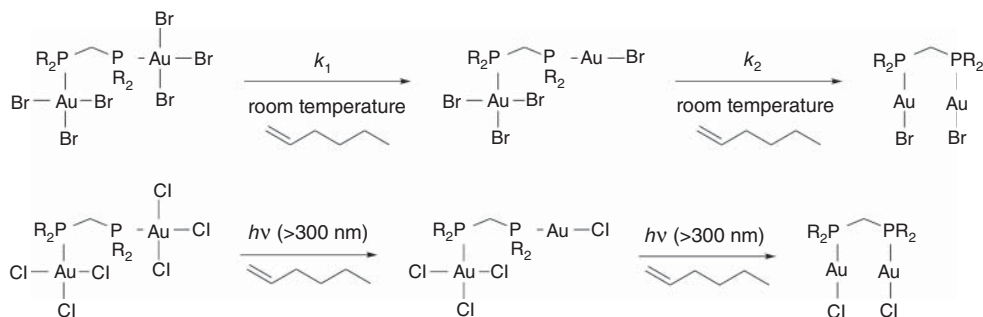
Energy storage is fundamental to large-scale utilization of the solar resource. Nocera and coworkers have developed redox reactions of dimetal centers that exploit aurophilic interactions and metal-philicity more generally.



R = Ph, cyclohexyl; X = Cl, Br

Figure 11.21 Semi-supported di-gold halo complexes.

Teets and Nocera [102] have disclosed a library of semi-supported di-gold bromo and chloro complexes, along with mixed-valence gold(III)/(I) and di-gold(I) analogs. Bridging ligands are as shown in Figure 11.21. Eight compounds were structurally characterized; only a di-gold(I) complex shows an aurophilic interaction, with a gold–gold distance of 3.262(9) Å. Thermal and photochemical reductive eliminations occur for di-gold(III) and Au(III)/Au(I) bromides, Scheme 11.1. Thermal reductions of gold(III) chlorides do not proceed cleanly, but photochemical reductions do. Reactions in solution, both photochemical and dark, proceed in the presence of olefins, which act as halogen traps. Olefins with two prochiral carbons yield *anti*-addition products in thermal reactions. The *anti*-stereochemistry is consistent with bromonium ion intermediacy and addition of the intact halogen. A diastereomeric mixture is expected for addition of a bromine radical; potential radical rearrangement products are not observed. Photochemical reactions show majority *anti*-addition, but the *syn*-addition diastereomer is a minor product when internal olefins are trapping agents.



Scheme 11.1 Thermal and photochemical reduction of di-gold(III) complexes.

Thermal reductive eliminations are faster for di-gold complexes and show evidence for bimetallic cooperation. Moreover, reductive elimination from a dibromide complex is accelerated by buildup or addition of the corresponding product. The authors do not speculate on the microscopic origin of any metal–metal cooperation, but aurophilic assistance is a plausible hypothesis.

Elemental chlorine and bromine add to the solid gold(I) compounds to yield gold(III) analogs that are the authors' initial photoreactants. This reaction is undone upon light excitation. The energy-storing attribute of these trap-free photoreactions is thereby proven.

11.2.3.4 Luminescent Complexes

Di-gold(I) aryls bridged by semirigid diphosphine ligands have been synthesized, structurally characterized, and found to be luminescent. Gray and coworkers [103] have described di-gold(I) aryls bridged by the pillared phosphines Xantphos, DPEphos, and DBFphos, Figure 11.22. These complexes are prepared in base-assisted reactions between the di-gold chlorides [104] or bromides [105] and arylboron reagents. Intermolecular gold–gold interactions are apparent in several (not all) structures. The crystal structure of one [(Xantphos)Au₂(1-pyrenyl)]₂ appears as Figure 11.23.

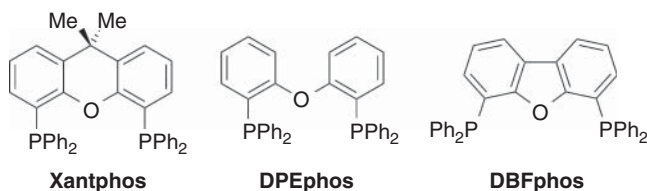


Figure 11.22 Pillared diphosphine ligands.

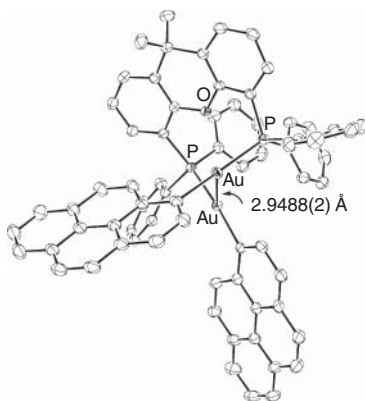


Figure 11.23 Crystal structure (50% ellipsoid) of a di-gold(I) 1-pyrenyl bridged by Xantphos. H atoms omitted for clarity; unlabeled atoms are carbon.

The compounds are luminescent at room temperature with structured emission profiles that suggest aryl ligand-centered emission. Time-dependent density-functional theory calculations support this assignment. Xantphos and related ligands are not spectroscopically innocent; the LUMOs of these compounds reside mostly on the connecting pillars and not on gold or the σ -aryl ligands.

Cano and coworkers [106] have prepared μ -pyrazolato di-gold(I) complexes; three structurally characterized complexes have aurophilically connected gold centers. Capping ligands are again diphosphines. The complexes are prepared by reaction of the sodium pyrazolate with $[\text{Au}_2\text{Cl}_2(\text{diphosphine})]$, where diphosphine = bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, DPEphos, and DBFphos. Complexes are isolated as light-sensitive, colorless solids. Two crystallographically characterized complexes and a dichloro precursor show gold–gold distances of 3.2766(5)–3.3728(9) Å. Bridging pyrazolato complexes luminesce at 77 K in CH_2Cl_2 glass; all except for one chloro complex emit in CH_2Cl_2 at room-temperature.

11.2.3.5 Reagents for Thin-Film Deposition

Coyle and coworkers [107] note that “the coinage metals possess the lowest resistivities of all elements that are suitable for the interconnects in microelectronics.” They report di-copper [108], di-silver, and di-gold [107] complexes that are fully supported by iminopyrrolidinate ligands (Figure 11.24). The metal centers are two-coordinate. Complexes are prepared by reaction of MCl ($\text{M} = \text{Ag}, \text{Au}$) with the lithium iminopyrrolidinate generated *in situ*. Crystal structures are reported for the silver and gold complexes. Both show metallophilic interaction; Ag–Ag and Au–Au distances are within 3σ of each other. The silver and gold complexes were used to form films by chemical vapor deposition (CVD). The resulting films showed different morphologies and electrical resistivities. Decomposition temperatures were evaluated by thermal gravimetric analysis, differential scanning calorimetry, and CVD. The order of thermal stability is $\text{Cu} > \text{Au} > \text{Ag}$. These results resolve an old question in

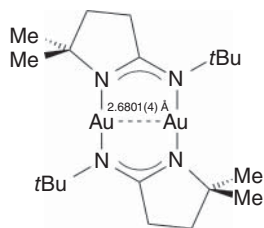


Figure 11.24 An (iminopyrrolidinato)gold(I) precursor for film deposition.

coinage metal chemistry namely the relative stability of the three complexes. Previously, di-gold complexes were held to be relatively unstable because of an inability to isolate them [54]. Similar gold(I) amidinate and guinidinate complexes have been reported [109]. Crystal structures show linear, di-coordinate gold(I) and aurophilic interactions. The related silver complexes are more complicated and undergo monomer $\rightleftharpoons$ dimer equilibria. A trimeric silver(I) complex was structurally characterized. Gold complexes were found to be more stable to heat and light than silver counterparts.

11.2.3.6 Photocatalysis with Di-gold(I) Complexes

The gold(I) complex $[\text{Au}_2(\text{dppm})_2]^{2+}$ emits long-lived yellow phosphorescence as reported independently by Fackler and Che [110–112]. Emission is assigned to a $d\sigma^* \rightarrow p\sigma$ excited state centered on gold. Metal atoms are bonded in the excited state. Many related complexes have been characterized. Absorption spectra show intense transitions assigned as Au_2 $d\sigma^* \rightarrow p\sigma$; weaker spin-forbidden transitions can appear at longer wavelengths.

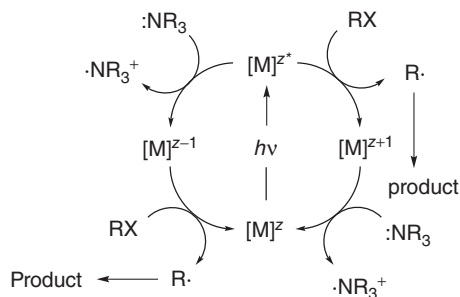
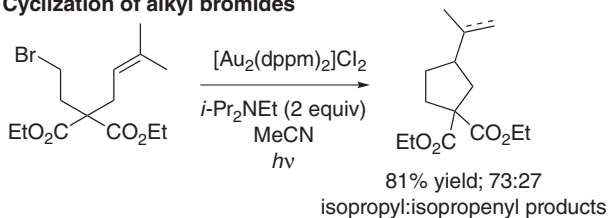
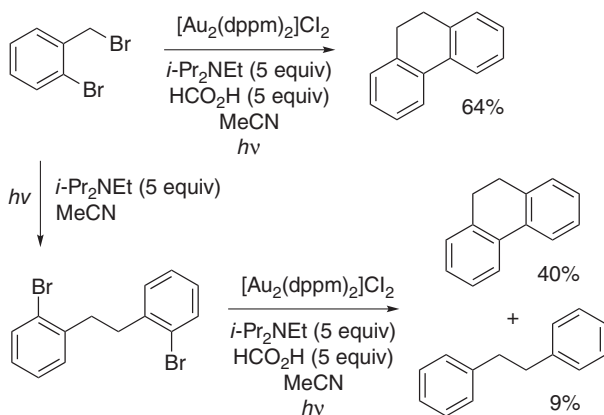
Very recently, $[\text{Au}_2(\text{dppm})_2]^{2+}$ has been developed as a photocatalyst in organic radical reactions such as the photoredox cyclization of alkyl bromides and the cyclization/dehalogenation of aryl bromides [113]. A generalized mechanism for these reactions is depicted in Scheme 11.2. The di-gold complex offers ultraviolet excitability ($\lambda_{\text{max}} = 295 \text{ nm}$), a high triplet-state quantum yield ($\Phi = 0.23$), and an excited-state reduction potential (-1.1 to -1.7 V vs sodium-saturated calomel electrode, SSCE) that is suitable for generating carbon-centered radicals in a single-electron transfer mechanism. Catalyst screening experiments show that the counterion moderates product yields. Unreacted starting material is recovered in the absence of di-gold catalyst. The chloride salt $[\text{Au}_2(\text{dppm})_2]\text{Cl}_2$ was chosen for studies of the reaction scope. Optimized reaction conditions employ diisopropylethylamine (*i*-Pr₂NEt) as a sacrificial hydrogen donor. Formic acid accelerates the reaction; the mechanism is obscure. Deuterium labeling experiments indicate *i*-Pr₂NEt to be the major, but not exclusive, hydrogen source. Both intra- and intermolecular reactions are effective.

11.2.4

Unsupported Gold(I)–Gold(I) Interactions

Balch and coworkers [114] report polymorphs of gold(I) di(isonitrile) salts that differ in the anion: PF_6^- versus AsF_6^- , Figure 11.25a. Both salts can be crystallized as yellow polymorphs upon exposure to solvent vapors. Dichloromethane, acetone, and acetonitrile can all trigger these interconversions. Diethyl ether, pentane, and water vapors appear to not do so. The crystalline, colorless polymorph is blue-emitting; the crystalline yellow polymorph is green-emitting. Both phases of the PF_6^- and AsF_6^- salts have been spectroscopically characterized. In no case does exposure to solvent vapor cause solvent molecules to incorporate into the crystal lattice.

Colorless polymorphs of the PF_6^- and AsF_6^- salts are isostructural. Gold(I) cations align in columns, with gold atoms in aurophilic contact. Gold–gold distances (colorless polymorph) are $3.1983(8) \text{ \AA}$ in the PF_6^- salt, $3.1822(3) \text{ \AA}$ in the AsF_6^- compound. Yellow polymorphs are not isostructural, but have stacks of di(isonitrile)gold(I) cations enchainned through unsupported aurophilic interactions. The longest gold–gold distance in the yellow polymorph, $3.0230(5) \text{ \AA}$ (AsF_6^- salt) is shorter than the shortest gold–gold distance in the colorless phase. Conversion is from the

General mechanism**Cyclization of alkyl bromides****Gold-catalyzed intermolecular radical cyclizations**

Scheme 11.2 General mechanism and selected examples of C–C bond-forming photoreduction catalyzed by $[Au_2(dppm)_2]Cl_2$. (Catalytic cycle redrawn from Ref. [113].)

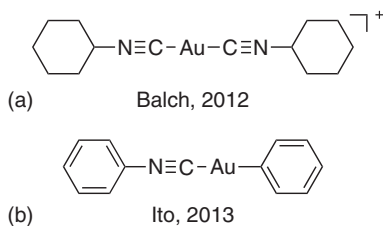


Figure 11.25 (a, b) Two gold(I) isonitriles that form crystalline polymorphs.

yellow, green-emitting polymorph to the colorless, blue-emitting polymorph. This study reports remarkable instances of the broader phenomena of vapochromism and vapoluminescence, which have been reviewed [115].

Conversion between polymorphs can also be attained through mechanical stimuli, as shown in another study of crystalline (isonitrile)gold(I) complexes. Ito and coworkers [116] describe polymorphs of (phenylisocyanide)gold(I) phenyl, Figure 11.25b. A less stable, colorless, blue-emitting polymorph crystallizes that can be transformed mechanically into a more stable yellow-emitting phase that is also crystalline. Crystal structures have been determined for both polymorphs. Auophilic interactions are absent in the structure of the less stable, blue-glowing phase, and present in the more stable yellow-emitting polymorph.

Conversion to the more stable, yellow-emitting polymorph is brought about by pricking the blue-emitting crystals with a needle or by contact with yellow-glowing crystals. The authors describe this change as “a self-replicating progression of phase transformation.” All crystals do not convert at the same rate. A mechanism is proposed whereby mechanical stimulus of the less-stable polymorph propagates throughout the crystal, like tumbling dominoes. The authors note that their crystalline polymorphs illustrate the Ostwald rule: Less-stable polymorphs crystallize early; more-stable phases thereafter.

11.2.5

Metallophilic Interactions Involving Gold(III)

Metallophilicity for gold(III) is less common than for gold(I). Several examples are discussed within broader reviews [4, 10, 117–119], a selective survey of recent results appears here. Che and coworkers [120] report the crystal structure of a bipyridylphenyl gold(III) alkynyl, Figure 11.26, that was prepared from the corresponding gold(III) acetate on reaction with the terminal alkyne and base. The *para*-NMe₂ moiety of the phenylalkynyl ligand was essential for prolonged stability; similar complexes degraded on standing in acetonitrile. The crystal structure shows a gold(III)–gold(III) distance of 3.495 Å, said to be the shortest when reported. Au(III)–Au(III) interactions occur in a pairwise manner, while π -stacking extends throughout columnar stacks in the crystal. Scanning electron micrographs of precipitates formed when diethyl ether is added to acetonitrile solutions showed “belt-like microstructures” with lengths in the tens of micrometers and widths of 1–10 μ m. An electron diffraction experiment on a single microbelt indicated it to be crystalline. The authors propose that metallophilic Au(III)–Au(III) interactions and π -stacking together drive the directional growth of these microbelt structures.

The complex is emissive in the solid state and weakly emissive in acetonitrile solution. Density-functional theory calculations employed a long-range dispersion-corrected functional. An energy

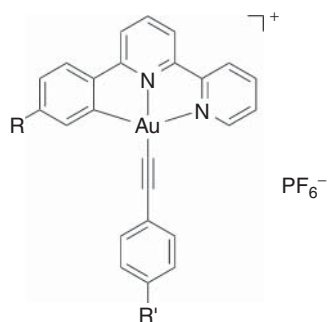


Figure 11.26 Gold(III) alkynyls that show intermolecular metallophilic interactions. Che: R = H, R' = NMe₂. Yam: R = Me, R' = Et.

decomposition analysis showed that dispersive Au...Au interactions and π -stacking are the major contributors to aggregation.

Shortly afterward, Yam and coworkers [121] reported a similar alkynyl with intermolecular gold–gold interactions of 3.6068 Å, and concomitant π -bonding, Figure 11.26. Gimeno, Villacampa, and collaborators [122] disclosed chlorogold(III) complexes of chelating aryl-acyclic carbene-type ligands. One complex of three shows intermolecular Au(III)...Au(III) interactions with a gold–gold distance of 3.514 Å. The individual complexes are linked in the crystal lattice by gold–gold and π -stacking interactions, but these are not mutually reinforcing.

11.3

Covalent Metal–Metal Bonding

11.3.1

Paddlewheel Complexes of Copper(II)

Dicopper(II) tetracarboxylates assume a cofacial arrangement with carboxylates bridging the two copper centers in the classic paddlewheel arrangement for metal–metal bonding. The close approach of two-square planar d^9 centers creates the possibility of a single copper–copper bond. Indeed, the magnetic susceptibility of copper(II) acetate and its analogs is anomalously low compared to most copper(II) salts, reflecting spin-pairing. Figgis and Martin measured a singlet–triplet energy gap of only 300 cm^{-1} for $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$, in which the copper centers lie 2.64 Å apart [123]. These authors ascribe the electron pairing to the formation of a δ -bond between copper(II) centers, through overlap of the singly occupied $d_{x^2-y^2}$ orbitals [124]. Forster and Ballhausen, however, argued for a strong interaction between the d_{z^2} orbitals, such that the σ^* orbital lies above δ^* in energy [125]. The net bond between copper centers would thus be described as a σ -bond, albeit one destabilized by the occupied π^* , δ , and δ^* orbitals lying above the σ -bonding orbital in energy (Figure 11.27) [126].

Exploring the copper–copper interactions in amidinate-bridged trinuclear and tetranuclear complexes, with both copper(I) and copper(II) present, Cotton, Murillo, and coworkers carried out computations on the model complex $\text{Cu}_2(\text{HN}(\text{NNH}))_4$ using density-functional theory [127]. The tri-azenido ligands bridge the copper(II) centers to form a geometry analogous to that of $\text{Cu}(\text{O}_2\text{CCH}_3)_4$. The results of these computations are more closely analogous to the Figgis/Martin scheme: Although the σ/σ^* splitting is large, both orbitals are occupied and lie well below the $d_{x^2-y^2}$ combinations in energy. All π and π^* combinations are fully occupied, as are both the δ and δ^* combinations of the d_{xy} orbitals. In these calculations, the HOMO is actually an antiphase combination with $d_{x^2-y^2}$ character from both metals; the corresponding in-phase combination is the LUMO. At a glance, then, the δ^* orbital is occupied and found below the unoccupied δ -bonding orbital in energy! Differing degrees of metal–ligand antibonding character in these combinations seem to outweigh their δ -bonding versus δ -antibonding character. In this paper, provocatively subtitled “Still No Copper–Copper Bonding” in reference to their earlier findings, the authors contend that spin-pairing in complexes of this type results strictly from strong antiferromagnetic coupling mediated by the bridging ligands [128].

11.3.2

Mixed-Valent Copper(I)/Copper(II) Complexes

Despite their very different functions, both cytochrome *c* oxidase and nitrous oxide reductase contain a dicopper core in which two cysteine thiolates bridge two copper centers separated by ~ 2.5 Å, designated as Cu_A (Figure 11.28a) [129]. The electron paramagnetic resonance (EPR) signal of the Cu_A resting state displays seven-line hyperfine coupling [129b], consistent with the interaction of an electron with two spin-3/2 copper centers. These and other spectroscopic studies support the characterization of Cu_A as a fully delocalized mixed-valent copper(I,II) complex, with each copper center in

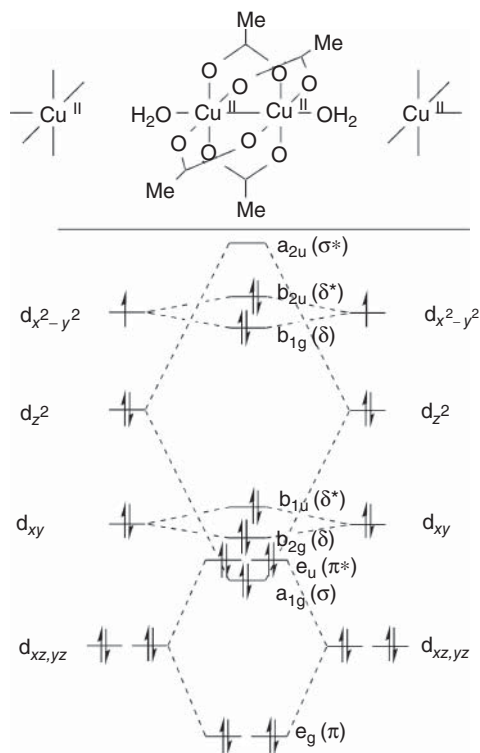


Figure 11.27 Proposed net σ -bonding interaction for $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$.

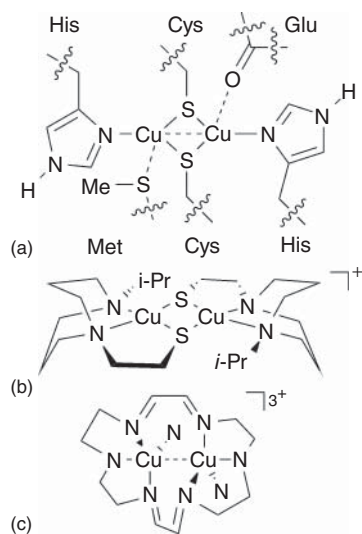


Figure 11.28 Dicopper cores in Cu_A (a), and in mixed-valent model complexes (b, c). Note: Ligand in (c) has $\sim D_3$ symmetry; bridges behind plane omitted for clarity.

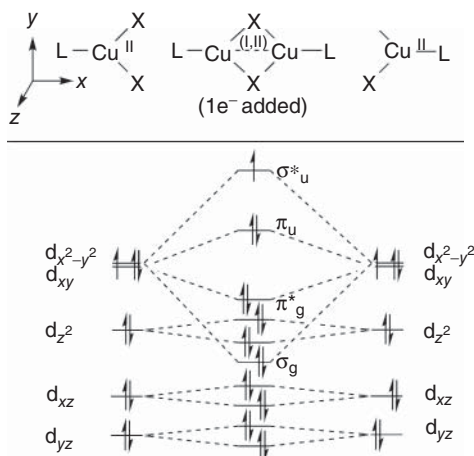


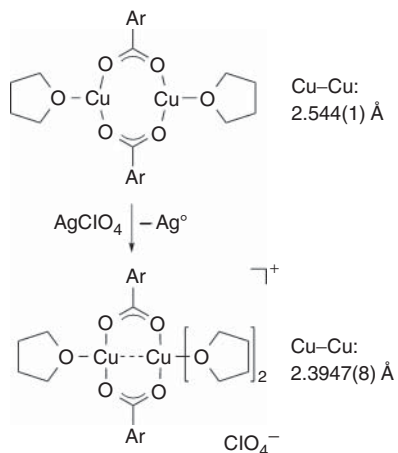
Figure 11.29 Proposed d-orbital interactions in fully delocalized, mixed-valent Cu_A [130]. For clarity, only key orbital combinations are labeled. Note inversion of π^* and π .

the +1.5 oxidation state [130]; the redox cycle of Cu_A occurs between this and the copper(I,I) state. In 1996, Tolman and coworkers reported the synthesis, structure, and spectroscopic characterization of a thiolate-bridged, mixed-valent model complex, also fully delocalized (Figure 11.28b) [131]. Although the copper–copper distance in this model at 2.9306(9) Å is longer than in Cu_A , and too long to suggest significant copper–copper covalency, studies of this complex aided greatly in the spectroscopic characterization of Cu_A . Indeed, a comparison between their absorption spectra led to the characterization of the copper–copper interaction in Cu_A as a net half-bond, with a delocalization energy of 7400 cm^{-1} (0.92 eV) [132].

Before the nature of the copper–copper interaction in Cu_A was understood, the possibility that metal–metal bonding might occur in biology and be relevant or even critical to the function of important electron transfer proteins inspired considerable interest in the synthesis of copper(I,II) model complexes with copper–copper bonding interactions. Threefold-symmetric octaazacryptate ligands were found to stabilize mixed-valent copper(I,II) complexes (Figure 11.28c); the seven-line EPR signal, like that of Cu_A , is consistent with full electronic delocalization between the copper centers [133]. Structural studies find Cu–Cu distances as short as 2.364(2) Å [134]; EPR studies indicate that the singly occupied molecular orbital is the σ^* combination of d_{z^2} orbitals [135]. The delocalization energy of 7100 cm^{-1} , corresponding to the energy of the copper–copper half-bond [136], is similar to that determined for Cu_A [137]. An orbital interaction scheme for Cu_A , adapted from Ref. [131], is depicted in Figure 11.29.

Subsequent studies explored the synthesis, structure, spectroscopy, and redox properties of a variety of Cu(I,II) model complexes [138]. In half-paddlewheel dicopper complexes bridged by sterically demanding carboxylates, for example, both the copper(I,I) and copper(I,II) states are structurally characterized; the one-electron oxidation leads to a shortening of the copper–copper distance from 2.524(1) to 2.3947(8) Å (Scheme 11.3) [139]. A complex with a $[\text{Cu}_2(\mu\text{-NR}_2)_2]$ diamond core, designed to mimic the low reorganization energy in the redox chemistry of Cu_A , likewise undergoes substantial Cu–Cu compression upon oxidation from the Cu(I,I) state to the Cu(I,II) state [140]. A series of such complexes and their $[\text{Cu}_2(\mu\text{-PR}_2)_2]$ analogs have been studied by X-band, S-band, and Q-band EPR spectroscopy, permitting comparison to Cu_A and illustrating the considerable ligand-based character of the orbital from which the electron is removed [141].

Following the discovery that the active site of particulate methane monooxygenase contains a dicopper site [142], evidence was obtained for a mixed-valent copper(I,II) species in the isolated form of this enzyme and for the lengthening of the metal–metal distance upon reduction to the Cu(I,I)



Scheme 11.3 Oxidation of Cu(I,I) to mixed-valent, fully delocalized Cu(I,II). Ar = 2,6-[2,4,6-(CH₃)₃C₆H₂]₂C₆H₃

state. Spectroscopic results, however, suggest that the mixed-valent species should fall under Class I (valence localized) or Class II (trapped-valence), rather than Class III (fully delocalized) [143].

11.3.3

Silver–Silver Bonding

Remarkably few isolable complexes exhibit silver–silver covalency. The ionization potential [144] and bond length (2.5310(10) Å) [145] of singly bonded Ag–Ag have been determined by spectroscopic studies on supersonic beams. Small clusters Ag_n (*n* = 2–5) have been synthesized and studied in an argon matrix [146], and the gas-phase synthesis and reaction chemistry of mixed-valent silver(0/I) clusters have been studied by mass spectrometry [147]. Pulse radiolysis of Ag⁺ solutions or glasses in water and ethanol has allowed the study of unstable clusters as intermediates in metal colloid formation; thus, the absorption and EPR spectra of [Ag₂]⁺, [Ag₄]⁺, and [Ag₄]³⁺ have been recorded [148]. These are fully delocalized Ag(0,I) ions in which partial occupation of silver 5s-orbital combinations leads to net metal–metal bonding.

Mixed-valent Ag(0,I) clusters have been stabilized in the solid state. The electrolytic reduction of concentrated silver fluoride solutions affords silver subfluoride, of empirical formula Ag₂F. The unit cell, established by both X-ray [149] and neutron diffraction [150] studies, consists of two Ag atoms at a distance of 2.8 Å, with eight corner-shared fluorides (Figure 11.30). The structure of silver suboxide, of empirical formula Ag₃O, consists of an array of [Ag₆]⁴⁺ octahedra, with charges balanced by O²⁻ anions. The short silver–silver distances within the octahedra, 2.863(2) and 2.757(2) Å, are ascribed to the presence of a pair of excess electrons in the a_{1g} bonding molecular orbital formed through the interaction of 5s orbitals from six Ag⁺ ions [151]. It is worth noting that these Ag–Ag separations, while shorter than in silver metal, are not necessarily shorter than those arising from many d¹⁰–d¹⁰ interactions discussed in Section 11.2.2. Both Ag₂F and Ag₃O exhibit metallic conductivity.

The [Ag₆]⁴⁺ cation, interspersed with Ag⁺, is also found in the structures of Ag(0,I) compounds such as Ag₅SiO₄ [152], Ag₅GeO₄ [153], and Ag₅Pb₂O₆ [154]. Startlingly, the metallic conductivity and antiferro magnetic behavior of Ag₂NiO₂, ostensibly an Ag(I)/Ni(II) oxide, are consistent with its formulation as a mixed-valent Ag(0,I) complex, [Ag₂]⁺ [Ni^{III}O₂][−] [155].

Finally, the Ag–Ag distances in adjacent pairs of the photoluminescent ion [Ag(CN)₂][−] decrease by as much as 0.58 Å upon electronic excitation. Extended Huckel molecular orbital calculations indicate the formation of an exciplex, with a transition from a 1σ²1σ^{*2}2σ⁰2σ^{*0} ground state with no formal bond (analogous to the orbital scheme shown in Figure 11.4 for two Cu(I) ions), to a 1σ²1σ^{*1}2σ¹2σ^{*0}

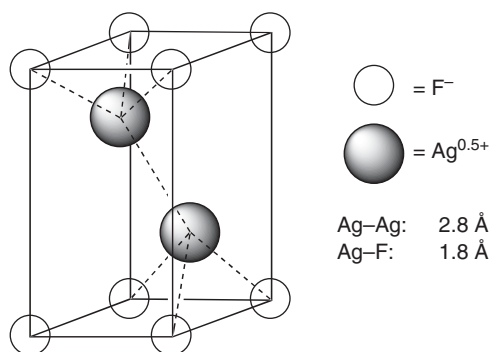


Figure 11.30 Unit cell representation for $[\text{Ag}_2\text{F}]$.

excited state with a formal single bond between metal centers [156]. The metal–metal bonding energy is calculated at 112 kJ mol^{-1} in the excited state, compared to 25 kJ mol^{-1} in the ground state [157].

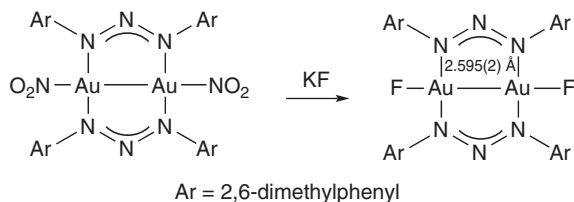
11.3.4

Gold–Gold Bonding

11.3.4.1 Semi- and Fully Supported Gold–Gold Bonds

By far the most numerous compounds having gold–gold single bonds are dinuclear gold(II) entities that are semi- or fully supported by bridging ligands. Common supporting ligands are 1,1-diphosphines, phosphorus ylides, dithiocarbamates, amidinates, and guanidinates. Such di-gold(II) complexes have been comprehensively reviewed¹⁾ [158–161]. Metallophilic interactions between singly bound gold–gold units can occur to form chains [162].

A notable recent contribution is the di-gold(II) fluoride of Fackler and coworkers [163]. This compound is prepared in a salt metathesis reaction from a di-nitrato precursor, Scheme 11.4. Both complexes have been characterized crystallographically. The gold–gold distance, $2.595(2) \text{ \AA}$, is longer than that of the analogous chloride, $2.567(2) \text{ \AA}$ [164], and is said to be longer than for the nitrato precursor, for which the bond length is unstated. The Au(II)–Au(II) bond is *trans*-influencing: The Au–F bond ($2.287(11) \text{ \AA}$) is longer than Au–F bonds in discrete $[\text{AuF}_4]^{2-}$ anions. For comparison, the $\text{Au}^{\text{I}}-\text{F}$ bond in the NHC complex (IDipp)AuF is $2.0281(2) \text{ \AA}$, shorter than the $\text{Au}^{\text{II}}-\text{F}$ bond.



Scheme 11.4 Synthesis of a supported gold(II) fluoride.

Toste and coworkers [165] have implicated a bimetallic reductive elimination mechanism in the oxidative heteroarylation of olefins. Electrochemical and stereochemical studies were made of mono- and di-gold(I) precatalysts; binuclear gold species had superior catalytic properties. Electrochemical markers of $\text{Au}(\text{I}) \cdots \text{Au}(\text{I})$ aurophilic interactions were discovered, including a 140-mV cathodic shift in the (irreversible) oxidation potential of di-gold species relative to mononuclear gold(I) analogs.

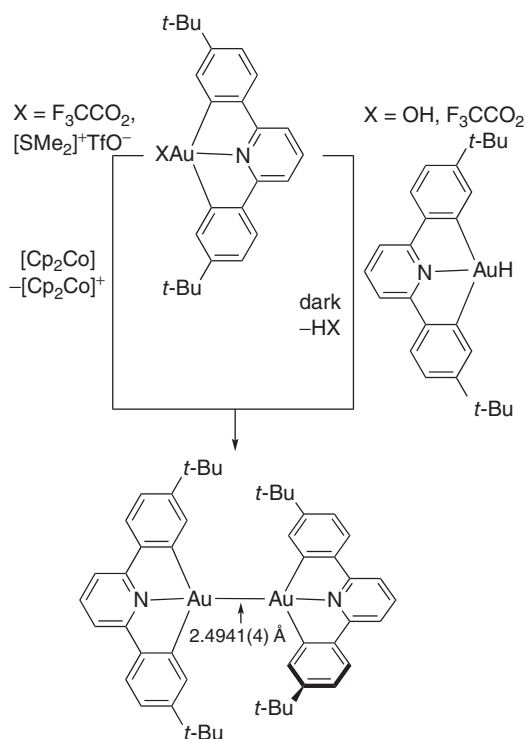
1) Numerous examples are given in Ref. [117].

Also noted was a 160-mV anodic shift in the (irreversible) reduction potential of a mixed-valence Au(III)/Au(I) species compared to the mono-gold(III) analog.

Catalytic mechanisms are proposed that invoke both aurophilic di-gold(I) intermediates and covalently bonded di-gold(II) entities. The proposed intermediates are semi-supported or unsupported, according to the definition of Figure 11.16. Geometries and energies of putative intermediates are calculated within density-functional theory; the computations support a bimetallic pathway. Reductive elimination, induced by an arylboronic acid, proceeds with retention of stereochemistry at carbon.

11.3.4.2 Unsupported Gold–Gold Bonds

Bochmann and coworkers [166] have prepared unsupported di-gold(II) complexes in reductive condensation reactions of a cyclometallated gold(III) reagents, Scheme 11.5. Thermal (dark) reaction of a chelated gold(III) hydride with the hydroxide or trifluoroacetate complex of the same cyclometallating ligand yields an unbridged gold(II) dimer with condensation of water or trifluoroacetic acid. The reaction proceeds in dichloromethane or benzene solvents in a timeframe of days ($X = \text{OH}$) or minutes ($X = \text{O}_2\text{CCF}_3$). The same gold(II) dimer is also accessed by reaction of the gold(III) dimethyl sulfide complex or the trifluoroacetate with cobaltocene. The dimer is isolated as luminescent yellow crystals. The complex is stable to air and moisture in the solid state and persists indefinitely in aerated dichloromethane solution at -25°C .



Scheme 11.5 Formation of an Au(II)–Au(II) dimer by reductive coupling or condensation of Au(III) precursors.

The gold(II) dimer was crystallographically characterized. The Au–Au distance of 2.4941(4) Å is among the shortest for unsupported di-gold(II) species.

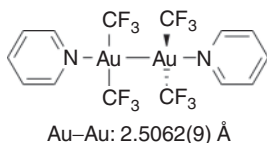


Figure 11.31 An unsupported gold(II) trifluoromethyl complex.

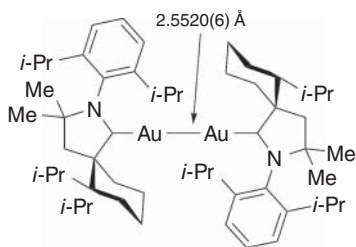


Figure 11.32 An unsupported Au(0) dimer.

Tyrre, Mathur, and coworkers [167] report the photoreaction of a silver(I) bis(trifluoromethyl) aurate(I) salt that leads to an unsupported gold(II) trifluoromethyl:



The sample is irradiated at 352 nm, and photolysis proceeds in CD_3CN or CDCl_3 ; metallic silver plates out as a byproduct. Attempts at preparing non-fluorinated alkyl complexes resulted in disproportionation. The di-gold(II) complex was crystallographically characterized. The gold–gold bond is unsupported, with a length of 2.5062(9) Å, Figure 11.31. Carbon–gold–carbon moieties are not eclipsed, but canted at $85.5(5)^\circ$; the complex resides on an inversion center. Intermolecular gold–gold contacts are not observed in the packing diagram. Their absence is attributed to steric blocking by the CF_3 ligands.

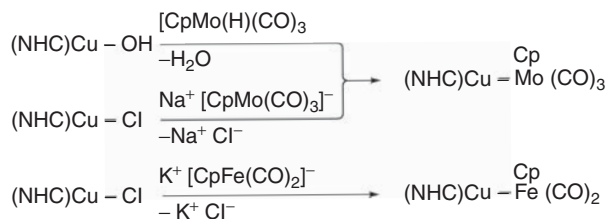
Until recently, examples of covalent, dinuclear Au–Au single bonds were limited to compounds of the +2 oxidation state. Bertrand and coworkers [168] have synthesized a di-gold(0) complex with an unsupported gold–gold bond (Figure 11.32). Cyclic (alkyl)(amino)carbene (CAAC) ligands cap the neutral Au_2 unit. The complex is prepared by reaction of the (CAAC)AuCl precursor with lithium sand in THF at room temperature. It is isolated as water- and air-sensitive light brown crystals (mp 98°C) in 20% yield. The compound is diamagnetic. In the ^{13}C NMR spectrum, the resonance for the carbene carbon atom, at δ 286 ppm, is shifted some 50 ppm downfield from that of the chlorogold(I) precursor. Density-functional theory calculations suggest that gold–gold bonding results from coupling of electrons in the 6s orbitals of Au(0).

11.4

Heterobimetallic Complexes of the Group 11 Metals

Extensive reviews of gold–heterometal interactions [169], and of complexes of d^{10} copper, silver, and gold with other metals, cover developments through 2011 [170]. A selection of recent advances appears here.

Copper–metal bonds have been synthesized by the condensation of (NHC)CuOH with the acidic metal hydride $\text{CpMo}(\text{H})(\text{CO})_3$ [171], or by halide displacement from (NHC)copper(I) using anions such as $\text{CpFe}(\text{CO})_2^-$ and $\text{CpMo}(\text{CO})_3^-$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; Scheme 11.6) [172]. The net metal–metal interaction in these complexes is a σ -bond: In (IDipp)Cu–Fe(CO) $_2$ Cp, with a Cu–Fe distance of only 2.3462(5) Å, the HOMO–1 and HOMO are Fe–Cu π^* orbitals, and the LUMO is the σ^* orbital. Natural population analysis indicates significant ionic character, consistent with unequal sharing of an



Scheme 11.6 Synthesis of (NHC)copper heterobimetallics. NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (Mo, Fe); 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene or 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (Fe).

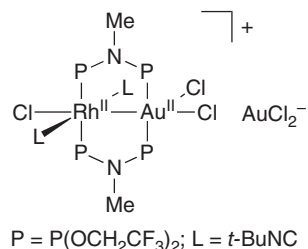
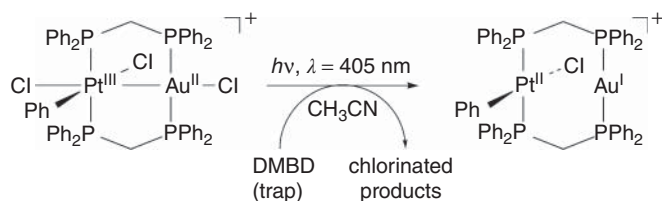


Figure 11.33 A Rh(II)–Au(II) core formed by oxidation of Rh(I)–Au(I).

electron pair between the CpFe(CO)₂[−] and (IDipp)Cu⁺ fragments [171]. This polarization is opposite to that calculated for a phosphinoamide-supported Cu/Fe bimetallic complex in which no bond is invoked [173]. The (IDipp)Cu–Fe(CO)₂Cp complex serves as an effective photocatalyst for the borylation of arene C–H bonds [174].

Much recent progress has come about from studies of heterobimetallic complexes of gold with late transition metals [175, 176]. Esswein *et al.* [177] have described a rhodium(I)–gold(I) complex that is fully supported by two bridging diphosphazane ligands. Oxidation with KAuCl₄ in acetonitrile leads to a Rh(II)–Au(II) product with a direct metal–metal bond (2.5649(4) Å), Figure 11.33. This complex is the first instance of a bond between rhodium and gold in these oxidation states. The Rh(II)–Au(II) complex decomposes at room temperature in CH₃CN and CH₂Cl₂ to yield mononuclear rhodium(III) and dinuclear gold(I) products. Its instability is partly attributed to a polarized Rh–Au bond, and the authors hypothesize that similar bonds between gold and platinum would be more covalent and more stable.

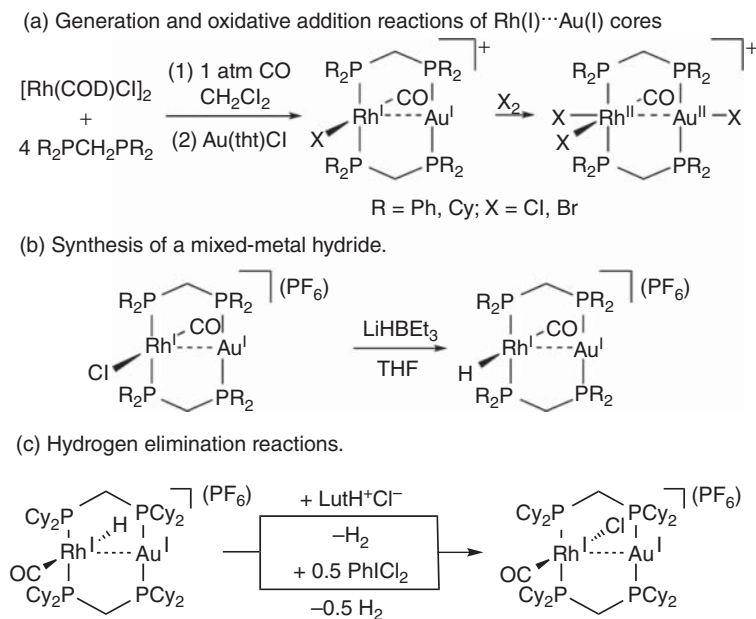
Reaction of [Pt^{II}Au^I(dppm)₂(Ph)Cl]PF₆ [178] with the chlorine source PhICl₂ yields [Pt^{III}Au^{II}(dppm)₂(Ph)Cl₃]PF₆, the first Pt(III)–Au(II) heterobimetallic [179]. The reduced complex lacks a metal–metal σ-bond, with a platinum–gold distance of 2.9646(3) Å. The oxidized complex has a 2.6457(3) Å Pt–Au bond. In the presence of an olefin trap, photolysis of [Pt^{III}Au^{II}(dppm)₂(Ph)Cl₃]PF₆ affords reduced [Pt^{II}Au^I(dppm)₂(Ph)Cl] (PF₆) along with chlorination products of the olefin, Scheme 11.7.



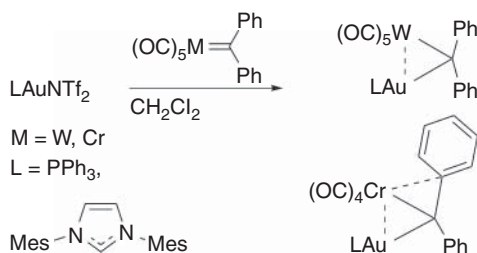
Scheme 11.7 Photoelimination of halogen from a Pt(III)–Au(II) core.

Teets, Neumann, and Nocera revisited two-electron redox reactions of the free phosphine with labile precursors. Oxidative addition reactions of Cl_2 (delivered as PhICl_2) and Br_2 across a non-bonded $\text{Rh}^{\text{I}} \cdots \text{Au}^{\text{I}}$ core were examined. Reactions yielded $\text{Rh}^{\text{II}} - \text{Au}^{\text{II}}$ entities with concomitant metal-metal bond formation. In an effort to combine halogen (X_2) elimination with H_2 elimination, hydride complexes of the $\text{Rh} - \text{Au}$ kernel were prepared as in Scheme 11.8a. The reaction is a salt metathesis where hydrogen displaces chlorine on rhodium, Scheme 11.8b. Bonding to rhodium is demonstrated by first-order rhodium-hydrogen coupling in the ^1H NMR spectrum. The mixed-metal hydride was structurally characterized, and the hydride was discerned in the difference map. Photolysis of the oxidized dihalide complexes led to halogen elimination with chemical assistance from olefin traps; protonolysis of the hydride complex in the presence of Cl^- sources yielded H_2 with regeneration of the initial $\text{Rh}(\text{I}) \cdots \text{Au}(\text{I})$ complex, Scheme 11.8c. A library of similar iridium-gold bimetallics was reported [180]. Oxidized $\text{Ir}(\text{II}) - \text{Au}(\text{II})$ species carry metal-metal bonds, as shown by metal-metal separations that contract on oxidation from non-bonded $\text{Ir}(\text{I}) \cdots \text{Au}(\text{I})$ reagents. Several of these compounds display chemically (trap-) assisted halogen elimination, but not all such reactions are clean.

Fürstner and coworkers [181] report heterobimetallic gold(I)-chromium(0) and gold(I)-tungsten(0) complexes bridged by alkylidene ligands, Scheme 11.9. Complexes of both group 6



Scheme 11.8 COD = 1,5-cyclooctadiene; tht = tetrahydrothiophene; Lut = 2,6-lutidine.



Scheme 11.9 Synthesis of alkylidene-bridged gold-(Group 6 metal) complexes.

metals were structurally characterized. Chromium bears one fewer-CO ligand than does tungsten in the analogous complex. A minor dative interaction occurs between Cr and an *ipso* carbon (Cr–C 2.281(10) Å) on the alkylidene phenyl; no such interaction is found in the structurally characterized tungsten complex. The authors state that this “interaction must be somehow constructive, because it prevents the collapse of the complex with release of the free carbenoid.” When similar transmetalation reactions were carried out with (heteroatom-substituted) Fischer carbene sources, carbene transfer to gold(I) proceeded without isolation of bimetallic intermediates.

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12

Group 12 Metal–Metal Bonds

Xian Wu and Sjoerd Harder

12.1

Introduction

The group 12 metals (G12) (zinc, cadmium, and mercury, also called zinc group metals) have a unique position in the periodic table. They occupy the last column of the d-block (the transition metals – TMs) and have fully filled valence d and s orbitals, making their chemical behavior more like main group (MG) metals rather than TMs. Due to the relativistic effect on the stabilization of the 6s orbital, the dimercury(I) ion is relatively stable and numerous dimercury(I) salts are known to exist. In contrast, dicadmium(I) and dizinc(I) ions are very rare. The first dicadmium(I) salt was prepared in the 1950s and the first dizinc(I) species was obtained in the 1960s. These are generally not stable and have a very high tendency to undergo disproportionation to bulk metal and metal 2+ cations.

The development of the molecular homobimetallic chemistry of G12 had a slow start. The first molecular Cd–Cd- and Hg–Hg-bonded compounds were reported in the 1990s and the first molecular Zn–Zn bond was not discovered until 2004. This breakthrough, however, stimulated intensive investigations on this topic and several research groups have successfully synthesized further Zn–Zn-bonded complexes, investigated their reactivities, and even found applications in catalysis. Some new Cd–Cd- and Hg–Hg-bonded complexes have also been prepared, although the number of these compounds is still relatively small.

In comparison to the homobimetallics, the heterobimetallics, that is, the chemistry of compounds containing bonds between G12 and metals from other groups, is much more varied. The G12 are able to form chemical bonds with group 13–15 metals, in particular Ga and Sn. Moreover, the field of G12–TM bonding is rich and numerous compounds have been prepared and characterized.

This chapter is divided into two parts: homobimetallics and heterobimetallics. In the homobimetallics part, the synthesis and structures of $[G12-G12]^{2+}$ ions (in particular Hg_2^{2+}) are presented, followed by those of molecular G12–G12-bonded compounds. Their reactivity is then summarized. The heterobimetallics part first deals with bonding between G12 and late MG and is organized according to group numbers. Subsequently, the field of metal–metal bonds between G12 and TM is discussed.

Within the limits of this book, this chapter does not intend to give a complete summary of all compounds related to this topic, but rather aims to cover the most important and representative compound classes, which highlight the historical development and current state of the area. More details and additional information can be found in research and review articles, which are cited in the main text.

12.2

Homobimetallics

12.2.1

Synthesis and Structures

12.2.1.1 [G12–G12]²⁺ Ions

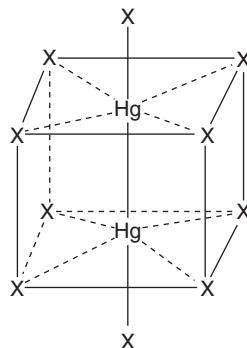
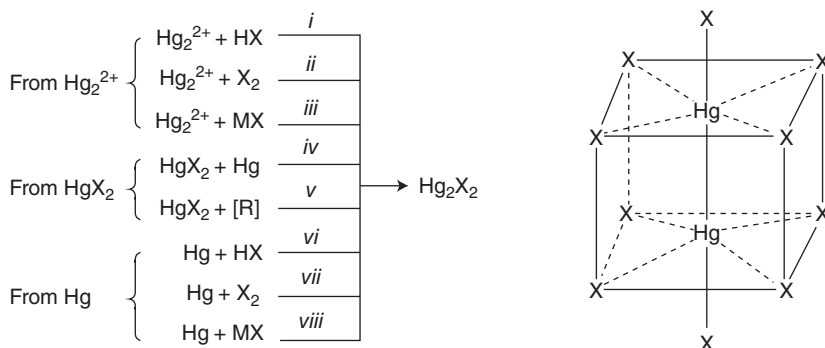
Mercurous dichloride Hg_2Cl_2 , also called calomel or sweet mercury, is undoubtedly one of the first and most well known metal–metal-bonded compounds. It is well known that calomel might have been prepared even in the dark ages of the fourteenth century from Hg , HNO_3 , and NH_4Cl (a detailed description of the history of calomel preparation in Europe can be found in the literature) [1]. Less known is the fact that in Asia calomel was already prepared and utilized almost two thousand years ago. The oldest recipe for the preparation of Hg_2Cl_2 appeared in the Eastern Han Dynasty (25–220 A.D.) in China.¹⁾ According to these old manuscripts, a snow-like sublimate could be obtained after heating a mixture of seven components including azurite, hematite, halite and mercury in a sealed oven for 4 days. Chinese alchemists improved and simplified this recipe during the next centuries. Even at an early stage, they could distinguish Hg_2Cl_2 from HgCl_2 by their preparation and used such preparations as medicines.

Surprisingly, there is little modern literature reviewing the chemistry of dimercury(I) salts [2]. The most important methods to prepare mercury(I) halides (Hg_2X_2) are summarized in Scheme 12.1. Depending on the mercury source, these methods can be divided into three groups: from dimercury(I) salts (Hg_2^{2+}), from mercury(II) halides (HgX_2), and from mercury metal (Hg). Hg_2^{2+} reacts with halogen hydride (HX) or dihalogen (X_2) or metal halide (MX) to give Hg_2X_2 (methods *i–iii*). HgX_2 could be reduced by comproportionation with Hg (method *iv*) or by other reducing agents (method *v*) to afford Hg_2X_2 . Treating mercury metal with HX , X_2 , or MX also produces Hg_2X_2 (methods *vi–viii*). The structures of Hg_2X_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were determined by X-ray powder diffraction [3] in 1926 and 30 years later the structure of Hg_2F_2 was revealed by this method [4]. The first single crystal X-ray diffraction analyses for Hg_2X_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) were reported in 1971 [5], and more recently structures of Hg_2F_2 and Hg_2I_2 were redetermined in 1992 and 2012, respectively [6, 7]. The structure of Hg_2Cl_2 was also measured by neutron powder diffraction [8]. The crystals of the four mercury(I) halides are tetragonal, and there are two molecules in each unit cell. There are five X atoms in the coordination sphere of each Hg atom, one with a short Hg–X distance, the other four with longer distances (Scheme 12.1). It can be described as an X–Hg–Hg–X fragment with a linear geometry in which mercury atoms interact with neighboring halogen atoms.

Another common class of dimercury(I) salts is those of the oxo-acids $\text{Hg}_2(\text{YO}_m)_n$. Like the mercury halides, $\text{Hg}_2(\text{YO}_m)_n$ could be prepared by different methods such as metathesis (anion exchange), comproportionation, or treatment of mercury with the corresponding acid. The anions could be either inorganic such as NO_3^- , CO_3^{2-} , SO_4^{2-} , HSO_4^- , XO_3^- ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), NO_2^- , H_2PO_4^- [9], or organic such as CH_3CO_2^- or CF_3CO_2^- [10]. Other important types of dimercury(I) salts are pseudohalides (e.g., $\text{Hg}_2(\text{SCN})_2$, $\text{Hg}_2(\text{N}_3)_2$) [11], metalates (e.g., Hg_2MoO_4 , Hg_2WO_4) [12], or Hg_2^{2+} species bearing neutral nitrogen ligands [13]. The Hg–Hg bond length in most Hg_2^{2+} species is between 2.46 and 2.60 Å.

Dicadmium(I) and dizinc(I) salts are scarce. The first dicadmium(I) salt was obtained in 1956 by dissolving Cd in molten CdCl_2 followed by addition of AlCl_3 to form $\text{Cd}_2(\text{AlCl}_4)_2$ [14]. This compound easily undergoes Cd(0)/Cd(II) disproportionation in water and organic solvents. Thirty years later, its structure was determined by X-ray diffraction revealing a Cd–Cd bond of 2.576 Å [15].

1) The procedure was described in the Chinese alchemy manuscript *Tai Qing Jin Ye Shen Dan Jing* which was written at the time of the Eastern Han Dynasty.

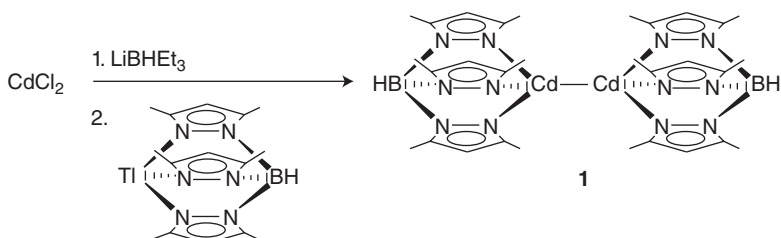


Scheme 12.1 Preparation and structure of mercury(II) halides Hg_2X_2 .

Evidence for the formation of the first dizinc(I) salt was observed in 1967 by introducing Zn into molten ZnCl_2 [16]. The existence of Zn_2Cl_2 was proven by UV–vis, Raman, and ESR (Electron Spin Resonance) spectroscopy as well as magnetic susceptibility measurement and chemical methods; however, no crystal structure has been obtained yet. Dizinc(I) dihydride, Zn_2H_2 , was claimed to be produced in 1995 by the matrix-isolation technique and could be identified by spectroscopic methods involving deuterium substitution and comparisons with quantum mechanical calculations [17].

12.2.1.2 Molecular G12–G12 Bonded Complexes

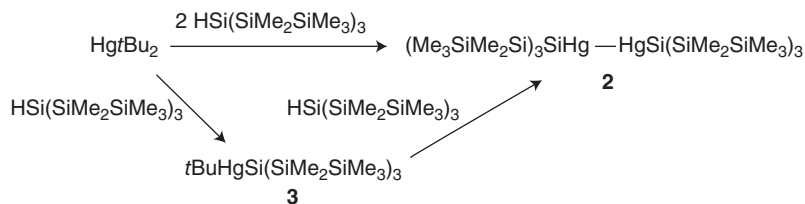
There are some excellent reviews concerning molecular G12–G12 bonds [2a, 18]. The first molecular G12–G12-bonded compound is the Cd–Cd complex **1** bearing two tridentate nitrogen ligands, which was synthesized in 1993 by treating CdCl_2 with LiBHET_3 followed by reaction with $\text{Ti}[\text{HB}(3,5\text{-Me}_2\text{pz})_3]$ (Scheme 12.2) [19]. Although no crystal structure was obtained, the large ^{111}Cd – ^{113}Cd coupling constant in ^{113}Cd NMR (Nuclear Magnetic Resonance) revealed unambiguously the existence of the Cd–Cd bond. Formation is presumably via a Cd–hydride complex that converts to the Cd(I) species and H_2 .



Scheme 12.2 Synthesis of the first molecular Cd–Cd-bonded complex **1**.

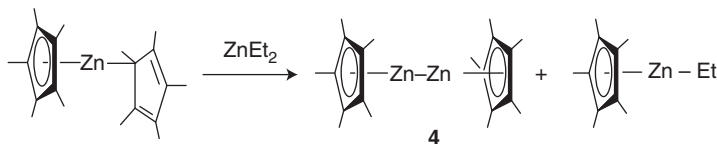
In 1999, Apeloig *et al.* reported the synthesis of the first molecular Hg–Hg-bonded complex **2** by reaction of $\text{Hg}t\text{Bu}_2$ with 2 equiv. of the sterically demanding silane $\text{HSi}(\text{SiMe}_2\text{SiMe}_3)_3$ (Scheme 12.3) [20]. Alternatively, **2** could be obtained by a stepwise route in which **3** was isolated as an intermediate. The X-ray crystal analysis showed a linear Si–Hg–Hg–Si arrangement with an Hg–Hg bond length of 2.6569(8) Å.

The synthesis of the first molecular Zn–Zn-bonded compound, however, was not achieved until 2004. Carmona's discovery of dizincocene $\text{Cp}^*\text{ZnZnCp}^*$ (**4**, $\text{Cp}^* = \text{C}_5\text{Me}_5$) by reaction of Cp^*_2Zn and Et_2Zn is shown in Scheme 12.4 [21]. The pyrophoric compound **4** is unstable when exposed to oxygen and moisture and is soluble in common organic solvents. It could be stored at room temperature under inert atmosphere indefinitely and undergoes sublimation in high vacuum at 70 °C without significant decomposition. The crystal structure shows that the Zn–Zn distance is very short



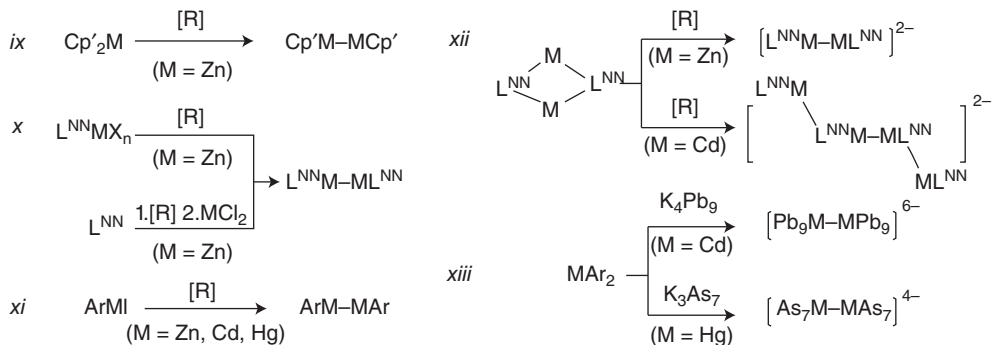
Scheme 12.3 Synthesis of the first molecular Hg–Hg-bonded complex **2**.

(2.305(±3) Å), indicating a direct Zn–Zn bond. This is the first experimentally observed 2c–2e covalent Zn–Zn bond. Cp*ZnZnCp* exhibits an almost linear arrangement with an average Cp_{center}*–Zn–Zn angle of 177.4(±1)°.



Scheme 12.4 Synthesis of the first molecular Zn–Zn-bonded complex **4**.

The successful isolation and characterization of Cp*ZnZnCp* not only filled a vacancy in the homobimetallic-bonded group of 12 elements but also became a turning point in this field. It initiated increased interest in G12–G12 chemistry and led to the preparation of numerous new complexes, especially those with Zn–Zn bonds. The synthetic methodologies for the formation of G12–G12 bonds are summarized in Scheme 12.5.

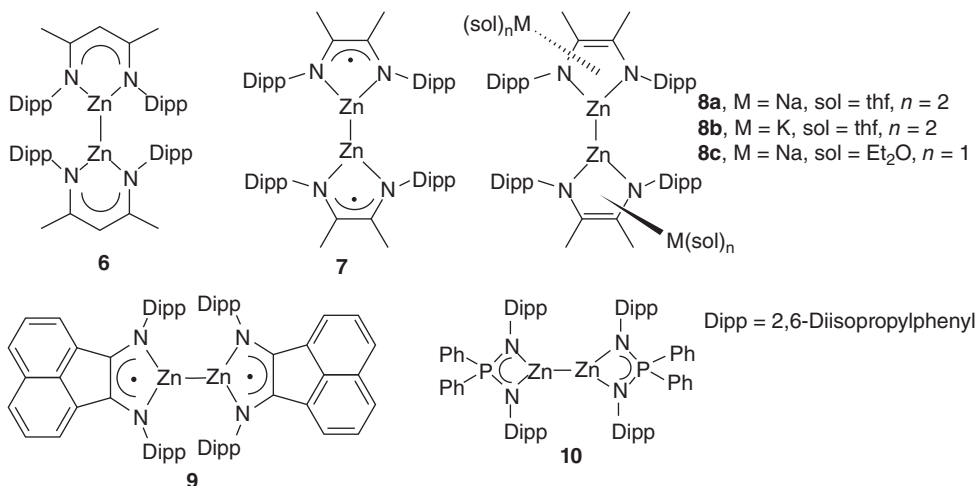


Scheme 12.5 Synthetic methodologies for the G12–G12 bond formation.

Method *ix* involves the reductive coupling of zirconocene compounds as applied in the discovery of Cp*ZnZnCp* (Scheme 12.4) in which case Et₂Zn is the reducing agent. This synthesis has been improved by using a mixture of ZnCl₂ and KH or CaH₂ for the reduction step [22]. The related compound [Zn₂(η⁵-C₅Me₄Et₂)] (**5**) could also be obtained and is thermally less stable than **4** [22]. Recently, Fischer *et al.* found that replacing the reducing mixture by ZnH₂ could lead to an even higher yield and suggested that in both cases similar mechanisms are operative [23]. Stephan *et al.* found that [Cp*₂Zn] under high pressure of H₂ could convert to **4** [24] (probably by formation of a zinc hydride species that decomposes to H₂ under Zn²⁺ reduction).

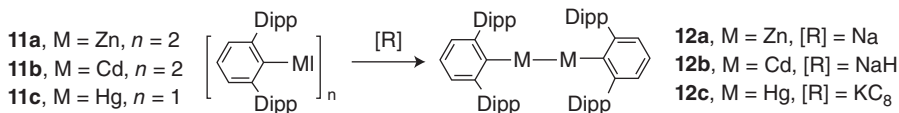
Reductive coupling is used for the preparation of zinc complexes bearing bidentate N-Ligands as the zinc source (method *x*, Scheme 12.5). The ligands (written as L^{NN} in Scheme 12.5) include

β -diketiminate [25], α -diimines [26], and aminoiminophosphonate [27]. Sodium, potassium, or Mg(I) complex are used as the reducing agent. In some cases, the protonated ligand is first treated with the reducing agent before reaction with ZnCl_2 . This method is more versatile than method *ix* since it allows for larger flexibility in ligand choice. Compounds prepared by method *x* are listed in Scheme 12.6.



Scheme 12.6 Complexes prepared by method *x*.

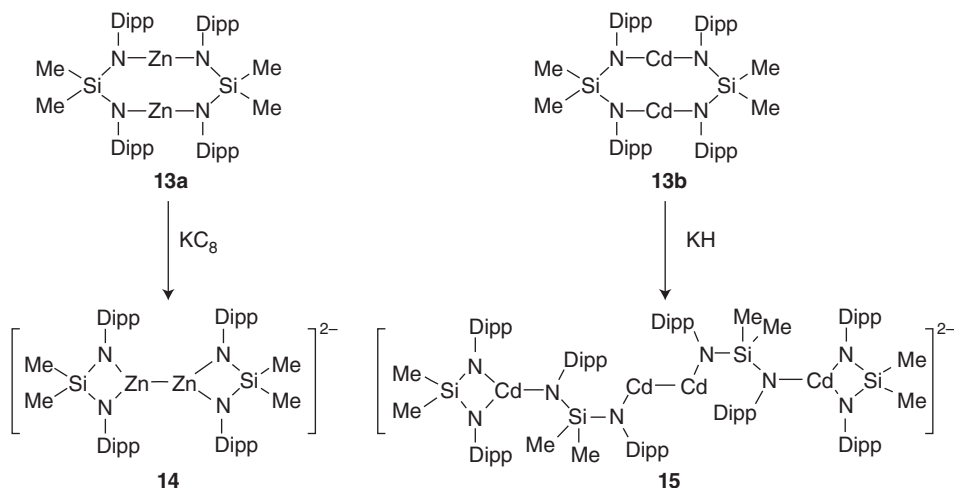
While methods *ix* and *x* are employed only for preparing Zn–Zn-bonded complexes, method *xi* developed by Power *et al.* was used to prepare the first homologous G12–G12-bonded compounds [28]. Reductive coupling of arylmetal iodide led to the formation of ArMMAr ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$) (**12a–c**) where the aryl group is the sterically demanding C_6H_3 -2,6-(Dipp)₂ (Scheme 12.7). The reducing agents were Na (for Zn), NaH (for Cd), and KC_8 (for Hg), respectively. It has been suggested that these reactions proceed through reactive arylmetal hydrides.



Scheme 12.7 The first homologous G12–G12-bonded compounds **12a–c** prepared by method *xi*.

Tsai *et al.* developed another reductive coupling method for the preparation of Zn–Zn- and Cd–Cd-bonded complexes (method *xii*) [29]. Cyclic dinuclear M(II) compounds bearing two silylene-bridged diamide ligands were treated with KC_8 (for Zn) or KH (for Cd) to afford $[\text{L}^{\text{NN}}\text{MML}^{\text{NN}}]^{2-}$ ($\text{M} = \text{Zn}$, **14**) or $[\text{L}^{\text{NN}}\text{ML}^{\text{NN}}\text{MML}^{\text{NN}}\text{ML}^{\text{NN}}]^{2-}$ ($\text{M} = \text{Cd}$, **15**), respectively (Scheme 12.8). Both products contain a direct M(I)–M(I) bond, and the latter contains two additional Cd(II) nuclei. Calculations suggested that the formation of the M(I)–M(I) complexes is via mixed-valent M(II)–M(I) intermediates.

Cd–Cd- and Hg–Hg-bonded complexes can also be synthesized by reacting diaryl cadmium or diaryl mercury with the intermetallic Zintl phases K_4Pb_9 or K_3As_7 , respectively (method *xiii*, Scheme 12.5) [30]. In both cases, a Zintl cluster anion ($[\text{Pb}_9\text{CdCdPb}_9]^{6-}$ or $[\text{As}_7\text{HgHgAs}_7]^{4-}$) is formed in which the metal atoms are connected by a single bond (**16–17**, Scheme 12.9). Complex **16** crystallized as two crystallographically independent molecules in which the Cd–Cd bond length is 2.697(1) and 2.715 (2) Å, respectively, while the Hg–Hg bond distance in **17** is 2.6792(9) Å.

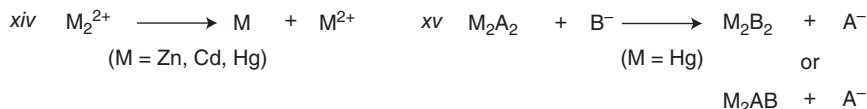
Scheme 12.8 Complexes prepared by method *xii*.Scheme 12.9 Complexes prepared by method *xiii*.

12.2.2

Reactivity

12.2.2.1 $[\text{G12-G12}]^{2+}$ ions

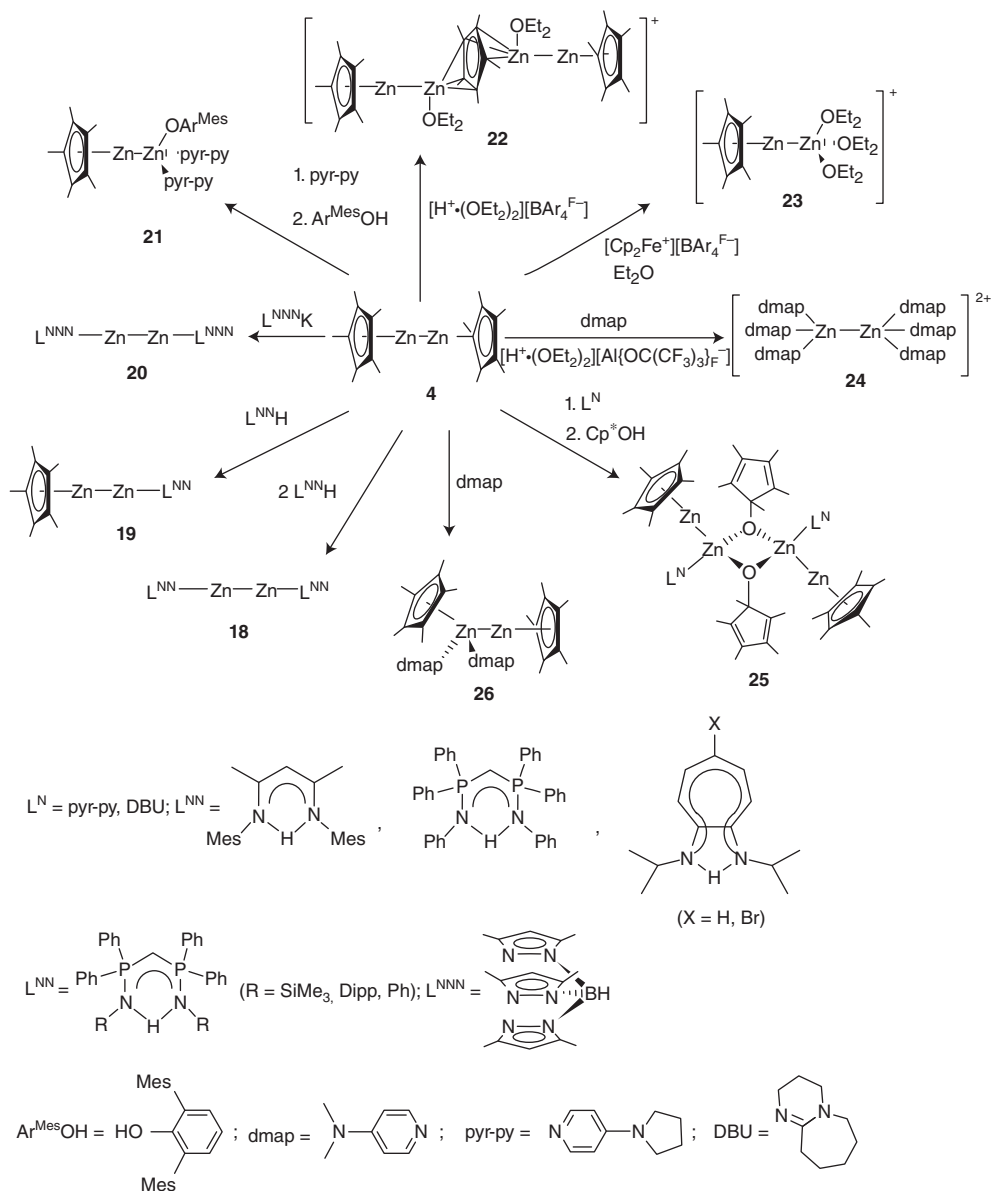
The reactivity of $[\text{G12-G12}]^{2+}$ ions is summarized in Scheme 12.10. Complexes containing the Zn_2^{2+} and Cd_2^{2+} ions are extremely unstable and decompose at room temperature into the corresponding $\text{M}/\text{M(II)}$ mixtures. In contrast, Hg_2^{2+} is much more stable and its disproportionation reactions are often reversible. Another important reaction type of the Hg_2^{2+} ion is the metathesis (reaction *xv*), where the anion in the starting compound is replaced or partially replaced. The metathesis reaction is highly useful for the preparation of different dimercury(I) salts.

Scheme 12.10 Reaction patterns of $[\text{G12-G12}]^{2+}$ ions.

12.2.2.2 Molecular G12–G12 Bonded Complexes

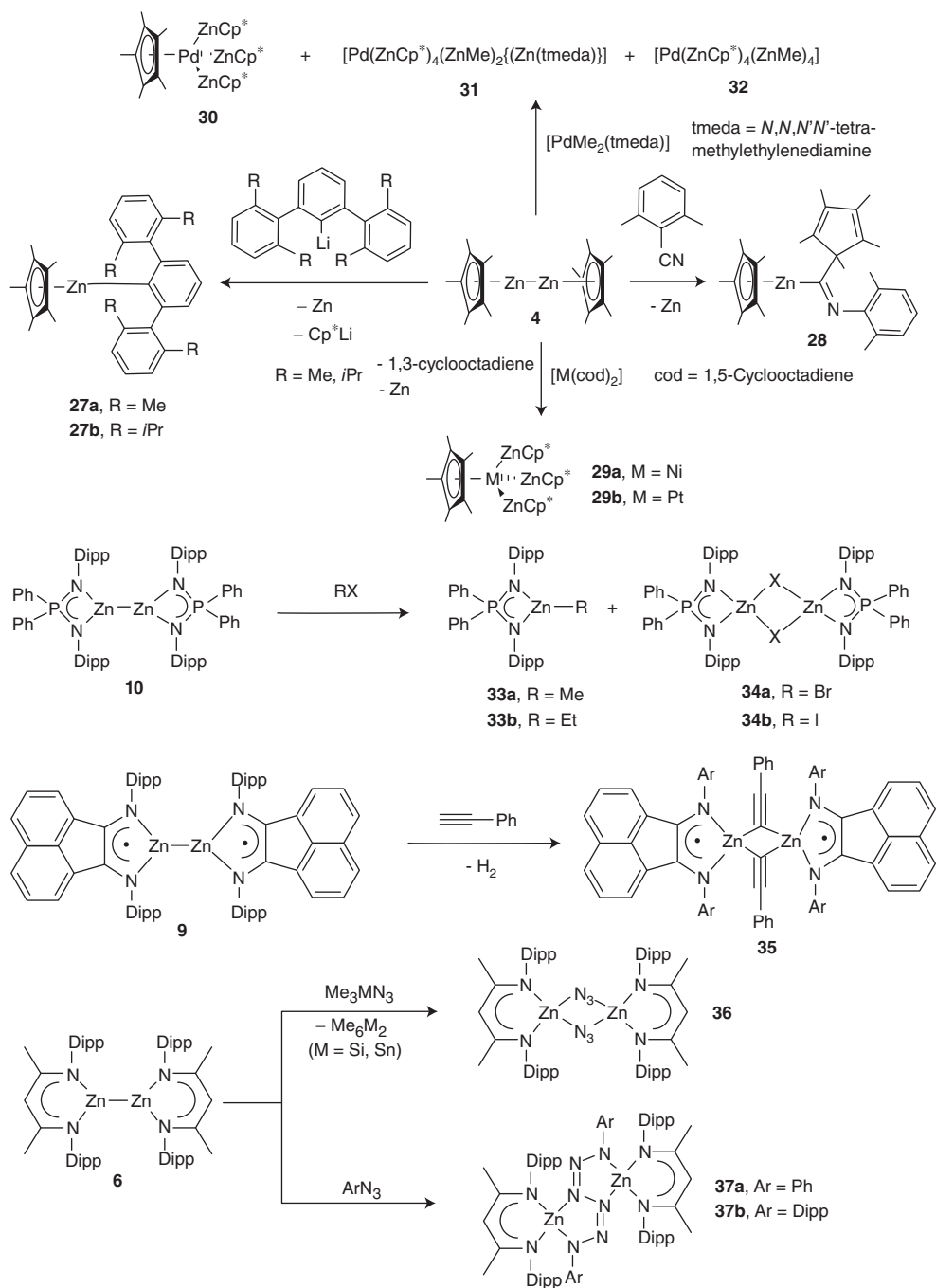
The typical reactivity of Zn–Zn-bonded complexes can be divided into two categories: reactions with preservation of the Zn–Zn bond (Scheme 12.11) and those with a cleavage of the Zn–Zn bond (Scheme 12.12).

Dizincocene $\text{Cp}^*\text{ZnZnCp}^*$ **4** readily undergoes ligand exchange reactions with preservation of the Zn–Zn bond. These reactions could be divided into three types: protonation of Cp^* by a protonated ligand (LH), ligand exchange with LK or addition of Lewis base. Complex **4** reacted with 1 or 2 equiv. of a bidentate or tridentate N-donor ligand to afford the corresponding mono- or disubstituted products (**18–20**) [31]. Treatment of **4** with pyr-py (4-pyrrolidinopyridine) followed by $\text{Ar}^{\text{Mes}}\text{OH}$ (2,6-dimesitylphenol) gave conversion to the half-sandwich complex **21** [32]. Similar reactions with pyr-py or DBU and Cp^*OH led to the formation of the dimer **25** [32]. The $\text{Cp}^*\text{-Zn}$ bond was oxidatively



Scheme 12.11 Reactivity of **4** with prevention of the Zn–Zn bond.

cleaved by the reaction of **4** with $[\text{Cp}_2\text{Fe}^+][\text{BAR}_4\text{F}^-]$ ($\text{BAR}_4\text{F} = \text{B}\{\text{C}_6\text{H}_3(\text{CF}_3)_2\}_4$) in diethyl ether giving the Et_2O -substituted cation **23** [23]. The same report describes Cp^*-Zn bond cleavage in reaction of **4** with $[\text{H}^+(\text{Et}_2\text{O})_2][\text{BAR}_4\text{F}^-]$ at low temperature in fluorobenzene. The product **22** was analyzed by single crystal X-ray diffraction and the structure shows a triple-decker sandwich containing two Zn–Zn bonds [23]. The zinc atoms coordinate with the Cp^* ring in both η^3 and η^5 fashion. By treatment with dmap (4-dimethylamino-pyridine) and $[\text{H}^+(\text{Et}_2\text{O})_2][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4^-]$, both Cp^*-Zn bonds underwent oxidative cleavage to form the $(\text{dmap})_6\text{Zn}_2^{2+}$ cation **24**, which represents the first structurally characterized dizinc(I) dication and features a Zn–Zn bond of 2.419(2) Å [33]. In the absence of $[\text{H}^+(\text{Et}_2\text{O})_2][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4^-]$, two dmap molecules coordinate to one of the zinc atoms and form the

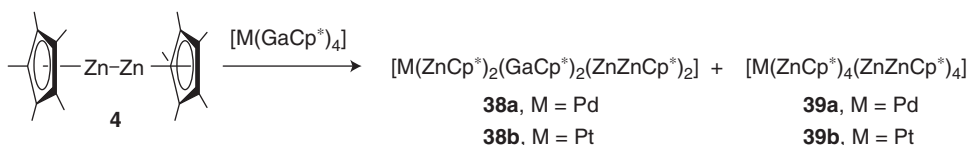


Scheme 12.12 Zn–Zn bond cleavage reactions of Zn–Zn-bonded complexes.

neutral bent sandwich complex **26** [34]. The reason for geminal dmap coordination instead of vicinal dmap coordination was explained by density functional theory (DFT) calculations. Coordination of the second dmap molecule in a vicinal position is calculated to be endothermic, whereas that in a geminal position is highly exothermic. This is due to the fact that, in contrast to expectation, the positive charge on Zn increases upon dmap coordination, whereas that on the neighboring Zn decreases [34].

For $\text{Cp}^*\text{ZnZnCp}^*$ (**4**) and other Zn–Zn-bonded complexes also reactions involving the cleavage of the Zn–Zn bond have been observed (Scheme 12.12). Complex **4** reacted with aryllithium compounds to afford $[\text{Cp}^*\text{ZnAr}]$ (**27**), Zn^0 and Cp^*Li [**33a**]. Treating **4** with *m*-xylolcyanide gave Zn and **28** [35]. The Zn–Zn cleavage also occurred by reaction of **4** with organometallic compounds such as $[\text{M}(\text{cod})_2]$ ($\text{M} = \text{Ni}, \text{Pt}$; $\text{cod} = 1,5\text{-cyclooctadiene}$) and $[\text{PdMe}_2(\text{tmeda})]$ ($\text{tmeda} = N,N,N',N'$ -tetramethylethylenediamine) [36]. In both cases, $[\text{Cp}^*\text{M}(\text{ZnCp}^*)_3]$ ($\text{M} = \text{Ni}, \text{Pt}, \text{Pd}$) (**29a**, **29b**, **30**) were obtained. The Zn–Zn-bonded complex **10** reacted with alkyl halide to give the monozinc complexes **33a** or **33b** as well as the halogen-bridged dimeric compounds **34a** or **34b** [27]. Phenylacetylene could be inserted into the Zn–Zn bond of **9**, affording the phenylacetylide bridged complex **35** and elimination of H_2 [37]. Most recently, Schulz *et al.* studied the reactivity of compound **6** toward azides [38]. Bond cleavage products **36** and **37** were obtained upon treatment of **6** with Me_3MN_3 ($\text{M} = \text{Si}, \text{Sn}$) and ArN_3 ($\text{Ar} = \text{Ph}, \text{Dipp}$), respectively.

Intermetallic complexes **38a**, **38b**, **39a**, and **39b** containing multiple metal nuclei have been obtained by treating **4** with $[\text{M}(\text{GaCp}^*)_4]$ ($\text{M} = \text{Pd}, \text{Pt}$) (Scheme 12.13) [39]. Complexes **38a** and **39a** have *hexa*-coordinated geometries, whereas **38b** and **39b** are *octa*-coordinated complexes. The Zn–Zn bond lengths in **38a** and **38b** are 2.345(1)/2.346(1) and 2.359(4)/2.335(3) Å, respectively, and the corresponding value in **39a** ranges from 2.347(3) to 2.351(3) Å. These are similar to the Zn–Zn bond distance in **4**.



Scheme 12.13 Reaction of **4** with both prevention and cleavage of the Zn–Zn bond.

The catalytic activity of **4** in intermolecular hydroamination of alkynes by anilines as well as in the intramolecular alkene and alkyne hydroamination has been reported [40]. The results show that in the presence of $[\text{PhNMe}_2\text{H}^+][\text{B}(\text{C}_6\text{F}_5)_4^-]$, **4** could catalyze these reactions very efficiently (2.5 mol% catalyst, 20–80 °C). It was suggested that the Cp^* moiety was protonolyzed to give Cp^*H , which was identified by NMR. In most cases, excellent yields were achieved, indicating a possible high potential of Zn–Zn-bonded complexes for catalytic organic transformations. As the presumed mechanism is not discussed further, it is hitherto unclear whether a Zn_2^{2+} species is prevalent in the catalytic cycle.

Surprisingly, there are no studies on the reactivity of molecular-bonded Cd–Cd and Hg–Hg complexes up to date.

12.3

Heterobimetallics

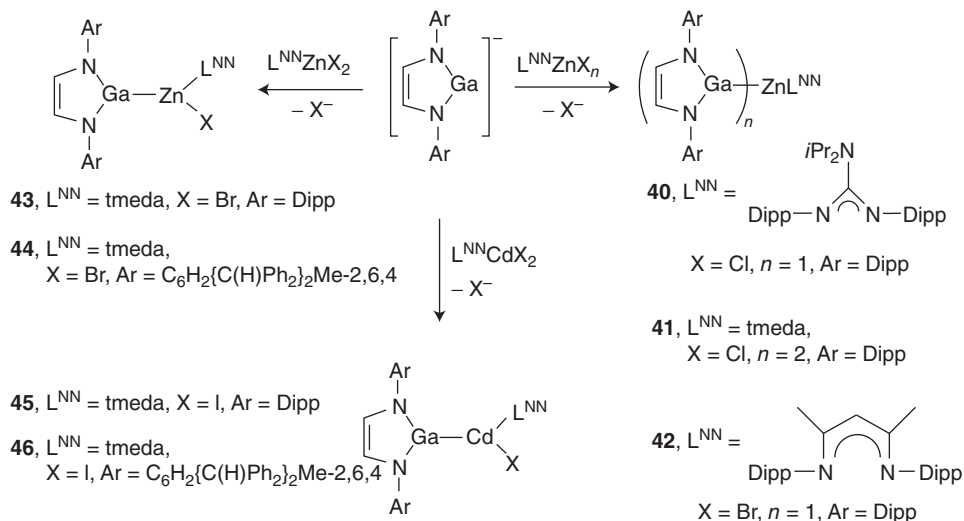
12.3.1

Bonding between G12 and Late Main Group Metals

12.3.1.1 G12–G13 Bonds

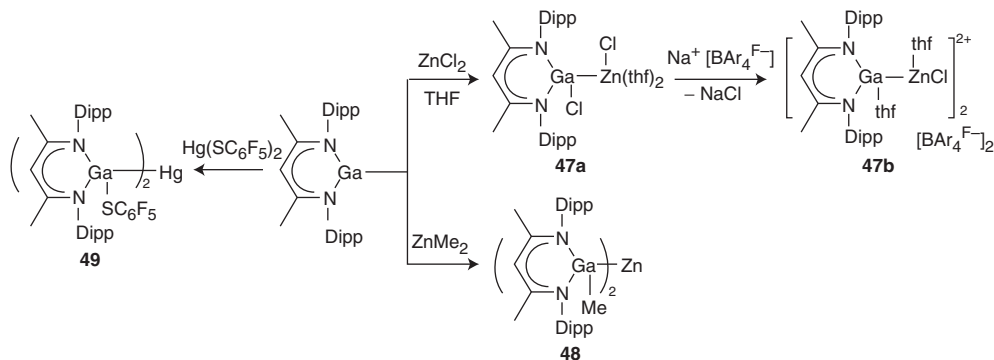
Based on the consideration that Zn and Ga are adjacent in the periodic table and in order to further explore the chemistry of M–Ga bonds, Jones *et al.* prepared a series of Zn–Ga-bonded complexes with the general formula $[\{(\text{DAB})\text{Ga}\}_n\text{ZnL}^{\text{NN}}]$ or $[\{(\text{DAB})\text{Ga}\}\text{ZnX}]$ ($\text{DAB} = \{\text{N}(\text{Ar})\text{C}(\text{H})\}_2$;

L^{NN} = amidinate, tmeda, β -diketimide; Ar = Dipp, $C_6H_2\{C(H)Ph_2\}_2Me$ -2,6,4; X = Cl, Br; $n = 1, 2$) by treating the anionic Ga(I) heterocycle $[(DAB)Ga:]^-$ with $L^{NN}ZnX_n$ (X = Cl, Br) or ZnX_2 , respectively (Scheme 12.14) [41]. Using the same strategy, they also obtained Cd–Ga-bonded complexes $\{[(DAB)Ga]CdI(tmeda)\}$ (**45** and **46**) [41b,c]. Complexes **40** and **41** are the first crystallographically characterized Zn–Ga-bonded compounds, whereas **45** is the first structurally known Cd–Ga-bonded compound. The Zn–Ga bond lengths are 2.3230(7) and 2.4491(17)/2.4307(17) Å in **40** and **41**, respectively, which are similar to the Zn–Zn bond lengths. The Cd–Ga bond in **45** has a length of 2.509(1)/2.5479(9) Å (two independent molecules in the unit cell), which is 0.1–0.2 Å longer than the Zn–Ga bond (2.3829(8) Å) in **43**.



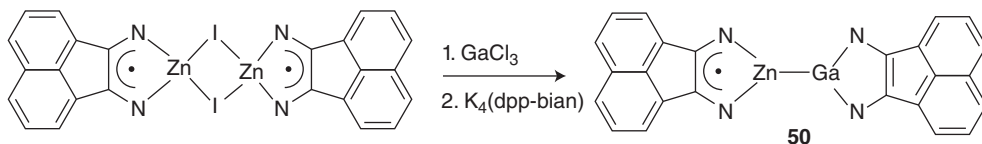
Scheme 12.14 Preparation of Zn–Ga and Cd–Ga-bonded complexes bearing DAB.

Another important method to prepare Zn–Ga-bonded complexes has been developed by Fischer *et al.* The β -diketiminato Ga(I) complex $[(DDP)Ga:]$ ($DDP = Dippnacnac = [HC\{C(Me)N(2,6-iPr_2C_6H_3)\}_2]$) reacted with $ZnCl_2$ or Me_2Zn to give $[(DDP)(Cl)GaZn(Cl)(thf)_2]$ (**47a**) or $\{[(DDP)(Me)Ga_2Zn]\}$ (**48**), respectively (Scheme 12.15) [42a]. This method was also applied to synthesize the first Hg–Ga-bonded complex $\{[(DDP)(SC_6F_5)Ga_2Hg]\}$ (**49**) (Scheme 12.15) [42b]. **47a** reacted with $Na^+[BAR_4F^-]$ to afford the dimer complex **47b**. The M–Ga bond lengths in **47–49** are 2.3920(6), 2.3960(11), 2.4631(7)/2.4609(7), and 2.5339(6) Å, respectively.

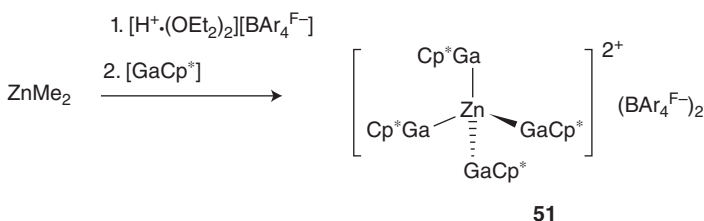


Scheme 12.15 DDP supported Zn–Ga complexes **47a**, **47b**, **48** and the first Hg–Ga complex **49**.

Two Zn–Ga-bonded complexes were synthesized and structurally characterized by Schumann's and Fischer's group, respectively. The dark-red compound [(dpp-bian)ZnGa(dpp-bian)] (**50**) (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)-imino]-acenaphthene) was prepared by treating the complex [(dpp-bian)ZnI]₂ with GaCl₃ followed by K₄[dpp-bian] (Scheme 12.16) [43]. The existence of the Zn–Ga bond was proven by ESR spectroscopy: coupling of the unpaired electron with ⁶⁹Ga and ⁷¹Ga could be observed. The X-ray structure shows that the Zn–Ga bond length has a value of 2.3531(8) Å. The compound [(Cp*Ga)₄Zn²⁺] [BAr₄^{F-}] (**51**) was synthesized by adding Cp*Ga to a mixture of ZnMe₂ and [H⁺·(Et₂O)₂] [BAr₄^{F-}] (Scheme 12.17) [42a]. The solid state of the colorless compound exhibits a distorted tetrahedral geometry around the zinc atom with Ga–Zn distances of 2.4036(6) and 2.4111(6) Å.



Scheme 12.16 Synthesis of **50**.

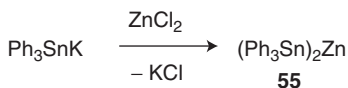


Scheme 12.17 Synthesis of **51**.

Two cluster compounds that might contain Zn–Ga bonds have been obtained by Fischer's group [44]. [Mo(GaCp*)₆] (**52**) reacted with Me₂Zn to afford a cluster compound of composition [MoZn₄Ga₄Me₄Cp*₄] (**53**), which converted into the cluster [MoZn₈Ga₂Me₆Cp*] (**54**) after further reaction with Me₂Zn. Due to the slight difference between the scattering power of Zn and Ga and uncertainty about the Me and Cp* distribution around the Zn and Ga atoms, the exact crystal structure of these compounds could not be confirmed. Therefore, the structures were provisionally predicted by DFT calculations that indicate the existence of Zn–Ga bonds in both compounds.

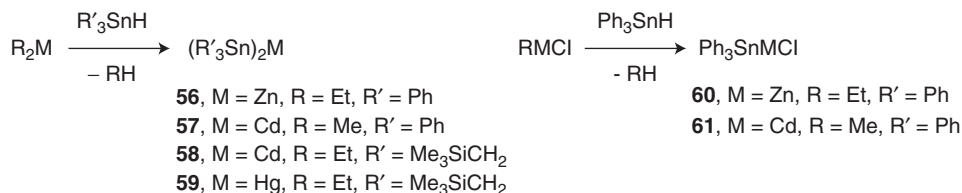
12.3.1.2 G12–G14 Bonds

The first G12–Sn-bonded complex (Ph₃Sn)₂Zn (**55**) was synthesized from ZnCl₂ and Ph₃SnK (Scheme 12.18) [45]. After that, a series of G12–Sn-bonded compounds have been prepared by hydrostannolysis of R₂M or RMCl (R = alkyl or aryl, M = G12) by a trialkyl-/triaryltin hydride reagent (Scheme 12.19) [46].



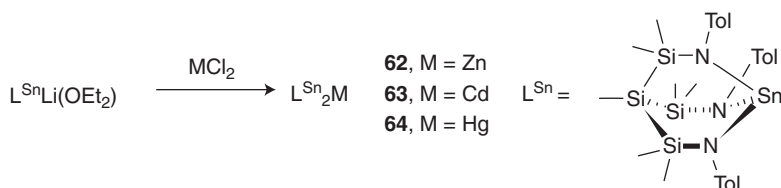
Scheme 12.18 Preparation of the first G12–Sn-bonded complex **55**.

However, none of these products have been crystallographically characterized. It is not until 2002 that first structural investigations on G12–Sn bonds were reported. Using the tripodal ligand



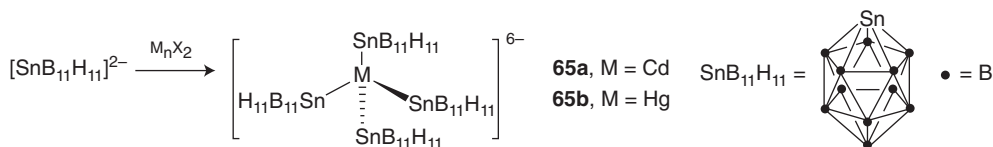
Scheme 12.19 G12–Sn-bonded complexes **56–61** prepared by hydrostannylation.

precursor lithium triamidostannate $[\text{MeSi}\{\text{SiMe}_2\text{N}(\text{p-Tol})_3\}\text{SnLi}(\text{OEt}_2)]$, Gade *et al.* successfully obtained the desired Zn–Sn-, Cd–Sn-, and Hg–Sn-bonded complexes **62–64** (Scheme 12.20) [47]. The Zn–Sn, Cd–Sn, and Hg–Sn bond lengths in these complexes are 2.5782(4)/2.9930(4), 2.6758(2), and 2.6495(2) Å, respectively. It should be noted that in complex **62**, the two Zn–Sn bonds are significantly different. One of the Zn–Sn bonds is unsupported, while the tripodal amido ligand in the second stannate unit binds both the Zn and Sn atoms.



Scheme 12.20 The first crystallographically characterized G12–Sn-bonded complexes **62–64**.

Wesemann *et al.* reported the synthesis of two cluster compounds **65a** and **65b** containing a Cd–Sn and Hg–Sn bond, which were generated by reacting the stanna-*closo*-dodecaborate salts $[\text{Et}_3\text{NH}^+]_2[\text{SnB}_{11}\text{H}_{11}^-]$ or $[\text{Me}_3\text{NH}^+]_2[\text{SnB}_{11}\text{H}_{11}^-]$ with CdBr_2 or Hg_2Cl_2 , respectively (Scheme 12.21) [48].

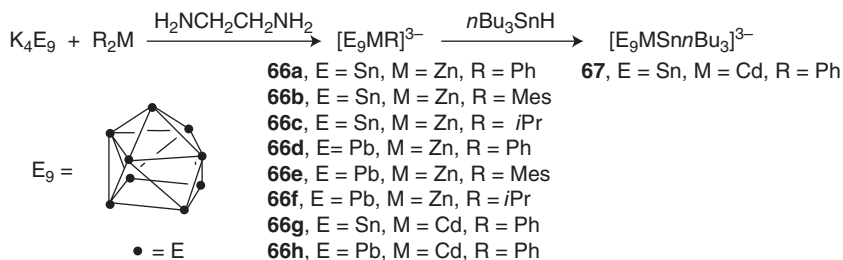


Scheme 12.21 Synthesis of **65a** and **65b**.

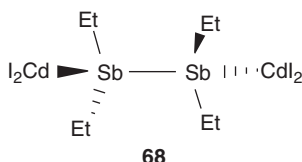
Some Zintl type organozinc and organocadmium ions with the general formula *closo*- $[\text{E}_9\text{MR}]^{3-}$ ($\text{E} = \text{Sn}, \text{Pb}$; $\text{M} = \text{Zn}, \text{Cd}$; $\text{R} = \text{Ph}, \text{Mes}, i\text{Pr}$) (**66a–h**) were obtained through reactions between potassium salts of the E_9^{4-} anions and dialkyl or diaryl zinc or cadmium in the presence of ethylenediamine (Scheme 12.22) [49, 50]. A reductive M–C bond activation by solvated electrons was supposed to be the reaction mechanism. The E_9^{4-} ligands in **66a–h** can be viewed as six-electron ligands, which are similar to the Cp^- ligand. Compound **66g** underwent a coupling reaction upon being treated with tri-*n*-butyltin hydride. Except **66e**, all the compounds have been analyzed by single crystal X-ray diffraction.

12.3.1.3 G12–G15 Bonds

The first crystallographically characterized Cd–Sb-bonded compound $[\text{Et}_4\text{Sb}_2 \cdot 2\text{CdI}_2]$ (**68**) with the Sb–Cd bond lengths of 2.821(2)/2.822(2) Å was generated by adding CdI_2 to Et_4Sb_2 (Scheme 12.23) [51]. Treating Me_2Cd with Et_4Sb_2 afforded a highly insoluble air-sensitive red-brown precipitate. The



Scheme 12.22 Preparation of Zintl type Zn–Sn- and Zn–Cd-bonded complexes **66a–h** and **67**.



Scheme 12.23 The first crystallographically characterized Cd–Sb-bonded compound **68**.

elemental analysis indicated the formation of the 1 : 1 adduct $[Me_2CdSb_2Et_4]$, but no crystal structure was obtained.

In 2005, Schulz *et al.* reported the crystal structure of a Zn–Sb-bonded cluster compound with the formula $[(\{MeZn\}\{Sb(SiMe_3)_2\}_3Zn_2\{SbSiMe_3\}_2)(ZnMe)Cl]$ (**69**) by reacting $[(dmap)AlMe_2Sb(SiMe_3)_2]$ with $ZnMe_2$ [52]. The chlorine atom stems probably from the impure Me_2Zn solution. In this molecule, the Zn_5Sb_4Cl core is connected by two $ZnSb_2$ fragments. The Zn–Sb bond lengths range from 2.604(1) to 2.686(1) Å. G12–Bi interactions have been found only in the two intermetalloid cluster compounds $[Zn_9Bi_{11}]^{5-}$ (**70**) and $[Zn_6Sn_3Bi_8]^{4-}$ (**71**) [53].

12.3.2

Bonding Between G12 and Transition Metals

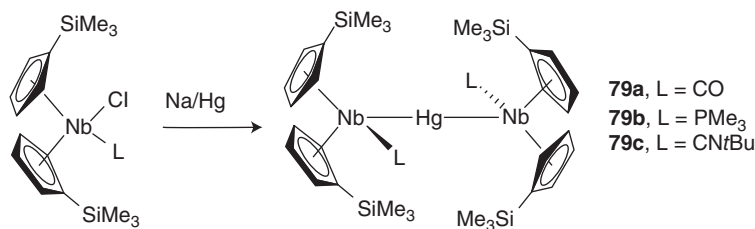
There is a large amount of G12–TM-bonded compounds, which have been prepared by different methods. Only some typical or important classes of these compounds are selected and discussed in this section. An excellent review on Zn–TM-bonded compounds has been written by Fischer *et al.* [54].

G12–G3- and G12–G4-bonded complexes are scarce. The Zn–Zr-bonded complex $[Cp_2Zr(ZnR)_2]$ ($R = C_6H_3-2,6-(2,4,6-iPr_3C_6H_2)_2$) (**72**) was generated from the reaction between $[RZnI]_2$ and $[Cp_2ZrCl_2]$ using sodium as the reducing agent [55]. Mazhar *et al.* prepared $[Cd_4Ti_4(dmae)_4(TFA)_8(OAc)_4O_6]$ ($dmae = N,N$ -dimethylaminoethanolate, TFA = trifluoroacetate, OAc = acetate) (**73**), which could be used as a precursor for generating $CaTiO_3$ thin films by aerosol-assisted chemical vapor deposition (AACVD) [56]. The crystal structure shows that two direct bonds between Cd and Ti are present in the dimer with distances of 3.3137(10) and 3.3132(12) Å.

The first G12–G5-bonded compounds $RHgTa(CO)_6$ (**74a**, R = Me; **74b**, R = Et; **74c**, R = Ph) were reported as early as 1964 [57]. In the 1970s, Ellis *et al.* prepared a series of Hg–G5-bonded complexes $[EtHgM(CO)_6]$ (**75a**, M = V; **75b**, M = Nb; **75c**, M = Ta) and $[EtHgM(CO)_5(PPh_3)]$ (**76a**, M = V; **76b**, M = Nb; **76c**, M = Ta) [58]. These compounds were all obtained from the reaction of $[K^+ \cdot (diglyme)_3][M(CO)_6^-]$, $[Na^+ \cdot (diglyme)_2][M(CO)_6^-]$, or $[Et_4N^+][M(CO)_5(PPh_3)^-]$ (M = V, Nb, Ta) with $RHgCl$ (R = Me, Et, Ph). Except for $[RHgTa(CO)_6]$, the IR spectra of all the above compounds have been measured. Some Zn–Nb- and Zn–Ta-bonded hydride complexes were

obtained from the reactions of $[\text{Cp}_2\text{NbH}_3]$ (**77**) or $[\text{Cp}'_2\text{TaH}_3]$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{Me}$) (**78**) with different stoichiometric amounts of Cp_2Zn [59, 60].

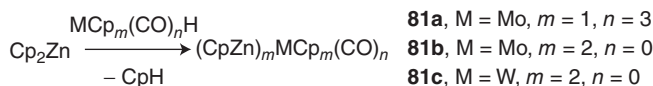
Bruno *et al.* reported a general method for the preparation of Nb–Hg-bonded complexes, involving the reduction of Nb(III) chloride species by sodium amalgam (Scheme 12.24) [61]. These reactions presumably proceed via intermediate Nb(II) radicals.



Scheme 12.24 Preparation of Hg–Nb-bonded complexes **79a–c**.

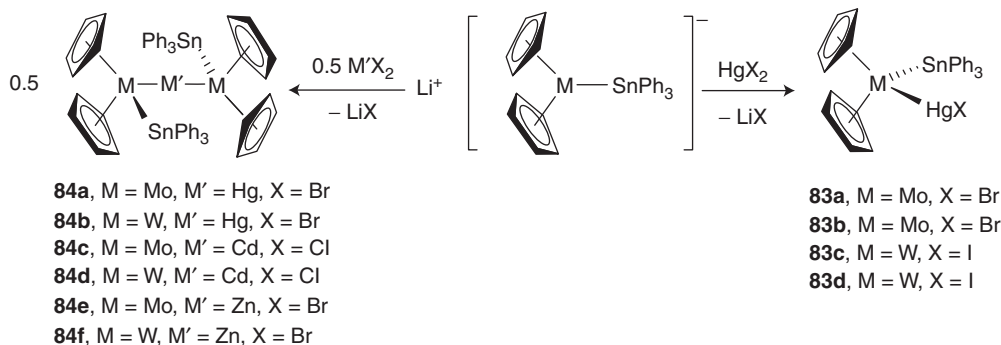
In 1976, Green *et al.* reported the formation of highly insoluble red-brown compounds with the composition $[(\text{Cp}_2\text{MZn})_n]$ (**80a**, M = Mo; **80b**, M = W) [62]. It is proposed that these complexes contain M–Zn bonds (M = Mo, W) and form cyclic tetramers or linear polymers.

Van der Kerk *et al.* developed a useful method for the synthesis of a series of Zn–Mo and Zn–W-bonded complexes with the general formula $[(\text{CpZn})_m\text{ML}_n]$ (M = Mo, W; L = CO, Cp; $m = 1, 2$; $n = 2, 3$) (Scheme 12.25) [63]. These solid compounds are soluble in benzene and monomeric according to ebulliometry measurements.



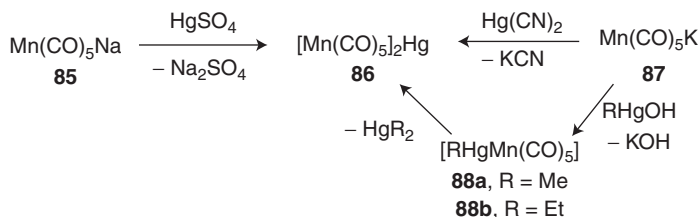
Scheme 12.25 Preparation of Zn–Mo- and Zn–W-bonded complexes **81a–c**.

The first crystallographically characterized Hg–Mo-bonded complex $[\text{Cp}_2\text{Mo}(\text{HgSEt}_2)]$ (**82**) was obtained by Kubicki *et al.* [64] Schubert *et al.* prepared some G12–M (M = Mo, W) bonded complexes from $\text{Li}[\text{Cp}_2\text{MSnPh}_3]$ (Scheme 12.26) [65].



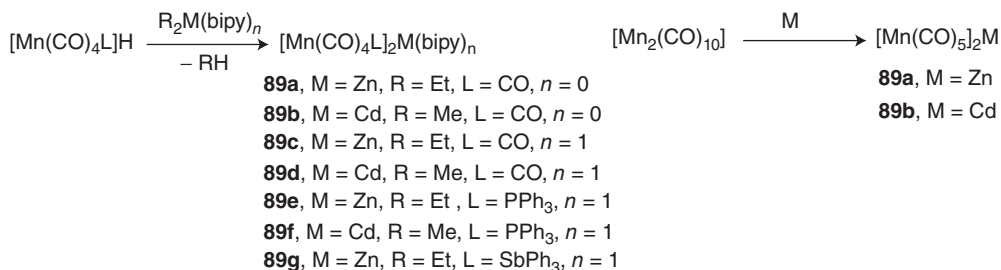
Scheme 12.26 Preparation of G12–Mo and G12–W-bonded complex **83a–d** and **84a–f**.

Studies on G12–G7-bonded complexes can be traced back to the preparation of the first Hg–Mn-bonded compounds by Hieber *et al.* (Scheme 12.27) [66].



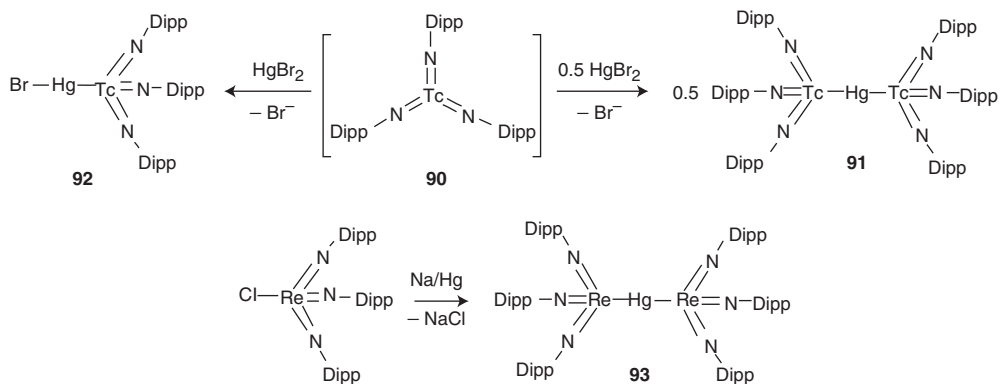
Scheme 12.27 Preparation of the first Hg–Mn-bonded complexes **88a** and **88b**.

The zinc and cadmium analogs of $[\text{Mn(CO)}_5]_2\text{Hg}$ were synthesized by treating $\text{Mn}_2(\text{CO})_{10}$ with the corresponding metal [67] (Scheme 12.28). Alternatively, $[\text{Mn(CO)}_4\text{L}]_2\text{M}$ ($\text{M} = \text{Zn, Cd}$) could also be achieved by reacting $[\text{Mn(CO)}_4\text{L}]\text{H}$ with dialkyl metal [68]. An electrochemical synthetic method for $[\text{Mn(CO)}_5]_2\text{M} \cdot \text{bipy}$ ($\text{M} = \text{Zn, Cd}$) was developed by Zhandire [69].



Scheme 12.28 Preparation of Zn–Mn- and Zn–Cd-bonded complexes **89a–g**.

Even G12–Tc-bonded complexes have been prepared. The tris(arylimido)technetium anion (**90**) reacted readily with 0.5 or 1 equiv. of HgBr_2 to afford $[\text{Hg}\{\text{Tc(NAr)}_3\}_2]$ (**91**) or $[\text{BrHgTc(NAr)}_3]$ (**92**, $\text{Ar} = 2,6\text{-diisopropylphenyl}$) (**92**), respectively (Scheme 12.29) [70]. The crystal structure of $\text{Hg}[\text{Tc(NAr)}_3]_2$ shows a linear geometry around the mercury atom and the bond length of Tc–Hg is $2.615(1)$ Å. Also the rhenium analog $[\text{Hg}\{\text{Re(NAr)}_3\}_2]$ (**93**) was obtained through reduction of tris(arylimido)rhenium chloride with sodium amalgam (Scheme 12.29) [70].

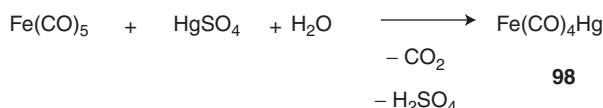
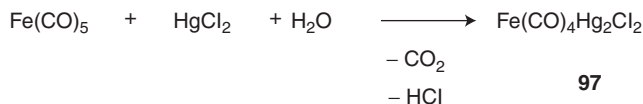


Scheme 12.29 Preparation of Hg–Tc- and Hg–Re-bonded complexes **91–93**.

G12–Re-bonded complexes $\text{M}[\text{Re(CO)}_5]_2$ (**94a**, $\text{M} = \text{Zn}$; **94b**, $\text{M} = \text{Cd}$; **94c**, $\text{M} = \text{Hg}$) and $\text{Cp}_2\text{ReHMX}_2$ (**95a**, $\text{M} = \text{Zn}$; **95b**, $\text{M} = \text{Cd}$) are also known [71]. Shapley *et al.* synthesized a series of

carbidoheptarhenate cluster compounds containing Zn–Re or Cd–Re bonds [72]. These compounds have a general formula of $[\text{Ph}_4\text{P}^+]_2[\text{Re}_7\text{C}(\text{CO})_{21}\text{MX}^{2-}]$ (**96**) ($\text{M} = \text{Zn}, \text{Cd}$; $\text{X} = \text{Cl}, \text{NO}_3, \text{SC}_6\text{H}_4\text{Br}$). The complex $[\text{Ph}_4\text{P}^+]_2[\text{Re}_7\text{C}(\text{CO})_{21}\text{ZnCl}^{2-}]$ was characterized by single crystal X-ray diffraction and represents the first structural evidence for a Zn–Re bond. The lengths of the three Zn–Re bonds are 2.689(2), 2.700(2), and 2.744(2) Å, respectively.

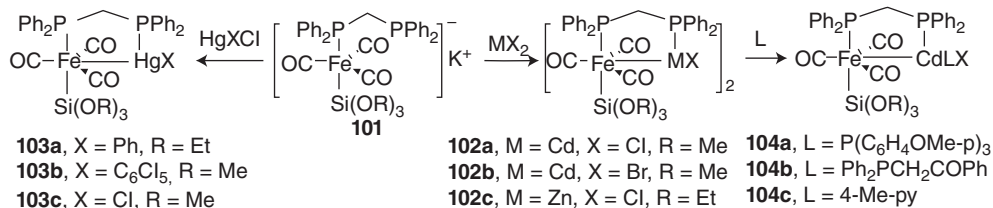
Hock and Stuhlmann were the first to explore the reaction between iron carbonyl and mercury salts and already at the end of the 1920s obtained compounds containing iron and mercury (Scheme 12.30) [73]. Similar compounds with cadmium instead of mercury were reported by Feigl and Krumholz [74]. Later, Hieber and Fack also prepared some iron carbonyl compounds containing zinc, cadmium, or mercury [75].



Scheme 12.30 Preparation of the first Fe–Hg-bonded compounds **97** and **98**.

The first direct evidence of the G12–Fe bonding was the crystal structure determination of the compounds $[\text{CdFe}(\text{CO})_4]$ (**99**) and $[(\text{byp})\text{CdFe}(\text{CO})_4]$ (**100**) in 1977 [76]. The former adopts a planar eight-membered ring of alternating Cd and $\text{Fe}(\text{CO})_4$ fragments, while the latter shows a planar six-membered ring of alternating Cd(byp) and $\text{Fe}(\text{CO})_4$.

Braunstein *et al.* prepared a series of G12–Fe-bonded complexes supported by the bidentate phosphine ligand dppm ($\text{Ph}_2\text{PCH}_2\text{PPh}_2$) (Scheme 12.31) [77]. Similar complexes were also synthesized by Zhang *et al.* and Mak *et al.* using different P,N-type bidentate donors as the supporting ligands (Scheme 12.32). The related ruthenium derivatives were prepared as well (Scheme 12.32) [78].

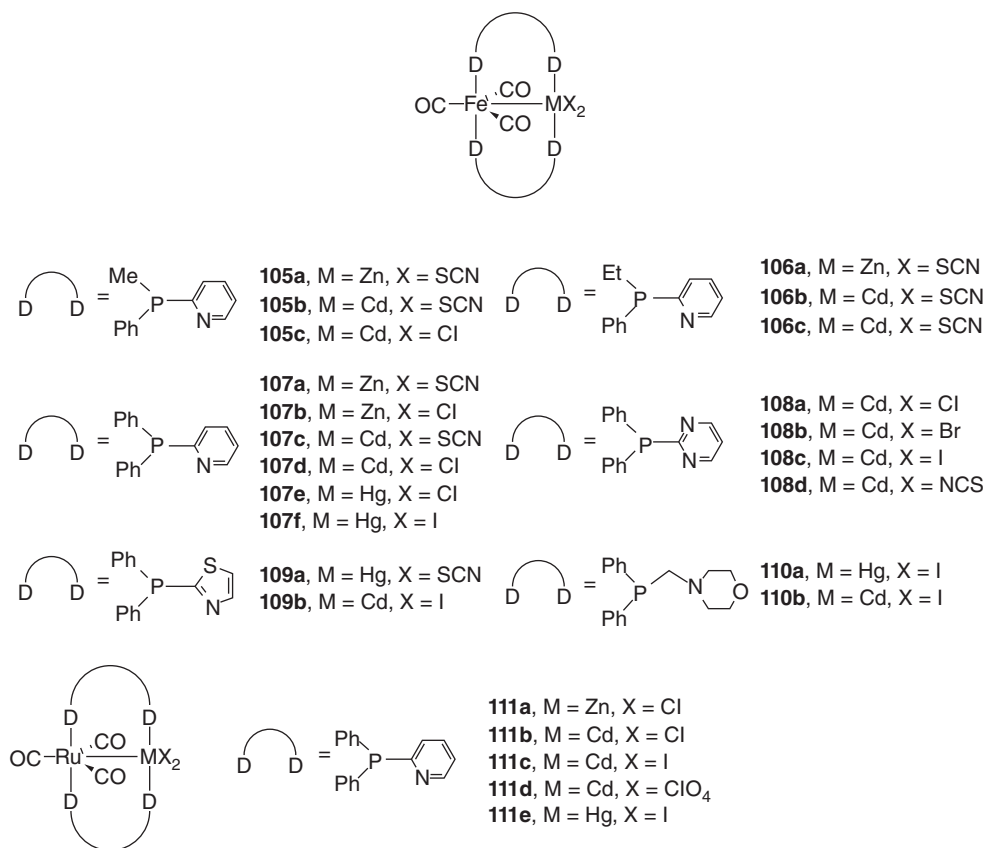


Scheme 12.31 Preparation of Zn–Fe- and Cd–Fe-bonded complexes **102–104**.

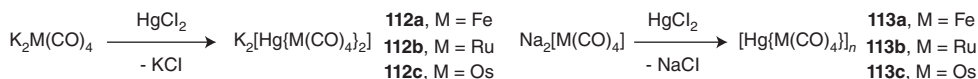
Convenient synthetic routes for the $[\text{Hg}\{\text{M}(\text{CO})_4\}_2]^{2-}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) anions were developed by Shore *et al.* (Scheme 12.33) [79].

$[\text{HCo}(\text{N}_2)(\text{PPh}_3)_3]$ reacted with $[\text{Cp}_2\text{Zn}]$ to give the Zn–Co-bonded complex $[(\text{CpZn})_2\text{Co}(\text{Cp})\text{PPh}_3]$ (**114**), which is the first structurally characterized TM–ZnR complex with the Co–Zn bond length of 2.289(1) Å [80].

Zn–Rh-bonded compounds $[\{(\text{dipp})\text{Rh}\}_2(\mu\text{-H})_2\{\mu\text{-Zn}(\text{CH}_2\text{Ph})\}_2]$ (**115**) and $[\{(\text{dipp})\text{Rh}\}_2(\mu\text{-H})_2\{\mu\text{-Zn}(\text{Cp})\}_2]$ (**116**) (dipp = 1,3-bis(diisopropylphosphino)propane) were synthesized by reacting $[\{(\text{dipp})\text{Rh}\}_2(\mu\text{-H})_2]$ with $[\text{Zn}(\text{CH}_2\text{Ph})_2]$ and $[\text{ZnCp}_2]$, respectively [81]. Tanase *et al.* prepared Hg–Rh-bonded tetranuclear complexes $[\text{Rh}_3(\text{HgX}(\mu\text{-Cl})_2(\mu\text{-X})(\mu\text{-dpmppp})(\text{CO})_2)\text{PF}_6]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$, dpmppp = *meso*-1,3-bis[(diphenylphosphinomethyl)phenylphosphino]propane). Replacement of



Scheme 12.32 G12-Fe- and G12-Ru-bonded complexes **105–110**.



Scheme 12.33 Preparation of Hg-G8-bonded complexes **112** and **113**.

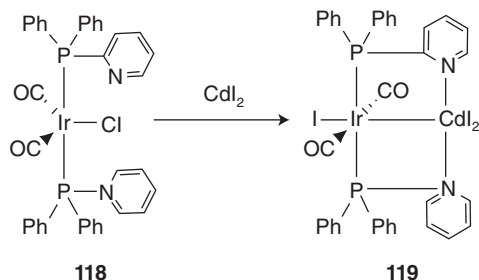
CO by xylyl-N≡C afforded the corresponding [Rh₃(HgX(μ-Cl)₂(μ-X)(μ-dpmp)(xylyl-N≡C)₂)]PF₆ (X = Cl, Br, I) [82].

Sutton *et al.* prepared the G12-Ir-bonded complexes [Cp^{*}(CO)₂IrMCl₂] (**117a**, M = Zn; **117b**, M = Cd; **117c**, M = Hg) by reacting [Cp^{*}Ir(CO)₂] with MCl₂ [83]. It should be mentioned that [Cp^{*}(CO)₂IrCdCl₂] is the first Ir–Cd-bonded complex.

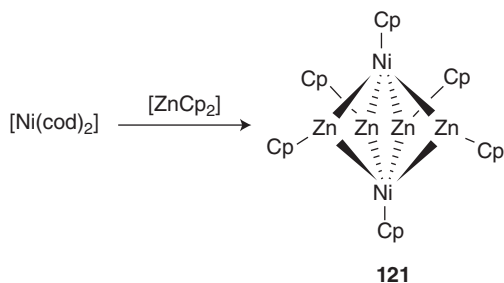
The first crystallographically characterized Ir–Cd complex (**119**) was obtained by the reaction of **118** with CdI₂ by Mak *et al.* (Scheme 12.34) [84]. Its preparation is similar to that of its Fe–Cd and Ru–Cd congeners.

Treatment of Vaska's complex [Ir(PPh₃)₂(CO)Cl] with [Hg(C≡CR)₂] (R = Ph, C₅H₁₁, C≡W(CO)₂(L) (L = HB(pz)₃, HB(pzMe₂)₃, pz = pyrazol-1-yl) afforded the Ir-Hg-bonded alkynyl complexes [Ir(PPh₃)₂(CO)(HgC≡CR)(C≡CR)Cl] (**120a**, R = Ph; **120b**, R = C₅H₁₁) and [Ir(PPh₃)₂(CO)(HgCl)(C≡CR)Cl] (**120c**, R = C≡W(CO)₂(L)) [85].

Van der Kerk *et al.* prepared [Ni₂Zn₄Cp₆] (**121**) containing the [Ni₂Zn₄] core by treating [Ni(cod)₂] with Cp₂Zn (Scheme 12.35) [86]. Its crystal structure shows that the eight Ni–Zn bonds have bond lengths of 2.398(2) Å. No Zn–Zn interactions were observed. This reaction presumably proceeds via



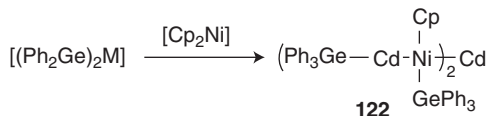
Scheme 12.34 The first crystallographically characterized Ir–Cd complex **119**.



Scheme 12.35 Preparation of the Zn–Ni-bonded complex **121**.

the highly reactive Ni–Zn bonded $[\text{CpNiZnCp}]$; the Ni–Zn-bonded intermediate $[\mu\text{-CpNi}(\text{PPh}_3)(\mu\text{-Cp})(\text{ZnCp})_2]$ could be trapped in the presence of Ph_3P .

In 1980, Domrachev *et al.* reported Cd–Ni bond formation by treating $[\text{Cp}_2\text{Ni}]$ with $[(\text{Ph}_3\text{Ge})_2\text{Cd}]$ (Scheme 12.36) [87]. Complex **122** is the first crystallographically characterized Cd–Ni-bonded compound with a Ni–Cd bond length of 2.476(2) Å; the second example was achieved 27 years later by Zacchini *et al.*, who prepared the dimeric cluster compound $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ by reacting $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ in THF with 2 equiv. of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ [88]. Its crystal structure shows that the two $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ fragments are connected to the Cd_2Cl_3^+ unit. The Cd–Ni distances have an average value of 2.736 Å.

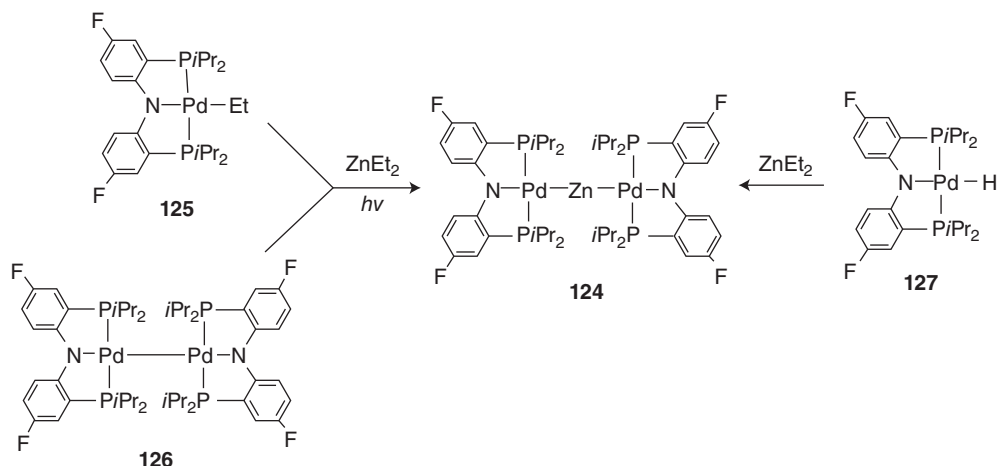


Scheme 12.36 Preparation of the first crystallographically characterized Cd–Ni-bonded complex **122**.

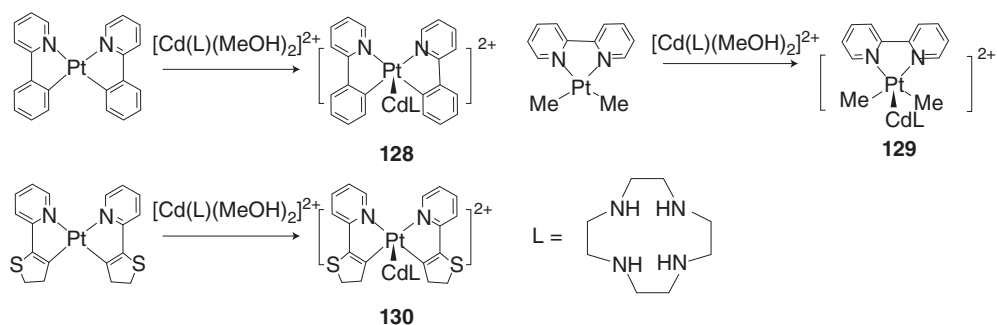
The Pd–Cd-bonded complex $[\text{CdPd}(\text{CH}_3\text{COO})_4 \cdot \text{CH}_3\text{COOH}]_2$ (**123**) was obtained from the reaction between palladium acetate and cadmium acetate in glacial acetic acid [89]. The crystal structure shows that the coordination sphere of cadmium adopts a trigonal-prismatic geometry. Ozerov *et al.* prepared the Pd–Zn-bonded complex **124** through different reaction pathways (Scheme 12.37) [90]. Complex **124** represents the first Pd–Zn-bonded compound with Pd–Zn distances of 2.3793(10) and 2.3723(10) Å.

The first Pt–Cd-bonded complexes were reported by Ito *et al.* in 1999 [91]. Treatment of different Pt(II) complexes with $[\text{Cd}^{2+}(\text{L})(\text{MeOH})_2](\text{ClO}_4^-)_2$ afforded the corresponding Pt–Cd-bonded compounds **128–130** (Scheme 12.38).

LaLinde *et al.* synthesized numerous Pt–Cd-bonded complexes bearing alkynyl groups: $[(\text{C}_6\text{F}_5)_2(\text{C}\equiv\text{CPh})_2\text{PtCdL}]$ (**131**), $[\text{cis-Pt}(\text{C}_6\text{H}_5)_2(\text{C}\equiv\text{CPh})_2\text{CdL}_n]$ (**132**), $[\text{Pt}(\text{C}\equiv\text{CTol})_4\text{Cd}(\text{py})_2]$ (**133**),

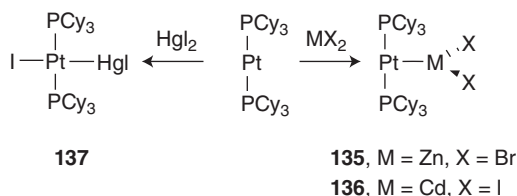


Scheme 12.37 Preparation of the first Pd-Zn bonded compound **124**.



Scheme 12.38 Preparation of the first Pt-Cd bonded complexes **128**–**130**.

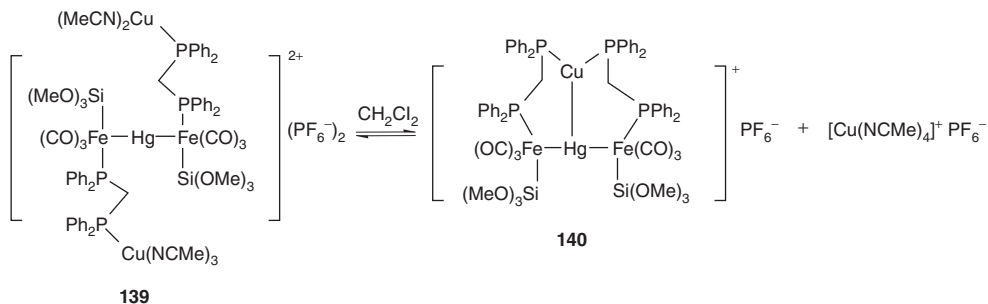
and $[Pt(C\equiv CTol)_4Cd(NC_5H_4CF_3-4)]_2$ (**134**) [92]. Jones *et al.* prepared three Pt-Zn-, Pt-Cd-, and Pt-Hg-bonded complexes by reacting $[Pt(PCy_3)_2]$ with the halide of the corresponding G12 metal (Scheme 12.39) [93].



Scheme 12.39 Preparation of G12-Pt-bonded complexes **135**–**137**.

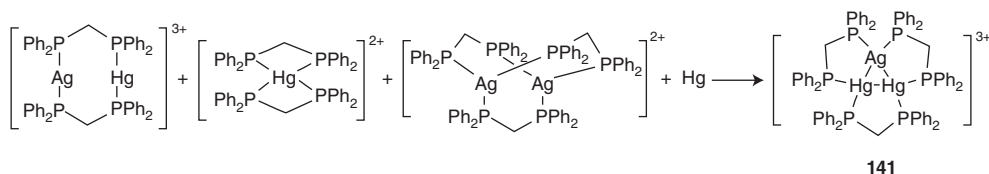
Chang *et al.* obtained the Pt-Cd-bonded compound $[Cd\{Pt(Bdt)(DTBbpy)\}_2](ClO_4)(H_2O)](ClO_4)$ (**138**) (Bdt = 1,2-benzenedithiolato, DTBbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine), in which the two Pt-Cd bonds have lengths of 2.7331(7) and 2.736(7) Å [94]. This compound was prepared from the reaction between $Cd(ClO_4)_2 \cdot 6H_2O$ and $[Pt(Bdt)(DTBbpy)]$. Interestingly, replacing cadmium chlorate for zinc chlorate did not give the analogous Pt-Zn-bonded complex, demonstrating the metal selectivity of this type of reaction.

A Cu–Hg bond of 2.689(2) Å was found in complex **140**, obtained from the Hg–Fe-bonded complex **139** (Scheme 12.40) [95].

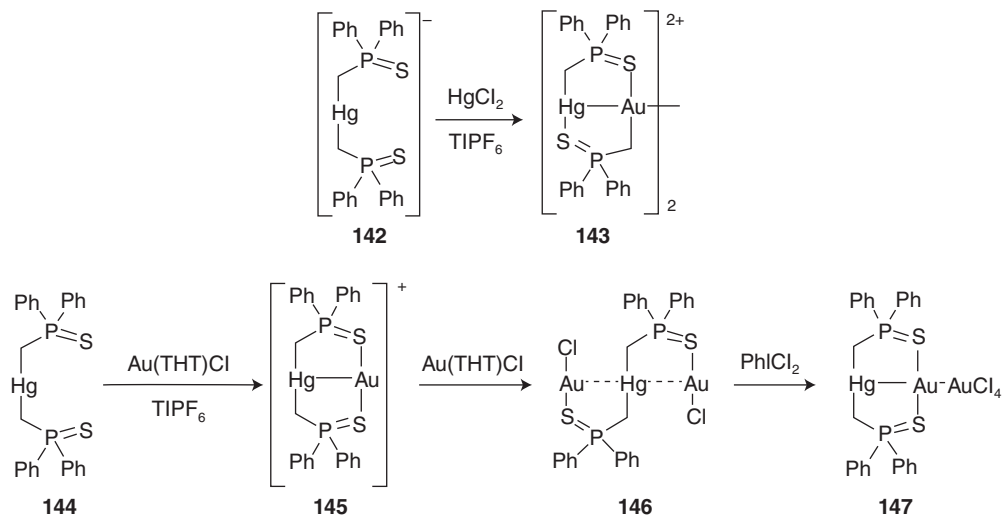


Scheme 12.40 Formation of the Cu–Hg-bonded compound **140**.

A silver–mercury centered cluster compound was prepared by Peringer *et al.* [96] (Scheme 12.41). The multi-component reaction led to quantitative formation of the complex **141**, which was analyzed by X-ray single crystal diffraction. The Hg–Ag distances in this compound are 2.853(2) and 2.805(2) Å, and the Hg–Hg distance is 2.6598(14) Å.



Scheme 12.41 Formation of the Hg–Ag-bonded compound **141**.

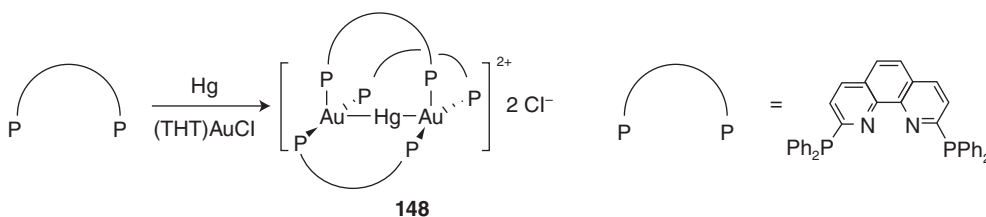


THT = tetrahydrothiophene

Scheme 12.42 Preparation of Hg–Au-bonded complexes **143** and **145–147**.

Gold–mercury cluster compounds have been obtained by different groups. Fackler *et al.* first prepared two Au–Hg-bonded complexes **143** and **145** in 1988 (Scheme 12.42) [97]. The two complexes are isomeric and the Au–Hg bond lengths are 3.088(1) and 2.989(1) Å, respectively. Compound **144** could also be converted into **146** by treating with Au(THT)Cl (THT = tetrahydrothiophene) without Tl salt. The solid structure of **146** showed the Hg–Au distances of 3.310(1) and 3.361(1) Å. These are significantly longer than the Au–Hg bond lengths in **143** and **145**. Complex **146** is the first trinuclear organometallic compound containing Au and Hg. Oxidation of **146** using PhICl_2 afforded quantitatively complex **147**, in which the Au–Hg bond has a length of 3.079(2) Å.

Some cluster compounds containing Hg–Au–Pd and Hg–Au–Pt centers have been prepared and crystallographically characterized by Steggerda *et al.* and Pignolet *et al.* [98] Catalano reported the formation of a linearly coordinated Hg(0) trapped in a Au(I) metallocryptand cage (Scheme 12.43) [99]. The Hg–Au distances are 2.7847(4) and 2.7804(4) Å, respectively. These are much shorter than the corresponding values in the compounds above (from 2.945(3) to 3.636(2) Å).



Scheme 12.43 Preparation of the Au–Hg-bonded complex **148**.

12.4

Summary and Perspectives

With examples of mercurous chloride prepared already as early as the Eastern Han Dynasty in China, compounds with G12–G12 bonds are likely among the oldest ever known metal–metal complexes. Despite these early examples of Hg–Hg compounds, the less stable Cd–Cd- and Zn–Zn-bonded complexes have been developed only during the last 60 years. The field of G12–G12 took especially off after the discovery of the first molecular metal–metal-bonded complexes involving group 12 metals. The successful synthesis of dizincocene $\text{Cp}^*\text{ZnZnCp}^*$ in 2004 certainly should be regarded as a milestone that has stimulated intensive follow-up research in this area. Since then, numerous zinc–zinc-bonded compounds have been prepared and characterized. More importantly, systematic investigations toward reactivity progressed significantly and catalytic activity of $\text{Cp}^*\text{ZnZnCp}^*$ in alkene and alkyne hydroamination has been reported. The number of molecular Cd–Cd- and Hg–Hg-bonded compounds is still very limited and no reactivity studies on these compounds have been reported yet.

In comparison to the homobimetallics, the heterobimetallics of group 12 metals exhibit much more diversity. Group 12 metals are able to form bonds with most TMs and late MG metals and numerous examples of such compounds can be found in literature. Identification of new metal–metal bonds is the main purpose of this research. Similar as for homobimetallic G12–G12 compounds, there is so far very little known on the potential applications of these heterobimetallic compounds. Further investigations toward utilization of these academically interesting compounds, for example, organic synthesis, catalysis, metal organic chemical vapor deposition (MOCVD), materials science, would move this rapidly developing field to the next step and would encourage an even stronger increasing interest.

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13

Group 13 Metal–Metal Bonds

Joseph A.B. Abdalla and Simon Aldridge

13.1

Preamble

This chapter is organized according to the sections of the Periodic Table, examining successively complexes from the s-, p-, d-, and f-blocks. Its scope – examining metal–metal bonds featuring the Group 13 metals aluminum, gallium, indium, and thallium – is potentially immense, with over 550 examples of homonuclear M–M bonds alone to be found in the Cambridge Structural Database. With this in mind, we have chosen to focus primarily on unsupported metal–metal bonds, and to focus on discrete systems, rather than multinuclear clusters described by delocalized schemes of bonding. While this means, inevitably, having to omit discussion of some seminal compounds – such as Schnöckel's Al_{77} cluster (and related sub-valent clusters), [1] it does still leave scope for discussion of numerous landmark compounds that have contributed to the recent “renaissance” in Main Group chemistry. In particular, this includes a variety of systems that have been instrumental in developing a better understanding of electronic structure in Group 13 derived systems. Notable highlights include Robinson's proposal of a $\text{Ga}\equiv\text{Ga}$ triple bond [2], Power's monovalent metal terphenyl systems [3, 4], Hill's homocatenated In_6 system [5], Jones's carbene-stabilized subvalent metal hydride $[(\text{IPr})\text{AlH}_2]_2$ [6], and Schnöckel's $\text{Al}_2(\text{PR}_2)_4$ biradicaloid – hinting at M–M bond formation/scission [7]. Heteronuclear systems have also offered new models of bonding, witness, for example, Fischer's terminal one coordinate Ga^+ ligand [8], Robinson's “ferrogallyne,” [9] and iron complexes of GaI isolobal with CO [10].

13.2

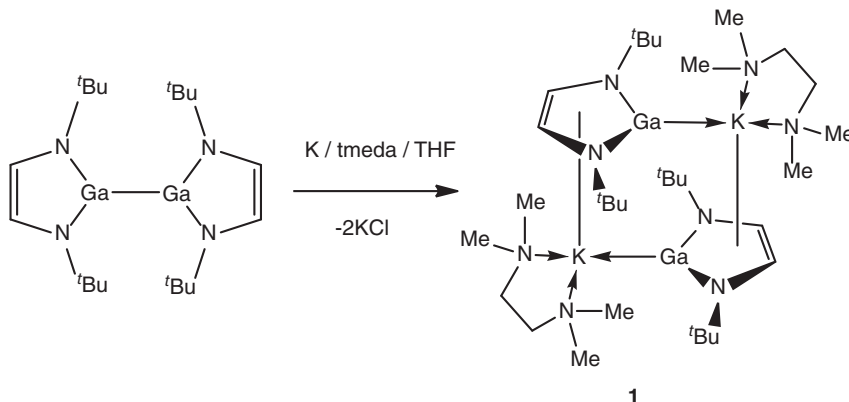
s-Block to Group 13 Metal Bonds

The synthesis of compounds featuring an appreciable interaction between a Group 13 metal center and a metal from the s-block is a relatively recent development, reflecting at least in part, a desire to synthesize nucleophilic reagents capable of delivering a formally anionic Group 13 moiety, for example, to a metal-based electrophile. While this class of compound remains relatively less numerous (and primarily focussed on gallium), its synthetic versatility is immediately apparent from the plethora of d- and f-block systems, which have been synthesized by employing such reagents in a salt metathesis process. Group 1 compounds have typically been synthesized by the formal reduction of M–M (typically Ga–Ga) bonded precursors or M^{III} dihalides with an appropriate source of the alkali metal; syntheses of Group 2 complexes exploit either similar reduction chemistry, or alternatively Group 1 derivatives in salt metathesis processes.

13.2.1

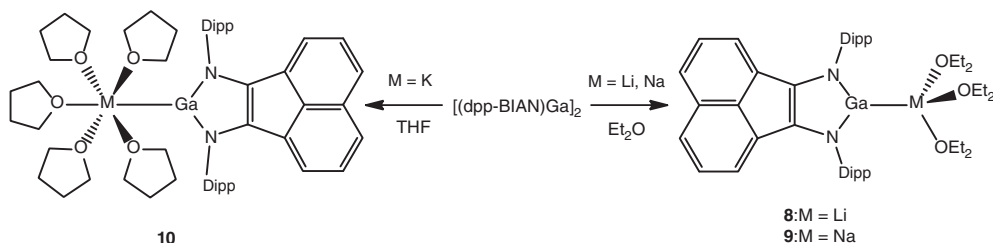
Group 1 Metal Complexes

Notwithstanding systems that feature relatively weak contacts between formally anionic (typically multinuclear) Group 13 metal fragments and a Group 1 metal [2, 11–16], a number of examples of isolated, unsupported Li–Ga, Na–Ga, and K–Ga bonds have been reported [17]. The first of these was reported in 2001 by Schmidbaur and coworkers (Scheme 13.1) [18, 19], who exploited the reaction of the Ga^{II} precursor, [(HC^tBuN)₂Ga]₂ with elemental potassium to generate dimeric [(HC^tBuN)₂GaK(tmeda)]₂ (**1**), which features a closest K⋯Ga contact of 3.538(1) Å (cf. 3.24 Å for the sum of the respective covalent radii) [20].



Scheme 13.1 Synthesis of [(HC^tBuN)₂GaK(tmeda)]₂.

Shortly afterwards, Jones and coworkers reported the related aryl-substituted systems [(HCDippN)₂GaK(tmeda)]₂ and [(HCDippN)₂GaK(OEt₂)₂] (2 and 3), which feature similar dimeric structures and K⋯Ga contacts in the order of 3.4 Å [21]. The use of 18-crown-6 allows access to the effectively “naked” anionic [(HCDippN)₂Ga][−] heterocycle by sequestering the potassium counter-ion. In this case, a more convenient Ga^{III} diiodide precursor was employed, and recently alkali metal derivatives of the closely related (backbone methyl-substituted) heterocycle [(MeCDippN)₂Ga][−] have been synthesized utilizing an analogous Ga^{III} dichloride starting material [22]. By employing alternative alkali metals, systems of the type {(MeCDippN)₂Ga}M(THF)₃ (M = Li, **4** or Na, **5**) or {(MeCDippN)₂Ga₂}K(THF)₄, **6**, can also be accessed. Here too, the highly polar nature of the alkali metal–gallium bond is reflected in metal–metal contacts (**4**: 2.686(14) Å; **5**: 2.972(4) Å; **6**: 3.687(1) Å), which are significantly in excess of the sums of the respective covalent radii (2.49, 2.87, and 3.24 Å, respectively) [20]. In addition, related systems featuring even more sterically encumbered pendant aryl substituents have recently been forthcoming [23]. Analysis of the solid-state structures of a series of compounds of the type {(HCArⁿN)₂Ga}Na(tmeda)L (7: L = Et₂O, THF, toluene, or pendant aryl group) reveals that the Na⋯Ga distance correlates well with the donor capabilities of the L substituent. Thus, complexes with L = THF or Et₂O feature Na⋯Ga contacts in excess of 3.0 Å (3.121(2) and 3.038(2) Å, respectively), while somewhat shorter distances are observed for more weakly bound donors (i.e., L = toluene or an intramolecularly coordinated aryl group: 2.940(1) and 2.910(3) Å, respectively). In a further variation on this theme, Fedushkin has developed routes to alkali metal complexes containing gallium heterocycles based on a 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (or dpp-BIAN) framework (**8–10**; Scheme 13.2) [24–26]. A range of complexes of this type have been synthesized for lithium, sodium, and potassium (and also for Group 2 metals), with an analysis of the Na⋯Ga contacts for sodium compounds of the type {(dpp-BIAN)Ga}NaL_n [L_n = (OEt₂)₃, (dme)₂, (OEt₂)(THF)₃] confirming that ancillary donor



Scheme 13.2 Synthesis of alkali metal–gallium bonds supported by BIAN heterocycles.

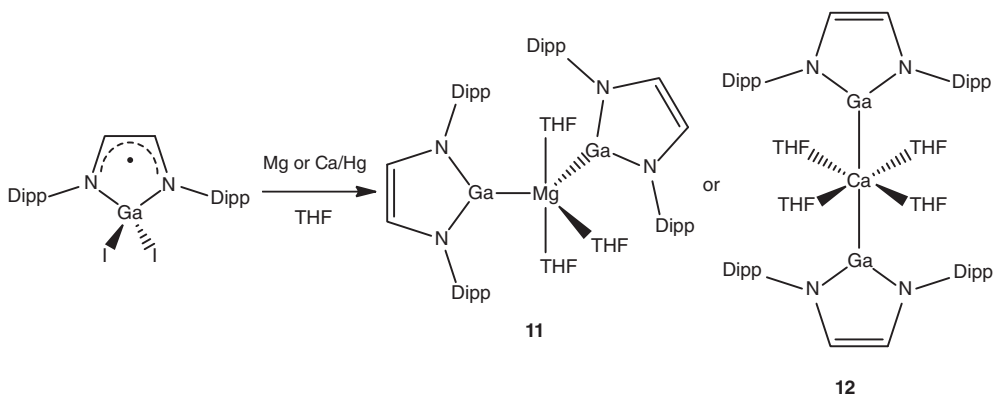
sterics are an important influence on this parameter. Thus, an increase of about 0.12 Å, for example, is observed between $\{(\text{dpp-BIAN})\text{Ga}\}\text{Na}(\text{dme})_2$ and $\{(\text{dpp-BIAN})\text{Ga}\}\text{Na}(\text{OEt}_2)(\text{THF})_3$.

The polar nature of the metal–metal bonds in these systems is reflected in natural bond orbital (NBO) analyses, which yield Wiberg bond indices of 0.52, 0.41, and 0.30, respectively for the model systems $\{(\text{HCXylN})_2\text{Ga}\}\text{M}(\text{THF})_3$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$). Moreover, consistent with the increasing electropositivity of the alkali metal, the natural charges at the metals are calculated to be 0.790, 0.822, and 0.852 for Li, Na, and K, respectively [22].

13.2.2

Group 2 Metal Complexes

Examples of structurally authenticated complexes featuring unsupported bonds between a Group 13 element and a Group 2 element are confined to gallium. Jones and coworkers were the first to report such complexes in 2006, employing a similar approach with magnesium and calcium, to that reported previously with Group 1 metals (**11** and **12**; Scheme 13.3) [27]. Mechanistically, this chemistry is thought to proceed by sequential reduction of the Ga^{III} diiodide precursor to give first Ga^{II} , and then Ga^{I} dimeric intermediates, with M-Ga bond formation ($\text{M} = \text{Mg}, \text{Ca}$) ultimately occurring via insertion into the Ga-Ga bond of the latter. That said, this approach does not appear to give analogous products with strontium or barium metal, yielding instead the partially reduced Ga^{II} species, $[(\text{HCDippN})_2\text{Ga}]_2$.



Scheme 13.3 Magnesium and calcium gallyl complexes via reduction chemistry.

The differing covalent radii of magnesium and calcium are reflected not only in the different coordination geometries of the metal centers in **11** (distorted trigonal bipyramidal) and **12** (distorted octahedral), but also in the $\text{M} \cdots \text{Ga}$ contacts (2.717(2) and 3.159(1) Å, respectively). The polar nature

of the metal–gallium interactions is revealed by NBO charges and Wiberg bond indices calculated for the model systems $\{(\text{H}(\text{CMeN})_2\text{Ga})_2\text{Mg}(\text{OMe}_2)_3\}$ and $\{(\text{H}(\text{CMeN})_2\text{Ga})_2\text{M}(\text{OMe}_2)_4\}$ ($\text{M} = \text{Ca}, \text{Sr}$). Thus, partial positive charges of 1.35, 1.54, and 1.58 are calculated for the Mg, Ca and Sr centers, with associated M–Ga bond orders of 0.377, 0.240, and 0.232, respectively.

An insertion approach has also been used to give access to related species featuring a BIAN-based heterocycle [26]. Thus, reactions of the elemental metals with the Ga^{II} precursor $[(\text{dpp-BIAN})\text{Ga}]_2$ in THF leads to the formation of the Group 2 complexes $\{(\text{dpp-BIAN})\text{Ga}\}_2\text{M}(\text{THF})_n$ ($\text{M} = \text{Mg}, n = 3$; $\text{M} = \text{Ca}$ or $\text{Sr}, n = 4$; $\text{M} = \text{Ba}, n = 5$).

An alternative entry point into Group 2 gallyl chemistry involves the reaction between a Group 1 metal salt of an anionic Ga^{I} heterocycle and a Group 2 electrophile. The choice of electrophile is clearly important, insofar as reactions of the potassium gallyl compound **2** with Group 2 diiodides, MI_2 , for example, are reported to yield intractable mixtures of products, whereas the corresponding chemistry with *in situ* generated $\text{MI}_2(\text{tmeda})_n$ brings about salt elimination and formation of the neutral bis(gallyl) systems $\{(\text{HCDippN})_2\text{Ga}\}_2\text{M}(\text{tmeda})_2$ (**13**: $\text{M} = \text{Ca}$; **14**: $\text{M} = \text{Sr}$; **15**: $\text{M} = \text{Ba}$) [26]. The increasing lability of the resulting M–Ga interaction as the group is descended is thought to be responsible for the lower yields obtained (e.g., 75%, 47%, and 14% for **13–15**, respectively).

A different class of Group 2–Group 13 metal bond has been reported to be formed via the reactions of the sandwich compounds Cp^*_2M ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) with pentamethyl-cyclopentadienylgallium(I), Cp^*Ga [28]. Thus, $\text{Ga} \rightarrow \text{M}$ linkages have been characterized crystallographically for $\text{Cp}^*_2\text{Ca}(\text{GaCp}^*)$, $\text{Cp}^*_2\text{Sr}(\text{GaCp}^*)(\text{THF})$, and $\text{Cp}^*_2\text{Ba}(\text{GaCp}^*)_2$, with the respective donor/acceptor linkages being defined by metal–metal separations of 3.183(2), 3.435(1), and 3.602(1)/3.580(1) Å, respectively. These interactions – which are thought to be due predominantly to dispersive forces – can be compared to 2.97, 3.16, and 3.36 Å for the sums of the respective covalent radii [20], and 3.198(1)/3.257(1), 3.324(1), and 3.466(1)/3.463(1) Å for the corresponding interactions involving $\text{Ca} \cdots \text{Ga}$, $\text{Sr} \cdots \text{Ga}$, and $\text{Ba} \cdots \text{Ga}$ linkages in complexes **13–15** [29].

13.3

p-Block to Group 13 Metal Bonds

13.3.1

Group 12 Metal Complexes

Direct reaction between Ga^{I} species and Group 12 halides and alkyls has proven the most common route to Group 12–Group 13 bond formation. The first such examples were obtained by salt metathesis between potassium gallyl reagent **2** and zinc halides. Accordingly, $\{^i\text{Pr}_2\text{NC}(\text{NDipp})_2\}\text{Zn}\{\text{Ga}(\text{NDippCH})_2\}$ is cleanly produced from the reaction of **2** with $\{^i\text{Pr}_2\text{NC}(\text{NDipp})_2\}_2\text{ZnCl}$, and the reaction of $(\text{tmeda})\text{ZnCl}_2$ with 2 equiv. of **2** yields $(\text{tmeda})\text{Zn}\{\text{Ga}(\text{NDippCH})_2\}_2$ [30]. The 1:1 reactions of **2** and ZnBr_2 or CdI_2 instead yield mono-substitution products, that is, $(\text{tmeda})\text{Zn}(\text{Br})\{\text{Ga}(\text{NDippCH})_2\}$ and $(\text{tmeda})\text{Cd}(\text{I})\{\text{Ga}(\text{NDippCH})_2\}$, respectively [29].

Insertion reactions using the neutral β -diketiminato stabilized Ga^{I} heterocycle $\{\text{HC}(\text{MeCDippN})_2\}\text{Ga}$ (**16**) can also afford Group 12–Group 13 bonds; reaction of **16** with ZnCl_2 yields the insertion product $\{\text{HC}(\text{MeCDippN})_2\text{Ga}(\text{Cl})\}\text{Zn}(\text{Cl})(\text{THF})_2$. Compound **16** also inserts into the Hg–S bonds of $\text{Hg}(\text{SC}_6\text{F}_5)_2$ to afford the only Ga–Hg bonded compound $\{\text{HC}(\text{MeCDippN})_2\text{Ga}(\text{SC}_6\text{F}_5)_2\}_2\text{Hg}$ [31, 32]. The homoleptic compound $[\text{Zn}(\text{GaCp}^*)_4]^{2+}$ may be obtained by addition of Cp^*Ga to a solution of ZnMe_2 and $[\text{H}(\text{OEt}_2)_2][\text{BAr}_4^{\text{F}}]$ [31].

The interesting paramagnetic Ga–Zn bonded species $\{(\text{dpp-BIAN})\text{Ga}\}\text{Zn}(\text{dpp-BIAN})$ may be obtained via the reaction of sodium gallyl $\{(\text{dpp-BIAN})\text{Ga}\}\text{Na}(\text{Et}_2\text{O})_3$ (**9**) with $(\text{dpp-BIAN})\text{ZnCl}$ [33, 34]. This compound features a radical mono-anionic dpp-BIAN ligand bound to zinc, and reacts with potassium metal to yield diamagnetic $[\text{K}(\text{THF})_5][\{(\text{dpp-BIAN})\text{Ga}\}\text{Zn}(\text{dpp-BIAN})]$, in which the dpp-BIAN unit attached to zinc has formally been reduced to a dianionic ligand.

While naphthalene-based mercuraindacyles have been purported to feature weak non-bonded Hg–In interactions [35], there have been no reports of direct Group 12–Group 13 bonds involving any other Group 13 elements.

13.3.2

Group 13–Group 13 Metal–Metal Bonds

Metal–metal bonds between Group 13 elements represent one of the defining characteristics of the elements in subvalent oxidation states (i.e., <3). While compounds featuring a metal–metal interaction and at least one metal in a formal oxidation state of +3 are known, most notably in donor acceptor systems of the type $RM \rightarrow MR'_3$, the vast majority of the more than 550 structurally authenticated M–M bonds necessarily feature a mean oxidation state of +2 or less. These include classes of compound that have been at the forefront of recent developments in Main Group chemistry, and a number for which bonding descriptions have been earnestly debated. Among the key developments in the field are the “metalloid” clusters of aluminum and gallium pioneered in the seminal work of Schnöckel, which offer insight into the relationship between molecular species and bulk metal phases. Such species are out of the scope of this chapter and the reader is directed to reference [36] for a fuller description. Likewise, recent reviews encompassing metal–metal bonded species in the +2 oxidation state, in the +1 oxidation state and in mixed valence species are also available [37–39].

13.3.2.1 Formal Oxidation State +2 and Related Systems

Dimeric systems of the types M_2X_4 and $M_2X_4L_2$, featuring the metal in the formal oxidation state +2, represent one of the largest classes of metal–metal bonded species. Unsupported systems of the type X_2M-MX_2 formed by formal dimerization of MX_2 fragments represent the norm for compounds of this stoichiometry, with tractable radical species of the type MX_2 only having been reported very recently, and then only in conjunction with highly sterically demanding and strongly electron-donating ancillary substituents [40]. The X_2M-MX_2 motif finds exemplars among systems featuring bulky monodentate alkyl/aryl and silyl donors, for example, and in *tetrakis*(amido) systems such as $[(HC^tBuN)_2Ga]_2$ featuring M–M linked heterocycles, which have much in common structurally with commercially available diboron(4) esters [18].

Thus, for example, systems of the type $M_2(SiR_3)_4$ are known for all four metals [41–45], with M–M distances of 2.751(2), 2.928(3), and 2.961(1) Å having been determined for the *tetrakis*-(Si^tBu_3) compounds of Al, In, and Tl and values of 2.599(4), 2.868(4), and 2.914(1) Å for the corresponding Ga, In, and Tl systems featuring related hypersilyl substituents, $-Si(SiMe_3)_3$. These metrics can be put into context by the covalent radii of the respective metals – 1.22, 1.21, 1.42, and 1.45 Å, respectively [20]. With this in mind, the Al–Al bond in $Al_2(Si^tBu_3)_4$ (**17**) is unusually long (2.751(2) Å) especially when compared to the analogous distance of 2.647(3) Å for Al_2Trip_4 , and presumably reflects the extreme steric demands of the Si^tBu_3 substituents [41, 46]. Although no evidence was seen for sterically induced fragmentation of **17** into radical species, it is interesting to note a tantalizing glimpse of the potential for such behavior in a report of the chemistry of the analogous dithallium system $Tl_2(Si^tBu_3)_4$, which has been shown to give rise to EPR-active solutions in benzene.

While the M–M bonds in systems of this type can therefore be weakened/lengthened by steric factors, one-electron reduction to give radical anions of the type $[M_2X_4]^-$ offers the potential for a net increase in the M–M bond order through the population of the π -symmetry LUMO. Thus, reduction of $Al_2\{CH(SiMe_3)_2\}_4$ (**18**) with lithium metal generates $[Al_2\{CH(SiMe_3)_2\}_4]^-$, the $[Li(tmeda)_2]^+$ salt of which (**19**) features a planar Al_2C_4 skeleton and a shortened Al–Al distance (2.53(1) vs 2.660(1) Å). On the basis of these metrical data and EPR measurements, the presence of a one-electron π -bonding interaction has been proposed [47, 48]. Similar structural trends have been reported by Power for systems of the type M_2Trip_4 and $[M_2Trip_4]^-$ (M = Al or Ga), with reductions in the M–M bond length

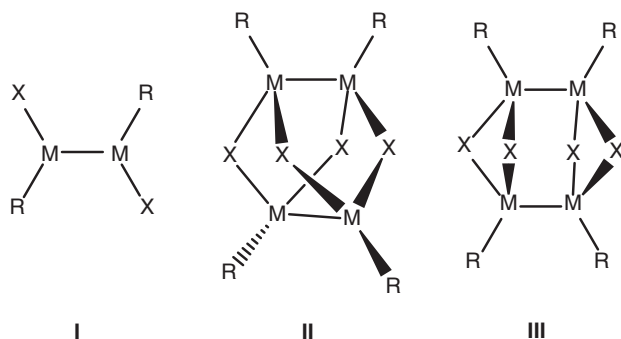


Figure 13.1 Aggregation of M^{II} systems.

from 2.647(3) to 2.470(2) Å being observed for $M = Al$, and from 2.515(3) to 2.343(2) Å for $M = Ga$ [46, 49–51].

Similar structural motifs (type I; Figure 13.1) are known for systems featuring halide substituents (predominantly iodides) in conjunction with very bulky ancillary ligands, as in $Ga_2(C_6H_3Mes_2-2,6)_2I_2$ [52–54], and $Al_2(C_6H_3Dipp_2-2,6)_2I_2$ [55–57], but more highly aggregated structures are also common, reflecting the inherent Lewis acidity retained by systems of the type $X(hal)M-M(hal)X$. Thus, $[Ga_2\{Si(SiMe_3)_3Br_2\}_2]$, $[Ga_2\{C(SiMe_3)_3Cl_2\}_2]$, $[In_2\{C(SiMe_3)_3Br_2\}_2]$, and $[In_2(C_6H_3Mes_2-2,6)_2I_2]_2$ adopt type **II** structures, featuring four bridging halide ligands, leading to the formation of five-membered $M_2(hal)M(hal)$ rings and $M-M$ bonds, which are approximately orthogonal [14, 52, 58, 59], while the related type **III** structure, featuring six-membered $M_2(hal)M_2(hal)$ rings and co-linear $M-M$ bonds, is observed for $[In_2(C_6H_3Mes_2-2,6)_2Cl_2]_2$ [52]. The latter structural type is very similar to that determined for related alkoxo derivatives, such as $[M_2(O^tBu)_4]_2$ ($M = Al, Ga$) [7, 60]. More interesting still is the Al^{II} phosphide derivative $Al_2(P^tBu_2)_4$, which features two μ_2 -bridging and two terminal P^tBu_2 groups and an $Al \cdots Al$ separation of >3.5 Å, and has consequently been described as a singlet biradicaloid – a “snapshot” on the route to $Al-Al$ σ -bond formation [7].

The ability of the systems outlined above to aggregate via additional donor/acceptor interactions is, of course, reflective of a more general phenomenon, with species of the types LX_2M-MX_2L and $L_2X_2M-MX_2L_2$ being well known in Group 13 chemistry [6, 61–81]. Equally familiar are related dianionic species of the type $[X_3M-MX_3]^{2-}$ [82–86]. A number of systems offer direct comparison of ligated and base-free forms: the structures of $In_2\{CH(SiMe_3)_2\}_4$ and its 1,2-bis(isonitrile) adducts, for example, reveal relatively little elongation of the $In-In$ bond in the adduct (e.g., 2.850(1) for the *tert*-butylisonitrile adduct cf. 2.828(1) Å). A more noticeable lengthening is observed for the $In-C$ bonds (2.247 (mean) vs 2.196(5) Å) [87, 88].

Numerous base-stabilized systems have also been synthesized in which the additional neutral Lewis base forms part of a chelating ligand system; here the additional possibility arises for the formation of 1,1 or 1,2 isomers (Figure 13.2). Within the field of O-donor systems, for example, a clear-cut division emerges between carboxylate-derived systems, which in general favor a 1,2-bridged (type **IV**) structure [89–96], and substituents offering a larger chelate tether such as acetylacetonate (“Acac”), for which the 1,1 (type **V**) isomer predominates [96–99]. This distinction reflects, at least in part, the inherent stability of five- and six-membered chelate rings, compared to the alternative four- and seven-membered conformations. Among N-donor systems, β -diketiminato (“Nacnac”) systems follow their O-donor counterparts in preferring type **V** structures; [97, 100, 101] amidinate [102, 103], guanidinate [104, 105], and aza-allyl systems [106], however, differ from carboxylates by adopting predominantly 1,1 (type **V**) arrangements [21, 107–109]. Here, the steric properties of the backbone and N-bound substituents – and their influence on the orientation of the donor atoms presumably causes the ligand to prefer a chelating (rather than bridging) mode of interaction – and consequently leads to the formation of four-membered rings within a type **V**

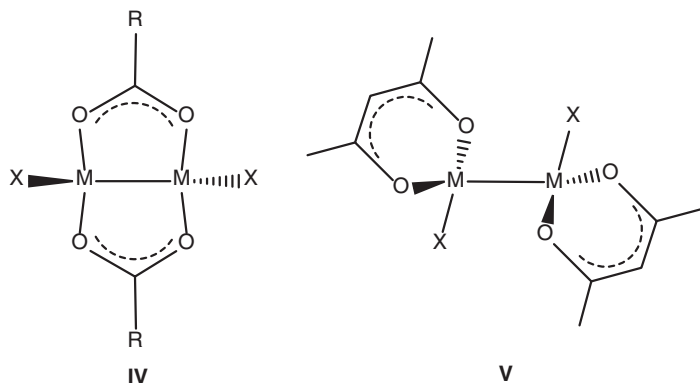


Figure 13.2 Terminal (1,1) and bridging (1,2) modes of coordination at M_2 units, exemplified by carboxylate and acetylacetonate derivatives.

structure [17]. In some cases, the energetic balance between the alternative isomeric forms is clearly a fine one. Thus, for example, Uhl and coworkers have reported that compounds of the stoichiometry $[Ga\{CH(SiMe_3)_2\}(EPPh_2NPPh_2E)]_2$ adopt a 1,1 (type V) formulation when $E = S$, featuring terminal $[EPPh_2NPPh_2E]^-$ ligands, while the analogous system with $E = O$ has a type IV structure, featuring seven-membered OPNPOGa₂ rings [110].

Finally, mention should be made of systems isomeric with the classical M^{II}_2 formulation, X_2M-MX_2 – that is, mixed valence species of the type $RM \rightarrow MR'_3$, which feature a donor/acceptor interaction between Lewis basic M^I and Lewis acidic M^{III} components. A number of M^I/M^{III} species of this sort have been reported for aluminum [111, 112], gallium [113–117], and indium [84, 118, 119], including several featuring mixed donor/acceptor combinations [112, 120, 121]. Syntheses of these systems rely on the availability of sources of the RM^I fragment, and with this in mind, the majority of complexes reported to date feature Cp^*M^I moieties. A series of related complexes of the types $Cp^*M \rightarrow Al^IBu_3$ (**20**: $M = Al$; **21**: $M = Ga$, **22**: $M = In$) and $Cp^*M \rightarrow Ga^IBu_3$ (**23**: $M = Al$; **24**: $M = Ga$; **25**: $M = In$) have been synthesized [112, 122], and the X-ray crystal structures of five of the six compounds determined. For the **20–22** $M-Al$ distances of 2.689(2), 2.629(2), and 2.843(2) Å have been measured, while corresponding distances of 2.680(2) and 2.845(2) Å are reported for **23** and **25**. Such data reveal very little difference in the $M-M'$ contacts for the isomeric Al/Ga systems, and between complexes featuring Al^IBu_3 as the Lewis acid versus Ga^IBu_3 . Consideration of the sum of the three $C-M'-C$ angles within the Lewis acid component does, however, allow some comment to be made regarding the relative strengths of the various donor/acceptor interactions. Stronger σ -donor Lewis bases tend to induce greater pyramidalization at alane-derived Lewis acids, and with this in mind it is apparent that the Lewis base strength of Cp^*M decreases with increasing mass of M [112].

Frenking has examined the energetic differences between isomeric systems of the types $RM \rightarrow M'R'_3$ and $RR'M-M'R'_2$ by quantum chemical methods, with the finding that systems featuring an RM^I component in which X has appreciable π donor capabilities, tend to favor the mixed valence formulation [123]. Such predictions are in line with experimental studies that have led to the isolation of complexes of the type $RM \rightarrow MR'_3$ typically with X being a Cp^* or *tris*(pyrazolyl)borate ligand.

13.3.2.2 Formal Oxidation State +1 and Related Systems

A wide variety of compounds featuring the Group 13 metals in the formal oxidation state of +1 are known, and aggregated structures featuring $M-M$ interactions are abundant. Singlet ground states have been calculated for a range of systems of the type RM^I ($M = Al-Tl$; $X = \text{alkyl, amido, } Cp^*$) [124], and the formation of oligo- or polymeric structures can be rationalized on the basis of the ambiphilic character of the RM^I fragment. Nonetheless, such tendencies are strongly dependent not only on

the metal, but also on the steric and electronic saturation provided by the ancillary ligand(s). Thus, among organometallic systems of In^{I} and Tl^{I} , for example, remarkable one-coordinate complexes of the type $\text{M}(\text{C}_6\text{H}_3\text{-2,6-Trip}_2)$ (**26**: $\text{M} = \text{In}$; **27**: $\text{M} = \text{Tl}$) were synthesized by Power and coworkers by exploiting the extremely high steric demands of these 2,6-diarylphenyl substituents [3, 4]. Ligand steric bulk is a critical factor in determining both redox stability and structure for such systems; thus, related Dipp-functionalized compounds $[\text{M}(\text{C}_6\text{H}_3\text{-2,6-Dipp}_2)]_2$ are dimeric in the solid state, featuring planar *trans*-bent geometries, while $[\text{Tl}(\text{C}_6\text{H}_3\text{-2,6-Xyl}_2)]_3$ is trimeric, and simple phenyl Tl^{I} systems are unstable with respect to disproportionation [125–127].

Within this sphere, a common structural motif is that based on a tetrameric array, and featuring a more-or-less regular tetrahedral arrangement of metal atoms. Such systems are known for all four metals, and encompassing bulky alkyl [88, 128–130], cyclopentadienyl [131], silyl [132–137], germyl [138], amido [139, 140], and even *tris*(pyrazolyl)borate substituents [141]. Related systems featuring a mixed substituent set are also known, as are formally lower valent systems, such as $\text{Ga}_8\{\text{C}(\text{SiMe}_3)_3\}_6$, which can be regarded as being comprised of exo-linked tetrahedral units [142].

Among the numerous tetrameric systems now reported in the literature, the *tris*(trimethylsilyl) methyl functionalized systems $\text{M}_4\{\text{C}(\text{SiMe}_3)_3\}_4$ (**28–31**: $\text{M} = \text{Al–Tl}$, respectively) represent a complete homologous series [88, 128–130]. The compounds of the lighter three elements (**28–30**) feature close-to-perfect tetrahedral cluster geometries with M–M–M angles very close to 60° and little internal variance in the M–M and M–C distances. Thus, mean M–M bond lengths of 2.739, 2.688, and 3.002 Å and M–C distances of 2.03, 2.08, and 2.25 Å have been measured for **28**, **29**, and **30**, respectively. While the trend in the M–M bond lengths largely fits expectations based on the respective covalent radii, it is notable that the contraction between aluminum and gallium occurs concomitantly with an increase in the M–C bond length. The effect of steric factors in this regard has also been noted in comparing the structures of **29** and $\text{Ga}_4\{\text{Si}(\text{SiMe}_3)_3\}_4$ (**32**). Compound **32** features somewhat shorter Ga–Ga distances (mean 2.584 Å) – an observation that has been related to the longer exo-polyhedral Ga–Si bonds (mean 2.41 Å) in comparison to the analogous Ga–C linkages. The pendant steric shrouding is thus more distant from the cluster core and allows for contraction of the Ga–Ga interactions [136]. Consistently, the Al–Al distances in $\text{Al}_4(\text{Si}^t\text{Bu}_3)_4$ (mean 2.605 Å) are markedly shorter than those in **28** [133].

The structure of the thallium tetramer (**31**) is less regular, featuring a triangular array of three thallium centers with a mean separation of 3.335 Å, and a fourth metal characterized by longer contacts of 3.461(1)–3.638(1) Å [130]. These distances can be put into context by considering the Tl–Tl single bonds in $\text{Tl}_2(\text{Si}^t\text{Bu}_3)_4$ and $\text{Tl}_2\{\text{Si}(\text{SiMe}_3)_3\}_4$ (2.961(1) and 2.914(1) Å, respectively) [45, 143], and by noting that the mean M–M distances measured for **28–30** are lengthened to a much smaller degree compared to the M–M single bonds found, for example, in the respective $\text{M}_2\{\text{CH}(\text{SiMe}_3)_2\}_4$ systems (2.660(2), 2.541(1), and 2.828(1) Å) [48, 51, 87]. Additionally, the Tl–C vectors in **31** are aligned not in a radial fashion with respect to the Tl_4 core, but in a paddlewheel arrangement. Uhl and coworkers suggest that the structure of **31** might best be viewed in terms of a basal Tl_3 unit held together by a cyclic array of three donor/acceptor interactions (akin to that found, albeit in a dinuclear system, for Lappert's distannene), together with a more weakly bound fourth $\text{TlC}(\text{SiMe}_3)_3$ moiety [144]. Moreover, such an analysis is consistent with cryoscopic measurements suggesting that **31** dissociates into monomeric $\text{TlC}(\text{SiMe}_3)_3$ units in benzene solution.

The observation of more weakly aggregated oligomeric species for the heavier metals is in accord with observations made for related $\text{Cp}^*\text{M}^{\text{I}}$ compounds ($\text{M} = \text{Al–Tl}$). Thus, although all four compounds vaporize as monomeric species [145–148], the aluminum compound crystallizes as a tetramer, with mean Al–Al distances (2.769 Å), which are not markedly different from **28** (2.739 Å), and which are shorter than the intermetallic separations in aluminum metal (2.86 Å) [131]. By contrast, both the gallium and indium compounds crystallize as loosely bound hexamers $(\text{Cp}^*\text{M})_6$, which have structures that can be viewed as octahedra, distorted by compression along a C_3 axis [147, 149]. In addition, and in contrast to $(\text{Cp}^*\text{Al})_4$, the $\eta^5\text{-Cp}^*$ centroid-M vectors lie not radial to the metal core, but tilted to give overall S_3 symmetry. One interpretation of these structural distortions is in terms of a second order Jahn–Teller effect, which maximizes M–M orbital overlap;

The observation of one-coordinate Group 13 metal centers *in the solid state* for complexes of the type RM' requires yet more steric protection, and some of the terphenyl ligand systems pioneered primarily by Power have been shown to offer the necessary bulk. Thus, as noted, **26** and **27** feature one-coordinate metal centers [3, 4]. While the marginally less encumbered $[M(C_6H_3-2,6-Dipp_2)]_2$ systems are dimeric [125]. In the case of gallium, the analogous systems $[Ga(C_6H_3-2,6-Dipp_2)]_2$ is also dimeric [12], as are the related systems featuring an additional ^tBu or CF₃ group in the 4-position of the central phenyl ring [151]. Dissociation into monomeric entities is observed in hydrocarbon solution, and this, together with calculated binding energies in the region of 20 kJ mol⁻¹ has led Power to conclude that the mode of association within these dimers resembles closed shell interactions [151]. Moreover, further increases in ligand steric profile can be introduced by incorporating ⁱPr substituents in the 3- and 5-positions, with the consequent effect on the positioning of the flanking aryl rings being sufficient to render $Ga(C_6H-3,5-^iPr_2-2,6-Dipp_2)$ (**33**) and $Ga(C_6H-3,5-^iPr_2-2,6-Trip_2)$ (**34**) monovalent (Figure 13.3) [151]. Analogous aluminum systems are highly reactive: the dialumine $[Al(C_6H_3-2,6-Dipp_2)]_2$, for example, undergoes [2+4] cycloaddition with toluene [55], and related systems show similar reactivity toward unsaturated substrates [152, 153].

In the cases of both aluminum and gallium dimers of the type $[M(C_6H_3-2,6-Ar_2)]_2$, further reduction is possible to give dianionic systems $[M(C_6H_3-2,6-Ar_2)]_2^{2-}$. The disodium supported dialuminyne $Na_2\{[Al(C_6H_3-2,6-Dipp_2)]_2\}$ (**35**) has been shown to have a *trans* bent structure, featuring C–Al–Al angles of $131.7(1)^\circ$, and an Al–Al distance of $2.428(1) \text{ \AA}$ [13]. The latter can be contextualized by values of $2.660(1)$ and $2.53(1) \text{ \AA}$ for **18** and **19**, which feature formal bond orders of 1 and 1.5, respectively [47, 48]. The corresponding E–E separation in the isoelectronic (and similarly *trans* bent) disilyne $RSiSiR$ [$R=Si^iPr\{CH(SiMe_3)_2\}_2$] – which is thought to feature a bond order between 2 and 3 – is somewhat shorter ($2.062(1) \text{ \AA}$). This wide discrepancy reflects, at least in part, the differing covalent radii of aluminum and silicon (1.22 and $1.11 \text{ \AA}$, respectively) [20], and the electrostatic repulsion between two formally negatively charged fragments in **35** [154]. Models of bonding in related gallium systems have been debated at length, with Robinson proposing a triple bond formulation for the anionic component of $Na_2\{[Ga(C_6H_3-2,6-Trip_2)]_2\}$ (**36**), which possesses a somewhat shorter M–M contact ($2.319(3) \text{ \AA}$) than **35**, but a similar *trans* bent configuration [2]. Power has proposed an alternative bonding description, which implies a bond order nearer 1. It is argued that the notion of a triple bond in a species of the type $[Ga(C_6H_3-2,6-Ar_2)]_2^{2-}$ would imply a bond order near 2 in the related neutral species. As such, the determination of a relatively long Ga–Ga bond length for

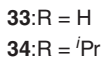


Figure 13.3 Structurally characterized monovalent Ga^I species.

$[\text{Ga}(\text{C}_6\text{H}_3\text{-2,6-Dipp}_2)_2]_2$ (2.627(1) cf. 2.515(3) Å for the single bond in Ga_2Trip_4) is more consistent with a weakly bound dimer than with a double bond, and hence with a bond order for the doubly reduced species $[\{\text{Ga}(\text{C}_6\text{H}_3\text{-2,6-Dipp}_2)_2\}_2]^{2-}$ of about 1 [49, 12, 151].

13.3.2.3 Formal Oxidation States of Less Than +1

One of the prominent developments in Main Group chemistry over the past 20 years has been the synthesis of a wide range of clusters, mainly for gallium, but also for aluminum and indium, featuring mean metal oxidation states of less than +1. Such systems feature a range of pendant (formally anionic) substituents (e.g., alkyl, aryl, silyl, amido, phosphido, and halide) and are perhaps most elegantly exemplified by the $[\text{Al}_{77}\{\text{N}(\text{SiMe}_3)_2\}_{20}]^{2-}$ cluster synthesized by Schnöckel and coworkers. This compound, synthesized from Al^{I} and $\text{Li}[\text{N}(\text{SiMe}_3)_2]$, features a central aluminum atom surrounded by concentric shells of 12, 44, and 20 metal atoms [1]. Interestingly, related cluster molecules for the heaviest Group 13 metal were unknown until recently, with the synthesis of a cubane system of stoichiometry Tl_8X_4 [40]. The vast scope of this chemistry, and the implication of extensively delocalized bonding models unfortunately puts it out of the scope of this chapter, and the reader is directed instead to a recent publication on the field by one of the main protagonists [36].

13.3.3

Group 14 Metal Complexes

Molecular species featuring metal–metal bonds between a Group 14 metal (i.e., Ge, Sn, or Pb) and a Group 13 metal are confined to aluminum, gallium, and indium, and represent a numerically small group of compounds. Schnöckel and coworkers described the reaction between Cp^*_2Ge and solutions of Al^{I} halides, leading to the formation of the tetrahedral *tetrakis*(aluminum)germanium system $\text{Ge}(\text{AlCl}_2\text{OEt}_2)_4$, which has been structurally characterized ($d(\text{Ge-Al}) = 2.449$ Å); the related silane has also been synthesized from Cp^*_2Si under similar conditions [155]. Salt elimination can also be used to construct Ge–Al bonds; thus the reaction between LiGePh_3 and Me_2AlCl generates the *tris*(germyl)aluminate $[(\text{Ph}_3\text{Ge})_3\text{AlMe}]^-$, featuring a tetrahedral aluminum center and a similar Ge–Al bond length of 2.520 Å [156]. Donor/acceptor linkages featuring a tin donor component and aluminum trihalide or gallium/indium trialkyl Lewis acids have also been reported [157, 158].

M–Ga bonds are slightly more common, with a number of examples being synthesized through various reactions involving isolated Ga^{I} heterocycles. Thus, Jones and coworkers have shown that $[(\text{HCDippN})_2\text{GaK}(\text{tmeda})]_2$ (**2**) reacts with ditetrelenes $\text{M}_2\{\text{CH}(\text{SiMe}_3)_2\}_4$ ($\text{M} = \text{Ge}, \text{Sn}$) to generate ionic species of the type $[\text{K}(\text{tmeda})][\{(\text{HCDippN})_2\text{Ga}\}_2\text{M}\{\text{CH}(\text{SiMe}_3)_2\}_2]$, which feature relatively long M–Ga bonds, while the analogous reaction with $\text{Pb}\{\text{CH}(\text{SiMe}_3)_2\}_2$ leads to oxidative coupling of the gallium heterocycle [159]. Similar chemistry giving access to Ge–Ga bonds has also been reported by Baines [160]. Salt metathesis can also be employed with **2** and Ge/Sn halides to generate charge neutral species of the type $\{^i\text{Pr}_2\text{NC}(\text{NDipp})_2\}\text{M}\{\text{Ga}(\text{HCDippN})_2\}$ ($\text{M} = \text{Ge}, \text{Sn}$) [159].

Fischer, on the other hand, has employed the *neutral* Ga^{I} heterocycle $\{\text{HC}(\text{MeCDippN})_2\}\text{Ga}$ (**16**) in the formation of M–Ga bonds ($\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$), exploiting the propensity of this system to insert into metal–halogen and metal–carbon bonds [32, 161]. In the case of SnCl_2 , the resulting gallium ligand stabilized Sn_7 and Sn_{17} clusters, reflect the reducing properties of Ga^{I} , while in the case of $\text{Cy}_3\text{P}^-\text{GeCl}_2$, addition of an external reducing agent leads to the formation of multimetallic Ge_n systems ($n = 2, 4$) stabilized by the coordination of **16** [162–164]. Related chemistry involving formal oxidative addition of Sn–H bonds at Ga^{I} has been reported by Linti [165].

13.4

d-Block-Group 13 Metal Bonds

It was in the 1970s that the first compounds containing direct bonds between transition metals and Group 13 elements were structurally characterized; these include $\text{In}[\text{Co}(\text{CO})_4]_3$ (the synthesis

of which was first reported in 1942) [166, 167] and $[\text{CpFe}(\text{CO})_2(\text{AlPh}_3)]^-$ [168]. However, reports of such compounds in the literature remained sporadic until the discovery that organometallic complexes of Group 13 metals containing direct metal–metal bonds could act as convenient single-source precursors for OMCVD (organometallic chemical vapor deposition). Interest in this field was first stimulated by reports of the deposition of CoGa films from $(\text{OC})_4\text{CoGaCl}_2(\text{THF})$ and PtGa_2 from $\text{Pt}[\text{N}_2\text{C}_2(\text{CH}_3)_2\text{O}_2(\text{GaMe}_2)]_2$ [169]. A wide range of complexes featuring two-center, two-electron bonds to transition metals was synthesized in the 1990s with a view to investigating their potential in OMCVD, primarily via salt metathesis reactions between carbonylmetallate anions and Group 13 halides [170–174].

More recently, the focus has shifted toward the study of novel structural types and bonding motifs. The isolation of low-coordinate, potentially multiply bonded systems in which the Group 13 element is in the +1 oxidation state has become particularly topical, allowing for a systematic investigation of fundamental structure and bonding, and comparison with related Group 14 ligands such as carbenes, silylenes, and carbynes [175–178]. The assertion of a Fe–Ga triple bond in the complex $(\text{OC})_4\text{FeGa}(\text{C}_6\text{H}_3-2,6\text{-Trip}_2)$ [9], led to much debate about the role of multiple bonding in these highly polar transition metal–Group 13 bonds [179, 180]. In general, quantum chemical calculations on transition metal complexes of Group 13 $\text{M}(\text{I})$ diyls and heterocycles systems indicate that σ -donation is typically the dominant covalent bonding interaction, with minor contributions from metal–metal backbonding; electrostatic contributions to the metal–metal bond often compete with – or are in excess of – the covalent contribution [181–185]. The availability of M^{I} Group 13 diyls, RM , including $[\text{Cp}^*\text{Al}]_4$, Cp^*Ga , and $\text{M}\{\text{C}(\text{SiMe}_3)_3\}_4$ ($\text{M} = \text{Al}, \text{Ga}, \text{In}$) has provided an additional (and very facile) route to diyl complexes of transition metals, $\text{L}_n\text{M}(\text{ER})$. Furthermore, two-coordinate metalladiyl complexes have also been isolated, such as $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_4$ [186–188] and $[\{\text{Cp}^*\text{Fe}(\text{CO})_2\}_2(\mu_2\text{-M})]^+$ [189] ($\text{M} = \text{Ga}, \text{In}$), which feature a Group 13 metal bridging two transition metals. Both these and more traditional diyl systems find useful comparison with the increasing number of systems featuring boron in superficially similar bonding modes [190–192].

Over the last two decades, transition metal complexes of *N*-heterocyclic carbene (NHC) ligands have been an area of enormous interest [175, 177, 193]. The syntheses of five-membered, anionic gallium analogs, $[(\text{HCRN})_2\text{Ga}]^-$, have led to wide-ranging synthetic investigations in d-block chemistry [21, 183, 194]. Such ligands are understandably strong σ -donors and can displace ligands such as CO and Cp from metal centers [183, 195, 196]. Neutral, six-membered heterocycles of the general form: $\text{M}\{(\text{NArCMe})_2\text{CH}\}$ ($\text{M} = \text{Al}, \text{Ga}, \text{In}$) can also be considered to be carbenoid systems, being isolobal to NHCs [17, 197]. These ligands demonstrate terminal and bridging coordination to transition metals, and recently the spontaneous metal-mediated dehydrogenation of the Ga^{III} system $\text{H}_2\text{Ga}\{\text{NDippCMe}\}_2\text{CH}\}$ has been shown to provide a new route into complexes of these ligand systems [198].

Transition metal bonds to Group 13 elements have been the subject of several extensive review articles [17, 183–185, 199–201]. In this section, a brief overview of the key routes employed to access such systems will be presented, together with a discussion of the nature of the metal–metal bonding.

13.4.1

Synthesis via Salt Elimination

Salt elimination between a transition metal anion and a Group 13 halide is the most extensively exploited route into the formation of transition metal–Group 13 bonds in which the Group 13 element is in the +3 oxidation state. Most initial work focused on indium and thallium species and their reactions with mono-anionic carbonylmetallates. Early examples include $[\text{CpMo}(\text{CO})_3]_3\text{Tl}$ formed via the reaction of Tl_2SO_4 with 3 equiv. of $\text{Na}[\text{CpMo}(\text{CO})_3]$ [202–204].

Salt elimination was later extended to gallium and aluminum systems, with complexes such as $\text{Cp}(\text{CO})\text{NiGa}(\text{CH}_2\text{'Bu})_2(\text{THF})$ [205], $(\text{OC})_4\text{CoGa}\{(\text{CH}_2)_3\text{NEt}_2\}(\text{Me})$ [170, 173], $\text{CpFe}(\text{CO})_2\text{AlCl}_2(\text{THF})$ (**37**), and $\text{CpFe}(\text{CO})_2\text{Al}\{(\text{CH}_2)_3\text{NMe}_2\}(\text{Cl})$ (**38**) being reported [171, 172]. The gallyl complex

(OC)₄CoGaCl₂(THF) (**39**) is of particular interest as it is an effective single-source precursor for OMCVD. The β -CoGa phase could be deposited directly from this complex, and could be grown epitaxially on to thin films of the widely used Group 13/15 semiconductor GaAs [169, 206].

The use of sterically bulky ligand sets is typically necessary in order to allow the isolation of monomeric complexes featuring a three-coordinate Group 13 center, thereby overcoming the propensity of aluminum (and to a lesser extent gallium) to adopt higher coordination numbers via oligomerization [207, 208]. Three-coordinate alanyl complexes are extremely rare; the first example, CpFe(CO)₂Al(tmp) (**40**) features very high steric shielding of the Al center [209]. As the three-coordinate aluminum center in **40** has a formally vacant p-orbital, there is the potential for backbonding from iron, which is not possible in four-coordinate alanyl complexes. However, the Fe–Al bond length in **40** (2.450(1) Å) is not significantly shorter than that found in most four-coordinate complexes (e.g., 2.456(1) Å for CpFe(CO)₂Al((CH₂)₃NMe₂)^tBu), indicating that there is only a modest contribution from backbonding. A somewhat wider range of three coordinate gallyl and indyl complexes have been reported, including CpW(CO)₃GaMe₂ (**41**) and Cp(CO)₂FeM(C₆H₂-2,4,6-^tBu₃)X (M = Ga, X = Cl; M = In, X = Br) [210, 211].

13.4.2

Synthesis via Alkane Elimination

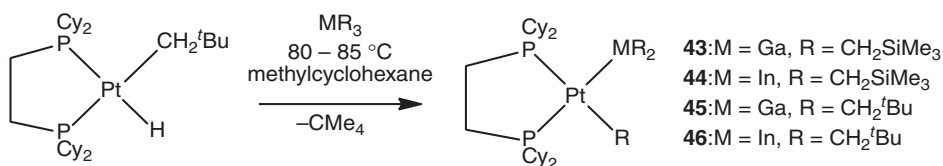
Transition metal complexes of Group 13 alkyls may be formed by alkane elimination, typically via reactions of transition metal hydrides with Group 13 trialkyls. The first dialkyl gallyl complex, **41** was isolated from the reaction of CpW(CO)₃H and GaMe₃ with evolution of CH₄ [211]. The solid state structure of **41** features secondary intermolecular isocarbonyl interactions with the gallium center, reflective of its high Lewis acidity; this phenomenon has subsequently been observed in several other aluminum and gallium alkyl complexes [212–214]. Related aluminum- and thallium-containing complexes CpMo(CO)₃Al^tBu₂ and CpMo(CO)₃TlMe₂ may be formed analogously [212, 215, 216].

A striking example of the application of alkane elimination is the reaction of Cp^{*}Ir(H)₂(PMe₃) with AlEt₃, which proceeds with loss of ethane to yield the dimeric species [Cp^{*}(PMe₃)IrAlEt]₂ (**42**) [217]. This compound is a rare example of a compound containing two M–Al single bonds to a single Al center [218]. It should be noted, however, that while a few examples of such complexes formed by alkane elimination have been reported in the literature, this route is of low general applicability. As high temperatures or photolytic conditions are generally required to initiate such reactions, this tends to lead to redistribution of alkyl groups and decomposition via elimination of MR₃ [199].

13.4.3

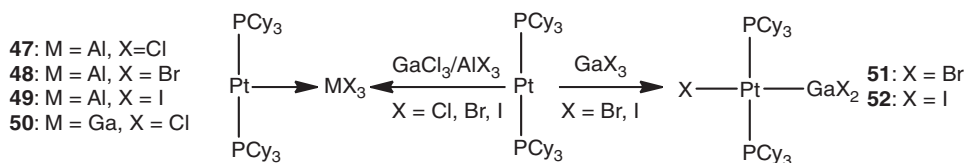
Oxidative Addition versus Adduct Formation: a Fine Electronic Balance

Oxidative addition at electron-rich transition metal centers has been exploited as an alternative route to transition metal complexes of Group 13 ligands. Sources of the highly reactive 14-electron species [Pt(dcype)] react with gallium and indium trialkyls MR₃ (M = Ga, In; R = CH₂^tBu, CH₂SiMe₃) via oxidative addition of a M–C bond to give species of the form (dcype)Pt(R)(MR₂) (**43–46**, Scheme 13.4) [219].



Scheme 13.4 Oxidative addition of M–C bonds (M = Ga, In) at [Pt(dcype)].

The reactions of Group 13 *halides* with $[L_2Pt]$ species (L = phosphine, NHC) have also been studied in detail. The reactions of boron halides with bis(phosphine)platinum(0) species have been found to give exclusively oxidative addition products, such as *trans*-(Cy_3P)₂Pt(Cl)(BCl₂) [220–224]. However, in marked contrast, aluminum trihalides AlX_3 (X = Cl, Br, I) do not give Al–X oxidative addition, but rather yield donor–acceptor complexes (Cy_3P)₂Pt(AlX_3) (**47–49**, Scheme 13.5), featuring Pt → Al dative bonds [225]. Gallium trichloride reacts similarly, forming an analogous platinum–gallane complex (Cy_3P)₂Pt(GaCl₃) (**50**) [226], but the heavier gallium trihalides undergo oxidative addition yielding halogallyl complexes *trans*-(Cy_3P)₂Pt(X)(GaX₂) (**51**: X = Br; **52**: X = I) [221]. The *trans* disposition of the halide and gallyl ligands in these complexes is consistent with the strong *trans* influence of the gallyl ligand. The observation that the Pt–Br bond in **51** (2.5087(3) Å) is significantly shorter than that in (Cy_3P)₂Pt(Br)(BBr₂) (2.5847(6) Å), suggests a weaker *trans* influence for gallyl versus boryl ligands. The differing reactivity of the respective gallium halides can be attributed to the much weaker Ga–X bonds with the heavier halides, thereby favoring oxidative addition. However, a similar trend exists for aluminum halides and yet oxidative addition of an Al–X (X = C, H, halide) bond at a transition metal center remains unknown [198, 219, 227].

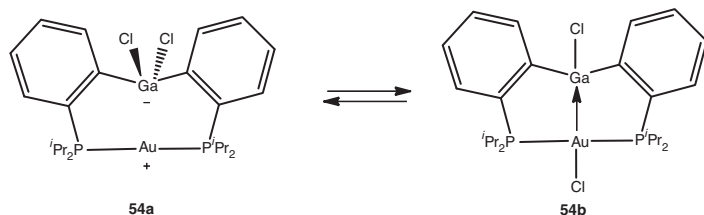


Scheme 13.5 Adduct formation and oxidative addition reactions of aluminum and gallium halides at $Pt(PCy_3)_2$.

13.4.4

Metal-Only Lewis Pairs

The dative Pt → Al and Pt → Ga bonds discussed in Section 13.4.3 represent members of a family of metal-only Lewis pairs containing Group 13 elements. Earlier work in this area focused on the isolation of terminally bound Group 13 acceptor fragments at electron-rich late transition metals [228]. Thus, the alane complex $Cp^*Ir(PMe_3)(H)_2(AlPh_3)$ (**53**) may be formed from $Cp^*Ir(PMe_3)(H)_2$ and $AlPh_3$, although the long Ir–Al bond length (2.864(2) Å) suggests that bridging three-center, two-electron Ir–H–Al interactions may be present in the solid state [217]. Complex **53** does not undergo alkane elimination, in contrast to the analogous reaction with $AlEt_3$ (Section 13.3.4), most likely to be due to the stronger Al–C bond to the sp^2 carbon. A range of anionic and neutral transition metal–gallane adducts have also been reported [229–232]. More recent work has probed the use of tethered ligands to facilitate binding between Group 13 metal Lewis acids and transition metal bases. By holding the two metal centers in close contact, several metalloboratrane have been isolated [233–235]. A similar approach has recently been applied to heavier Group 13 elements; Reaction of $\{o\text{-}^iPr_2P(C_6H_4)\}_2GaCl$ with $AuCl(SMe_2)$, for example, yields complex **54**, which in the solid state adopts zwitterionic form **54a** (Scheme 13.6) [236]. The long Au–Ga separation (3.02 Å) and the similarity of the Ga–Cl bond lengths (2.266(1), 2.278(1) Å) are consistent with complete transfer of chloride from gold to gallium. However, in solution, this species is in equilibrium with a neutral form **54b**, featuring an Au → Ga interaction. A similar approach has been applied to the formation of metalloalumatranes, featuring the late transition metals including iron, cobalt, and nickel [237]. The extent of metal–metal bonding in such tethered complexes is hard to ascertain, however, as the metal atoms might also be regarded as being held in place by the restraints of the chelating ligand framework.



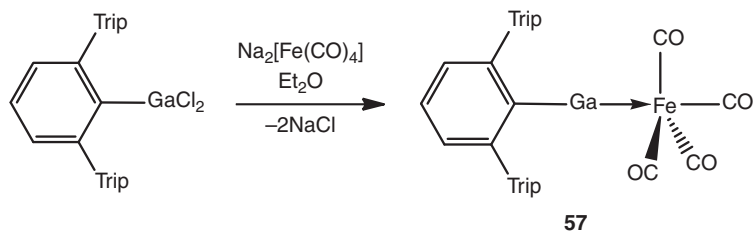
Scheme 13.6 Neutral and zwitterionic forms of the metal-only Lewis pair **54**.

13.4.5

Double Salt Elimination as Access to the +1 Oxidation State

While the majority of early work on metal–metal bond formation via salt metathesis used mono-anionic transition metal ions, the use of di-anionic carbonylmetallates has given access to compounds where the Group 13 element is formally in the +1 oxidation state, including some featuring coordinated AlX and GaX (X = halide, alkyl) moieties [238–241]. A representative example is the reaction between $\text{K}_2[\text{Cr}(\text{CO})_5]$ and MCl_3 (M = Al, Ga) in the presence of a neutral multidentate N-donor ligand such as *tmeda*, yielding $(\text{OC})_5\text{CrGaCl}(\text{tmeda})$ (**55**). Compound **55** may subsequently be treated with $\text{Li}[\text{BEt}_3\text{H}]$ to give $(\text{OC})_5\text{CrGaH}(\text{tmeda})$ (**56**), which represents an example of donor-stabilized “GaH” trapped at a transition metal [240]. Several such species have been examined as potential precursors for the deposition of thin films using OMCVD, with compounds such as $(\text{OC})_5\text{CrGa}(\text{Et})(\text{tmeda})$ showing promise [239].

A landmark compound formed using double salt metathesis is $(\text{OC})_4\text{FeGa}(\text{C}_6\text{H}_3\text{-2,6-Trip}_2)$ (**57**), isolated from the reaction of $\text{Na}_2[\text{Fe}(\text{CO})_4]$ with $(2,6\text{-Trip}_2\text{C}_6\text{H}_3)\text{GaCl}_2$ (Scheme 13.7) [9]. Compound **57** features a linear, two-coordinate gallium atom, and the Fe–Ga distance (2.2248(7) Å) is the shortest reported in a neutral species. These structural parameters led to an initial description as a Fe–Ga triple bond (a “ferrogallyne”), formally featuring two back-bonds from filled orbitals at iron into vacant p-orbitals at the *sp*-hybridized gallium. In this way, **57** can be viewed formally as related to a cationic Fisher carbyne complex [242, 243]. However, this bonding description has since been questioned, with DFT calculations implying that the extent of backbonding from Fe to Ga is very low, and suggesting that a description as a single $\text{Ga} \rightarrow \text{Fe}$ bond (analogous to a phosphine) is more appropriate [179, 180].



Scheme 13.7 Synthesis of “ferrogallyne” **57**.

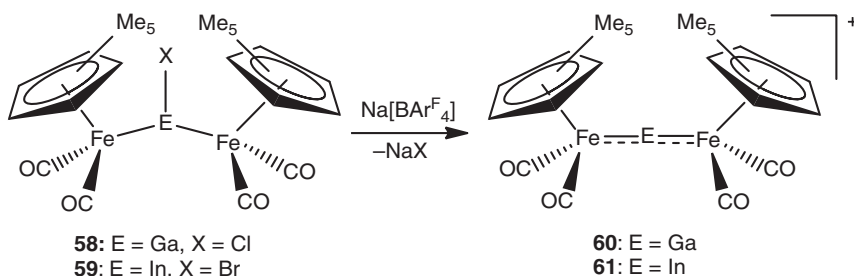
A range of compounds has been synthesized by double-salt metathesis in which a two-coordinate, substituent-free gallium atom sits in an essentially linear environment between two transition metals. Compounds of the form $(\eta^5\text{-C}_5\text{R}_5)(\text{dppe})\text{FeGaM}(\text{CO})_n$ (M = Fe, n = 4; M = Cr, W, n = 5; R = H, Me) may be accessed via reactions of $(\eta^5\text{-C}_5\text{R}_5)(\text{dppe})\text{FeGaCl}_2$ with carbonylmetallate dianions $\text{K}_2[\text{M}(\text{CO})_n]$ [186–188, 244]. In such complexes, the bridging gallium atom is formally *sp*-hybridized and hence has two vacant p-orbitals, which may accept electron density from metal d-orbitals

through backdonation. Indeed, in $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_4$, both Fe–Ga bonds are significantly shorter than Fe–Ga single bonds ($\text{Cp}^*(\text{dppe})\text{Fe–Ga} = 2.2479(10) \text{ \AA}$; $\text{Ga–Fe}(\text{CO})_4 = 2.2931(10) \text{ \AA}$; cf. 2.36–2.46 for Fe–Ga single bonds) [199], which is suggestive of significant π backbonding contributions from both iron fragments.

13.4.6

Halide Abstraction as a Route to Cationic Diyl Systems

Halide abstraction from M^{III} systems has proved to be a versatile route into many charged, low-coordinate species featuring unusual bonding interactions. Cationic analogs of species featuring two-coordinate, bridging Group 13 atoms may be obtained by halide abstraction from compounds in which XM fragments ($\text{M} = \text{Ga}, \text{In}, \text{Tl}$) bridge two transition metal centers (Scheme 13.8). Suitable precursors such as $[\text{Cp}^*(\text{CO})_2\text{Fe}]_2\text{GaCl}$ (**58**) and $[\text{Cp}^*(\text{CO})_2\text{Fe}]_2\text{InBr}$ (**59**) can be prepared by the reaction of Group 13 trihalides with 2 equiv. of carbonylmetallate anions [210]. Subsequent halide abstraction yields cationic complexes featuring bridging gallium or indium atoms, $[\{\text{Cp}^*(\text{CO})_2\text{Fe}\}_2\text{Ga}][\text{BAR}_4^{\text{F}}]$ (**60**) and $[\{\text{Cp}^*(\text{CO})_2\text{Fe}\}_2\text{In}][\text{BAR}_4^{\text{F}}]$ (**61**) [189, 245]. A significant shortening of the Fe–Ga bonds is observed on halide abstraction (e.g., from 2.352(1) $\text{\AA}$ in **58** to 2.266(1)/2.272(1) $\text{\AA}$ in **60**) reflective of the lower coordination number and increased back-bonding. An anionic thallium analog, $[\{(\text{OC})_5\text{Cr}\}_2\text{Tl}]^-$ may be synthesized in a contrasting manner, by the reaction of excess $\text{K}_2\text{Cr}(\text{CO})_5$ with TlCl_3 [246].

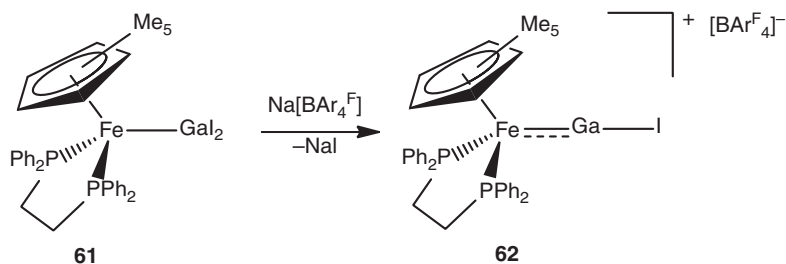


Scheme 13.8 Formation of cationic bridging diyl systems by halide abstraction.

Three coordinate halogallyls and –indyls have been used as precursors to cationic diyl complexes by halide abstraction, mimicking a common route to cationic borylene complexes [247–249]. Related attempts to isolate terminal diyl species of the form $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{FeM}(\text{C}_6\text{H}_2\text{-2,4,6-}^t\text{Bu}_3)]^+$ by halide abstraction from $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{E}(\text{C}_6\text{H}_2\text{-2,4,6-}^t\text{Bu}_3)\text{X}$ ($\text{R} = \text{H}, \text{Me}$; $\text{M} = \text{Ga}, \text{In}$; $\text{X} = \text{Cl}, \text{Br}$) are frustrated by the formation of halide bridged dimers $[\{(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{E}(\text{2,4,6-}^t\text{Bu}_3)\}_2(\mu\text{-X})][\text{BAR}_4^{\text{F}}]$ [189]. This is in marked contrast to analogous boron chemistry: abstraction of bromide from $\text{Cp}^*\text{Fe}(\text{CO})_2\text{B}(\text{Br})\text{Mes}$ yields the terminal cationic borylene complex $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{BMes})]^+$ [190]. However, the use of bulky N,N' -chelating substituents, in particular amidinato, guanidinato, and β -diketiminato ligands, has allowed for the isolation of terminally coordinated cationic diyl complexes, presumably due to steric protection of the highly electrophilic Group 13 center, and thermodynamic stabilization conferred by the strong σ -donor properties of these ligands [17, 250]. Accordingly, salt elimination using amidinate stabilized Group 13 dihalides has been utilized to form complexes of the type $\text{CpFe}(\text{CO})_2\text{M}(\text{X})\{(\text{NCy})_2\text{C}^t\text{Bu}\}$ ($\text{M} = \text{Al}, \text{Ga}, \text{X} = \text{Cl}$; $\text{M} = \text{In}, \text{X} = \text{Br}$), as potential precursors to terminally coordinated three-coordinate cationic systems [251]. However, halide abstraction to form such a system was only successful in the case of gallium, yielding a donor-stabilized cationic gallylene complex $[\text{CpFe}(\text{CO})_2\text{FeGa}(\text{OEt}_2)\{(\text{NCy})_2\text{C}^t\text{Bu}\}][\text{BAR}_4^{\text{F}}]$. Two examples of non-donor stabilized cationic three-coordinate terminal gallylene complexes featuring the bulkier β -diketiminato ligand $[\text{HC}(\text{MeCDippN})_2]^-$ have however been prepared via halide abstraction,

namely $[\{HC(MeCDippN)_2Ga\}Au\{Ga(NDippCMe)_2CH\}][Bar^F_4]$ [252] and $[(OC)_4Co\{Ga(NDippCMe)_2CH\}][Bar^F_4]$ [198]. More recent work has expanded significantly the library of haloalanyl complexes in which the aluminum center is supported by N,N' -chelating ligands, including bulky β -diketiminates as in $CpFe(CO)_2Al(Cl)\{NDippCMe)_2CH\}$ [253]. However, no cationic complexes of transition metals featuring direct metal–aluminum bonds have been reported; this presumably stems from the much stronger Al–X bond in haloalanyls, hindering halide abstraction, and the likely highly Lewis acidic (and therefore highly reactive) nature of the aluminum center in any such cationic species.

By employing a highly electron rich and sterically encumbered transition metal fragment, the very unusual terminal iodogallylene complex $[Cp^*Fe(dppe)(GaI)][Bar^F_4]$ (**62**) can be formed by halide abstraction from $Cp^*Fe(dppe)GaI_2$ (**61**) (Scheme 13.9) [10]. Compound **62** represents the only reported example of the unsupported, terminal coordination of a Group 13–Group 17 analog of the ubiquitous CO and N_2 ligands; despite attempts to isolate similarly coordinated BF and BCl moieties, it has only been possible to date to isolate complexes in which these ligands bridge between two metal centers, namely $\{Cp^*Mn(CO)_2\}_2(\mu-BCl)$ [254] and $\{CpRu(CO)_2\}_2(\mu-BF)$ [255]. The Fe–Ga and Ga–I bond lengths in **62** [2.2221(6) and 2.4436(5) Å, respectively] are exceptionally short (cf. 2.322 Å (mean) for the Fe–Ga bond length in precursor **61**), which reflects the low coordination number at Ga and the presence of some multiple bond character in the Fe–Ga bond. Indeed, DFT calculations show that the GaI fragment acts as both a σ -donor and π -acceptor, although the covalent contribution to the Fe–Ga bond is comparatively low (-236 kJ mol^{-1} , compared to -469 , -397 , and -262 kJ mol^{-1} for BF, CO, and N_2 , respectively, bound to $[Cp^*Fe(dppe)]^+$) and is comparable to the electrostatic contribution of -234 kJ mol^{-1} . The metal–ligand interaction in **62** is, however, relatively weak and in light of this, GaI can be quantitatively displaced from **62** by CO to form $[Cp^*Fe(dppe)CO][Bar^F_4]$.



Scheme 13.9 Synthesis of a terminally coordinated complex of GaI (**13.62**).

Complexes have also been isolated featuring terminally bound, naked M^+ cations as ligands. Reaction of $Pt(GaCp^*)_4$ with $[Ga_2Cp][Bar^F_4]$, yields $[GaPt(GaCp^*)_4][Bar^F_4]$ (**63**), a trigonal bipyramidal species in which the Ga^+ ion occupies an axial position. The related complex $[InPt(PPh_3)_3][Bar^F_4]$ (**64**) can be prepared by treating $Pt(PPh_3)_4$ with $In[Bar^F_4]$ [8]. Extensive computational studies suggest that the terminal gallium atom in **63** carries only a small positive charge compared to platinum, and it acts both as a σ -acceptor and π -acceptor from the 18-electron $Pt(GaCp^*)_4$ unit. Similarly, in **64** the terminal indium atom acts as an almost pure acceptor from the 16-electron $Pt(PPh_3)_3$ unit. This bonding description arises due to the fact that the lone pair of the naked M^+ ions is located in a non-directional s-orbital, and hence does not contribute significantly as a donor to the transition metal. Such naked cations can hence be considered analogs of H^+ . Such bonding models are in marked contrast to M^I diyl fragments RM , which act as strong σ -donors and weak acceptors, in part as a result of the lone pair being located in a higher energy orbital with greater p character (see Section 13.4.7.2).

13.4.7

Direct Reactions with M^I Species

While insertion reactions of M^I halides have long been known (see Section 13.4.7.1), formation of transition metal–Group 13 bonds has been dominated by reactions exploiting other more recently developed M^I precursors, such as alkyl and Cp* substituted diyls, and heterocycles featuring two-coordinate Group 13 centers. Although similar compounds may be accessed via the use of double-salt metathesis (e.g., (OC)₄FeGa(C₆H₃-2,6-Trip₂) (57)), these reactions are often low yielding and require the use of highly reducing carbonyl-metallate dianions, which limits the range of accessible complexes. The use of M^I diyls and heterocycles in direct ligand displacement reactions has greatly enlarged the family of transition metal complexes featuring Ga^I, In^I, and especially Al^I donors. The chemistry of Group 13 diyls and heterocycles in this regard has been the subject of several recent review articles [17, 183, 185], and hence only a brief overview of such chemistry will be provided here.

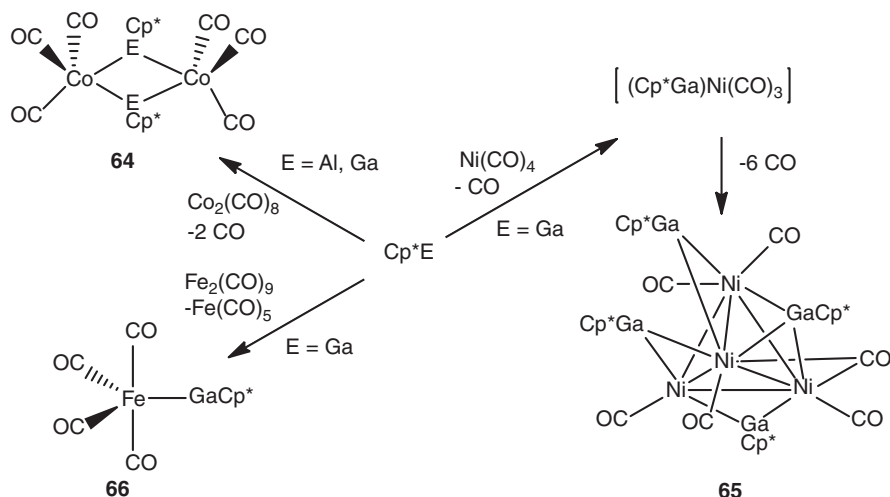
13.4.7.1 Insertion of M^I Halides into M–X and M–M Bonds

Insertion reactions of Group 13 M^I halides into transition metal–halide or metal–metal bonds have been dominated by the reactivity of In^I halides, which are much more stable than Ga^I and Al^I analogs, and are commercially available. Many insertion reactions into the M–M bonds of dinuclear metal carbonyl compounds have been reported; [256, 257, 204, 258] crystallographically characterized systems including the halide-bridged dimer [InBr{Mn(CO)₅}₂]₂, formed via the reaction of InBr with Mn₂(CO)₁₀ [259], and dimeric [InBr{MCp(CO)₃}₂]₂ (M = Cr, Mo, W) from insertion of InBr into the M–M bonds of [CpM(CO)₃]₂ [260, 261]. Related gallium chemistry is dominated by a reagent that reacts as a source of GaI; [262, 263] Green's sonochemically prepared "GaI" inserts into the Mo–I bonds of Cp'Mo(CO)₃I and (η⁷-C₇H₇)Mo(CO)₂I to yield (Cp'Mo(CO)₃GaI₂·OEt₂) and (η⁷-C₇H₇)Mo(CO)₂GaI₂·THF, respectively [262]. The insertion of InBr and InI into the Fe–Fe bond of {(η⁵-C₅R₅)Fe(CO)₂}₂ (R = H, Me) has been shown to proceed to give the XM-bridged species {(η⁵-C₅R₅)Fe(CO)₂}₂InX (R = Me, X = Br, I; R = H, X = I), whereas the reaction of {(η⁵-C₅Me₅)Fe(CO)₂}₂ with GaI instead yields [(η⁵-C₅Me₅)Fe(CO)₂GaI₂]₂ [210, 260]. Nothing is known of the insertion of ALX species into M–X and M–M bonds [264].

13.4.7.2 Ligand Displacement Reactions Utilizing Group 13 Diyls, RM

Among the Group 13 diyls, the coordination chemistry of Cp*M (M = Al, Ga, In) is by far the most extensively developed. A range of alkyl-substituted species RM: [M = Al, Ga, In; R = C(SiMe₃)₃, CH(SiMe₃)₂, Si(SiMe₃)₂] has also been used as ligands. Species of this sort feature an sp-hybridized Group 13 element center. In the monomeric state, the Group 13 element possesses a singlet lone pair in a σ-orbital as the HOMO, alongside two vacant p-orbitals, which are generally the LUMOs that lie orthogonal to the Cp* centroid-M vector. These ligands are hence isolobal to CO, with the potential to participate in synergistic σ-donor/π-acceptor bonding to transition metals [181, 265, 266]. However, the ability to act as a π-acceptor is largely dependent on the nature of the substituent R; strongly π-donating groups, such as Cp*, donate into the p-orbitals at the Group 13 center, raising their energy and reducing the propensity to participate in π-backbonding. The π-acceptor capability is increased with less π-donating substituents, such as C(SiMe₃)₃, as this reduces the population of the p-orbitals at the metal center.

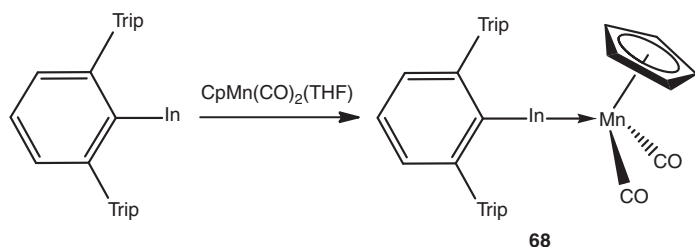
The most commonly used strategy for the coordination of Group 13 diyls is displacement of more weakly coordinating ligands such as alkenes, phosphines, and CO. RM units may act as a terminal, μ₂-bridging or μ₃-bridging ligands, in an analogous manner to CO (Scheme 13.10). CO displacement is especially common, as in the reaction of Cp*M (M = Al, Ga) with Co₂(CO)₈, yielding [Co₂(CO)₆(μ₂-MCp*)₂] (64) [267–269]. Reaction of Cp*Ga with Ni(CO)₄ is thought to proceed via initial CO displacement to yield the terminally coordinated complex (OC)₃Ni(GaCp*), which has been detected spectroscopically. However, this species is unstable and the final product of the reaction is the cluster compound Ni₄(GaCp*)₄(CO)₆ (65), in which the Cp*Ga ligands demonstrate both μ₂ and μ₃ bridging



Scheme 13.10 CO displacement reactions involving Cp*M (M = Al, Ga).

modes between nickel centers [267]. Reaction with homoleptic metal carbonyls does not, however, always proceed with CO displacement; $(\text{OC})_4\text{Fe}(\text{GaCp}^*)$ (**66**) is formed in the reaction of Cp^*Ga with $\text{Fe}_2(\text{CO})_9$, with the elimination of $\text{Fe}(\text{CO})_5$ [267]. The structural characterization of both **66** and $(\text{OC})_4\text{Fe}(\text{AlCp}^*)$ (**67**) allows for comparison of the electronic properties of the Cp^*M fragment down Group 13 [270]. The Fe–Al bond length (2.231(1) Å) is slightly shorter than the Fe–Ga bond length (2.273(1) Å) in **67**; this, coupled with red-shifted carbonyl stretching frequencies for **66** (2037, 1966, and 1942 cm^{-1} , compared to 2024, 1948, and 1903 cm^{-1} for **67**), is suggestive of a stronger σ -donor role for Cp^*Al as compared to Cp^*Ga , which can be accounted for by the lower *s*-character of the lone pair in Cp^*Al . The behavior of the alkyl substituted diyl tetramers $\text{M}_4\{\text{C}(\text{SiMe}_3)_3\}_4$ (M = Ga, In) toward metal carbonyls is often found to be similar to that of Cp^*M [271, 272].

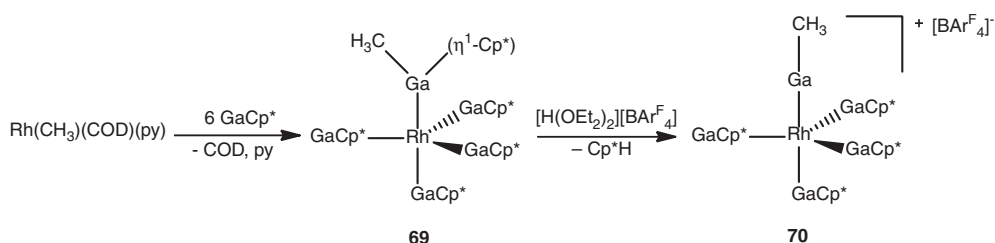
Displacement of more weakly coordinating ligands such as alkenes or solvent molecules has also been probed. Thus, the reaction of the one-coordinate terphenyl indium diyl $\text{In}(\text{C}_6\text{H}_3\text{-2,6-Trip}_2)$ (**26**) with $\text{CpMn}(\text{CO})_2(\text{THF})$ yields $\text{CpMn}(\text{CO})_2\text{In}(\text{C}_6\text{H}_3\text{-2,6-Trip}_2)$ (**68**, Scheme 13.11) [3]. This compound is purported to contain a strong Mn–In single bond, with the $\text{In}(\text{C}_6\text{H}_3\text{-2,6-Trip}_2)$ ligand acting as a very weak π -acceptor; this contrasts with the initial description of the related complex $(\text{OC})_4\text{FeGa}(\text{C}_6\text{H}_3\text{-2,6-Trip}_2)$ (**57**) as containing a Fe–Ga triple bond [9]. Other terphenyl indium and gallium complexes of early transition metals may be accessed, via *in situ* reduction of $\text{Cl}_2\text{M}(\text{C}_6\text{H}_3\text{-2,6-Trip}_2)$ [273, 274].



Scheme 13.11 Complexation of a one-coordinate indium diyl at $[\text{CpMn}(\text{CO})_2]$.

Two prototypical examples of alkene displacement are the displacement of cyclooctene (COE) from $\text{Cr}(\text{CO})_5(\text{COE})$ by Cp^*Ga to yield $\text{Cr}(\text{CO})_5(\text{GaCp}^*)$, and that of cycloheptatriene (CHT) in **66** from

$\text{Fe}(\text{CO})_3(\text{CHT})$, yielding the dinuclear complex $(\text{OC})_3\text{Fe}\{\mu_2-\eta^5\text{-GaCp}^*\}_2\{\mu_2-\eta^3\text{-GaCp}^*\}\text{Fe}(\text{CO})_3$, featuring both η^3 and η^5 coordinated Cp^* ligands (Scheme 13.12) [267]. Changes in hapticity of the Cp^* ligand, most commonly to a η^3 or η^1 coordination mode, are relatively common, and allow the Cp^*M ligand to act as a better π -acceptor and reduce steric repulsion. Alkene displacement also allows relatively facile access into homoleptic complexes featuring RM: fragments [275, 276], as successive displacements of more strongly π -accepting CO ligands is often not possible in the presence of strong σ -donors. For example, the homoleptic complexes $\text{Ni}(\text{MCp}^*)_4$ ($\text{M} = \text{Al}, \text{Ga}$) and $\text{Ni}\{\text{MC}(\text{SiMe}_3)_3\}_4$ can be prepared from $\text{Ni}(\text{COD})_2$ [277–280]. The nature of the Ni–M bonding in these homoleptic species is very different to that in species featuring ancillary carbonyl ligands. Energy decomposition analysis (EDA) on compounds of the type $(\text{OC})_4\text{Fe}(\text{GaR})$ suggest that σ -donation is dominant, and electrostatic interactions are also very strong, but π -backbonding is minimal [281]. However, in homoleptic complexes, the π -backbonding contribution is much increased, accounting for around 40% of the overall orbital contribution in the model compounds $\text{Ni}(\text{MMe})_4$ and $\text{Fe}(\text{MMe})_5$ ($\text{M} = \text{Al}, \text{Ga}, \text{In}$) [279, 281]. This is a result of the lack of competing π -acceptor CO ligands in the coordination sphere of the transition metal [282].

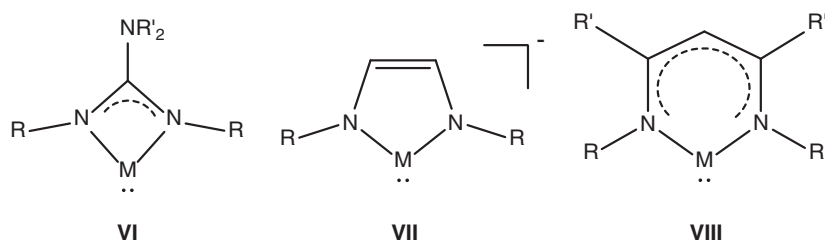


Scheme 13.12 Insertion of Cp^*Ga into an Rh–C bond; subsequent protonolysis to form **70**.

Coordination of Group 13 diyls may also be achieved by addition or insertion reactions [283]. The ability of Cp^*M fragments to insert into M–X bonds has been demonstrated in the formation of $\text{Cp}^*\text{Fe}(\text{CO})_2\text{Ga}(\text{Cl})(\eta^1\text{-Cp}^*)$ and $(\text{Cp}^*\text{Ga})_4\text{Rh}\{\text{Ga}(\text{CH}_3)(\eta^1\text{-Cp}^*)\}$ (**69**) [284, 285]. Protonolysis of **69** gives access to $[(\text{Cp}^*\text{Ga})_4\text{Rh}\{\text{Ga}(\text{CH}_3)\}]^+$ (**70**), featuring a very rare example of GaMe as a terminally coordinated ligand (Scheme 13.12).

13.4.7.3 Reactions with M^{I} Heterocycles

The coordination chemistry of heterocycles featuring the Group 13 element in the +1 oxidation state and supported by an *N,N*-chelating substituent has been developed in the last decade. Monomeric heterocycles of types **VI**–**VIII** have been isolated and used as ligands; the neutral four- and six-membered heterocycles are isolobal to NHCs in that they bear a singlet lone pair and a formally vacant p-orbital at the metal center, and the anionic five-membered heterocycles are valence isoelectronic to NHCs.



There are no stable four-membered heterocycles of boron or aluminum, but coordination chemistries of $\text{Ga}\{\text{NDipp}_2\text{CNCy}_2\}$ (**71**) and $\text{In}\{\text{NDipp}_2\text{CNCy}_2\}$ (**72**) have been investigated [286]. Coordination modes of **71** to transition metals are reminiscent of those of gallium diyls, and synthetic methods employing the displacement of ligands such as COD and CO are commonplace. **71** may act as a terminally bound ligand, as in *cis*- $[\text{Ni}(\text{COD})\{\text{Ga}(\text{NDipp})_2\text{CNCy}_2\}_2]$, or a bridging ligand as in $\text{Co}_2(\text{CO})_6(\mu_2\text{-}\{\text{Ga}(\text{NDipp})_2\text{CNCy}_2\}_2)$ [287–289]. Compound **71** is less nucleophilic than Cp^*Ga and some of its complexes are very labile in solution [287, 288, 290]. Compound **72** is a weaker donor still, on account of its more diffuse lone pair, and is hence a more labile ligand; of the few examples of coordination complexes, several including *trans*- $[\text{Pt}(p\text{-C}_6\text{HF}_4)_2\{\text{In}(\text{NDipp})_2\text{CNCy}_2\}_3]$, display short $\text{In}\cdots\text{F}$ contacts, in accordance with the higher Lewis acidity of the In center in the $[\text{In}\{\text{NDipp}_2\text{CNCy}_2\}]$ fragment as compared to $[\text{Ga}\{\text{NDipp}_2\text{CNCy}_2\}]$ [288, 289].

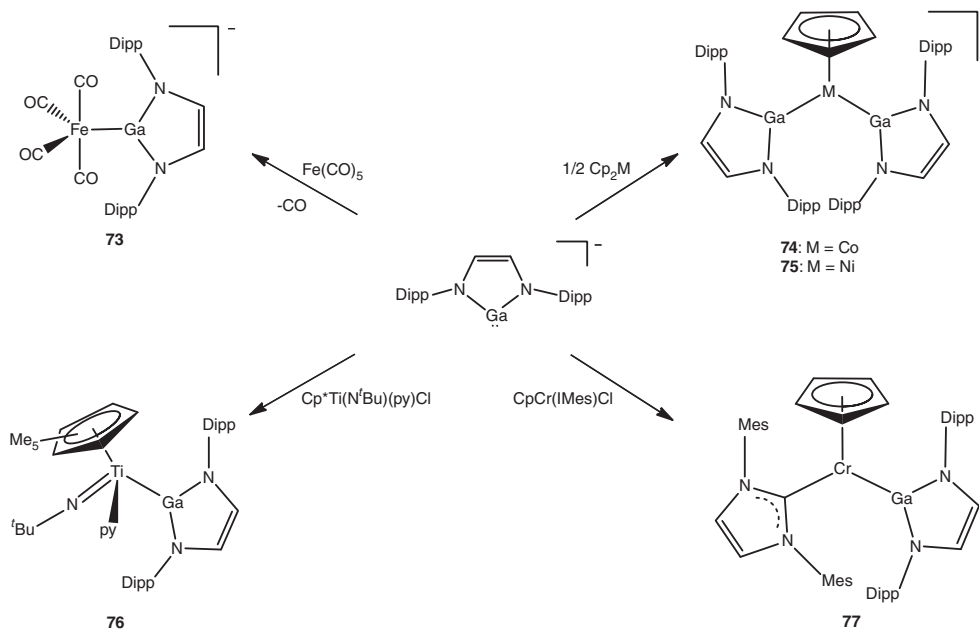
Anionic, five-membered heterocycles have been isolated featuring boron and gallium [21, 291]. Theoretical studies on systems of the type $[\text{E}(\text{NHCH})_2]^-$ ($\text{E} = \text{B} - \text{In}$) have demonstrated that the HOMO is a singlet lone pair at the Group 13 center, while the LUMO is associated with the formally vacant p-orbital orthogonal to the heterocycle plane. Although the LUMO at the metal center for Al, Ga, and In interacts with the adjacent nitrogen atoms in the heterocycle to a far lower extent than in NHCs, it lies relatively high in energy, which disfavors π -backbonding in transition metal complexes [181, 219, 281, 292].

The coordination chemistry of anionic gallium heterocycles is limited to that of $[(\text{HCDippN})_2\text{Ga}]^-$ pioneered by Jones, featuring very bulky aryl groups that can provide kinetic stabilization to coordination complexes. $[(\text{HCDippN})_2\text{Ga}]^-$, and the analogous boryl anion, have been shown to stabilize many unusual Main Group and transition metal species [17, 183, 293]. $[(\text{HCDippN})_2\text{Ga}]^-$ is a very strong σ -donor ligand, and accordingly readily displaces ligands such as CO and Cp^- (Scheme 13.13). This allows access to compounds such as $[\text{Fe}(\text{CO})_4\{\text{Ga}(\text{HCDippN})_2\}]^-$ (**73**), $[(\text{C}_5\text{H}_4\text{R})\text{M}(\text{CO})_n\{\text{Ga}(\text{HCDippN})_2\}]^-$ ($\text{R} = \text{H}, \text{Me}$; $\text{M} = \text{V}, n = 3$, $\text{M} = \text{Mn}, n = 2$; $\text{M} = \text{Co}, n = 1$) and $[\text{CpM}\{\text{Ga}(\text{HCDippN})_2\}_2]^-$ (**74**: $\text{M} = \text{Co}$; **75**: $\text{M} = \text{Ni}$), with the formation of the latter from Cp_2M mimicking the chemistry of NHCs [195, 196, 294]. While salt elimination appears an obvious route into transition metal complexes of $[(\text{HCDippN})_2\text{Ga}]^-$, most complexes formed in this way feature d^0 or d^{10} configurations. Examples include *trans*- $[\text{Pt}(\text{PEt}_3)_2\{\text{Ga}(\text{HCDippN})_2\}_2]$ and $\text{Cp}^*\text{Ti}\{\text{Ga}(\text{HCDippN})_2\}(\text{N}^t\text{Bu})(\text{py})$ (**76**) [295, 296]. Examples of complexes so formed with open d-shell configurations, such as $\text{CpCr}(\text{IMes})\{\text{Ga}(\text{HCDippN})_2\}$ (**77**), are extremely rare and require the presence of strong electron-donating ancillary ligands (usually NHCs) in order to prevent reduction of the metal halide precursor [297, 298].

Neutral, six-membered M^{I} heterocycles of Group 13 elements most commonly feature the β -diketiminate ligand $[\text{HC}(\text{MeCDippN})_2]^-$. Theoretical investigations of the model systems $\text{M}\{(\text{NMeCMe})_2\text{CH}\}$ confirm that they feature a sp-hybridized metal-centered lone pair. However, the p-orbital orthogonal to the heterocycle plane is not the LUMO, but the LUMO + 1, and lies high in energy, resulting in large HOMO–LUMO + 1 gaps ($\text{M} = \text{Al}$: 98 kcal mol $^{-1}$; $\text{M} = \text{Ga}$: 110 kcal mol $^{-1}$; $\text{M} = \text{In}$: 99 kcal mol $^{-1}$) [197, 299, 300]. These compounds therefore act as strong σ -donors, but weak π -acceptors. As with diyls such as Cp^*E , the increasing s character of the lone pair on descending the group means that the indium heterocycles are significantly less nucleophilic than the corresponding aluminum and gallium species [301].

Only two six-membered aluminum heterocycles, $\text{Al}\{\text{NDippCMe}_2\text{CH}\}$ (**78**) and $\text{Al}\{\text{NDippC}^t\text{Bu}_2\text{CH}\}$ (**79**) have been isolated; these compounds represent rare examples of two-coordinate aluminum [299, 302]. Their coordination chemistry is limited to that of **78** with palladium [17, 183, 200, 201, 303, 304]. Accordingly, reaction with 1 equiv. of $\text{Pd}_2(\text{dvds})_3$ forms a 1:2 complex in which the aluminum heterocycle bridges two palladium centers; reaction with an excess of **78** generates $(\text{dvds})\text{PdAl}\{\text{NDippCMe}_2\text{CH}\}$, featuring a rare example of a three-coordinate aluminum center in the coordination sphere of a transition metal [305, 306].

The coordination chemistry of the gallium heterocycle $\text{Ga}\{\text{NDippCMe}_2\text{CH}\}$, **80**, has developed to a far greater extent than that of the aluminum and indium congeners. In common with other Ga^{I} species, displacement of more weakly coordinating ligands is a primary route to

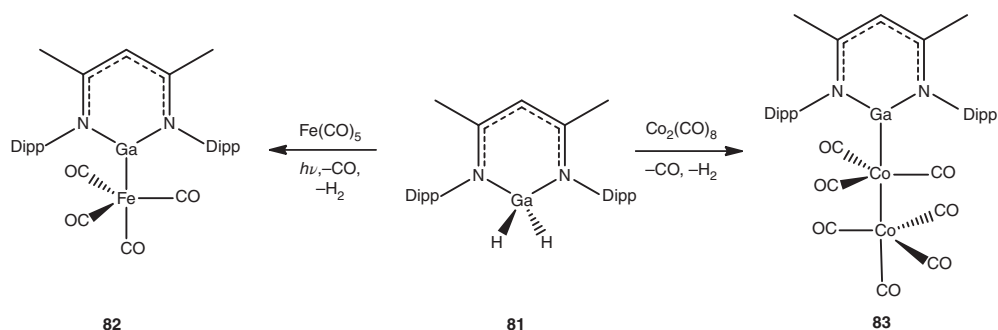


Scheme 13.13 Coordination complexes of the anionic gallium heterocycle $[(\text{HCDippN})_2\text{Ga}]^-$.

access transition metal complexes. Examples include the displacement of CO from $\text{Fe}(\text{CO})_5$ to yield $(\text{OC})_4\text{Fe}\{\text{Ga}(\text{NDippCMe})_2\text{CH}\}$ [307], and displacement of COD from $\text{Pt}(\text{COD})_2$ to form $\text{Pt}\{\text{Ga}(\text{NDippCMe})_2\text{CH}\}_2(\eta^2\text{-1,3-COD})$ [306, 308]. Besides ligand displacement, **80** also undergoes a range of insertion reactions into metal-halide bonds. Reaction with $\text{Pt}(\text{COD})\text{Cl}_2$, for example, leads to the formation of $\text{Pt}(\text{Cl})(\text{COD})\{\text{Ga}(\text{Cl})(\text{NDippC}(\text{Me})_2\text{CH})\}$, the result of formal insertion into a Pt–Cl bond. The reaction of **80** with $(\text{Ph}_3\text{P})_3\text{RhCl}$ provides further insight into insertion processes: one PPh_3 ligand is displaced, and the product, $(\text{Ph}_3\text{P})_2\text{RhGa}\{\text{NDippC}(\text{Me})_2\text{CH}\}(\mu_2\text{-Cl})$ features a chloride-bridged Rh–Ga unit [252].

Most recently, a new route has been developed to access the terminally coordinated complexes of **80** without having to employ a Ga^{I} precursor. The Ga^{III} hydride $\text{H}_2\text{Ga}\{\text{NDippC}(\text{Me})_2\text{CH}\}$ (**81**) undergoes spontaneous dehydrogenation at a range of transition metal carbonyls (Scheme 13.14). Thus, for example, photolysis of $\text{Fe}(\text{CO})_5$ with **81** does not yield a σ -gallane complex, but rather provides an alternative route directly to $(\text{OC})_4\text{Fe}\{\text{Ga}(\text{NDippC}(\text{Me})_2\text{CH})\}$ (**82**) in somewhat higher yield than the thermal reaction with **80** itself [198]. Moreover, products may be accessed which are not accessible by direct reaction with **80**: reaction of **81** with $\text{Co}_2(\text{CO})_8$ yields the terminally coordinated complex gallylene $(\text{OC})_4\text{CoCo}(\text{CO})_3\{\text{Ga}(\text{NDippC}(\text{Me})_2\text{CH})\}$ (**83**), whereas direct combination of **80** with $\text{Co}_2(\text{CO})_8$ produces instead the salt $[(\text{OC})_3\text{Co}\{\text{Ga}(\text{NDippC}(\text{Me})_2\text{CH})_2\}][\text{Co}(\text{CO})_4]$ [309]. Mechanistic investigations suggest that the dehydrogenation reactions of **81** proceed via oxidative addition of a Ga–H bond, followed by the elimination of H_2 . This offers a marked contrast to the aluminum congener $\text{H}_2\text{Al}\{\text{NDippC}(\text{Me})_2\text{CH}\}$, which yields σ -alane complexes with the same metal fragments, consistent with the dearth of examples of Al–X oxidative addition as discussed in Section 13.4.3 [310].

The coordination chemistry of six-membered In^{I} heterocycles is restricted to one example; the reactions of $\text{In}\{(\text{NArCMe})_2\text{CH}\}$ (Ar = Mes, Dipp) with $\text{CpFe}(\text{CO})_2\text{I}$ yield the insertion products $\text{CpFe}(\text{CO})_2\text{In}(\text{I})\{(\text{NDippCMe})_2\text{CH}\}$ [115]. The much lower nucleophilicity of these indium heterocycles is likely to be behind the more restricted development of their coordination chemistry.



Scheme 13.14 Spontaneous dehydrogenation of $\text{H}_2\text{Ga}\{(\text{NDipp})\text{CMe}\}_2\text{CH}\}$ (**81**) at transition metal carbonyls.

13.5

f-Block-Group 13 Metal Bonds

As with boron, the synthesis of molecular species containing bonds between Group 13 metals and f-block elements has largely been predicated on the availability of nucleophilic sources of the Group 13 fragment [311]. As such, lanthanide and actinide complexes featuring bonds to aluminum or gallium can be divided into two classes – those involving formally anionic five-membered gallium heterocycle ligands, derived typically from salt elimination or Ga–Ga oxidative addition, and relatively weakly bound systems featuring neutral M^{I} donors such as Cp^*Al or Cp^*Ga (see Chapter 3).

The latter class of compound includes the first example of an actinide–Group 13 metal bond, reported by Arnold in 2008. Here, the reaction between $(\text{Cp}^*\text{Al})_4$ and $\text{Cp}^{\text{Si}}_3\text{U}$ gave access to $\text{Cp}^{\text{Si}}_3\text{UAlCp}^*$ (**84**) [312], a methodology that was subsequently extended to the Cp^*Ga ligand, and to *tris*(cyclopentadienyl) derivatives of neodymium [313]. The structures of $\text{Cp}^{\text{Si}}_3\text{UMCp}^*$ have been determined crystallographically for both $\text{M} = \text{Al}$ (**84**) and $\text{M} = \text{Ga}$ (**85**), revealing U–Al and U–Ga distances of 3.117(3)/3.124(4) and 3.065(1) Å, respectively (compared to 3.17 and 3.16 Å for the sum of the covalent radii) [20]. DFT calculations, however, reveal that the potential energy well for deformation along the U–M bonds is very shallow and may therefore be influenced to a significant degree by intermolecular forces. NBO analyses indicate that the predominant bonding interaction involves the Cp^*M fragment acting as a σ -donor into the 7s/6d acceptor orbitals at U^{III} , with negligible π back-bonding. The related neodymium complexes $\text{Cp}^{\text{Si}}_3\text{NdMCp}^*$ have also been synthesized and the gallium system, **86**, structurally characterized. The Nd–Ga contact (3.153(1) Å) is also shorter than the sum of the respective covalent radii, although competition experiments between **86** and $\text{Cp}^{\text{Si}}_3\text{U}$ reveal stronger binding of the Cp^*Ga donor to the uranium Lewis acid [313].

A related approach has been adopted by Roesky and coworkers in the synthesis of Cp^*Al and Cp^*Ga derivatives of Eu^{II} and Yb^{II} [314, 315]. However, in systems of the type $\text{Cp}^*_2\text{LnAlCp}^*$ (**87**: $\text{Ln} = \text{Eu}$; **88**: $\text{Ln} = \text{Yb}$) the Ln–Al interaction is very weak (about 30 kJ mol^{−1}), being almost exclusively electrostatic in nature, and reflected in metal–metal contacts (**87**: 3.365(1) Å; **88**: 3.198(1) Å) which are outside the sums of the respective covalent radii (3.20 and 3.09 Å, respectively) [20]. More robust complexes featuring Ln–Ga bonds have been synthesized by the use of a salt elimination approach utilizing formally anionic gallyl precursors and Ln^{II} or Ln^{III} halides [316, 317]. These include Nd^{III} , Sm^{II} , Eu^{II} , Yb^{II} , and Tm^{III} compounds prepared from $[(\text{HCDippN})_2\text{GaK}(\text{tmeda})_2]$ (**2**) and lanthanide iodide precursors. For the series of isostructural Ln^{II} bis(gallyl) complexes $\text{Ln}(\text{tmeda})_2\{\text{Ga}(\text{HCDippN})_2\}_2$, the measured Ln–Ga distances (Sm: 3.312(1); Eu: 3.312(1); Yb: 3.226 (mean) Å) fit with the trend expected on the basis of the respective ionic radii. The relatively polar nature of the bonds in each case is reflected by the fact that each contact lies comfortably outside of the sum of the relevant covalent radii (3.20, 3.20, and 3.09 Å) [20]. Fedushkin has reported the synthesis of similar Ln^{II} compounds featuring a BIAN-derived gallium heterocycle, both by analogous salt elimination chemistry, and

interestingly also by insertion of the lanthanide metal into a Ga–Ga bond [34, 318]. Finally, salt elimination has also been applied to the synthesis of a U–Ga bond [319]. The U–Ga distances measured for $\{N(CH_2CH_2NSiMe_3)_3\}U\{Ga(HCDippN)_2\}(THF)$ (**89**; 3.212(1) and 3.298(1) Å) are somewhat longer than that determined for the Cp^*Ga complex **85** (3.065(1) Å), and, consistently, DFT calculations imply that the U–Ga bond in **89** has >70% electrostatic character.

Abbreviations

Ar [*]	2,6-(Ph ₂ CH) ₂ -4-Me-C ₆ H ₂
Ar ^F	3,5-bis(trifluoromethyl)phenyl
Cp [*]	C ₅ Me ₅
Cp'	C ₅ H ₄ Me
Cp ^{Si}	C ₅ H ₄ SiMe ₃
COD	1,5-cyclooctadiene
COE	cyclooctene
CHT	cycloheptatriene
Cy	cyclohexyl
DFT	density functional theory
Dipp	2,6- <i>i</i> Pr ₂ C ₆ H ₃
Dppe	1,2-bis(diphenylphosphino)ethane
Dcype	1,2-bis(dicyclohexyl-phosphino)ethane
Dvds	1,1,3,3-tetramethyl-1,3-divinyldisiloxane
Dme	1,2-dimethoxyethane
dpp-BIAN	1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene
EPR	electron paramagnetic resonance
HOMO	highest occupied molecular orbital
IPr	<i>N,N'</i> -bis(2,6-diisopropylphenyl)imidazol-2-ylidene
IMes	<i>N,N'</i> -bis(2,4,6-trimethyl-phenyl)imidazol-2-ylidene
LUMO	lowest unoccupied molecular orbital
Mes	2,4,6-Me ₃ C ₆ H ₂
NBO	natural bond orbital
OMCVD	organometallic chemical vapor deposition
THF	tetrahydrofuran
Tmeda	<i>N,N,N',N'</i> -tetramethylethylenediamine
tmpH	2,2,6,6-tetramethyl piperidine
Trip	2,4,6- <i>i</i> Pr ₃ C ₆ H ₂
Xyl	2,6-Me ₂ C ₆ H ₃

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14

Group 14 Metal–Metal Bonds

Robert J. Less and Dominic S. Wright

14.1

Introduction

Metal–metal bonded compounds of Group 14 encompass an exceptionally broad range of materials, including cluster compounds with electron-deficient bonding, multiply bonded analogs of carbon-based alkenes and alkynes, main group metal–Group 14 metal bonded compounds, and transition metal–Group 14 metal bonded compounds. As such, it is impossible to provide a fully comprehensive treatment of this area within the domain of this relatively short chapter. Rather, this chapter aims to identify the major areas of interest in this field, to identify general structural classes, and to define the nature of the metal–metal interactions involved. The emphasis is very much on structurally characterized compounds and the structural rules and bonding patterns within them.

14.2

Homoatomic Group 14–Group 14 Bonds

14.2.1

Cluster Compounds

Homoatomic and heteroatomic cluster compounds of Group 14 can be regarded as falling into three general classes, *Zintl compounds* (containing “naked” metal centers) [1–5], *metalloid cages* (of formulae $[\text{RE}]_n$) [6, 7], and *metalloid clusters* (of formulae $[(\text{RE})_n(\text{E})_m]^{x\pm}$) [8–11]. The bonding in these species is highly varied and can cover the entire range of electron-precise metal–metal single bonds, electron-deficient metal–metal bonds, and pseudo-aromatic ring bonding.

The simplest Zintl compounds comprising homoatomic $[\text{E}]_n^{x-}$ anions ($\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$) were first reported by Zintl in 1933 [12]. Ions of this type were originally obtained by the reduction of the metals or semimetals with alkali metals in liquid ammonia. Switching the reaction solvent to ethylene diamine and the use of alkali metal sequestering agents such as 2,2,2-crypt (2,2,2-crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane) first allowed Corbett to obtain Zintl compounds as crystalline solids which were amenable to structural characterization [13]. Nowadays, a range of macrocyclic Lewis bases (L) and solvents (S) are employed, and it is well recognized that among other factors, the thermochemical radius of the $[(\text{L})\text{M}]^+$ counter-ion has a key thermodynamic structure directing influence on the Zintl anion obtained in such reactions (Eq. 14.1). The structurally characterized homoatomic Zintl anions of Group 14 are shown in Figure 14.1, ranging from $[\text{E}]_4^{4-}$ to $[\text{E}]_{10}^{2-}$.



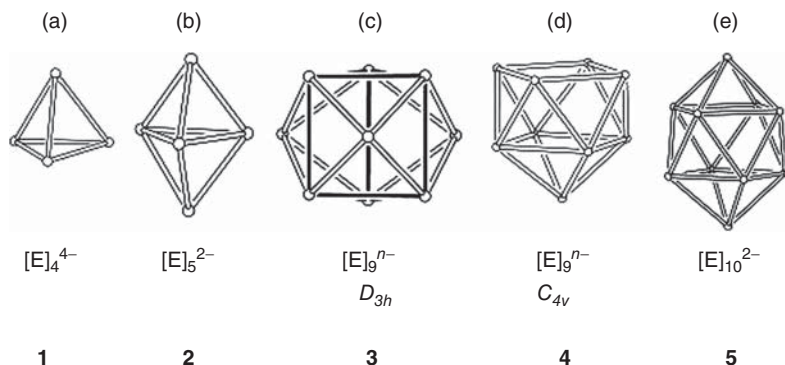


Figure 14.1 Structurally characterized Zintl ions of Group 14.

The $[E]_4^{4-}$ anions **1** are valence-isoelectronic with P_4 and contain electron-precise ($2c, 2e$) E–E bonds, whereas the other clusters are best described in terms of a delocalized bonding model that is analogous to that used for boranes (with each E atom contributing $2e$ to cluster bonding and with a lone pair of electrons *exo* to the cage). The clusters $[E]_5^{2-}$ (**2**) (Figure 14.1b), $[E]_9^{n-}$ (**3**) (Figure 14.1c, $n = 4$) and $[E]_{10}^{2-}$ (**5**) (Figure 14.1e) all conform to Wade's rules, having $n + 1$ pairs of cluster electrons and adopting *closo* deltahedral arrangements. In the case of $[E]_9^{4-}$, a *nido*-type structure is also consistent with Wade's rules (having $n + 2$ cluster electron pairs) (Figure 14.1d). However, the paramagnetic $[E]_9^{3-}$ anions (**5**) do not conform to these rules. Removal of an electron from the degenerate, filled HOMO of the $[E]_9^{4-}$ anion (**4**) (C_{4v}) or addition of an electron into the σ -antibonding LUMO of the $[E]_9^{2-}$ anion (**5**) (D_{3h}) produces Jahn–Teller or prismatic (height) distortion of either arrangement, so that the observed structures of $[E]_9^{3-}$ anions in the solid state normally lie between the two extremes of D_{3h} and C_{2v} symmetry. The E–E bond distances in these clusters of 2.4–2.7 Å (E = Si), 2.5–2.9 Å (E = Ge), 2.9–3.3 Å (E = Sn), and 3.0–3.5 Å (E = Pb) are considerably longer than normal E–E single bonds [2.353 Å (α -Si), 2.445 Å (α -Ge), 2.810 Å (α -Sn), and 2.88 Å (twice the Pb valence radius)].

Oligomerization and polymerization of $[E]_9$ units can also occur by oxidative coupling of $[E]_9^{4-}$ using Ag^+ , through the relatively stable $[E_9 \cdot]^{3-}$ radicals (**6**). The dimers $[E_9 - E_9]^{6-}$ [E = Ge (**7a**) and Sn (**7b**)] (Figure 14.2a,b, respectively) [14] and $[Ge_9^{2-}]_\infty$ (**8**) (Figure 14.2c) [15] have been structurally characterized. In the case of $[Ge_9]^{6-}$, two possible conformers (**7a** and **7b**) are observed containing different Ge_9 units [14c]. Dimers and tetramers result from the formation of two non-classical inter-cluster bonds between the Ge_9 units in the anions $[Ge_9 = Ge_9 = Ge_9]^{6-}$ (**9**) (Figure 14.2d) and $[Ge_9 = Ge_9 = Ge_9 = Ge_9]^{8-}$ (**10**) [16].

Group 14 Zintl ions can also function as ligands to a range of transition and main group metals. Interesting examples containing less than nine Group 14 atoms are $[E\{M(CO)_5\}]_6^{2-}$ (**11**) (E = Ge, Sn; M = Cr, Mo, W) (Figure 14.3a) [17] and $[Pb_5\{Mo(CO)_3\}_2]^{4-}$ (**12**) (Figure 14.3b) [18]. The $[E]_6^{2-}$ anion of **11** is obtained from the reactions of $Na_2[M_2(CO)_{10}]$ with GeI_2 or $SnCl_2$, and is valence-isoelectronic with *closo*- $[B_6H_6]^{2-}$, while complex **12** is produced in the reaction of $[Pb]_9^{4-}$ with $[\{\eta^6\text{-}2,4,6\text{-Me}_3\text{C}_6\text{H}_3\}Mo(CO)_3]$ and contains a planar 2π aromatic $[Pb]_6^{2-}$ dianion. The $[Sn]_6^{12-}$ anion (**13**) has also been reported and is valence-isoelectronic with S_6 [19].

Overall, the formation of complexes with d-block elements is rare for Zintl ions containing less than nine Group 14 atoms. *Nido*- $[E]_9^{4-}$ anions normally behave as η^4 -ligands with the transition metals occupying the vacant vertex position. Such an example is seen in the *nido*-to-*closo* transformation of $[E]_9^{4-}$ to $[(\eta^4\text{-}E_9)M(CO)_3]^{4-}$ (**14a**) (M = Cr, Mo, W) (Scheme 14.1) [17]. This conforms to Wade/Mingos rules since the $Mo(CO)_3$ fragment contributes no electrons formally to the cluster, thus the electron count of the $[E]_9^{4-}$ Zintl ion (number of electron pairs = $n + 2 = 11$) is conserved while the number of cluster atoms (n) increases by one (i.e., number of electron pairs now = $n + 1$). Interestingly, in this case, structural isomers have also been observed (depending on the reagents

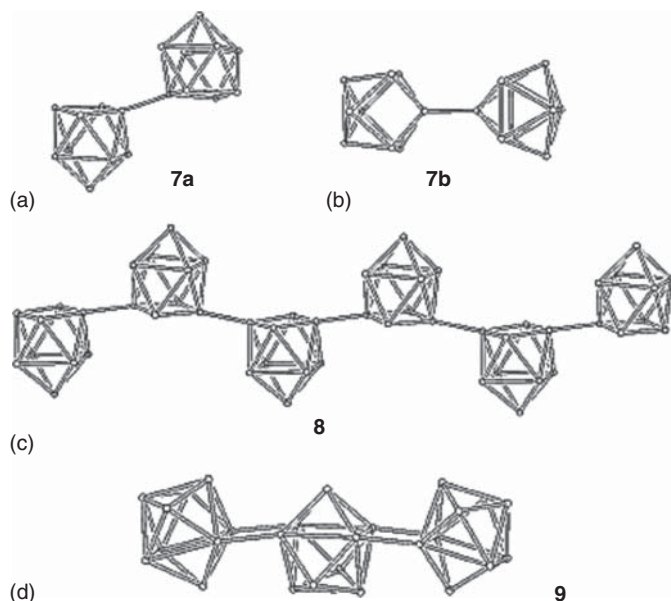


Figure 14.2 Structures of $[E]_9$ -based anions formed by (a) dimerization, (b) polymerization and (c) trimerization.

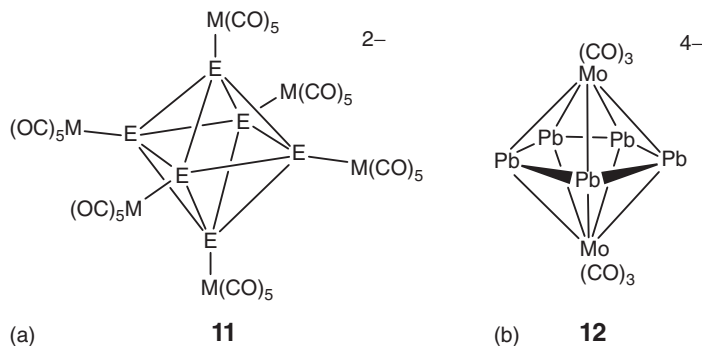
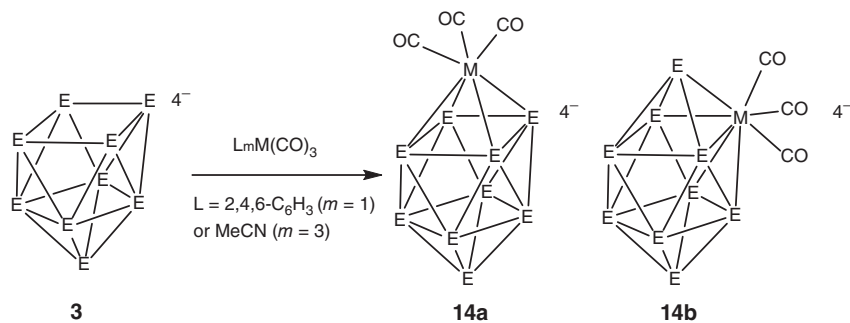


Figure 14.3 Examples of naked Zintl ions acting as ligands to d-block organometallic fragments, (a) $[E(M(CO)_5)]_6^{2-}$ (**11**) ($E = \text{Ge, Sn}$; $M = \text{Cr, Mo, W}$) and (b) $[Pb_5\{\text{Mo(CO)}_3\}]^{4-}$ (**12**).

and reaction conditions employed), with the X-ray structures of *closo*- $[(\eta^5-E_9)M(CO)_3]^{4-}$ (**14b**) ($M = \text{Mo, W}$) exhibiting an alternative η^5 -coordination of the $[E]_9^{4-}$ anion to the $M(CO)_3$ units [18].

A large number of endohedrally filled anionic Group 14 clusters have been reported, in which interstitial guest metal atoms are found within the surrounding arrangement of Group 14 atoms [3]. These species are formed by the loss of the organic substituents from the previously described organometallic complexes. Group 14 endohedral clusters of the general type $[M_m@E_n]^{x-}$ (where M is the guest metal atom and E_n the surrounding host arrangement) roughly span the range $[M@E_9]^{3-}$ to $[M_2@E_{18}]^{4-}$, although some examples of clusters incorporating more than two guest metal atoms have been reported [19]. A representative of the smallest of these clusters is $[Ni@Ge_9]^{3-}$ (**15**) obtained from the reaction of $[Ge]_9^{4-}$ with $Ni(\text{cod})_2$ ($\text{cod} = \text{C}_8\text{H}_{12}$) in dimethyl formamide (Figure 14.4a) [20]. The paramagnetic nature of the latter is ascribed to the presence of $Ni(0)$ in the cluster. More frequently, however, rearrangement and expansion of the initial framework of



Scheme 14.1 Transformation of $[\text{E}_9]^{4-}$ into the two potential isomers of $\text{closo-}[(\text{E}_9)\text{M}(\text{CO})_3]^{4-}$ (**14**).

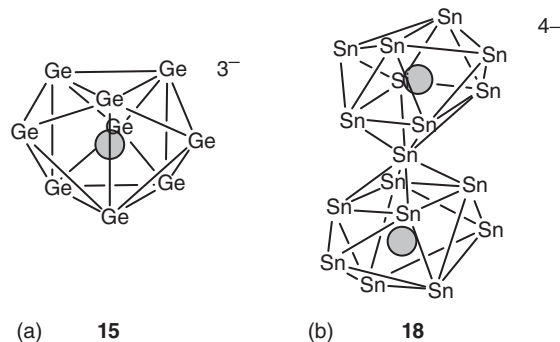
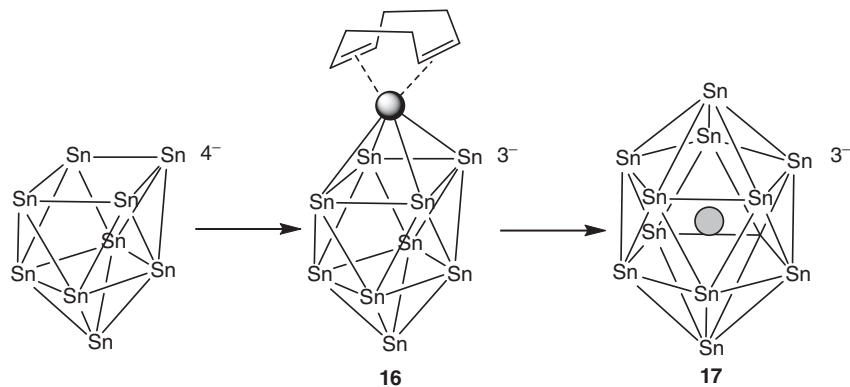


Figure 14.4 Structure of (a) the $[\text{Ni}@\text{Ge}_9]^{3-}$ anion (**15**) and (b) $[\text{Pt}_2@\text{Sn}_{17}]^{4-}$ (**18**).

the Zintl ion occurs during reactions of this type, which are accompanied by oxidation processes involving organic ligands and/or solvent molecules. For example, in the stepwise reaction of $[\text{Sn}]_9^{4-}$ with $[\text{Ir}(\text{cod})\text{Cl}]_2$, initial formation of the intermediate cage $[\text{Sn}_9\text{Ir}(\text{cod})]^{3-}$ (**16**) is followed by an oxidation step in which the free cod ligand is lost to give $[\text{Ir}@\text{Sn}_{12}]^{3-}$ (**17**) (Scheme 14.2) [21]. This oxidation is accelerated by the presence of dppe [1,2-bis(diphenylphosphino)ethane] which can act as an oxidizing agent. Examples of clusters at the higher end of the size spectrum are $[\text{Pt}_2@\text{Sn}_{17}]^{4-}$ (**18**) (constructed from two interconnected Sn_9 tricapped trigonal prisms, Figure 14.4b) [22] and



Scheme 14.2 Stepwise reaction of $[\text{Sn}]_9^{4-}$ with $[\text{Ir}(\text{cod})\text{Cl}]_2$ followed by thermal oxidation with the loss of the cod ligand.

[Pd₂@Sn₁₈]⁴⁻ (**19**) (in which the two Pd atoms are housed within a deltahedral Sn₁₈ framework) [23]. These clusters are generated from reactions of K₄Sn₉ with [Pd(PPh₃)₄] and [Pt(PPh₃)₄] in ethylene diamine. DFT calculations on structurally characterized transition metal [M@E₉]^{x-}, [M@E₁₀]^{x-}, and [M@E₁₀]^{x-} clusters support the view that the transition metals (M) are all found in the d¹⁰ electronic configurations, for example, Ni(0) in the cage [Ni@Ge₉]³⁻ (**15**) and Ir(1-) in the cage [Ir@Sn₁₂]³⁻ [3]. Like main group metal guest atoms in these species, the transition metal atoms do not contribute electrons to the skeletal E_n cage electron counts, although their s, p, and d orbitals are involved in cage stabilization. In the case of [Ir@Sn₁₂]³⁻ (**17**) (Scheme 14.2), for example, this is best regarded as a Wade's rule *closo*-Sn₁₂²⁻ anion (valence-isoelectronic with [B₁₂H₁₂]²⁻) which encapsulates the guest metal atom, while [M@E₉]^{x-} cages like [Ni@Ge₉]³⁻ clearly do not conform to Wade's rules.

Metalloid cages and clusters can be regarded as ligand-substituted Zintl ions containing exo-covalent bonds to organic substituents. Direct reactions of Group 14 Zintl anions with organic groups is, however, not generally an effective way of making these cages and clusters owing to the strong reducing power of the Zintl anions. Alternative strategies that are employed are reduction of ER_{4-n}X_n (R = alkyl, aryl; X = halogen) with the formation of ligand-free E-atoms by ligand elimination [24], the reduction of low-valent molecules E^{II}R'₂ (R' being either aryl or halide) [25], or the disproportionation of Ge^I and Sn^I subhalides [8–11]. This last route has been pioneered by Schnepf and relies on the fact that during decomposition of element(I) halides into metals and element(IV) halides, metastable cluster compounds are generated at relatively low temperatures that can be trapped and kinetically stabilized by the introduction of ligands on their surfaces. Although complicated by the specific reaction conditions required for each cluster, this route has been found to be particularly useful for larger metalloid cages.

The bonding in these species mirrors that in Zintl anions themselves, but the structures are generally more diverse in terms of their polyhedral arrangements. The simplest members of this class are electron-precise tetrahedro-tetrasilane cages [E{Si(Si^tBu₃)₃}]₄ [E = Si (**20a**), Ge (**20b**)], valence-isoelectronic with P₄ (Figure 14.5a) [26]. The Si₄ cage is generated by the reaction of ^tBu₃SiSiBr₂SiBr₂Si^tBu₃ with ^tBu₃SiNa (Eq. (14.2)), whereas the Ge₄ analog is best prepared by a more direct route involving GeCl₂ (dioxane) (Eq. (14.3)). For less sterically demanding organic and silyl substituents (R), *triprismo*-octagermanes [Ge₆R₆] (**21**) (e.g., R = CH(SiMe₃)₂) [27] and *hexahedro*-octasilanes [E₈R₈] (**22**) (E = Si, Ge, e.g., R = SiMe^tBu₂, CMe₂CHMe₂, 2,6-Et₂C₆H₃) [28] have been observed (Figure 14.5b,c, respectively). These are generally prepared by the Wurtz-type coupling of RE(hal)₃ with s-block metals.

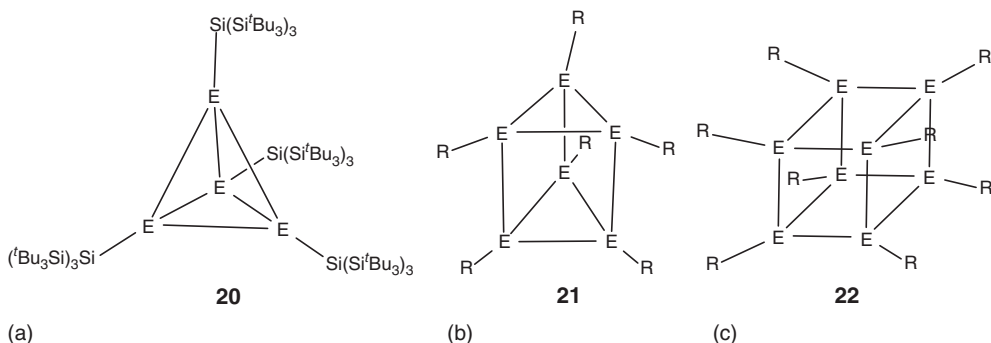
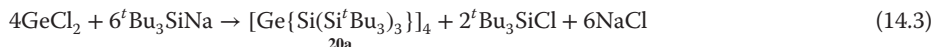


Figure 14.5 The structures of some Group 14, ligand-stabilized electron-precise cages, (a) [Si{Si(Si^tBu₃)₃}]₄ (**20a**), (b) [Ge₆R₆] (**21**) (e.g., R = CH(SiMe₃)₂) and (c) [E₈R₈] (**22**).

A very broad variety of electron-deficient clusters of Ge, Sn, and Pb are known which encompass a range of structures comprising 6–17 Group 14 atoms, many of which conform to Wade's rules [1–5, 8–11]. The use of the Zintl ions $[\text{E}]_9^{4-}$ (**3**) as the precursors for ligand-stabilized clusters is limited by the fact that only one or two positions on the naked cages can be functionalized. In the case of reactions of Ge_9^{4-} with electrophiles, the D_{3h} -tricapped trigonal prismatic arrangement is transformed into the alternative C_{4v} -arrangement. Such an example is seen in the reactions of $[\text{Ge}]_9^{4-}$ with PnPh_3 ($\text{Pn} = \text{Sb}$ or Bi) which lead to the difunctionalized $22e$ -cages $[\text{Ge}_9(\text{PnPh}_2)_2]^{2-}$ (**23**) (Figure 14.6a), a process that presumably involves reduction of the phenyl-pnictinides to $[\text{PnPh}_2]^{2-}$ anions and corresponding oxidation of the Ge_9 precursor [29]. Coupling of the Ge_9 units can also be observed in some cases, as in the cluster $[\text{Ph}_2\text{SbGe}_9-\text{Ge}_9-\text{SbPh}_2]^{4-}$ (**24**) (Figure 14.6b) which probably occurs via a radical coupling mechanism [30]. In the tri-substituted cage $[\text{Ge}_9\{\text{Si}(\text{SiMe}_3)_3\}_3]^-$ (**25**) (Figure 14.6c), which is obtained by the reaction of $\text{Ge}^{\text{I}}\text{Cl}$ with $[\text{LiSi}(\text{SiMe}_3)_3]$, the skeletal $22e$ count of the $[\text{Ge}]_9^{4-}$ cage and its arrangement are retained (i.e., $3 \text{ R-Ge } (3 \times 3e) + 6 \text{ Ge } (6 \times 2e) + \text{charge}$

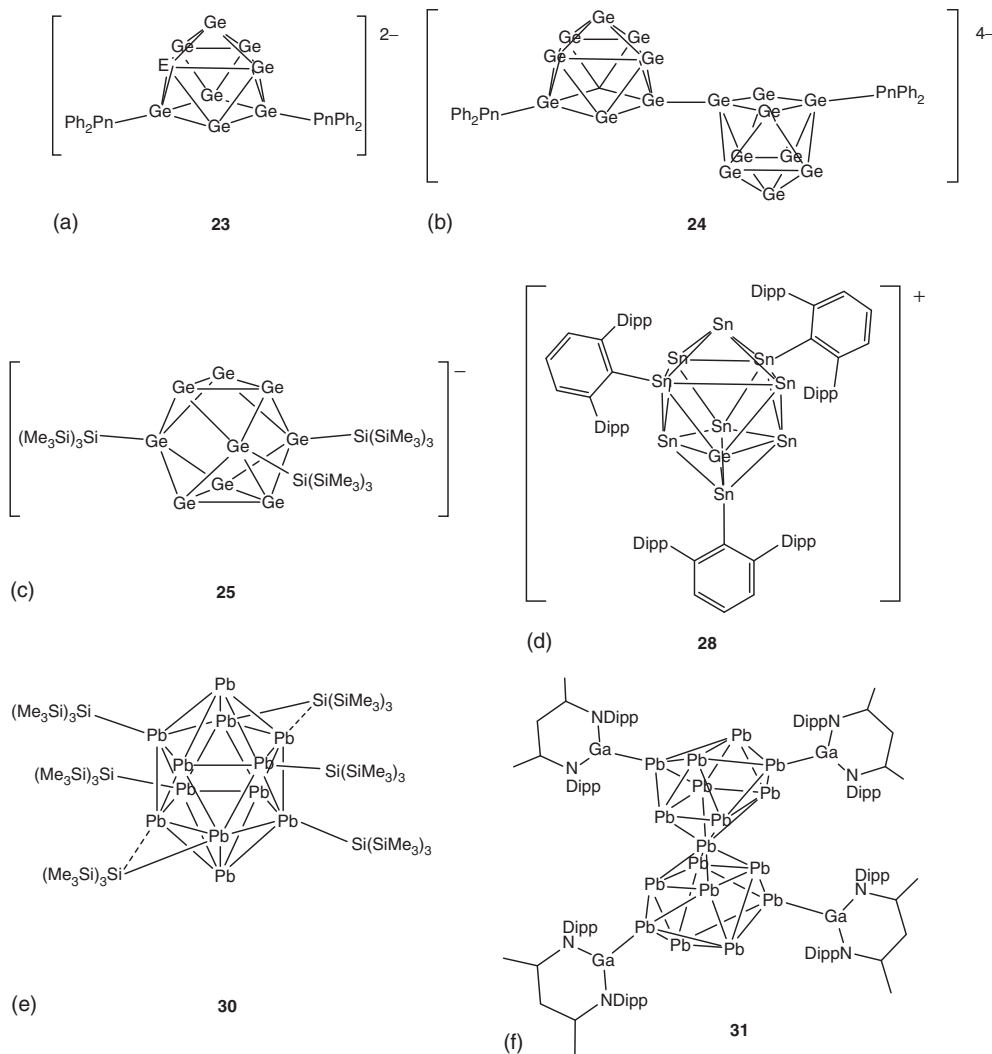


Figure 14.6 Selected examples of electron-deficient, ligand-supported clusters.

(1e) = 22e) [31]. The cluster structures of $[\text{Ge}_2\text{Sn}_4\{2,6\text{-(Dipp)}_2\text{C}_6\text{H}_3\}_2]$ (**26**) (Dipp = 2,6-*i*-Pr₂C₆H₃) [32], $[\text{Sn}_7\{2,6\text{-(Dipp)}_2\text{C}_6\text{H}_3\}_2]$ [33] (**27**), and $[\text{Sn}_{10}\{2,6\text{-(Dipp)}_2\text{C}_6\text{H}_3\}_3]^+$ (**28**) (Figure 14.6d) [25a] all adopt *closo*-polyhedral arrangements and conform exactly to Wade's rules (in which the distribution of the organic substituents can be regarded as resulting in order to minimize steric congestion). However, Wade's rules cannot be applied directly to the structures of clusters like $[\text{Pb}_{10}\{\text{Si}(\text{SiMe}_3)_3\}_6]$ (**29**) and $[\text{Pb}_{12}\{\text{Si}(\text{SiMe}_3)_3\}_6]$ (**30**) (Figure 14.6e) [34]. For example, in the latter case, an *arachno*-cluster would be expected on the basis of the skeletal electron count of 30e, rather than the observed deltahedral arrangement. The structure of $[\text{Sn}_{17}\{\text{Ga}(\text{ddp})\}_4]$ (**31**) [ddp = HC(CMeNC₆H₃-2,6-*i*-Pr₂)₂] (Figure 14.6f) [25c], obtained by reduction of SnCl₂ by the low-valent Ga^I β-diketiminato $[\text{Ga}(\text{ddp})]$, has a dumbbell shape comprising two interlocked Sn₉ fragments and represents the current maximum number of Group 14 metal atoms in this area. The cluster can be seen a ligand-stabilized Sn₁₇^{4−} anion (see Figure 14.4b).

14.2.2

Group 14–Group 14 Single Bonds (E–E)

14.2.2.1 Molecules and Oligomers

A comprehensive survey of all compounds bearing homoatomic group 14–group 14 single bonds is well beyond the scope of this review. Instead, this chapter will briefly highlight some of the main trends in synthesis and reactivity as the group is descended. Many detailed reviews have been published focusing on Si [35], Ge [36], Sn [37], and Pb [38] derivatives which the reader is encouraged to consult.

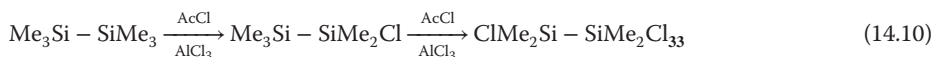
The first Si–Si organometallic was hexaethyldisilane synthesized in 1869 [39] and for the greater part of the next 100 years most Si–Si bond chemistry revolved around R₆Si₂ dimers. Since the development of techniques to access longer chains, there has been an explosion of interest in polysilane chemistry and those of the heavier group 14 congeners, mainly due to the unusual properties conferred on molecules forming bonds with orbitals, more diffuse than those on carbon, the main consequences being poorer orbital overlap resulting in low HOMO–LUMO energy gaps between σ and σ* orbitals of the E–E bonds.

The synthetic techniques used to make Si–Si bonds have changed little since the earliest developments. By far the most widely used methods involve variations on the Wurtz-type coupling where chlorosilanes are reductively coupled using an alkali metal (Eq. (14.4)) [35, 40]. Various metals have been employed under a variety of conditions with Na and Li remaining the most popular. Other techniques include reaction of metallosilanes with halosilanes (e.g., Eq. (14.5)) [41], photolysis of hydrosilanes [42], and silylene insertion reactions (e.g., Eq. (14.6)).



In terms of reactivity, Si–Si bonds may be cleaved by halogens (Eq. (14.7)) [35], by OH groups or reductively to produce metallosilanes (Eq. (14.8)) [43], with alkyl silanes being much more resistant to Si–Si bond cleavage than aryl derivatives. A classic example is the cleavage of tetrakis(trimethylsilyl)silane to produce the versatile anion tris(trimethylsilyl)lithium (**32**) (Eq. (14.9)) [44]. Under acidic conditions, R groups can be replaced by halogens (leaving Si–Si bonds intact) to provide useful intermediates for further transformation (e.g., such as **33**, Eq. (14.10)) [35].





Cyclic silanes are a much studied class which can be accessed using methods described above. Wurtz coupling of dihalosilanes typically gives mixtures of polymers and different ring sizes, though control of products can be effected by careful control of reaction conditions. For example, reaction of Ph_2SiCl_2 with 2 equiv. of Li produces $(\text{Ph}_2\text{Si})_4$ (**34**), whereas excess Li and longer reaction times results in formation of the thermodynamic product $(\text{Ph}_2\text{Si})_5$ (**35**) [45]. Other types of reaction include skeletal rearrangements of polysilanes in the presence of AlCl_3 [46], photolysis to eliminate R_2Si silenes [47] and additions to C–C multiple bonds catalyzed by palladium [48].

One category of singly bonded Si compounds, which merits special attention is the bis-silylenes, which have been reviewed recently [49]. The monomeric silylenes (e.g., **36**, Figure 14.7a) are a well-established class of compound with highly developed reaction chemistry (containing Si^{II}). The related bis-systems where the Si centers are linked by a single bond but still possessing lone pairs display unique reactivity (e.g., **37**, Figure 14.7b). Si centers can either react as isolated silylenes with retention of the Si–Si bond or via Si–Si bond cleavage. Reactions include cycloadditions with various unsaturated organic systems and oxidations [49].

Synthetic strategies employed in the preparation of oligosilanes can also be applied to making Ge–Ge single bonds. Although there are a range of reactions which can give rise to Ge–Ge bonding, none are as general and widely applicable as using Wurtz coupling [50] or reaction of a germanium–alkali metal compound with a germanium–halide [51]. A convenient method for extending the chain length of organogermanium compounds involves the replacement of one of the organic groups with a halide using SnCl_4 (Eq. (14.11)) [50]. The resulting halide can then be further reacted or self-coupled.



The most common methods of forming the Sn–Sn linkage are similar to those of Ge and Si (Eq. (14.12)). Another technique is through use of tin hydrides, which can be dehydrocoupled with loss of H_2 (Eq. (14.13)) or reacted with Sn-heteroatom compounds (Eq. (14.14)) [52].

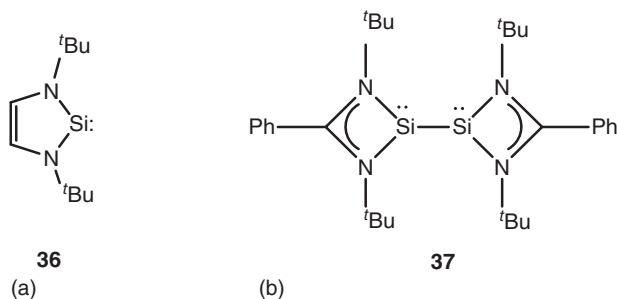
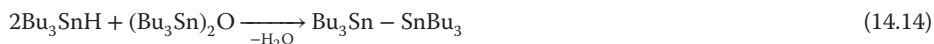
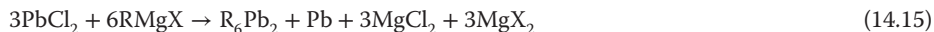


Figure 14.7 Mono- and bis-silylenes.



The cyclic oligostannanes are an important class of compounds, synthesized in a similar manner to the Sn_2 units above [53]. Larger R groups lead to lower degrees of association and the formation of isolated of R_2Sn stannylene units and doubly bonded dimers discussed below. In terms of reaction chemistry, the principal modes of reactivity of oligo- and polystannanes are through oxidative or reductive cleavage of Sn–Sn bonds [37].

The Pb–Pb derivatives are by far the least numerous of the Group 14 singly bonded compounds due to the inherent weakness of the metal–metal bonding. Chain compounds are limited to up to four linked lead units. The hexaorganodilead compounds represent the most studied class. Synthetic routes to access $\text{R}_3\text{Pb} - \text{PbR}_3$ include Wurtz coupling of triorganolead halides as well as reaction of lead(II) chloride with Grignards (Eq. (14.15)) [54].



These systems are, however, all unstable and react via cleavage of the Pb–Pb bond, either reductively, oxidatively, or by disproportionation into Pb(IV) and Pb or Pb(II) [55].

14.2.2.2 Polymers

Of particular interest have been the $[\text{ER}_2]_n$ polymers based on a singly bonded backbone of group 14 units bearing two side groups (Figure 14.8). As with the other singly bonded organometallics discussed above, by far the greatest number of derivatives are known for the silicon polymers [56] where the field has progressed rapidly since the 1970s, which saw the development of high molecular weight materials. The synthesis of polymers of the heavier group 14 elements (Ge, Sn, Pb) has been limited by the difficulties in obtaining longer chain lengths due to the increasing weakness of element–element bonds as the group is descended, although there have been some recent developments in the synthesis of high molecular weight germanium and tin polymers [57].

Of primary interest is the unusual electronic structure of the polymer backbone. The diffuse nature of the valence orbitals in the heavier group 14 elements results in far lower low-band gaps between bonding and antibonding bands than those present in carbon-based materials. The resulting “ σ -conjugation” is unprecedented in carbon–polymer chemistry and gives rise to electronic and optical properties more normally associated with π -conjugated polymers [58]. Thus, these materials have attracted considerable interest because of their unusual optical and electronic properties.

The first reports of polymeric silanes appeared in the 1920s when Kipping produced oligomeric polysilanes via a Wurtz coupling of Ph_2SiCl_2 with sodium metal [40]. The resulting material was, however, highly crystalline and insoluble which limited potential interest in the field. Subsequent derivatives suffered from the same problems of low molecular weights and poor solubility. It was not until the pioneering work of West and Trujillo in the late 1970s, by co-polymerization or by careful choice of side groups that high molecular weight, soluble materials could be obtained [59]. From then on, there followed an explosion of interest in the area of polysilanes. The synthetic strategies most favored have, however, remained almost unchanged since the very earliest developments: Wurtz coupling of dichlorosilanes in an inert hydrocarbon solvent still remains the most effective method of Si–Si bond formation. The mechanism of chain growth has been studied intensely [56]. Various

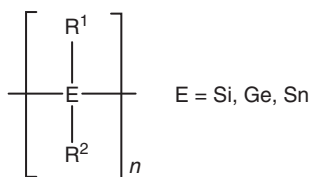


Figure 14.8 The backbone of Group 14 polymers.

alkali metals have been tried as reducing agents including Li, K, and Na–K alloy, although these often cause problems of over-reduction or side-chain cleavage [60]. The use of more polar solvents or donors tends to result in shorter chain lengths. Alternative synthetic routes to polysilanes include catalytic dehydrocoupling of Si–H bonds, catalyzed by early transition metals [61] and ring-opening polymerization of cyclic polysilanes [62]. However, these methods have yet to approach the versatility and high molecular weights achieved through sodium-mediated Wurtz coupling.

The corresponding germanium and tin polymers have also been targets of interest due to the even greater levels of σ -conjugation and lower band gaps these systems exhibit [63]. Similar approaches of using Wurtz coupling tend to yield only lower molecular weight materials although high molecular weight germanes have been reported [63]. Most advances in this field have been, however, in the use of transition metal-catalyzed dehydrocoupling [57]. Early breakthroughs were made by Tilley using Zr catalysts under mild conditions to generate high molecular weight polystannanes [64].

14.2.3

Group 14–Group 14 Double Bonds (E=E)

14.2.3.1 Structure and Bonding

The heavier congeners of Group 14 forming Double-bonded species of the heavier congeners of Group 14 have only been successfully prepared since the early 1980s due to the general lack of stability of these species and the increasing preference for σ - over π -bonding as the group is descended. This mirrors the general trend expected for multiply bonded heavier elements such as those in group 15, where the increasing size of p orbitals and consequent poorer orbital overlap give rise to rather weak π -bonds. However, unlike the multiply bonded species of Group 15 those containing Si–Pb exhibit vastly different patterns of structure and reactivity from C than might be expected purely on the basis of an increase in orbital size; bond lengths between multiply bonded atoms are often little different from, and in some cases even longer than their singly bonded counterparts and are subject to facile dissociation and high reactivity. Given that the structures and behavior of these more exotic multiply bonded species have challenged previous notions of what exactly constitutes a chemical bond, the previous descriptions of clearly defined single, double, and triple bonds no longer become applicable in the face of such widely differing behavior. Assignments of multiple bonds in this area have been primarily made based upon the stoichiometry of the species involved rather than a consideration of bond strength and chemical properties. The area of Group 14 heavy alkenes [65] and p-block multiple bonding in general has been reviewed extensively [65, 66].

The first example of a homoatomic double-bonded group using heavier elements from the group 14 family was the famous distannane species $R_2Sn=SnR_2$ (**38**) [$R = CH(SiMe_3)_2$] presented by Lapert and co-workers in 1976 (Figure 14.9) [67]. This was found to have a *trans*-bent geometry with pyramidal Sn centers and a deviation from planarity of 41° . The observed Sn–Sn distance in the solid state [$2.768(1) \text{ \AA}$] was found to be only slightly shorter than a Sn–Sn single bond. The compound was also found to dissociate readily in solution into R_2Sn stannylene monomer units (as shown in Figure 14.9).

The bonding pattern and behavior were explained by a bonding model consisting of two donor–acceptor interactions from an sp^2 -type lone pair into the vacant p orbital on the Sn atoms, a manifestation of the inert-pair effect which reduces involvement of s electrons in bonding (Figure 14.10) [68].

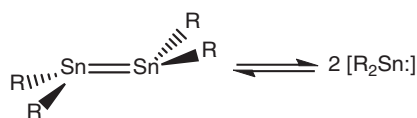


Figure 14.9 *Trans*-bent structure of **38** [$R = CH(SiMe_3)_2$] and its dissociation into monomers in solution.

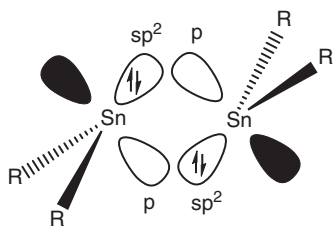


Figure 14.10 The bonding in distannanes like **38**.

The initial explanation for the unusual *trans*-bent geometries of heavier Group 14 alkenes, that of a donor–acceptor pair, has since been extended with the help of calculations into a more general model correlating increasing levels of orbital mixing with more distorted geometries (Figure 14.11). Generally speaking, as the group is descended, there is an increasing tendency for π -bonding molecular orbitals to mix with an antibonding σ^* set. Although this results in a lowering in energy of the π -bonding combination, there is also a move toward non-bonding, lone-pair character as well as a bending of the R groups. Also, there is a weakening of the σ -bonding [68b, 69].

The range of distannenes since prepared shows similar trends in structure and solution behavior [65, 66] in addition to one notable exception. The trialkylsilyl derivative $[(^t\text{BuMe}_2\text{Si})_2\text{Sn}]_2$ (**39**) shows an almost planar geometry about the Sn centers and the shortest Sn=Sn bond yet reported [2.6682(7) Å] and retains its dimeric nature in solution [70]. These strong differences have been attributed to the electronic effects of the silyl substituent in reducing the singlet–triplet energy gap, favoring an alkene-like bonding situation [71].

The first stable $\text{R}_2\text{Si}=\text{SiR}_2$ derivative was prepared by West (R = Mes) [72] and since then, the library of known compounds of this type has increased rapidly to include many examples of linear, cyclic, and conjugated disilylenes [65]. Si–Si bond distances vary between 2.132(2) and 2.360(2) Å and in contrast to the Sn derivatives are generally significantly shorter than the corresponding single bonds and also display planar or almost planar geometries, with reduced bending angles (0–13°). The silyl species also show a much reduced tendency to dissociate into monomers in solution, and thus overall bear more similarities to alkenes in bonding and chemical properties than the weak donor–acceptor interactions prevalent in distannyls.

The digermes $\text{R}_2\text{Ge}=\text{GeR}_2$ have more in common with their distannene counterparts, displaying *trans*-bent geometries, corresponding to a reluctance to undergo hybridization [65, 66]. Some examples with trialkylsilyl substituents have shorter Ge=Ge bonds and retain planar structures more reminiscent of the silenes, as does the lithium-substituted derivative $[(1,4\text{-dioxane})\text{Et}_2\text{OLi}_2\text{Ar}^*\text{GeGeAr}^*]$ (**40**) (R = $\text{C}_6\text{H}_3\text{-2,6-Mes}_2$) which has a planar Li_2Ge_2 core [73]. Like the distannenes, most digermenes display a tendency toward dissociation in solution to monomeric R_2Ge units.

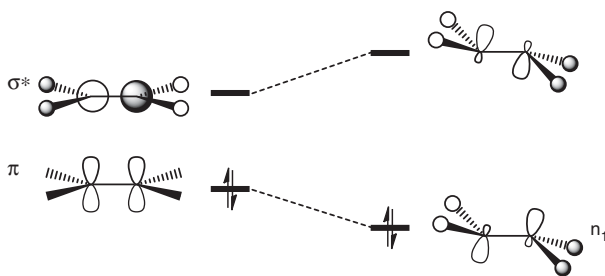


Figure 14.11 Refined bonding model for E=E bonded dimers.

The final members of the heavy alkene family, the diplumbenes R_2PbPbR_2 only appeared in 1994 following the expected trend, showing *trans*-bent pyramidal geometries and a further reluctance to retain their dimeric structures in solution. $Pb \cdots Pb$ separations are even longer than the corresponding $Pb-Pb$ single bonds (e.g., 2.844(4) Å in Pb_2Ph_6) [74] and vary widely from 2.9033(9) to 4.129 Å [65, 66]. In the case of such weak bonding, it would make more sense to consider lead derivatives as weakly associated R_2Pb monomers rather than formally double-bonded.

Moving on from symmetric $R_2E=ER_2$ systems, the diversity of structural types discovered has increased rapidly, most notably in the area of silicon chemistry, where a large number of conjugated and cyclic systems have been characterized [65, 66]. Some examples of these are given (Figure 14.12). Several trisilacyclopropenes and tetrasilacyclobutenes have been prepared. These tend to display more planar geometry at the silicon centers, but because of the ring strain inherent in these systems, frequently undergo photochemically induced ring rearrangements into linear species, although the reverse reaction, that is, cyclization to form rings has also been reported. The germanium and tin analogs of the cyclopropenes have also been reported, although examples are less numerous.

The unusual pentasila-dispiro compound **43** is worthy of note, not least because of the high degree of ring strain present, but also that the two three-membered rings are not perpendicular to each other as might be expected, but rather inclined at 78.3° [75]. A number of derivatives of sila-butadienes have been prepared which show rich reaction chemistry with small inorganic molecules, often giving rise to further heterocyclic products (Figure 14.13) [76]. The silaallene **45** is unusual when compared to the respective carbon analogs, in that the central Si_3 unit is not linear as might be expected but bent at an angle of 137.2(1)° [77]. The all-Ge derivative has also been prepared as have the mixed Si/Ge species [78]. The nature of bonding in these compounds to the central E(0) atom is still a matter of considerable debate.

Some recent additions to the series of doubly bonded Group 14 species also include the unusual compounds $[L \rightarrow E = E \leftarrow L]$ [$E = Si, Ge; L = C(NDippCH)_2$] (**53**) which contain the dimeric E_2 unit with both tetrel atoms in the zero oxidation state, stabilized by *N*-heterocyclic carbene donor groups. The small $L-Si=Si$ angles in the silicon derivative (93.4°) imply a high degree of p-orbital involvement in bonding, with minimal contributions from s electrons, which remain localized at the E centers [71, 79].

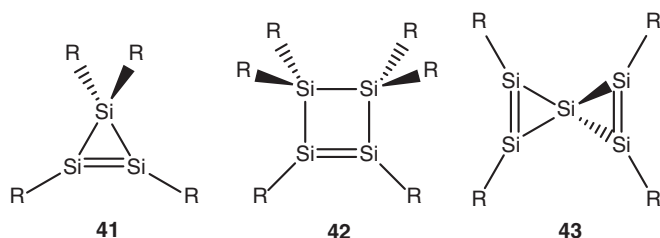


Figure 14.12 Some examples of cyclic silylenes.

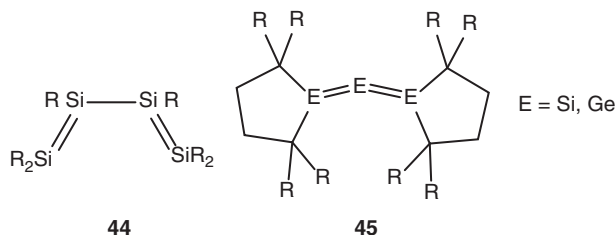
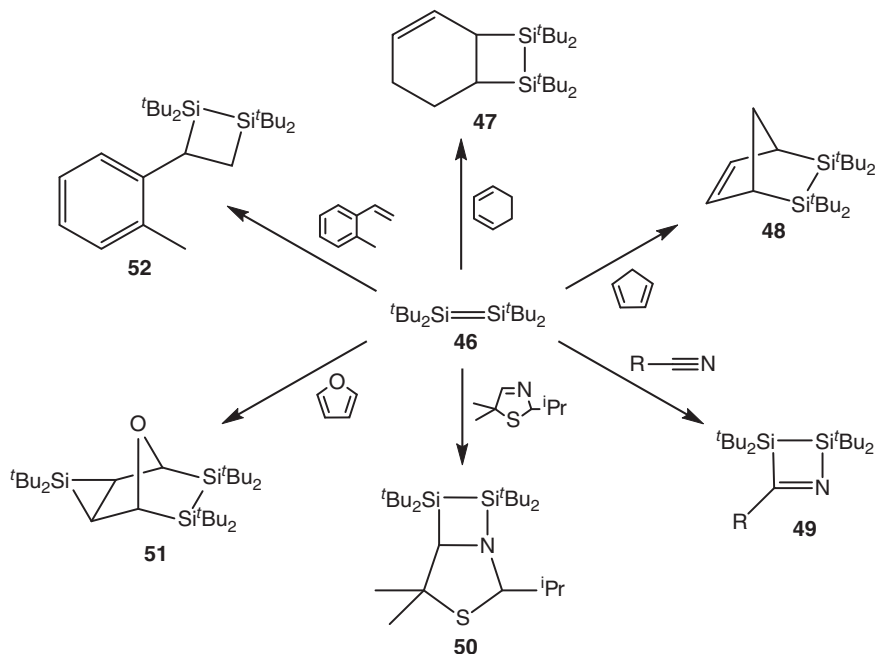


Figure 14.13 Examples of sila-butadienes.

14.2.3.2 Reactivity of Si=Si and Ge=Ge Bonds

Of the series of heavier Group 14 double-bonded species, the silyl derivatives are somewhat unique in retaining their double-bond character while in solution. As such, they are subject to a plethora of cycloaddition reactions with unsaturated organic molecules, forming both [2+2] and [2+3] cycloadducts with much enhanced reactivity over their carbon analogs (Scheme 14.3) [65, 80]. The digermenes also undergo similar, although less extensive cyclisation reactions, although their increased tendency to dissociation means reactivity proceeds via isolated R_2Ge units, often through insertion into multiple bonds to generate cyclopropene-type ring structures. The preference to react as isolated R_2E units is even stronger for the tin and lead derivatives due to the ever-increasing trend to exist as monomeric units in solution.



Scheme 14.3 Cycloaddition reactions of silylenes as exemplified by the silylene **46**.

The ditetrenes $R_2Si=SiR_2$ (R =aryl) are subject to reductive cleavage of the Si–R bond by reaction with alkali metals resulting in the formation of $R_2E=ERM$, the silicon equivalent of vinyl anions [76]. Several linear and cyclic derivatives have been prepared and show an increase in the $E=E$ bond length and a strong localization of charge over one silicon atom rather than over the whole framework [81]. Dianionic species $[ArEEAr]^{2-}$ have been prepared for $E = Ge, Sn$ by reduction of the dihalides $[ArE(Cl)]_2$ by alkali metals [82]. Like their neutral counterparts, these display strongly *trans*-bent geometries.

14.2.4

Group 14–Group 14 Triple Bonds ($E\equiv E$)

The description of the bond order within the Group 14 alkyne analogs is even more contentious than those of the doubly bonded derivatives. It is only fairly recently that the series of REER species has been prepared and characterized. They are valence-isoelectronic with the triply bonded dianion $[Ar^*_2Ga_2]^{2-}$ (**54**) ($Ar^* = 2,6\text{-Dipp-C}_6\text{H}_4$) first synthesized by Robinson [83], which provoked vigorous

debate about the precise nature of the bonding and what could formally be considered a triple bond, considering the conflicting conclusions reached by different research groups on whether s electrons were significantly involved in bonding, or isolated on Ga centers as non-bonding lone pairs.

The preparation of the complete series of Group 14 alkyne analogs has allowed a detailed comparison of bonding and structural trends on descending the group. As with the series of doubly bonded alkene derivatives, all the corresponding REER species display varying degrees of *trans*-bent geometries with an increasing tendency toward non-linearity with increasing atomic number.

The initial bonding model provided by Robinson to explain the bent geometry in **54** was a donor–acceptor interaction, similar to Lappert's heavy alkenes but with sp -hybridization (rather than sp^2) and an additional π -bond formed from overlap of p orbitals each containing one electron (Figure 14.14). As in the case with the series of heavy alkenes, a more generalized bonding scheme links the increasing deviation from linearity of the REER unit with a greater degree of π – σ^* orbital mixing as the group is descended and a decrease in formal EE bond order toward single bonds and localized lone pairs [84, 85]. The completion of the Group 14 series allows for a detailed comparison of the changing geometry and bond order with increasing atomic number [66c]. In general, the heavier alkynes all require extremely bulky ligands to provide steric protection to the highly reactive E_2 unit. The Ge, Sn, and Pb derivatives are prepared via reduction of the $ArE^{II}Cl$ halides. The heaviest member of the series $Ar^*PbPbAr^*$ (**55**) ($Ar^* = 2,6\text{-Dipp-C}_6\text{H}_4$) was prepared first in 2000 by Power [86] and shows an extreme bending angle (α) of $94.26(4)^\circ$ at the metal center and a long Pb–Pb distance of $3.1881(1) \text{ \AA}$, even greater than typical Pb–Pb single bonds ($2.844(4) \text{ \AA}$ in Pb_2Ph_6 [73]). Such geometry is incompatible with Robinson's proposed donor–acceptor triple-bond scheme and the presence of near 90° bond angles can only be interpreted as a single bond between unhybridized Pb centers. The lead derivative was followed by the Ge and Sn species with various bulky ligands attached (often 2,6-disubstituted aryls) [87]. In contrast to the case of the lead derivative, these usually have E–E bond distances shorter than corresponding single-bond lengths, indicative of significant multiple bonding. In the case of Ge, these are typically at around $2.26 \text{ \AA}$ ($\alpha \sim 128^\circ$), consistent with a double bond whereas Sn exhibits more bending ($\alpha \sim 124^\circ$) and relatively longer bonds ($3.06 \text{ \AA}$) as might be expected for partial multiple-bond character. In all cases, the bond lengths and bending angles are highly sensitive to subtle changes in the organic ligands. The first stable disilyne $RSi\equiv SiR$ (**56**) ($R = Si^iPr[CH\{SiMe_3\}_2]_2$) was prepared by Sekiguchi in 2004 [88]. Although having a slight *trans*-bent structure [$Si\equiv Si-Si = 137.44(4)^\circ$], the silyl derivative shows an extremely short $Si\equiv Si$ bond [$2.0622(9) \text{ \AA}$], and thus has more in common with carbon-based alkynes which have a higher degree of s-orbital involvement in bonding than the other members of the group. The Si, Ge, and Sn alkyne analogs can all be reduced to the corresponding double-bonded radical dianions $[REER]^{2-}$ (**57**), which have been mentioned above [76], as well as to radical monoanions (**58**) where EPR spectroscopy indicates a delocalization of the unpaired electron about the E_2 core [89]. The radical dianions all show an increase in *trans*-bending and increased E–E separation upon reduction consistent with lowering of bond order by population of π^* antibonding orbitals. The recent access to the heavier Group 14 alkynes has opened up a rich reaction chemistry (as exemplified in Scheme 14.4 for the $Ge\equiv Ge$ species **59** [$Ar = C_6H_3-2,6\{C_6H_3-2,6\text{-}^iPr_2\}_2$]) [85]. Transformations include cycloadditions with unsaturated organic groups [90], donation from Lewis bases [91], and E–E bond cleavage with diradical formation [92]. Recent examples of formation of π -donor complexes with

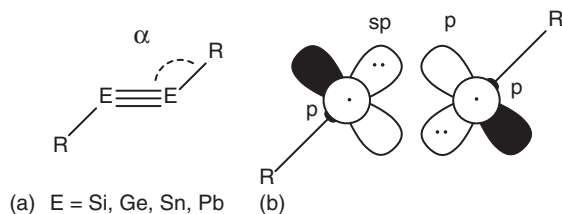
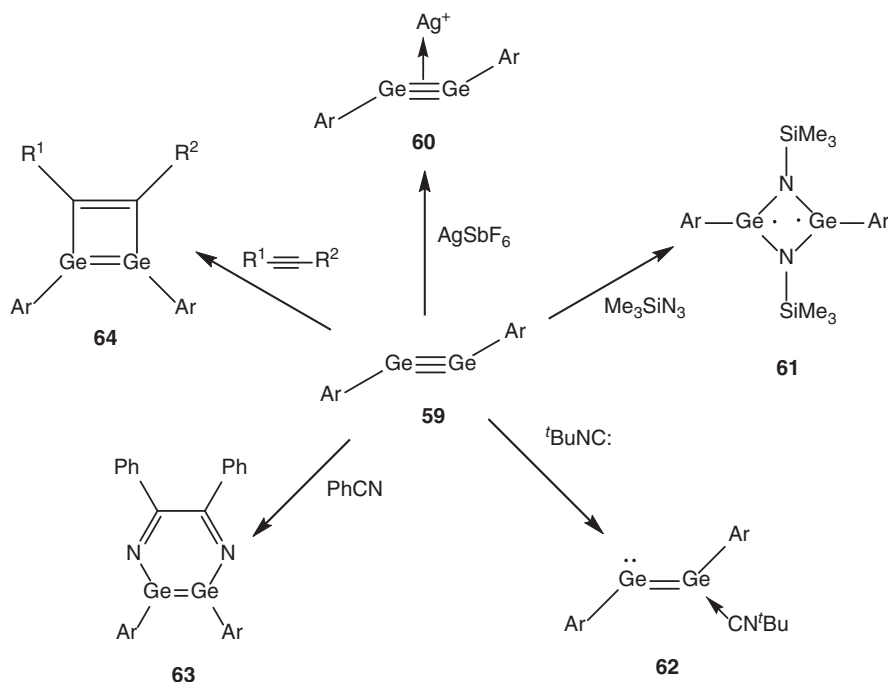


Figure 14.14 (a) *Trans*-bent arrangements of Group 14 REER and (b) Robinson's bonding model for **54**.



Scheme 14.4 Reactions of the germyne **59**.

transition metals include the Ge–Ag(I) species **60** reported by Power [93] and the related Si–Pd(II) and Si–Pt(II) complexes prepared by Ishida and Iwamoto [94].

14.3

Heteroatomic Metal–Metal Bonds

14.3.1

s-Block Metal–Group 14 Metal Bonds

Bonds between s block and Group 14 metals are frequently observed in a large number of compounds containing organometallic Group 14 anions and are especially common in the structures of Group 14 Zintl and related compounds (discussed previously in Section 14.2.1). The bonding and structures in s-block organometallics containing C–metal bonds (such as n BuLi and t BuLi) have been a major area of study for several decades because of their ubiquitous use as sources of organic anions (R) and as strong bases for deprotonation reactions. Less well developed has been the analogous chemistry of the heavier congeners of Group 14, especially those of Ge, Sn, and Pb [95]. While it is recognized that bonds between Group 14 elements (E = Si–Pb) and Group 1 and 2 metals (M) will be predominantly ionic, one of the interesting background issues in this area is the expected increase in covalency of E–M bonds as Group 14 is descended (as a result of the decrease in the electronegativity of the elements). A further issue is that of orbital use by the Group 14 atoms in these compounds, particularly the increase in the s character of the lone pair of electrons carried by the Group 14 elements within the E–Li bonds.

In addition to Zintl compounds, the main class of structurally characterized molecular species containing E–M bonds are of the type $[(R_3E)_n ML_m]$ (where L is a Lewis base donor ligand). These are directly analogous to organometallic C–M bonded complexes and contain R_3E^- anions.

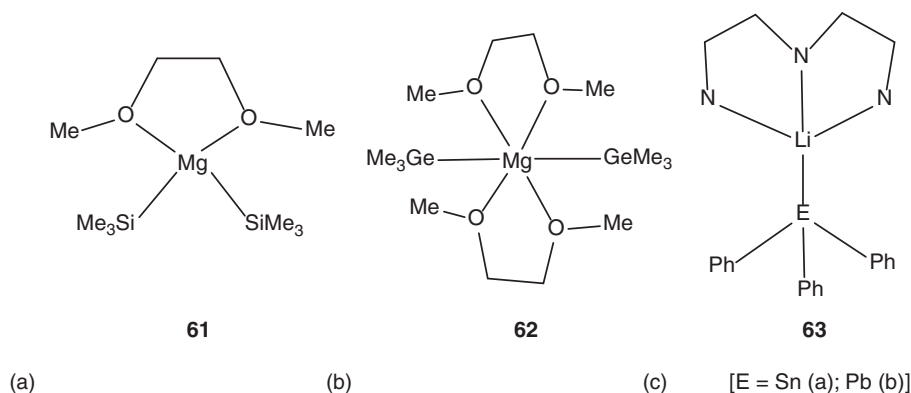


Figure 14.15 The structures of the first structurally characterized examples of E–M bonded compounds of the type $[(R_3E)_nML_m]$ reported.

The first representative of this family of compounds was the ion-paired Mg–Si bonded complex $[(DME)Mg(SiMe_3)_2]$ (**61**) (DME = dimethoxyethane) (Figure 14.15a) reported by Oliver and co-workers in 1977 [96]. Shortly after, the first example of a Ge–M bond was also published (complex **62**, Figure 14.15b) [97]. Not surprisingly, since the strength of C–E bonds decreases significantly going down Group 14 and R_3E^- anions become less thermally stable, bonds between s-block metals and the heavier Group 14 elements become far less common and only a few Sn–M [98] and Pb–M [99] (Figure 14.15c) bonded compounds have been reported to date. An example of this instability is seen in the case of the Pb–Li bonded complex **63b**, which gradually decomposes into Ph_4Pb at room temperature. Like the more conventional C–M bonded counterparts, the potential for oligomerization in these complexes increases as the extent of Lewis base solvation of the M^+ or M^{2+} cations and/or the steric bulk of the R groups decrease. Good examples of this are seen in the structures of the unsolvated trimer $[Me_3SiLi]_3$ (**64**) [100] and the tetramer $[(Me_3Si)Me_2SiLi]_4$ (**65**) [101], which adopt the expected ring and cubane arrangements in the solid state (respectively). A survey of the Cambridge Crystallography Data Base (this review) reveals that Si–M bond lengths in molecular Group 14 complexes of this type are normally at or above the sum of the atomic radii of Si and M, whereas, other E–M bonds involving the heavier Group 14 elements are usually shorter than the expected covalent bond lengths¹⁾.

A particularly interesting feature in this area is the way in which the hybridization of the Group 14 R_3E^- anions varies on descending the group, showing a progressive decrease in s/p mixing of the valence orbitals. This variation is of course exactly the same as that found for the neutral, isoelectronic triorgano-Group 15 molecules R_3E , however, the effect is particularly dramatic in Group 14. Ion-separated or -paired Ph_3C^- anions, for example, are planar about their central sp^2 hybridized C-atom, in which the lone pair is housed within an orbital with p character [102]. In contrast, ion-separated R_3E^- anions (containing no E–M bonds) [103, 104] and ion-paired R_3E^- anions of the heavier elements are *all* pyramidal, suggesting far greater s character in the lone-pair orbitals of the

1) Search of the CCDC (January, 2014) (values in Å): Si–Li range 2.51–2.95 (mean 2.70) ($\Sigma_{Si/Li} = 2.55$), Si–Na range 2.88–3.47 (mean 3.07) ($\Sigma_{Si/Na} = 2.90$), Si–K range 3.27–3.94 (mean 3.68) ($\Sigma_{Si/K} = 3.30$), Si–Rb range 3.44–3.98 (mean 3.68) ($\Sigma_{Si/Rb} = 3.45$), Si–Cs (no examples). Ge–Li range 2.42–2.76 (mean 2.70) ($\Sigma_{Ge/Li} = 2.70$), Ge–Na 2.97 ($\Sigma_{Ge/Na} = 3.05$), Ge–K range 3.35–3.42 (mean 3.38) ($\Sigma_{Ge/K} = 2.55$), Ge–Rb 3.48 ($\Sigma_{Ge/Rb} = 2.68$), Ge–Cs

3.77 ($\Sigma_{Ge/Cs} = 3.85$), Sn–Li range 2.74–3.14 (mean 2.87) ($\Sigma_{Sn/Li} = 2.70$), Sn–Na 3.07–3.08 (mean 3.07) ($\Sigma_{Sn/Na} = 3.25$), Sn–K range 3.55–3.72 (mean 3.66) ($\Sigma_{Sn/K} = 3.65$), Sn–Rb (no examples), Sn–Cs (no examples), Pb–Li 2.85–2.95 ($\Sigma_{Pb/Li} = 3.25$), Pb–Na (no examples), Pb–K range 3.59–3.69 (mean 3.63) ($\Sigma_{Pb/K} = 4.00$), Pb–Rb (no examples), Pb–Cs (no examples).

Group 14 atoms homologs. Although there are as yet no complete series of structurally characterized complexes of the type $[(R_3E)_n ML_m]$, which would allow a full analysis of the trend in pyramidalization of a specific R_3E^- anion as Group 14 is descended (for a given s-block metal (M)), comparison of the key C–Sn–C and C–Pb–C bond angles in the homologous complexes **63a** (mean 96.1°) [97] and **63b** (mean 94.3°) (Figure 14.15) [98], as well as in other closely related Si and Ge complexes of this type [105], indicates a trend toward 90° (i.e., predominant use of p-orbitals in the σ -bonding). Further, comparison of the C–Sn–C bond angles in **63a** with those found in the “naked” Ph_3Sn^- anion (mean 97.9°) [103] reveals only a small compression of the anion geometry, indicative of the weakness of the Sn–Li bonding involved.

Beyond the chemistry of simple complexes of the s-block elements containing R_3E^- anions is a very extensive and diverse range of species which are far too numerous to describe in detail here. Some interesting examples of other E–M bonded compounds are shown in Figure 14.16. Mentioned previously (in Section 14.2.3) are multiply bonded compounds containing $[REER]^{2-}$ anions which commonly contain E–M interactions with a range of alkali metals (M). Such an example is $[2,6-Trip-C_6H_2]_2Ge_2Na_2$ (Trip = 2,4,6-*i*-Pr₃C₆H₂) (**66**) (Figure 14.16a) in which the two unsolvated Na⁺ cations bridge the Ge=Ge bond [82]. The complex $[(^iPr_3Si)_2Si(Li\cdot 2thf)_2]$ (**67**) (Figure 14.16b) [106] is also of particular interest in that it contains a rare example of an R_2E^{2-} dianion (isoelectronic with an amide anion), while the series of homologs $[(Me_3Si)_2(SiMe_2)_n(SiMe_3)_2]\{K(18-crown-6)\}_2$ (**68**) [$n = 0$ (Figure 14.16c), 1, 2, 3] [107, 108] (and related compounds) contain $\{[(Me_3Si)_2(SiMe_2)_n(SiMe_3)_2]^{2-}$ dianion chains. Several examples of heteroatom cages, like $[Sn_3(P^tBu)_4Na]\{Na\cdot PMDETA\}_2$ (**69**) [PMDETA = Me₂NCH₂CH₂)₂NMe] [109], have also been reported which contain E–M bonds at their peripheries (Figure 14.16d). Also worthy of mention are heavier Group 14 cyclopentadienide analogs like $\{[Ph_4C_4Pb]Li(thf)_4\}^+ [Li(thf)_4]^-$ (**70**) in which the $[Ph_4C_4Pb]^-$ anion is π -bonded to the Li⁺ cation within the anion unit (Figure 14.16e) [110, 111].

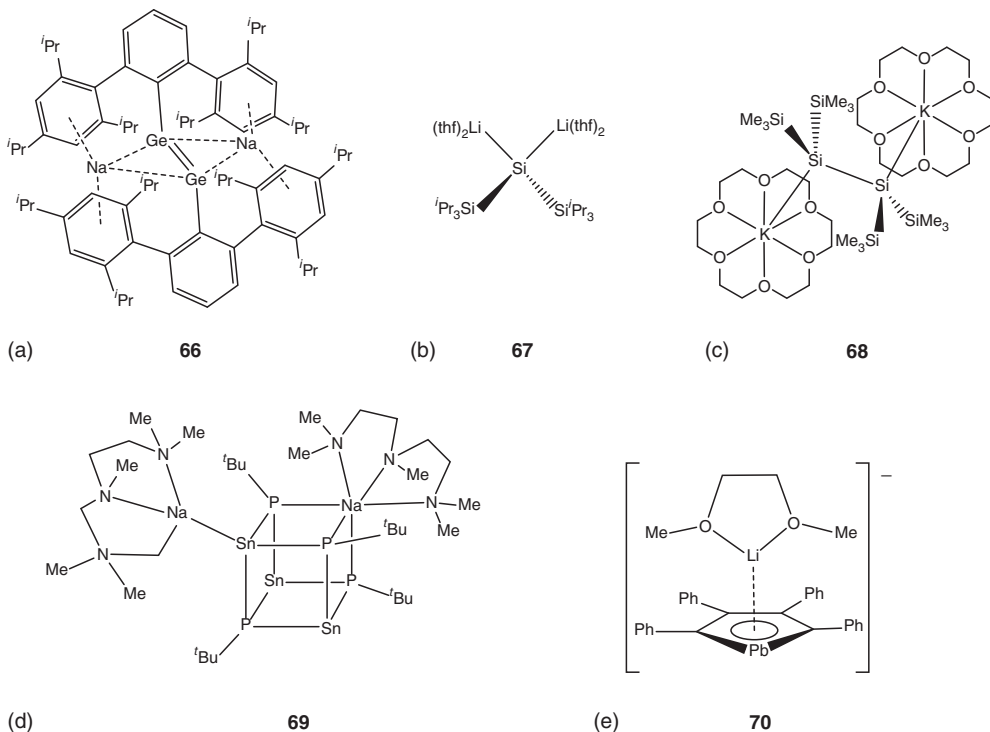


Figure 14.16 Examples of structurally characterized complexes with more elaborate bonding arrangements.

14.3.2

p-Block Metal–Group 14 Bonds [Group 13 (Al–Tl and Group 15 (As–Bi)]

This section will focus mainly on bonds between the most metallic Group 14 elements (Ge, Sn, and Pb) and the most metallic Group 13 (Al, Ga, In, Tl) and 15 (As, Sb, and Bi) elements. While a very large number of Si–Group 13 and 15 bonded compounds have been investigated in the past 30 years, almost all of these contain silyl-family ligands of the type R_3Si- (R = alkyl, aryl, or R'_3Si), which play a conventional role as stabilizing, sterically demanding ligands in this area.

The first examples involving bonds between the most metallic elements in Group 13 and 14 were reported by Veith in 1985. The imido Sn(II) or Ge(II) cubanes $[EN^tBu]_4$ (**71**) coordinate two molecules of $AlCl_3$ to give the donor–acceptor adducts $(AlCl_3)_2[EN^tBu]_4$ (**72**) (Figure 14.17a.) [112]. Further coordination to $AlCl_3$ is prevented presumably on steric grounds, partly as a result of the expansion and distortion of the E_4N_4 frameworks resulting from coordination to the Al^{III} centers. Like the silyl counterparts, ligands of the general type R_3Ge- have often been employed as supporting ligands in a range of arrangements. An interesting case is that of the $[(Ph_3Ge)_3Ga]Ga^-$ anion (**73**), obtained from the reaction of sonochemically prepared “GaI” with Ph_3GeLi . The anion contains a linear Ga_3 fragment in which the central Ga atom is a two-coordinate (Figure 14.17b) [113]. Another notable example of this type is the $[(^tBu_2MeSi)_2Ge]_2In^-$ anion (**74**) which is valence-isoelectronic with the allyl anion (Figure 14.17c) [114]. Triorganogermyl groups (R_3Ge-) have also been employed as supporting ligands in various cluster compounds, such as in the two metalloid clusters $[Ga\{Ge(SiMe_3)_3\}]_4$ (**75**) and $[Ga_{22}\{Ge(SiMe_3)_3\}_8]$ (**76**) [115].

Other examples of Group 14–Group 13 bonds are also worthy of mention. The reactions of solutions containing Al^I halides with Cp^*_2E (E = Ge, Sn; Cp^* = C_5Me_5) give a mixture of products which include the unusual $Ge-$ and $Si-Al$ bonded species $[E(AlCl_2 \cdot OEt_2)]_4$ (**77**), containing a central, tetrahedral E atom coordinated by four $AlCl_2 \cdot OEt_2$ fragments [116]. A particularly interesting area of investigation has been the ligand chemistry and reactivity of gallium(I) *N*-heterocyclic carbene analogs like $[Ga\{N(Ar)C(H)_2\}]^-$ (Ar = 2,6- i -Pr $_2$ - C_6H_3) with heavier Group 14 metals [117, 118]. For example, 1 : 1 stoichiometric reactions of the salt **78** (Scheme 14.5) with the alkene analogs $[Ar_2E=EAR_2]$ give compounds **79**, which contain $Ga-E$ as well as $K-E$ bonds, while 4 : 1 reaction gives a bis-substituted Sn^{II} center in the anion of **80**. DFT calculations confirm the presence of single $Ga-E$ bonds in these species, with the bonds being formed using largely Sn *p* orbitals and *s* to *sp* orbitals from Ga. There is no back-bonding of the lone pairs on *E* into the vacant Ga orbital of the carbene-like ligand.

Moving to Group 15, a common class of Group 15–Group 14 bonded compounds are cages containing RE' ligands (E' = Group 15). Neutral oligomeric cages of the type $[E(AsR)]_n$ (E = Ge, Sn, Pb) are well known in this area with n = 4 [119], 6 [120] or 7 [121]. These arrangements are well known for analogs containing the lighter congeners (N and P) in Group 15. The arsenic cages are normally prepared by the reactions of Group 14 dichlorides with $RAs(SiMe_3)_2$ (with the elimination of Me_3SiCl) or with $RAsLi_2$ (with the elimination of $LiCl$). Examples of each are shown in Figure 14.18. (i.e., the cages **81**, **82**, and **83**). An interesting situation, however, occurs in an attempt to extend the synthesis of cage **83** (obtained from the reaction of $(^iPr_3Si)As(SiMe_3)_2$ with $SnCl_2$) to Sb in the

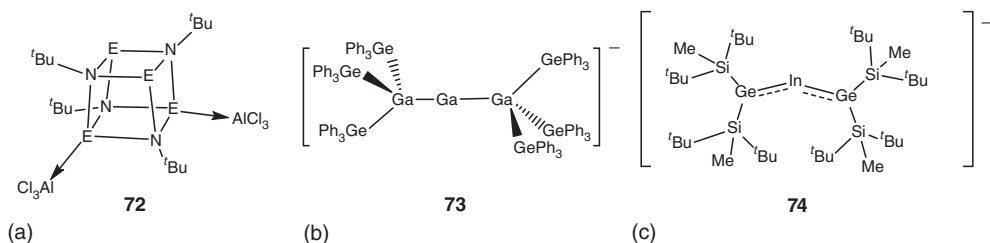
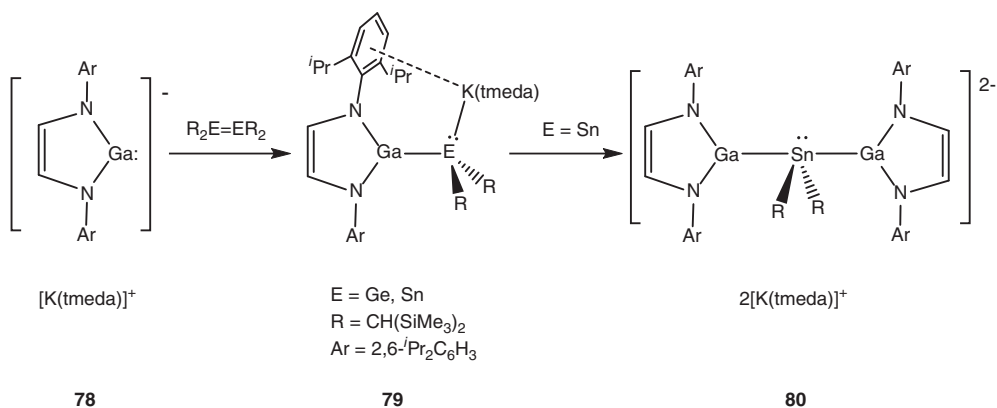


Figure 14.17 (a) Structure of the adduct $(AlCl_3)_2[EN^tBu]_4$ (**72**), (b) the $[(Ph_3Ge)_3Ga]Ga^-$ anion (**73**), and (c) the $[(^tBu_2MeSi)_2Ge]_2In^-$ anion (**74**).



Scheme 14.5 An example of the coordination of an *N*-heterocyclic carbene analog to a Group 14 center, generating single Ga–E bonds.

reaction of $PbCl_2$ with $(i\text{-Pr}_3\text{Si})\text{Sb}(\text{SiMe}_3)_2$. The product is the $P_4\text{Sb}_6$ cage $[(i\text{-Pr}_3\text{Si})\text{Sb}]_6\text{Pb}_4$ (**84**) in which Sb–Sb bond formation has occurred alongside the formation of Sb–Pb bonds [119b]. Another rare occurrence of the Sb–Pb bond is found in the sandwich compound $[\eta^5\text{-Cp}^*\text{Pb}\{\eta^5\text{-C}(i\text{-Bu})_2\text{P}_2\text{Sb}\}]$ (**85**) [122], but here with longer range (3.3065(12) Å) interactions than seen in **84** (mean 2.89 Å) which reflect the weak π -bonding nature of the cyclopentadienide-like diphosphastibolyl $[\text{C}(i\text{-Bu})_2\text{P}_2\text{Sb}]^-$ ligand. Closely related cage compounds to the neutral $[E(\text{AsR})]_n$ oligomers are cages containing $[E_x(E'R)_y]^{n-}$ anions, such as in the cages $[\{\text{Sn}_4(\text{AsSi}^i\text{Pr}_3)_6\}\text{Li}_4\cdot(\text{OEt}_2)_2]$ (**86**) (Figure 14.18e) [121] and $[\{t\text{-BuGe}(\text{AsSi}^i\text{Pr}_3)_3\}_2\text{Li}_6]$ (**87**) [123], which are constructed from the cyclic $[\text{Sn}_4(\text{AsSi}^i\text{Pr}_3)_6]^{4-}$ dianion and the tripodal $[t\text{-BuGe}(\text{AsSi}^i\text{Pr}_3)_3]^{3-}$ trianion, respectively. Analogs of these types of arrangements also exist for N- and P-based counterparts [124] and it is interesting to note that the cyclic dianion unit of **86** is valence-isoelectronic and isostructural with neutral phosph(III)azanes of the type $[P_4(\text{NR})_6]$ [125].

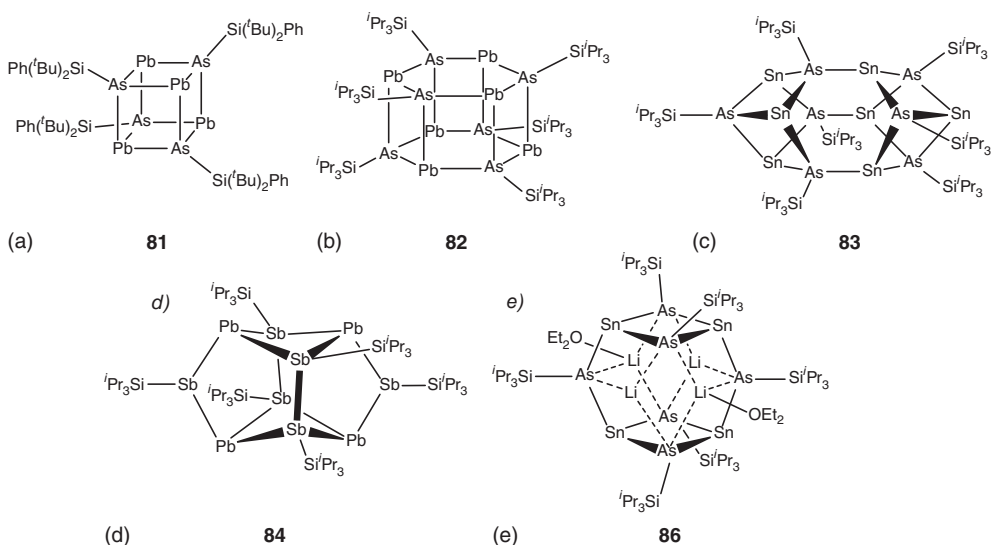


Figure 14.18 Examples of neutral and anionic E–E' bonded cages (a) **81** [6], (b) **82** [7b], (c) **83** [8], (d) **84** [6], and (e) **86** [8].

Also worth mentioning in this area are several notable examples of compounds in which R_3E^- or R_2E^{2-} ligands have been used to stabilize electron-precise Group 15 metal–metal bonded arrangements. A simple example is the distibane $[(Me_3Sn)_2Sb]_2$ (**88**) in which the Sb–Sb bond is supported by Me_3Sn –ligands [126], while a more elaborate arrangement is seen in the structure of $[Bi_8\{Sn(SiMe_3)_3\}_6]$ (**89**), a product of the reaction of $BiBr_3$ with $[(Me_3Si)_3SnLi \cdot 2thf]$ and containing a bicyclic Bi_8 unit composed of two fused Bi_5 rings [127]. Further, interesting examples are obtained by the deprotonation of germanes with organo-bismuth reagents. The deprotonation of $[(C_6F_5)_2GeH_2]$ with Me_3Bi gives the unusual Ge–Bi bonded compound $[Bi_2\{\mu-Ge(C_6F_5)_2\}_3]$ (**90**), having a trigonal bipyramidal arrangement of heavy atoms which is supported by $[(C_6F_5)_2Ge]^{2-}$ ligands (Figure 14.19a) [128]. While reaction of Et_3Bi with the Ge–Ge bonded precursor $[(C_6F_5)_2Ge(H)Ge(H)(C_6F_5)_2]$ gives the related compound $[Bi_2\{(C_6F_5)_4Ge_2\}_2]$ (**91**) in which the Bi–Bi bond is stabilized by two $[(C_6F_5)_2GeGe(C_6F_5)_2]^{2-}$ ligands (Figure 14.19b) [129].

14.3.3

f-Block Metal–Group 14 Bonds (including Sc, Y, La)

The chemistry of lanthanide and actinide metals containing non-classical, metal-based ligands is still relatively undeveloped compared to transition metal compounds of this type (see section 14.3.4), as highlighted in recent reviews by Liddle *et al.* [130, 131]. Generally speaking, the bonding is of two types, polarized covalent and donor–acceptor. Figure 14.20 shows some examples of the types of structurally characterized compounds that have been reported. The first example of an organolanthanide complex to be structurally characterized that featured a lanthanide–Group 14 bond to a heavier element was $[(\eta^5-C_5H_5)_2Ln(SiMe_3)_2]^- [Li(DME)_3]^+$ ($Ln = Sm, Lu$) (**92**) (the anion of which is shown in Figure 14.20a), obtained from the reactions of $[Me_3SiLi]$ with $[(\eta^5-C_5H_5)_2LnCl \cdot NaCl \cdot 2DME]$ [132, 133]. Later, the first Sn–Ln bonded $[(tBuCH_2)_3Sn]_2Yb \cdot 2THF$ (**93**) compound was obtained (Figure 14.20b), the presence of the Yb–Sn bond was further supported by the observation of satellite coupling to ^{117}Sn (8254 Hz) and ^{119}Sn (8627 Hz) in the ^{171}Yb NMR spectrum [134, 135]. Typical of compounds containing covalent polar bonds of this type, the Group 14–lanthanide bonds in **92** and **93** are shorter than expected for purely covalent bonds (i.e., the sum of the atomic radii). The first example of such a lanthanide complex containing a dative bond was the silylene compound $[(C_5Me_5)_3Ln\{Si(NCH_2^tBu)\}-1,2-C_6H_4]$ ($Ln = Y, Yb$) (**94**) (Figure 14.20c) which was prepared by mixing the *tris*-metallocene with the silylene in toluene [136, 137]. The Si–Ln bonds in silylene complexes of this type are at or marginally above the sum of the covalent radii for the respective elements involved. Rare examples of a donor–acceptor Sn–lanthanide bonds have been seen recently in the structures of the trimetallic compounds $[THF \cdot Li(4-Me-C_5H_3-2-)_3 SnLn(\eta^5-C_5H_5)_3]$ ($Ln = Y, La$) (**95**) (Figure 14.20d) [138]. Although an extensive range of Group 14–lanthanide bonded compound has been structurally characterized to date, a large number of metal–metal bonds have not yet been observed. Lanthanide–Ge bonds are still rare [133e, 139] and there are apparently no reported examples of Pb–lanthanide or actinide bonds. The U^{IV} compounds

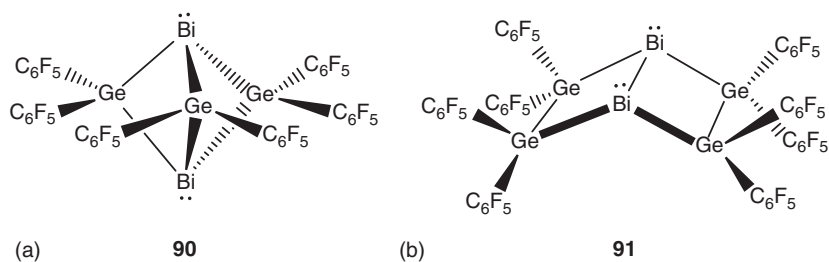


Figure 14.19 Structures of the Ge–Bi bonded compounds, (a) $[Bi_2\{\mu-Ge(C_6F_5)_2\}_3]$ (**90**) and (b) $[Bi_2\{(C_6F_5)_4Ge_2\}_2]$ (**91**).

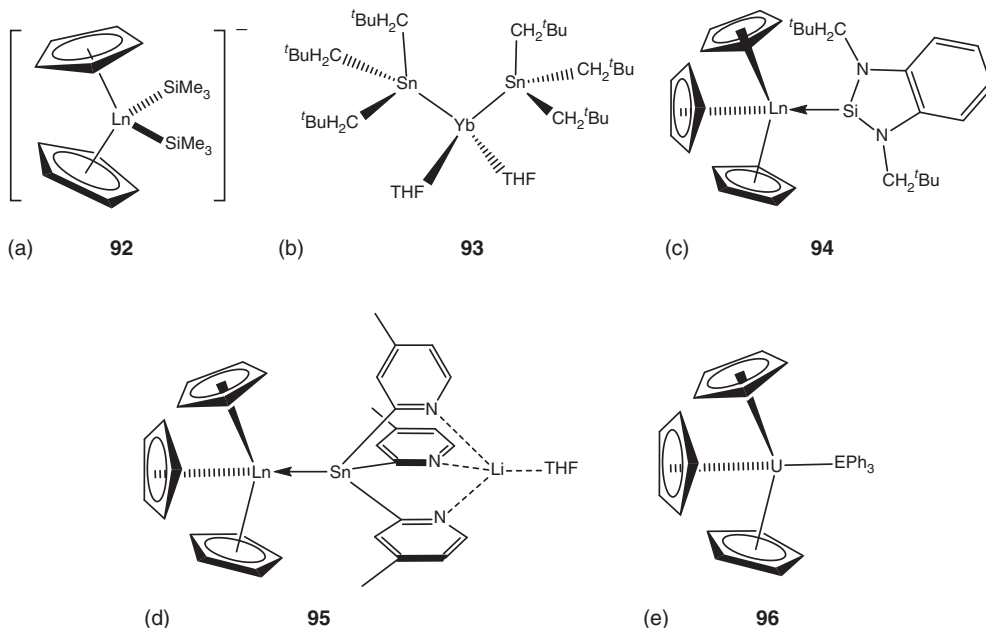


Figure 14.20 Selected examples of Group 14–lanthanide and actinide-bonded compounds, (a) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ln}(\text{SiMe}_3)_2][\text{Li}(\text{DME})_3]^+$ ($\text{Ln}=\text{Sm}$, Lu) (**92**), (b) $[(t\text{BuCH}_2)_3\text{Sn}]_2\text{Yb}\cdot 2\text{THF}$ (**93**), (c)

$[(\text{C}_5\text{Me}_5)_3\text{Ln}(\text{Si}(\text{NCH}_2^t\text{Bu})\text{-}1,2\text{-C}_6\text{H}_4)]$ ($\text{Ln}=\text{Y}$, Yb) (**94**), (d) $[\text{THF}\cdot\text{Li}(4\text{-Me-C}_6\text{H}_3\text{-}2\text{-})_3\text{SnLn}(\eta^5\text{-C}_5\text{H}_5)_3]$ ($\text{Ln}=\text{Y}$, La) (**95**) and (e) $[(\eta^5\text{-C}_5\text{H}_5)_3\text{UEPh}_3]$ ($\text{E}=\text{Si}$, Ge , Sn) (**96**).

$[(\eta^5\text{-C}_5\text{H}_5)_3\text{UEPh}_3]$ ($\text{E}=\text{Si}$, Ge , Sn) (**96**) (Figure 14.20e) are some of the very few Group 14–actinide bonded compounds to have been structurally characterized [140a–c].

In addition to the interest in new types of metal–metal bonds in this area, interesting reactivity has also been uncovered. A case of this is seen in a series of reactions of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{SmCH}(\text{SiMe}_3)_2]$ (**97**) with silanes. Reaction of **97** with excess $\text{H}_2\text{Si}(\text{SiMe}_3)_2$ leads to a simple deprotonation reaction, giving the new compound $[\text{Cp}^*_2\text{SnSiH}(\text{SiMe}_3)_2]$ (**98**) which has a loosely linked dimeric arrangement in the solid state formed by agnostic $\text{Sm}\text{--}\text{Me}$ interactions [141]. However, reaction of **97** with PhSiH_3 produces a complicated mixture of products which result from Ph -migration and dehydrocoupling of $\text{Si}\text{--}\text{H}$ bonds (Scheme 14.6). [142] The reaction appears to proceed through the rapid formation of an intermediate $[\text{Cp}^*_2\text{SnSiMe}_3]$ which then trimerizes to compound **99**, while the use of Ph_2SiH_2 as the substrate favors the formation of compound **100**.

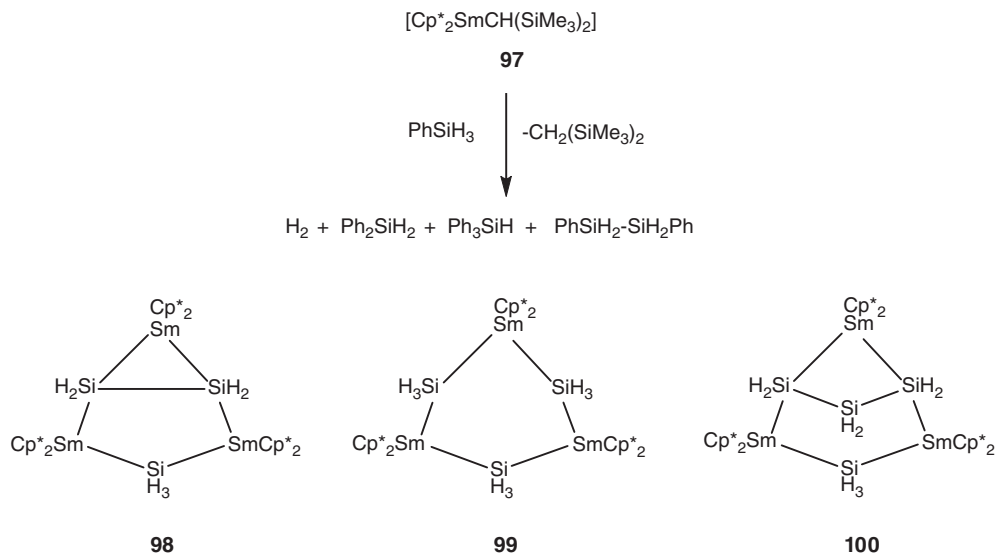
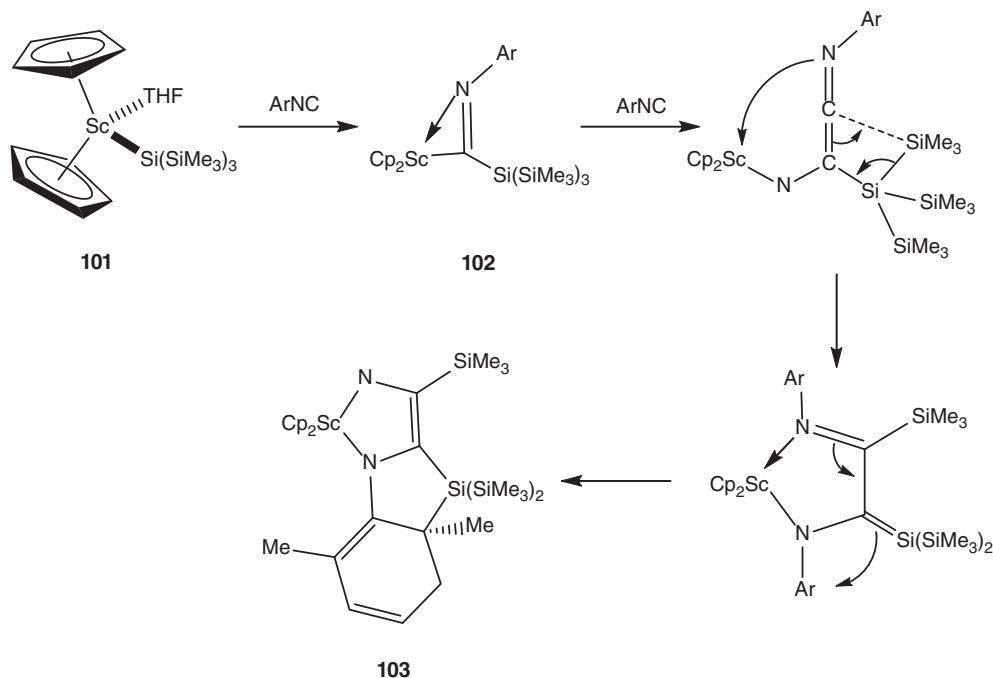
Insertion reactions of small molecules into the $\text{Sc}\text{--}\text{Si}$ bond of the Sc^{III} compound $[(\eta^5\text{-C}_5\text{H}_5)_2(\text{THF})\text{ScSi}(\text{SiMe}_3)_3]$ (**101**) are also worthy of note, and parallel some related transition metal chemistry [133c]. For example, **101** reacts with aryl isocyanides (ArNC) initially *via* insertion into the $\text{Sc}\text{--}\text{Si}$ bond giving intermediate η^2 -iminosilaacyl compound **102**, which then reacts further by the proposed mechanism shown in Scheme 14.7 to give the fused ring compound **103**.

14.3.4

Transition Metal–Group 14 Bonds

14.3.4.1 Single and Partial–Single Bonds (Tm–E)

There are almost 4000 examples of compounds containing single (or electron-deficient) bonds between transition metals and the heavier Group 14 elements that have been structurally characterized, which cover an incredibly diverse range of chemistry and bonding situations. It would

Scheme 14.6 Reaction of **97** with PhSiH_3 .Scheme 14.7 Insertion reaction of **101** with ArHC ($\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$).

clearly be impossible within the scope of this chapter to address this area fully. Nonetheless, it is possible to categorize most of the structurally characterized compounds reported into just few classes, (i) compounds containing terminal or bridged R_3E -ligands (e.g., **104** [143] and **105** [144], Figure 14.21), (ii) compounds containing metal–bridging R_2E -ligands (including N -heterocyclic

carbene analogs [145]) (e.g., compounds **106** [146] and **107** [147], Figure 14.21), (iii) compounds containing metal-bridging RE-ligands (e.g., Compound **108** [148], Figure 14.21), and (iv) compounds containing “naked” E atoms (including Zintl compounds and organometallic transition metal cluster compounds) (e.g., Compound **109** [149], Figure 14.21; see also section 14.2.1 of this chapter). By far, the largest class are those of type (i).

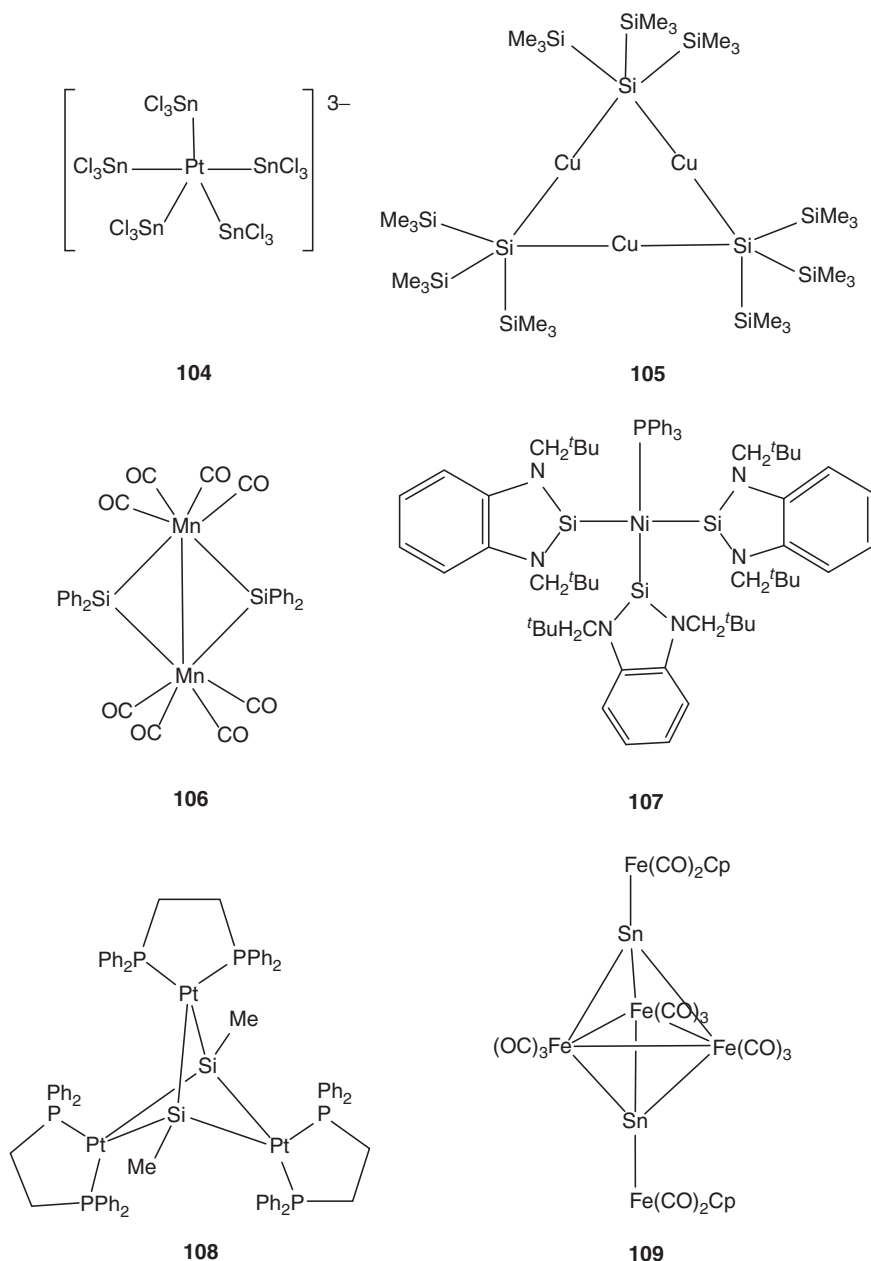


Figure 14.21 Selected examples of single or electron-deficient bonds in this area.

Additional aspects of this extremely large area of research can be found in reviews of the role of secondary Si–H–Tm interactions [150], synthesis, reactivity and catalysis involving transition metal silyls [151, 152], structural aspects of transition metal–Si bonds [153], aspects of the structural chemistry of Tm–E bonds [154], and Si–Si bond activation [155].

14.3.4.2 Double Bonds (Tm=E)

A large number of compounds containing formal double bonds between Group 14 elements and transition elements (Tm=E) have been reported in the literature. The majority of these involve silicon and germanium, while only a few examples of bonds involving the heavier elements tin and lead are known. The first example of a structurally authenticated double bond of this type was found in $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2]_2\text{Ge}$ (**110**), obtained on treatment of $\text{K}[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{GeH}_3]$ (**111**) with acetic acid (Figure 14.22) [156]. Treatment of **110** with Hg^{2+} ions was also shown to result in a small amount of the remarkable bimetallic compound $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2]_3\text{Ge}$ (**112**), containing a Mn_2Ge triangle (Figure 14.22) [156].

The full extent and structural diversity of compounds in this class are too numerous to catalog within the confines of this chapter. However, broadly speaking, compounds containing Tm=E bonds can be divided into two classes, *donor-free* (containing $[\text{Tm}]=\text{ER}_2$ units) [157] and *donor-stabilized* (containing $[\text{Tm}]=\text{E}(\leftarrow\text{L})\text{R}_2$ units) [158, 159]. Compounds **110** and **112** are clearly examples of donor-free double bonds. Further, selected examples of these two types of arrangement are depicted in Figure 14.23. An extensive range of ligand functionality has been employed in the donor-free derivatives, notable examples being the *N*-heterocyclic silylenes, such as that in **115** (which are analogous to the carbon-based *N*-heterocyclic carbene counterparts) and the unusual example **116** in which an *N*-heterocyclic carbene is directly involved in stabilizing the $\text{Cr}=\text{Si}$ bond. As far as donor-stabilized examples are concerned, this can take the form of a monodentate Lewis base (e.g., **117**), an intramolecular Lewis base (e.g., **118**), or, in the unusual example of **119**, take the form of intermolecular association. According to model *ab initio* SCF MO calculations, increased acceptor ability is predicted for nucleophilic attack on the Si atom of $[(\text{OC})_5\text{Cr}=\text{SiH}(\text{OH})]$ in comparison with the carbene complex [160]. The coordination of a donor ligand to such a Tm=E bond obviously results in considerable loss of double-bond character, with the occupancy of the acceptor orbital involved in the double bond by the lone pair on the donor ligand. This reduction in π -bonding and the associated pyramidalization of the Group 14 center (E) depends on the strength of donor interaction, as shown not only by MO calculations [161] but also by the observation of unrestricted rotation of Tm–E bonds [162]. However, it is also found that facile dissociation of the Lewis base ligand can occur in solution, with the formation of the ligand-free complexes. For example, ^1H NMR line-shape analysis of $[\text{Cp}^*(\text{Me}_3\text{P})_2\text{Ru} \cdots \text{SiPh}_2(\text{NCMe})]$ (**117**) shows that rapid exchange of the Si–bonded MeCN ligand occurs with MeCN solvent, with the $\Delta S^\ddagger = +14 \text{ J mol}^{-1} \text{ K}^{-1}$ indicating a dissociative process [160a,b].

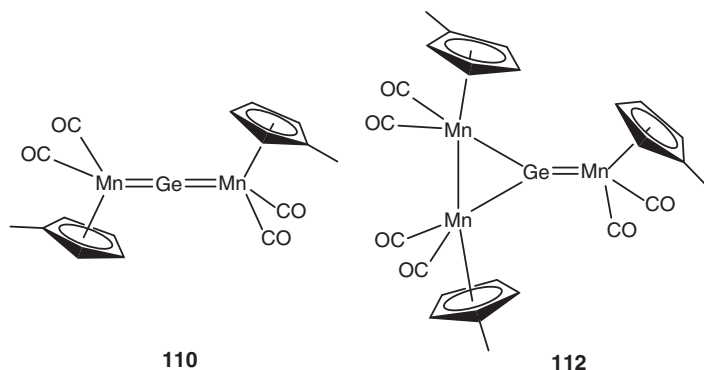


Figure 14.22 Structures of **110** and **112**.

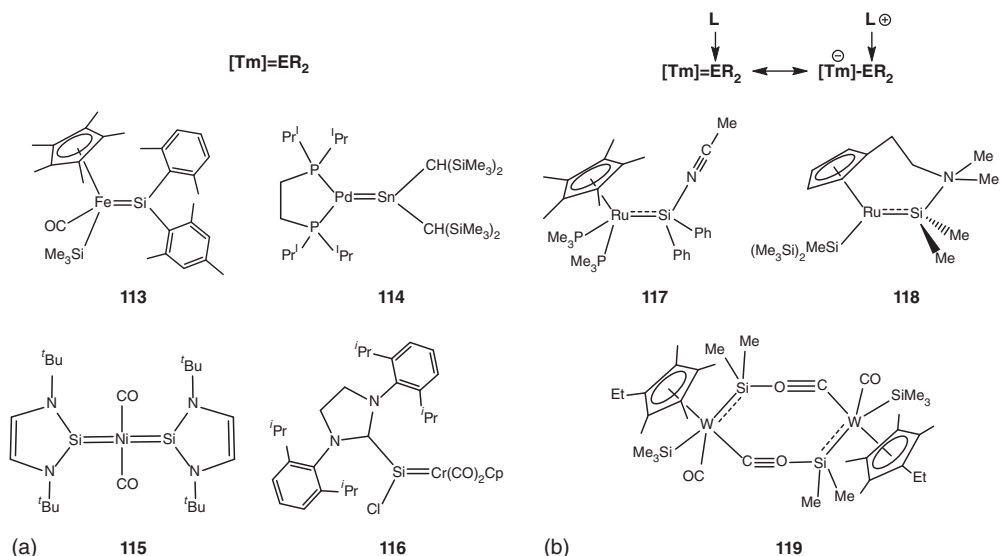
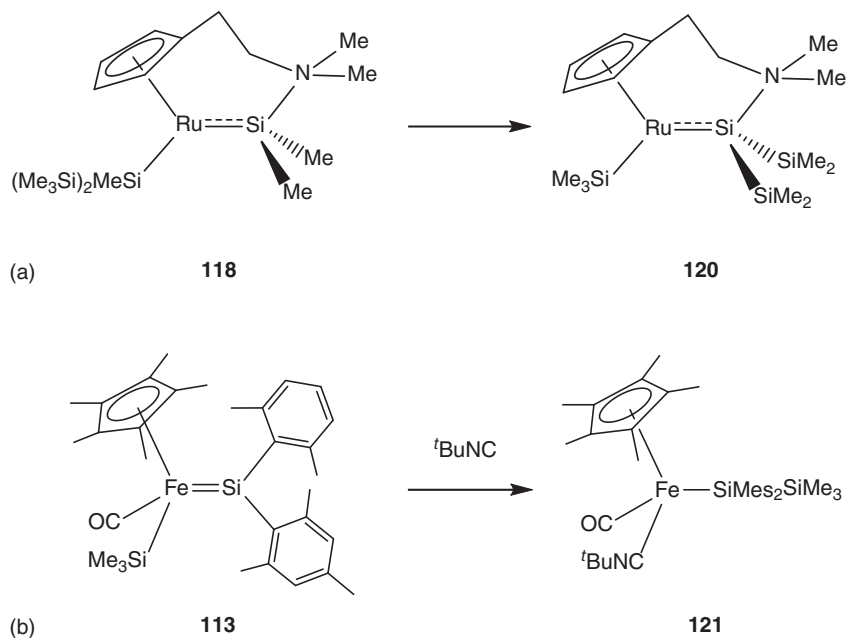


Figure 14.23 Selected examples of (a) donor-free and (b) donor stabilized $\text{Tm}=\text{E}$ double bonds ($\text{Cp}=\text{C}_5\text{H}_5$, $\text{Mes}=2,4,6\text{-Me}_3\text{C}_6\text{H}_2$).

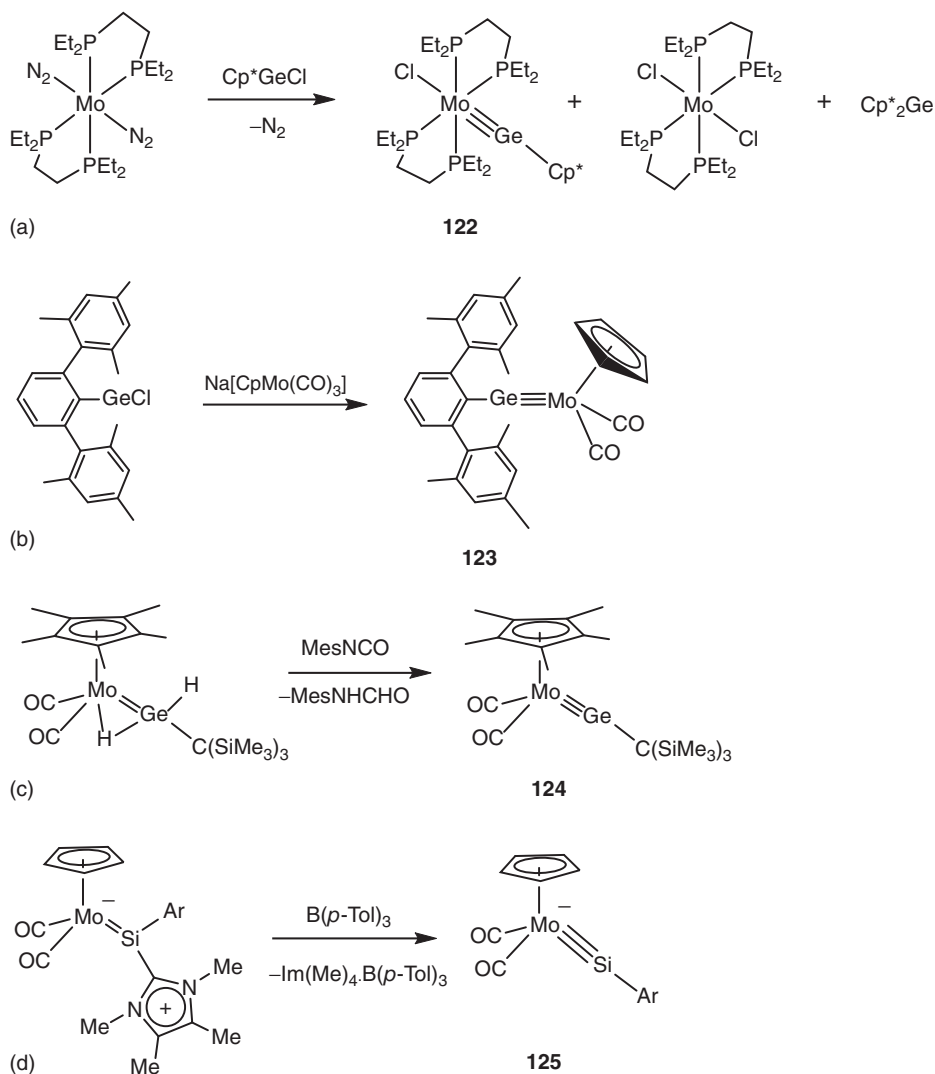
This type of dissociation can unlock further potential for reaction, as is seen in the example of **118** in which formation of the intermediate silylene is followed by rearrangement via a 1,3-sigmatropic transfer of the methyl group (Scheme 14.8a) [158c]. A related example of this type is seen in the reaction of **113** with $t\text{BuNC}$, which involves transfer of the metal–bonded SiMe_3 group onto the SiMe_2 group (Scheme 14.8b) [157i].



Scheme 14.8 (a) 1,3-Sigmatropic rearrangement of **118**. (b) Mes_3Si –transfer to the silylene group of **113**.

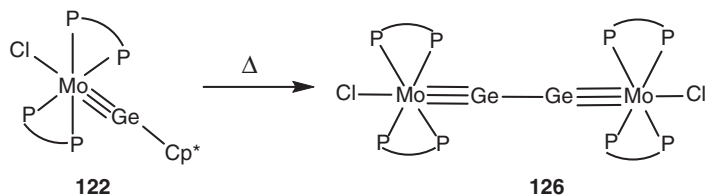
14.3.4.3 Triple Bonds ($\text{Tm}\equiv\text{E}$)

The vast majority of triply bonded compounds which have been structurally characterized are of the type $[\text{L}_n\text{Tm}\equiv\text{ER}]$, in which L is a supporting ligand or ligand set, R is a sterically bulky organic ligand, and Tm is a Group 6 element (Cr, Mo, W) [163a,b, 164a–164h, 165a,b, 166]. The area of triple bonds between transition metals and the heavier elements of Groups 14 and 15 was reviewed earlier by Scheer [167]. A variety of synthetic strategies have been employed in the formation of triply bonded compounds of this type. Most commonly, reactions of Group 6 dinitrogen compounds (e.g., compound **122**, Scheme 14.9a) with II-oxidation state oligomers $(\text{REX})_n$ ($\text{X} = \text{halogen}$) have been employed. Alternative strategies have included reactions of transition metal organometallic anions with $(\text{REX})_n$ (e.g., compound **123**, Scheme 14.9b) [164a], dehydrogenation of Group 6 metal hydride complexes (e.g., compound **124**, Scheme 14.9c) [164g], Lewis acid activated carbene-transfer



Scheme 14.9 Selected synthetic routes to $\text{E}\equiv\text{Tm}$ bonded compounds
 $[\text{Cp}^* = \text{C}_5\text{Me}_5, \text{Im}(\text{Me}_4) = \text{tetramethylimidazol-2-ylidene}]$.

reactions (e.g., compound **125**, Scheme 14.9d) [164b] and Pb–N bond activation [166c]. The formation of a particularly unusual example of a triply bonded transition metal Group 14 compound is seen in the thermal Ge–Cp* bond-cleavage reaction of [*trans*-(depe)₂Mo≡Ge(η⁵-Cp*)] (**122**) (depe = Et₂PCH₂CH₂PEt₂), which results in [ClTm(depe)₂≡Ge–Ge≡Mo(depe)₂Cl] (**126**) (Scheme 14.10) [164e].



Scheme 14.10 Thermolysis of **122** to give **126**.

Theoretical calculations have been employed in several studies to probe the nature of E≡Tm bonds and to compare their character to that of transition metal carbynes.[164b, 166a,b]. These studies give a consistent view of triple bonds that are polarized toward the Tm side and that are best described by a Dewar–Chatt–Duncanson Model, involving a combination of [RE] → [Tm] σ-donation and [Tm] → [RE] back π-donation. Calculations on model germlylidyne of the type [CpL₄W≡GeCp] (**127**) shows a similar situation to the carbene analog. However, the germanium-based ligand is a poorer σ-donor and a better π-acceptor. Further calculations on cations of the type [(PMe₃)₅W≡Pb(2,6-Trip₂C₆H₃)⁺] (**128**) confirm the analogy with Fischer carbynes.

A few studies have also explored the reactivity of Tm≡E bonds. Although so far limited in their range, studies show two types of reactivity, (i) ligand-exchange reactions which preserve the Tm≡E bonds [164d,e, 166a,b] and (ii) nucleophilic addition reactions to the E-atoms [157o]. An example of the first type of reaction is seen in the exchange of the W-bonded Cl-ligand of [(PMe₃)₄ClW≡Ge{(2,6-Trip)₂C₆H₃}] (**129**) with various nucleophiles (Nu[−]), giving [(PMe₃)₄(Nu)W≡Ge{(2,6-Trip)₂C₆H₃}] (**130**) for Nu[−] = I[−], NCS[−]. Interestingly, however, reaction with a source of Me₂N[−] gives the hydride [(PMe₃)₄(H)W≡Ge{(2,6-Trip)₂C₆H₃}] (**131**) which presumably results from initial replacement of the Cl-ligand with the Me₂N-ligand followed by β-H elimination. In contrast, reactions of [Cp(CO)₂Mo≡Si{(2,6-Trip)₂C₆H₃}] (**132**) with nucleophiles (Nu[−] = I[−], N₃[−], Me[−]) give the silylene anions [Cp(CO)₂Mo = Si(Nu){(2,6-Trip)₂C₆H₃}][−] (**133**).

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15

Group 15 Metal–Metal Bonds

James S. Jones, Baofei Pan, and François P. Gabbaï

15.1

Introduction

Among the Group 15 elements, antimony and bismuth are both classified as poor metals and thus exhibit distinct metallic properties. Although arsenic does have metalloid properties, its chemistry tends to parallel that of the non-metal phosphorus. Because of these distinctions and for the sake of conciseness and focus, this chapter will be solely dedicated to the metal–metal bonded compounds containing antimony and bismuth. Page restrictions also require us to make additional choices regarding our coverage of the topic. A review of the literature shows that metal–metal bonds involving antimony and bismuth are present in a plethora of organometallic derivatives and coordination complexes [1–9]. An exhaustive treatment of this area of chemistry cannot be provided in a single book chapter. Therefore, we have chosen to focus on the chemistry of metal–metal bonded compounds featuring an organometallic antimony or bismuth fragment.

Within the coverage limits defined above, we will see that this field of research has experienced considerable growth with ongoing development in new exciting directions. The first part of this chapter is concerned with the chemistry of main group only compounds in which two or more antimony or bismuth atoms are covalently linked via single or multiple bonds. The second part of the chapter deals with the chemistry of transition metal complexes containing organometallic antimony or bismuth fragments in their coordination sphere. While one could argue that stibine and bismuthine complexes could fall in this category, we will recognize that stibines and bismuthines are donor ligands that interact with metal centers via coordination bonds. Formation of such complexes is well precedented [1–9] and will not be covered per se in this chapter. Instead, an effort will be made to document advances concerned with the chemistry of complexes featuring R_2Pn , RPn , or simply terminal Pn fragments ($Pn = Sb, Bi$). Finally, we will also discuss recent advances made in the chemistry of complexes containing pentavalent antimony moieties bound to d-block metals.

15.2

Complexes with Sb–Sb and Bi–Bi Bonds

15.2.1

Synthesis and Structures of Distibines and Dibismuthines

15.2.1.1 Synthesis

The simplest representatives of this class of compounds are the antimony and bismuth analogs of tetraalkyl or tetraaryl hydrazines. Since their discovery over 80 years ago [10–12], the synthesis of these compounds has been pursued in several laboratories around the world. These efforts, which have been reviewed on several occasions [3, 13–18], have led to a large collection of distibines and

dibismuthines, some of which are presented in Table 15.1. Different synthetic approaches have been employed to access these compounds. One of the most commonly used approach consists in the generation of a diorganyl stibide or bismuthide as a sodium salt followed by oxidative coupling with 1,2-dichloroethane. This approach is illustrated in entry 1 with the synthesis of Et_4Sb_2 (**1-Et**) as described by Notles in the 1970s [19]. Ashe also demonstrated that this approach can be applied to the synthesis of dibismuthines such as Me_4Bi_2 (**2-Me**, entry 2) [20]. Over the years, alternative synthetic routes have been reported. In particular, it has been shown that direct reduction of R_2PnX synthons into the corresponding dipnictines (**3**, **4**) can be carried out with metals such as magnesium (entries 3 and 4) [21, 22, 30], thereby alleviating the need for a sodium-pnictide intermediate. Mild reducing agents have also been proven to be effective in inducing Pn–Pn bond formation. This is the case of the reaction in entry 5 where a phosphonite serves as a reducing agent to produce an intramolecularly base-stabilized dibismuthine (**5**) [23].

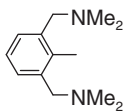
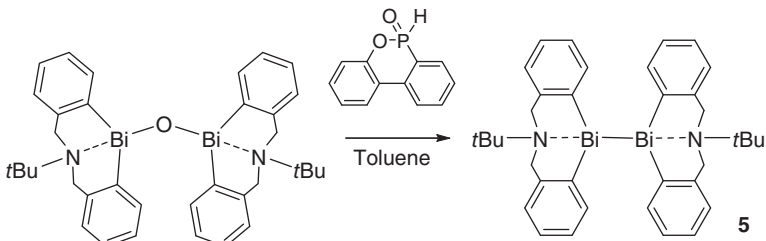
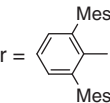
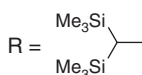
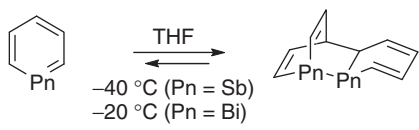
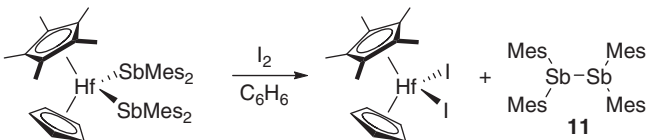
Secondary stibines and bismuthines can also be used as precursors (see entries 6 and 7). In these reactions, Pn–Pn bond formation results from H_2 elimination, a process facilitated by the weakness of the Sb–H and Bi–H bonds. This approach has been successfully applied to $(2,6\text{-Mes}_2\text{C}_6\text{H}_3(\text{Me})\text{Sb})_2$ (**6**) which necessitates daylight to undergo coupling [24]. In the case of $((\text{Me}_3\text{Si})_2\text{CH})_2\text{BiH}$, hydrogen elimination occurs spontaneously upon elevation of the temperature, leading to formation of the coupled product **7** [25]. Another interesting coupling is observed upon reaction of $((\text{Me}_3\text{Si})_2\text{CH})_2\text{SbCl}_2$ with LiAlH_4 (entry 8) [26]. In this case, the reaction produces a rare bis(hydridostibine) (**8**), which reacts with MeI under the action of a base (1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)) to form the corresponding dimethyldistibine complex [27]. While the mechanism of the Sb–Sb bond forming reaction has not been fully clarified, it is speculated that it proceeds via a hydrido-chloride derivative which reacts with an equivalent of $((\text{Me}_3\text{Si})_2\text{CH})_2\text{SbH}_2$ generated *in situ*.

Formation of Pn–Pn bonds is sometimes observed upon dimerization of derivatives in which the pnictogen is π -bonded to carbon. This is, for example, the case for stibabenzene, and bismabenzene, which undergo a head-to-tail Diels–Alder dimerization (see entry 9 for the formation of the dipnictines **9** and **10**) [28]. Related dimerizations have also been observed during the attempted synthesis of stibaallenes [31]. Finally, some less common routes have also been reported over the past few years. For example, Sb–Sb bond formation can also be promoted by transition metals, as in the case of $\text{CpCp}^*\text{Hf}(\text{SbMes}_2)_2$ which eliminates an equivalent of $\text{Mes}_2\text{Sb–SbMes}_2$ (**11**) upon reaction with I_2 in toluene (entry 10) [29].

15.2.1.2 Structures

Several distibines and dibismuthines have been characterized by X-ray diffraction. In all cases, the bond angles at the pnictogen element are close to 90° , indicating little *s/p* hybridization as is often observed for heavy main group elements. The pnictogen–pnictogen bond distances measured for these compounds fall in the rather narrow range of 3.834–3.863 Å [24, 32–39] for the stibines and 2.983–3.087 Å [25, 36, 38, 40–42] for the dibismuthines. A more interesting facet of the structural chemistry of these species comes from their thermochromic properties. For instance, Me_4Sb_2 (**1-Me**) forms a red crystalline solid which turns yellow upon melting or dissolution [12]. Solutions of **1-Me** in organic solvents like alcohol, ether, or benzene turn back to red upon freezing [12]. This reversible thermochromic phenomenon has also been observed for other distibines featuring substituents with small steric profiles [42]. Similar to antimony derivatives, less sterically encumbered dibismuthines also possess reversible thermochromic properties [33–35, 39, 43–45]. For example, violet, crystalline Me_4Bi_2 (**2-Me**) turns orange upon melting [45]. As discussed by Ashe [17], not all dipnictines are thermochromic, thus pointing to the importance of the role played by the organic substituents. The structure of two representative examples of thermochromic derivatives (**1-Me** and $(\text{CH}=\text{CMe})_4\text{Bi}_2$ (**12**)) are shown in Figure 15.1. These two compounds, which possess a Pn–Pn bond of 2.862(1) Å for **1-Me** and 2.990(1) Å for **12**, form short intermolecular Pn⋯Pn interactions of 3.645(1) Å for **1-Me** and 3.660(1) Å for **12**, respectively (Figure 15.1). These interactions lead to an extended chain-like structure with almost linear Pn⋯Pn–Pn angles (179.2° and 166.5° for **1-Me** and **12**, respectively) [35].

Table 15.1 Examples of reactions affording distibines and dibismuthines.

Entry	Reactions	References
1	$\text{Et}_3\text{Sb} \xrightarrow[\text{NH}_3]{\text{Na}} \text{Et}_2\text{SbNa} \xrightarrow{\text{Cl}(\text{CH}_2)_2\text{Cl}} 0.5 \text{ Et}_2\text{Sb} - \text{SbEt}_2$ 1-Et	[19]
2	$\text{Me}_3\text{Bi} \xrightarrow[\text{NH}_3]{\text{Na}} \text{Me}_2\text{BiNa} \xrightarrow{\text{Cl}(\text{CH}_2)_2\text{Cl}} 0.5 \text{ Me}_2\text{Bi} - \text{BiMe}_2$ 2-Me	[20]
3	$(\text{Me}_3\text{SiCH}_2)_2\text{SbBr} \xrightarrow[\text{THF}]{\text{Mg}} (\text{Me}_3\text{SiCH}_2)_2\text{Sb} - \text{Sb}(\text{Me}_3\text{SiCH}_2)_2 + \text{MgBr}_2$ 3	[21]
4	$\text{Ar}_2\text{BiCl} \xrightarrow[\text{THF}, -20^\circ\text{C}]{\text{Mg}} \text{Ar}_2\text{Bi} - \text{BiAr}_2 + \text{MgCl}_2$ 4 Ar = 	[22]
5	 5 + other products	[23]
6	$\text{Ar}(\text{Me})\text{SbH} \xrightarrow[\text{daylight}]{\text{C}_6\text{D}_6} \begin{array}{c} \text{Ar} \quad \text{Me} \\ \quad \\ \text{Sb} - \text{Sb} \\ \quad \\ \text{Me} \quad \text{Ar} \end{array} + \text{H}_2$ 6 Ar = 	[24]
7	$\text{R}_2\text{BiH} \xrightarrow[\text{RT}]{\text{Et}_2\text{O}} \begin{array}{c} \text{R} \quad \text{R} \\ \quad \\ \text{Bi} - \text{Bi} \\ \quad \\ \text{R} \quad \text{R} \end{array} + \text{H}_2$ 7 R = 	[25]
8	$\text{RSbCl}_2 + \text{LiAlH}_4 \xrightarrow[-78^\circ\text{C}]{\text{Et}_2\text{O}} [\text{RSb}(\text{H})\text{Cl}] \xrightarrow{\text{RSbH}_2} \begin{array}{c} \text{R} \quad \text{H} \\ \quad \\ \text{Sb} - \text{Sb} \\ \quad \\ \text{H} \quad \text{R} \end{array}$ 8 R = 	[26, 27]
9	 9 (Pn = Sb) 10 (Pn = Bi)	[28]
10	 11	[29]

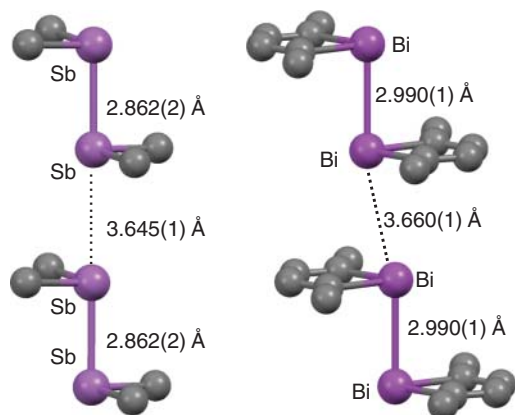


Figure 15.1 Supramolecular structure of Me_4Sb_2 (**1-Me**) and $(\text{HC}=\text{CMe})_4\text{Bi}_2$ (**12**) in solid state. Hydrogen atoms are omitted for clarity.

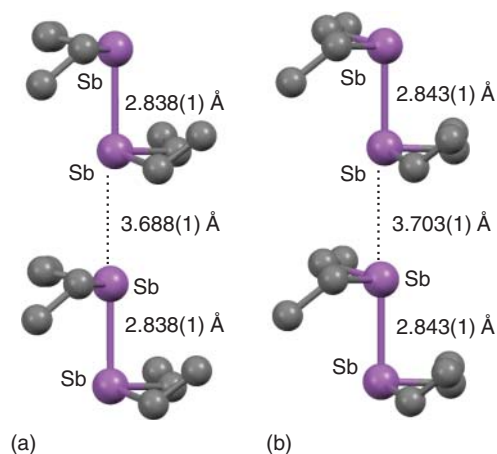


Figure 15.2 Supramolecular structure of the red (a) and yellow form (b) Et_4Sb_2 (**1-Et**). Hydrogen atoms are omitted for clarity.

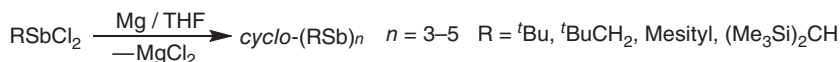
It was proposed by Ashe [17, 42] that the disruption of these intermolecular $\text{Pn}\cdots\text{Pn}$ interactions, which are shorter than twice the van der Waals of the pnictogen element (4.12 Å for Sb and 4.14 Å for Bi) is responsible for the thermochromic properties of these compounds.

Some theoretical work, aimed at clarifying the origin of this thermochromism, is available in the literature [46–48]. Unfortunately, these theoretical investigations deal only with the special case of distiboles and their conclusions cannot be extended to explain the thermochromism of simple compounds such as Me_4Sb_2 (**1-Me**). Moreover, some recent investigations suggest that the origin of the thermochromic properties of these compounds may not be as simply explained as originally assumed. While it has usually been accepted that disruption of the intermolecular $\text{Pn}\cdots\text{Pn}$ interactions is responsible for the color change observed at certain temperature, Schulz and coworkers have recently reported that Et_4Sb_2 (**1-Et**) converts from a red form into a yellow form at about -80°C . Structural analysis of these two forms shows that they both possess comparable intermolecular $\text{Sb}\cdots\text{Sb}$ contacts of 3.688(1) Å for the red form and 3.703(1) Å for the yellow form (Figure 15.2) [36, 37]. These results suggest that the thermochromic behavior of these compounds is still poorly understood and does not necessarily originate from a disruption of intermolecular $\text{Pn}\cdots\text{Pn}$ interactions.

15.2.2

Synthesis and Structures of *cyclo*-Organostibines and -Organobismuthines15.2.2.1 *cyclo*-Stibines

cyclo-Organostibines, which can be regarded as oligomers of organostibinidenes, constitute another type of compounds with single Sb–Sb bonds. Since an original report in the 1960s [49], the chemistry of such compounds has continued to develop, leading to a family of compounds of different ring sizes. As documented by Breunig *et al.* in several recent reviews, one of the most common methods for the preparation of these compounds is the reductive dehalogenation of organoantimony dihalides using magnesium as a reducing agent (Scheme 15.1) [13, 15, 16, 18, 50, 51].



Scheme 15.1

The simplest members of this class of compounds are the cyclic trimers of the general formula *cyclo*-(RSb)₃. Although the possible existence of such species like *cyclo*-(RSb)₃ (R = Me, Et, Ph) was originally derived from mass spectrometry studies [52–54], synthetic efforts based on the reductive dehalogenation depicted in Scheme 15.1 only afforded trace amounts of the relevant compound. The first fully characterized example of such a compound, namely *cyclo*-((Me₃Si)₂CHSb)₃ (**13**), was obtained using a different route based on the reaction of (Me₃Si)₂CHSbCl₂ with Li₃Sb in tetrahydrofuran (THF) at low temperature [55]. A crystallographic analysis of **13** shows an essentially equilateral Sb₃ triangle with Sb–Sb bond distances in the 2.819(1)–2.845(1) Å range (Figure 15.3). With two alkyl ligands up and one alkyl ligand down with respect to the Sb₃ plane, the molecule has mirror symmetry, a conclusion consistent with its ¹H and ¹³C NMR spectra in C₆D₆.

Several examples of *cyclo*-(RSb)₄ compounds are known [27, 53, 56–64]. One of the simplest representatives of such compounds is *cyclo*-(^tBuSb)₄ (**14**), which is obtained by reduction of ^tBuSbCl₂ over Mg in THF [56]. In the crystal, the central Sb₄ ring of **14** adopts a puckered conformation (folded angles: 132.7° and 132.8°), with the ^tBu groups at the 1,3-positions *trans* from those at the 2,4-positions. This conformation is most likely dictated by the steric bulk of the ^tBu groups. All four Sb–Sb bonds fall within the narrow 2.814(2)–2.821(2) Å range and are comparable to the Sb–Sb distances observed in *cyclo*-((Me₃Si)₂CHSb)₃ (ranging from 2.819(1) to 2.845(1) Å) [55]. Several other examples of *cyclo*-(RSb)₄ species have been reported, and all but one feature a puckered Sb₄ ring with

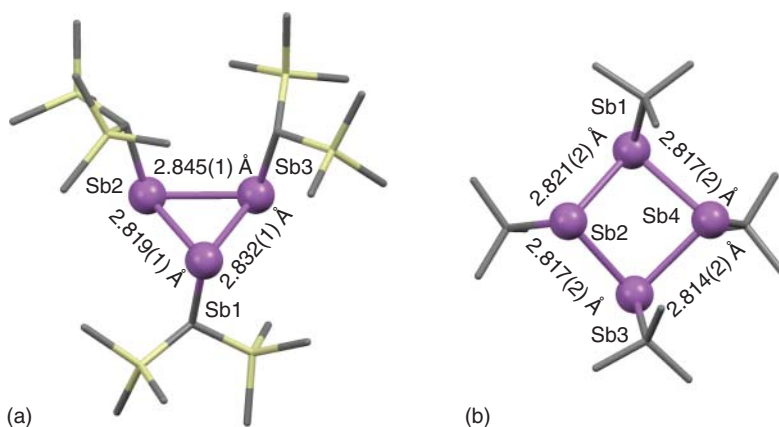


Figure 15.3 Solid state structure of *cyclo*-((Me₃Si)₂CH)Sb₃ (**13**, a) and *cyclo*-^tBu₄Sb₄ (**14**, b). Hydrogen atoms are omitted for clarity.

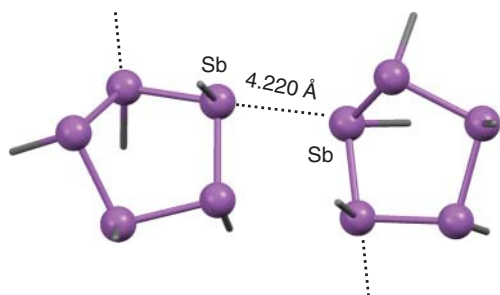
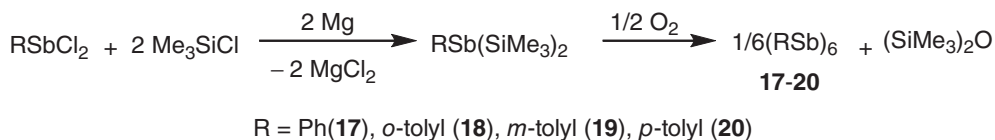


Figure 15.4 Supramolecular structure of *cyclo*-(*t*BuCH₂Sb)₅ (**16**). The *tert*-butyl groups and hydrogen atoms are omitted for clarity.

the ligands at the 1,3-positions *trans* from those at the 2,4-positions. The only exception is a kinetically trapped isomer of the *cyclo*-((Me₃Si)₂CHSb)₄ (**15**) with the ligands at the 1,2-positions *trans* from those at the 3,4-positions [27]. It is important to note that *cyclo*-organostibines will tend to favor tetrameric structures because the resulting intracyclic Sb–Sb angles are close to 90°, a value most compatible with the p-orbital dominated bonding of trivalent organoantimony species. This view is reinforced by the scarcity of *cyclo*-(RSb)₅ species. To date, the only structurally characterized example of such a compound is *cyclo*-(*t*BuCH₂Sb)₅ (**16**) [65]. While the Sb–Sb bonds within the five-membered ring (2.812–2.819 Å) are close to those in other *cyclo*-oligomers, this molecule presents a unique supramolecular structure with the individual molecules arranged in a zigzag chain-type framework as a result of Sb⋯Sb interactions of 4.220 Å (Figure 15.4). These interactions are much longer and thus weaker than those observed in Me₄Sb₂ (1-Me, 3.645(1) Å) [46–48].

Hexameric *cyclo*-organostibines have also been reported. Such species are best prepared by the reaction of bis(trimethylsilyl)organostibines with oxygen (Scheme 15.2) rather than by the more conventional reductive dehalogenation route used to access the lower oligomers (Scheme 15.1) [54, 66]. The strategy outlined in Scheme 15.2 can be used to access *cyclo*-(RSb)₆ (**17–20**) derivatives that differ by the nature of the R substituent. Example of such hexamers include the phenyl (**17**), *o*-tolyl (**18**), and *m*-tolyl (**19**, Figure 15.5), which have all been structurally characterized. In all three cases, the Sb₆ ring adopts a chair conformation with the aryl substituents in equatorial positions. The *m*-tolyl derivative **19** shows intermolecular Sb⋯Sb contacts of 4.192 Å, which are reminiscent of those observed in *cyclo*-(*t*BuCH₂Sb)₅ (**16**, Figure 15.4) [65]. While *cyclo*-organostibines of larger nuclearity than six have remained elusive, mixed valence species such as ((Me₃Si)₂CH)₄Sb₈ (**21**) have been isolated (Figure 15.6) [67]. This octanuclear derivative can be regarded as a Sb₄ tetrahedron whose edges are capped by a bridging ((Me₃Si)₂CH)Sb unit.



Scheme 15.2

15.2.2.2 Cyclo-bismuthines

cyclo-Organobismuthines have also been investigated. Like their antimony analogs, these compounds can also be prepared from the dichloride precursors using magnesium [68]. Other methods have also been developed, including dihydrogen elimination from RBiH₂ to generate *cyclo*-(RBi)_{*n*} (*n* = 3, 5; R = 2-(Me₂NCH₂)C₆H₄, Me₃SiCH₂ (**22**)) [65, 69], RH elimination from R₂BiH to form *cyclo*-(RBi)₄ (R = 2-(Me₂NCH₂)C₆H₄) [30], and reduction of RBiCl₂ by sodium in liquid ammonia to form *cyclo*-(RBi)₃ (R = 2-(Me₂NCH₂)C₆H₄) [30]. Although *cyclo*-(RBi)_{*n*} species with *n* = 3–5 have been reported,

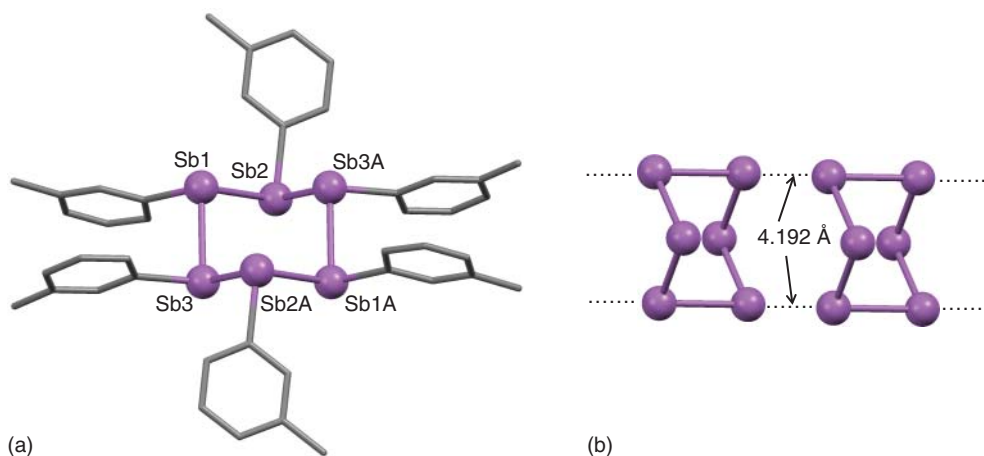


Figure 15.5 Molecular (a) and supramolecular structure (b) of *cyclo*-(*m*-tolylSb)₆ (**19**). Hydrogen atoms on the left structure and *m*-tolyl substituents on the right supramolecular structure are omitted for clarity.

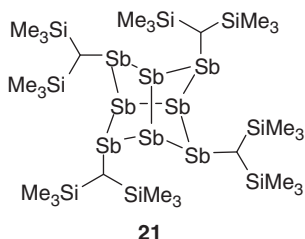


Figure 15.6 Diagram of the octanuclear mixed valence compound ((Me₃Si)₂CH)₄Sb₈ (**21**).

the only structurally characterized examples are the two tetramers *cyclo*-((Me₃Si)₂CH)₄Bi₄ (**23**) and *cyclo*-(2-(Me₂NCH₂)C₆H₄)₄Bi₄ (**24**) both of which possess a puckered structure with the substituents at the 1,3-positions trans from those at the 2,4-positions [30, 68].

15.2.3

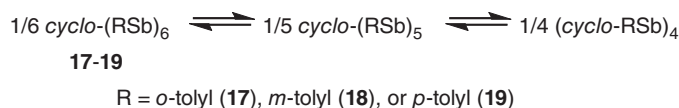
Stability and Reactivity

15.2.3.1 Thermal and Photochemical Stability

Owing to the diffuseness of the bonding orbitals, the stability of covalent bonds involving a main group element typically decreases as a group is descended. This trend is certainly observed in the thermal behavior of distibines and dibismuthines which disproportionate upon elevation of the temperature to produce the corresponding metal and tri-organylpnictine. The reactions of the tetramethyl derivatives have been investigated in detail. Neat Me₄Sb₂ (**1**-Me) survives heating at 100 °C for a week, but starts depositing Sb metal when the temperature is raised above 160 °C [70]. The corresponding dibismuthine (**2**-Me) is much less stable, and decomposes in benzene at 25 °C [20]. The kinetics of this decomposition are relatively fast, with only 50% of the compound remaining after 6 h. The lability of these complexes can be exploited for material synthesis applications as in the case of Et₄Bi₂ (**2**-Et), which deposits Bi nanoparticles in THF at low temperature [71]. Gas phase stability studies are also available for some of the distibines. Interestingly, while **1**-Me survives in the gas phase up to temperatures of 300 °C [72], Et₄Sb₂ (**1**-Et) is much less stable, decomposing at temperatures above 100 °C [72].

The lability of these compounds is also reflected by their photochemistry. Irradiation of Ph_4Sb_2 (**1-Ph**) with a sun lamp has been proposed to produce $\text{Ph}_2\text{Sb}^\bullet$ radicals, which can readily be trapped by reaction with alkyl iodides [73]. It has also been shown that the radical polymerization of styrene, among other monomers, is effectively retarded in the presence of **1-Ph** which delivers a Ph_2Sb moiety as a polymer-end radical capping unit [74]. Compound **1-Ph** can also be used to provide the end units of catenated polystibines [24]. An elegant example of such a process is the synthesis of a $\text{Ph}_2\text{Sb-SbPh-SbR-SbPh}_2$ chain ($\text{R} = \text{CH}_2\text{SiMe}_3$) in the coordination sphere of a chromium tetracarbonyl $\text{Cr}(\text{CO})_4$ moiety by reaction of **1-Ph** with *cyclo*-($\text{Me}_3\text{SiCH}_2\text{Sb}$)₅ in the presence of $[\text{nbdCr}(\text{CO})_4]$ (nbd = norbornadiene) [75]. Free diorganopnictogen radicals have also been proposed in the reaction of Me_4Sb_2 (**1-Me**) and Me_4Bi_2 (**2-Me**) with benzylbromide, which affords the corresponding bromide (Me_2PnBr) and benzyl (Me_2PnBz) derivatives [76].

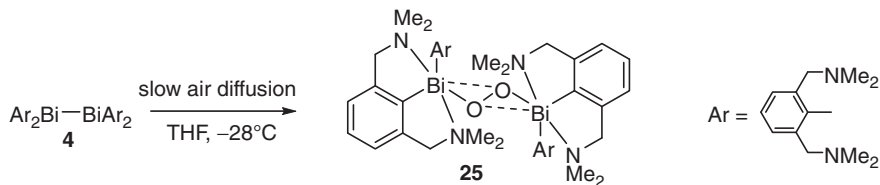
The propensity of Sb–Sb bonds to undergo homolytic cleavage is also evident in the behavior of *cyclo*-(RSb)₆ derivatives [66]. Indeed, while such species are stable in the solid state, they readily enter equilibrium with lower oligomers when dissolved in organic solvents. When **17–19** are dissolved in C_6D_6 under dilute conditions, the major species of the resulting mixture is the tetramer while under more concentrated solution, the pentamer dominates (Scheme 15.3). At very low concentrations, mass spectrometry studies suggest that the trimer becomes the most abundant species. The facile interconversion observed between these different oligomers reflects the inherent weakness of the Sb–Sb bonds present in these derivatives [66]. Related observations are made with *cyclo*-organobismuthines, which can also exist in solution as mixtures of oligomers [30, 65, 68].



Scheme 15.3

15.2.3.2 Reactivity

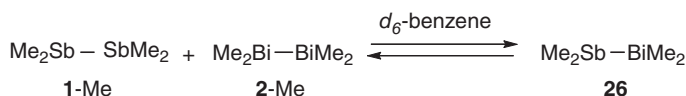
When exposed to slow diffusion of air in Et_2O , the tetraaryl distibines Ar_4Sb_2 ($\text{Ar} = \text{Ph}$ (**1-Ph**), *o*-tolyl (**1-*o*-tol**), *p*-tolyl; (**1-*p*-tol**)) undergo clean conversion into the corresponding $\text{Ar}_2\text{Sb-O-SbAr}_2$ [77]. Mass spectral studies show that similar reactions are also observed with the tetraalkyl derivatives [78]. Related results have been obtained with simple tetraalkyldibismuthines such as Me_4Bi_2 (**2-Me**) and ${}^n\text{Pr}_4\text{Bi}_2$ (**2-ⁿPr**) [79, 80]. In the case of Ph_4Bi_2 (**2-Ph**), a stoichiometric amount of oxygen is consumed, but the product of the reaction cannot be readily isolated because of subsequent reactions [40]. The course of this oxygen insertion reaction can be altered by the nature of the aryl substituents. The bridged oxide is readily isolated when mesityl substituents are employed [81, 82]. With the 2,6-(Me_2NCH_2)₂ C_6H_3 ligand (see **4** in Scheme 15.4), a peroxide bridged intermediate featuring an O_2 fragment sandwiched between two Ar_2Bi units can be isolated at -30°C upon slow reaction with air [22]. This compound, which has been structurally characterized, is not stable and quickly converts into the expected $\text{Ar}_2\text{BiOBiAr}_2$ (**25**) [22].



Scheme 15.4

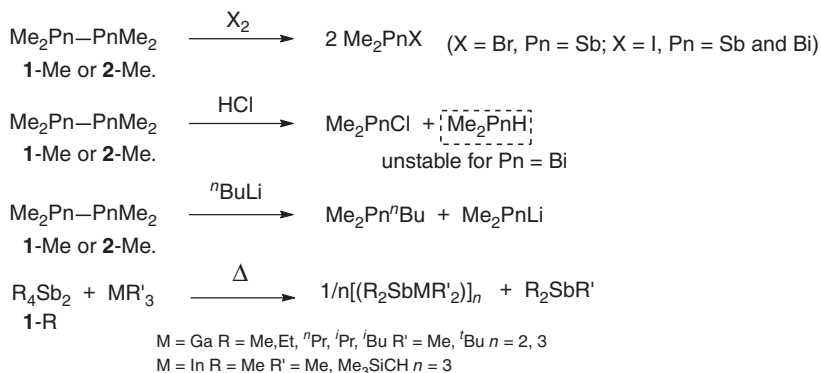
In general, dipnictines react cleanly with sulfur, selenium, or tellurium to afford corresponding chalcogen (Ch) insertion products of general formula $\text{R}_2\text{Pn-Ch-PnR}_2$. Such reactions occur with

both alkyl and aryl substituted derivatives [40, 78–81, 83–87], provide another illustration of the weakness and reactivity of the central metal–metal bond of these derivatives. There have been numerous reports showing that the homonuclear bond of dipnictines can be cleaved by reactions with dichalcogenides of general formula $R'Ch-CHR'$ (R' = alkyl or aryl), leading to the corresponding chalcogenostibines [88–91] and chalcogenobismuthines of general formula $R_2Pn-CHR'$ [84, 85]. Analogous exchange reactions also occur when two different dipnictines are allowed to react with each other [80]. An example of such a reaction is provided in Scheme 15.5 where **1-Me** and **2-Me** undergo exchange to produce the corresponding heterobimetallic derivative [92]. NMR studies of this reaction in d_6 -benzene shows that the product, $Me_2SbBiMe_2$ (**26**), is in a dynamic equilibrium with the starting distibine and dibismuthine.



Scheme 15.5

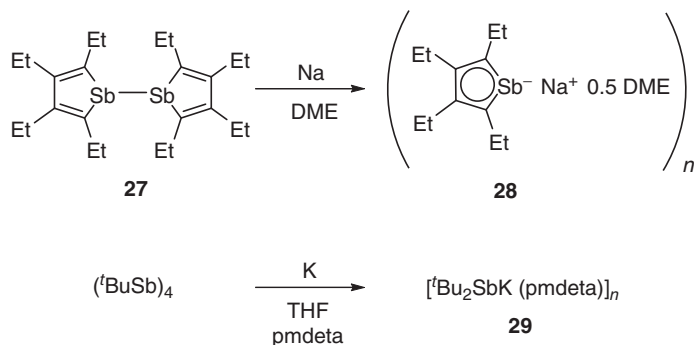
Cleavage of the central $Pn-Pn$ bond of distibines and dibismuthines is also observed with several reagents, including halogens [40], HCl , and $nBuLi$, as depicted in Scheme 15.6 for the tetramethyl derivatives **1-Me** and **2-Me** [76, 93]. Related $Pn-Pn$ bond heterolysis reactions are also observed when distibines are allowed to react with gallanes and indanes (Scheme 15.6) [94–97]. Such reactions provide a convenient access to the corresponding diorganogallium- and diorganylindium-stibide derivatives, which exist as cyclic dimers or trimers [5].



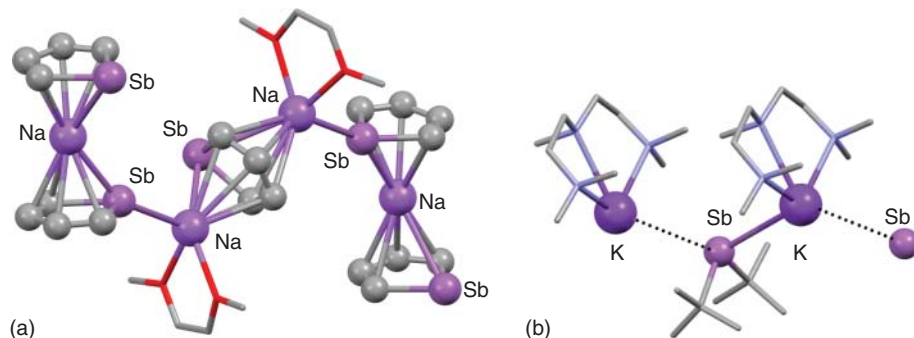
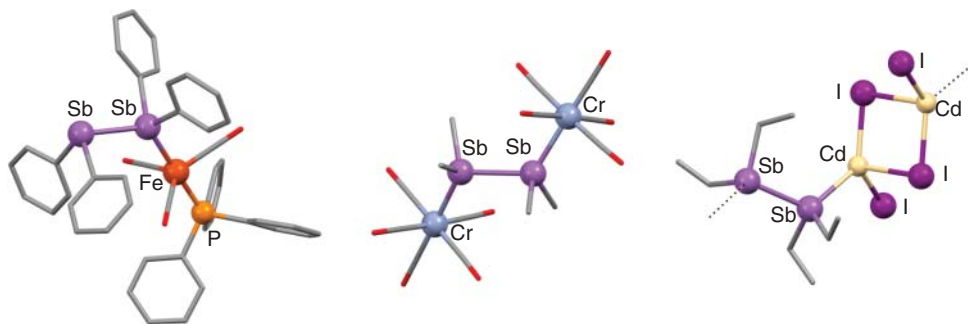
Scheme 15.6

The pnictogen–pnictogen bond of dipnictines is also easily cleaved under reducing conditions [98–100]. Such a process is illustrated in Scheme 15.7, with the reaction of octaethyldistibole (**27**) with sodium. This reaction affords the corresponding sodium stibolide (**28**), the structure of which has been elucidated by X-ray diffraction [100]. The sodium salt shows both η^1 and η^5 coordination of the stibolide to adjacent alkali metal centers, resulting in the formation of a bent chain structure (Figure 15.7). Related reactions are observed for *cyclo*-organostibines such as *cyclo*-($tBuSb$)₄ (**14**) [101, 102]. The reaction of this compound with potassium in the presence of pentamethyldiethylenetriamine (pmdeta) is accompanied by a redistribution of the *tert*-butyl ligands to produce the pmde-ta-stabilized postassium salt of tBu_2Sb^- (**29**).

Distibines are sufficiently stable to be used as donor ligands toward both main group [103, 104] and transition metal centers (Figure 15.8) [58, 105–116]. Distibines can adopt a monohapto coordination mode as in $(Ph_2SbSbPh_2)Fe(CO)_3PPh_3$ (**30**) [114], a complex obtained by the reaction of $K_2[Fe(CO)_3(PPh_3)]$ with Ph_2SbCl . The bridging dihapto mode is also known, as illustrated by



Scheme 15.7

Figure 15.7 Sections of the structures of **28** (a) and **29** (b). Hydrogen atoms are omitted for clarity.Figure 15.8 Structures of **30**, **31**, and **32**. For **32**, a portion of the polymeric chain is shown. Hydrogen atoms are omitted for clarity.

complexes such as $(\text{CO})_5\text{Cr}(\text{Me}_2\text{SbSbMe}_2)\text{Cr}(\text{CO})_5$ (**31**), which is obtained by reaction of the distibine with $(\text{CO})_5\text{Cr}(\text{THF})$ [75, 107]. Since both antimony atoms can become engaged in coordination bonds, polymeric structures are also possible [117] as is observed for the bis(CdI_2) adduct of Et_4Sb_2 (**32**), which forms extended chains [118]. The coordination chemistry of the dibismuthines is much less developed, a situation that can be assigned to the lability of the Bi–Bi bond [95]. The only such complexes reported to date are the $(\text{tBu}_3\text{M})(\text{Et}_2\text{BiBiEt}_2)(\text{M}^t\text{Bu}_3)$ ($\text{M} = \text{Al}, \text{Ga}$) derivatives, which can be isolated by simply mixing the Lewis acidic and basic components neat or in pentane at low temperatures [94].

cyclo-Stibines have also been used as ligands. The coordination chemistry of *cyclo*- $((\text{Me}_3\text{Si})_2\text{CHSb})_3$ (**13**) was investigated by Breunig and coworkers in 2003, who showed that this cyclic compound

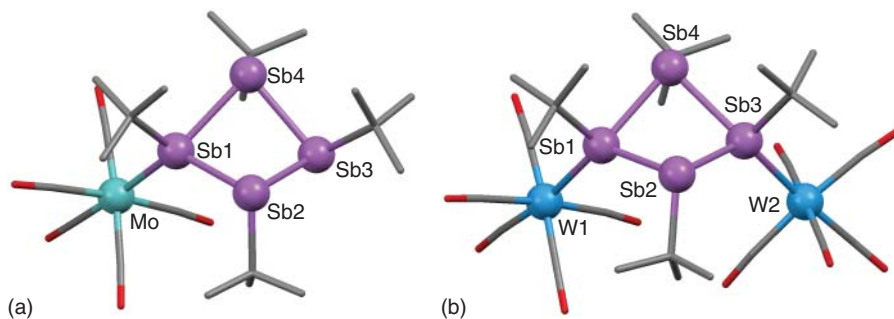


Figure 15.9 Structures of 14-Mo(CO)₅ (a) and 14-(W(CO)₅)₂ (b) Hydrogen atoms are omitted for clarity.

remains intact when coordinated to a W(CO)₅ fragment [119]. Related results have been obtained with other *cyclo*-stibines, such as *cyclo*-(^tBuSb)₄ (**14**), which can act as a ligand toward Fe(CO)₄ or Mo(CO)₅ moieties. This *cyclo*-stibine can also support the coordination of two transition metal moieties, as seen in bis(W(CO)₅) adduct, in which W(CO)₅ fragments coordinate at the 1 and 3 positions (Figure 15.9) [58, 61].

15.2.4

Compounds with Pn–Pn (Pn = Sb, Bi) Multiple Bonds

15.2.4.1 Double-Bonded Species

Some of the first evidence for the existence of distibenes [120] of general formula RSb=SbR [121] was derived from W(η²-Ph₂Sb₂)(CO)₅(W(CO)₅)₂ (**33**), which was obtained by reaction of PhSbCl₂ with Na₂W₂(CO)₁₀ [122]. This complex possesses three W(CO)₅ fragments which stabilize the distibene. Two of these fragments are coordinated to the two antimony atoms in a terminal fashion. The third W(CO)₅ fragment bridges the two antimony atoms (Figure 15.10). The existence of a Sb=Sb double bond in this complex is supported by the Sb–Sb bond distance (2.705(2) Å) which is notably shorter than the Sb–Sb single bond of Ph₄Sb₂ (**1-Ph**, 2.844(1) Å) [39].

Although a few more transition metal-stabilized distibenes have been reported [123–126], the isolation of free distibenes could be achieved only through the use of extremely bulky aryl substituents [127, 128]. Tokitoh and coworkers showed that the triselenatristibine (TbtSbSe)₃ (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) can be reduced by hexamethylphosphorus triamide (Me₂N)₃P in toluene at 100 °C to afford TbtSb=SbTbt (**34-Tbt**, Scheme 15.8) [120]. This compound features a short Sb=Sb distance of 2.642(1) Å, which is almost 7% shorter than the Sb–Sb single bond of Ph₄Sb₂ (**1-Ph**, 2.844(1) Å) [129]. The Sb–Sb–C bond angle of 101.4° in **34-Tbt** is

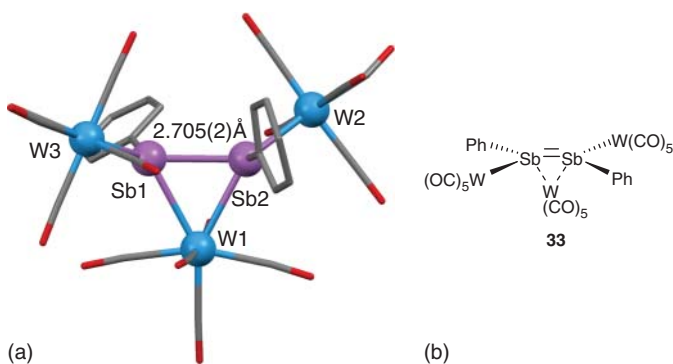
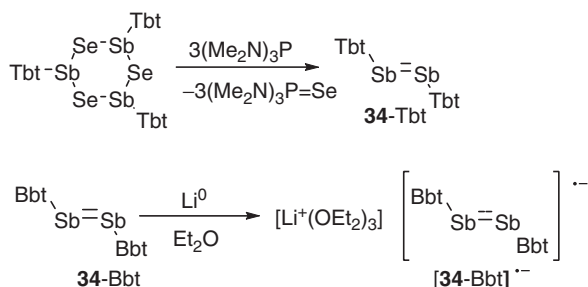


Figure 15.10 Structure of **33**. Hydrogen atoms are omitted for clarity.



Scheme 15.8

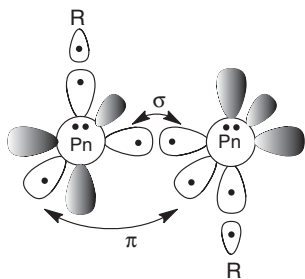


Figure 15.11 Simplified molecular orbital representation accounting for the structure of dipnictenes. This representation is extreme as it assumes no s/p hybridization [130].

thought to be a manifestation of the core-like character of the 5s pair and the consequentially high p character of the Sb–C σ -bonds, the Sb–Sb σ -bond, and the Sb–Sb π -bond (Figures 15.11 and 15.12) [130–132]. Continued efforts in the chemistry of these multiple-bonded species have shown that different bulky substituents can be employed [132]. These additional studies have also demonstrated the viability of the reduction of organoantimony dihalides with LiAlH_4 , K, or Mg as synthetic alternatives in the preparation of distibenes. Known distibenes are listed in Table 15.2 along with key geometric parameters [131, 133, 134, 135]. All are characterized by an acute Sb–Sb–C bond angle and a short Sb=Sb bond. All reported distibene compounds are also intensely colored as a result of π – π^* and n – π^* electronic transitions.

A number of reactions of distibenes have been observed. For example, **34-Tbt** reacts with Br_2 , I_2 , or O_2 to afford TbtSbBr_2 , TbtSbI_2 , and the dioxadistibine $(\text{TbtSbO})_2$, respectively. Some of these compounds are also amenable to reversible redox processes. The distibene $\text{BbtSb}=\text{SbBbt}$ (**34-Bbt**, Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl) displays an irreversible oxidation wave at around +1.02 V, and a reversible one electron reduction at –1.65 V, suggesting formation of a stable radical anion ($[\mathbf{34-Bbt}]^{\bullet-}$) [131]. Radical $[\mathbf{34-Bbt}]^{\bullet-}$ can be generated by reaction with lithium metal and isolated as a $[\text{Li}(\text{OEt}_2)_3]^+$ salt (Scheme 15.8). The crystal structure of this salt shows a lengthening of the Sb–Sb bond from 2.704(1) Å in the neutral distibene to 2.751(1) Å in the radical anion, a phenomenon consistent with the population of the Sb–Sb π^* orbital by one electron (Figure 15.12).

Analogous strategies to those employed for the stabilization of distibenes have also proved successful for dibismuthenes. A metal-stabilized example of a dibismuthene (**35**) was obtained by the reaction of an equilibrating mixture of *cyclo*-trimer and -pentamer of $[(\text{Me}_3\text{SiCH}_2)\text{Bi}]$ with $\text{W}(\text{CO})_5(\text{THF})$ in THF (Scheme 15.9) [140, 141]. A structural analysis of the product shows a *cis*-dibismuthene which is coordinated side-on to two $\text{W}(\text{CO})_5$ fragments (Figure 15.13). The Bi–Bi bond of 3.003(1) Å is quite long and in the range of that typically observed for Bi–Bi single bonds as in 2-Ph (2.990(2) Å) [40]. This long Bi–Bi bond indicates that the formal Bi=Bi double bond of the dibismuthene unit experiences strong activation by the two transition metal centers. A much shorter

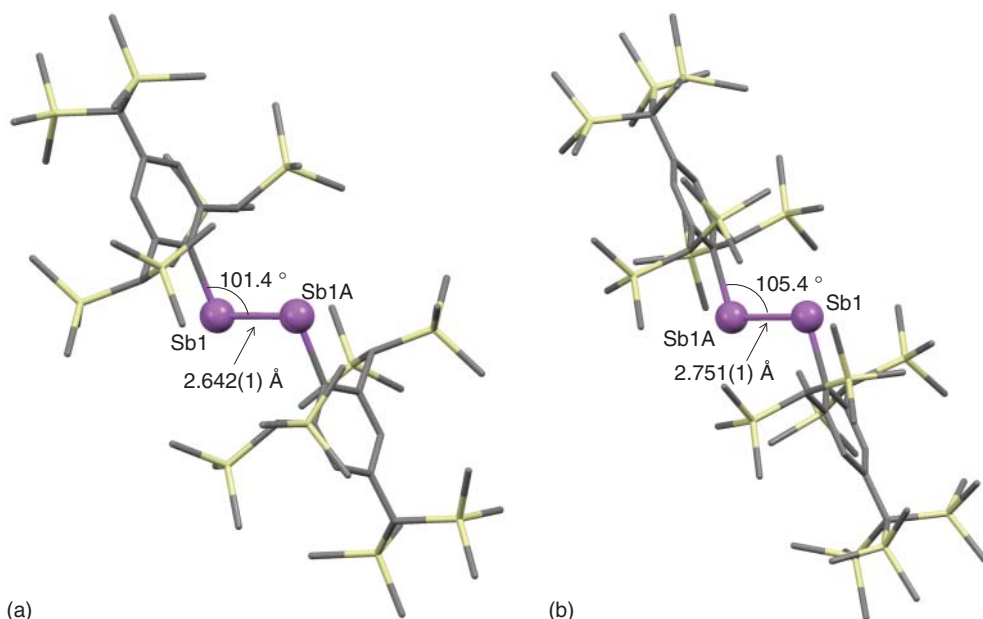
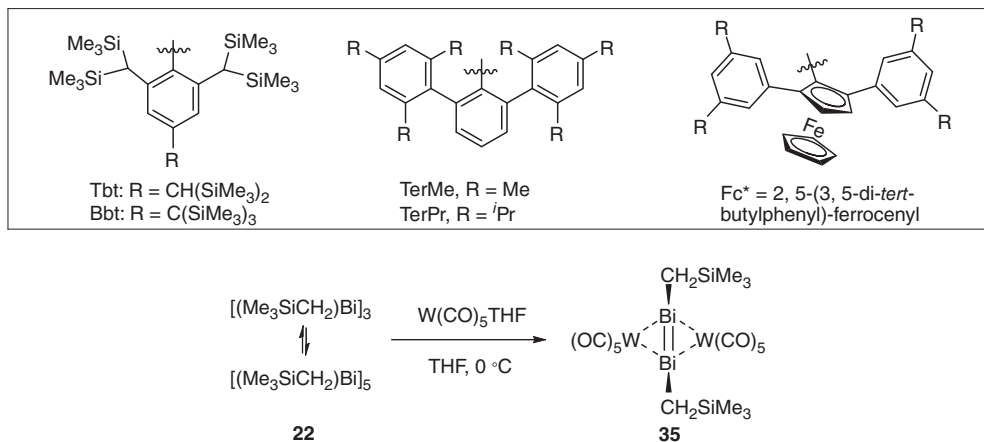


Figure 15.12 The structure of **34-Tbt** (a) and **[34-Bbt]^{•–}** (b). Hydrogen atoms are omitted for clarity.

Table 15.2 Selected structural data for compounds with Pn=Pn double bonds (Pn = Sb, Bi).

Compound	Pn=Pn (Å)	C–Pn–Pn (°)	References
TbtSb=SbTbt (34-Tbt)	2.642(1)	101.4(1)	[120]
BbtSb=SbBbt (34-Bbt)	2.7037(6)	105.4(1)	[133]
(TerMe)Sb=Sb(TerMe) (34-TerMe)	2.6558(5)	94.1(1)	[134]
(TerPr)Sb=Sb(TerPr) (34-TerPr)	2.668(2)	98.9(2)	[131]
Fc ⁺ Sb=SbFc ⁺ (34-Fc⁺)	2.7511(4)	102.29(8)	[135]
TbtBi=BiTbt (36-Tbt)	2.8206(8)	100.5(2)	[136]
BbtBi=BiBbt (36-Bbt)	2.8699(6)	104.1(1)	[133]
(TerMe)Bi=Bi(TerMe) (36-TerMe)	2.8327(14)	92.5(4)	[134]
(TerPr)Bi=Bi(TerPr) (36-TerPr)	2.8560(3)	105.44(6)	[134]
Fc ⁺ Bi=BiFc ⁺ (36-Fc⁺)	2.8307(3)	96.17(9)	[135]
((^t Bu ₂ PhSi) ₂ P)Bi=Bi(P(^t Bu ₂ PhSi) ₂)	2.8206(9)	89.38(4)	[137]
[K-2.2.2-Cryptand] ₂ [Bi ₂]	2.8377(7)	n/a	[138]
[Cs·(18-crown-6)(NH ₃) ₂] ₂ [Bi ₂]	2.8645(4)	n/a	[139]

bond of 2.821(1) Å is observed in metal-free examples of dibismuthenes such as TbtBi=BiTbt [136] (**36-Tbt**), which was synthesized by a route analogous to that employed for the antimony analog (Scheme 15.8). This short bond distance unambiguously supports the presence of a Bi=Bi double bond. As for the distibenes, the Bi–Bi–C angle of 100.5° of **36-Tbt** shows that all bonding orbitals at bismuth have a dominant p character (Figure 15.11). Since these pioneering studies, additional examples of dibismuthenes that differ by the nature of the substituent have been reported [133, 134, 135, 137, 142, 143]. Selected structural data for these dibismuthenes are summarized in Table 15.2. The formation of Bi=Bi double bonds is not restricted to dibismuthenes. They have also been observed in salts containing the [Bi=Bi]^{2–} units [139]. One of these salts ([K-2.2.2-Cryptand]₂[Bi₂], **37**) is obtained by reaction of K₅In₂Bi₄ in ethylenediamine in the presence 2.2.2-Cryptand [138].



Scheme 15.9

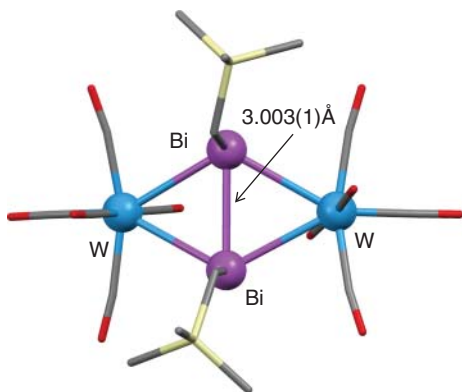
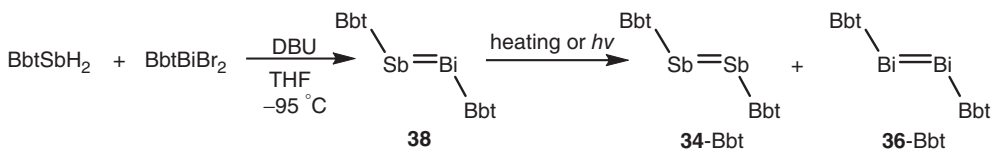


Figure 15.13 Structure of 35. Hydrogen atoms are omitted for clarity.

The [Bi₂]^{2−} dianion of **37** features a Bi=Bi bond distance (2.838(1) Å) comparable to that observed in dibismuthenes (Table 15.2) [138]. It is also interesting to note that while isoelectronic with O₂, [Bi₂]^{2−} appears to have a singlet ground state.

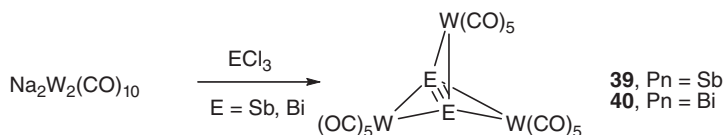
In addition to the homobimetallic dipnictenes (Sb and Bi) discussed above, Tokitoh and coworkers reported BbtSb=BiBbt (**38**), the only example of a heterobimetallic dipnictene species between Sb and Bi, via the condensation of the primary stibine and the dibromobismuthine in the presence of DBU (Scheme 15.10) [144]. This stibabismuthene, which is stable in the absence of light, undergoes disproportionation upon heating or irradiation to generate the corresponding symmetrical distibene (**34-Bbt**) and dibismuthene (**36-Bbt**).



Scheme 15.10

15.2.4.2 Triple-Bonded Species

The diatomic molecules Sb_2 and Bi_2 have been studied in the gas phase. The presence of a triple bond in these molecules is supported by the $\text{Sb}\equiv\text{Sb}$ (2.341 Å) and $\text{Bi}\equiv\text{Bi}$ (2.659 Å) bond lengths, which are noticeably shorter than the corresponding $\text{Pn}=\text{Pn}$ double bond distances summarized in Table 15.2 [145]. In the condensed state, these triply bonded diatomic units have been observed in the coordination spheres of transition metals. For example, the reaction of SbCl_3 or BiCl_3 with $\text{Na}_2\text{W}_2(\text{CO})_{10}$ produces complexes of general formula $(\text{Pn}\equiv\text{Pn})(\text{W}(\text{CO})_5)_3$ ($\text{Pn} = \text{Sb}$ (**39**), Bi (**40**)) with the dipnictogen molecule coordinated in a threefold, dihapto fashion to the $\text{W}(\text{CO})_5$ fragments (Scheme 15.11) [122, 146]. This coordination mode leads to a considerable weakening of the triple bond, which is reflected by the relatively long $\text{Pn}\text{--}\text{Pn}$ distances of 2.663 Å for **39** and 2.818 Å for **40** (Figure 15.14). A theoretical investigation of the arsenic analog of such complexes favors a bonding model in which the dipnictogen acts as a $6e^-$ donor to the three coordinated $\text{W}(\text{CO})_5$ fragments (Figure 15.14) [147]. A similar bonding situation can be envisioned for complexes of general formula $(\text{Pn}\equiv\text{Pn})(\text{Mn}(\text{CO})_2\text{Cp})_3$, which have also been described [146].



Scheme 15.11

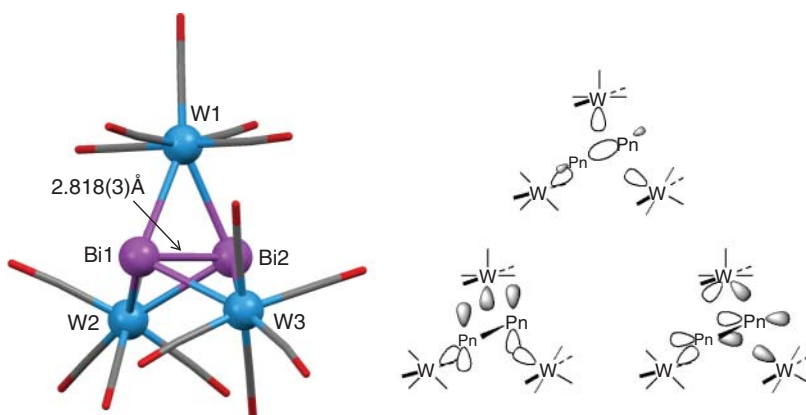


Figure 15.14 Structure of **40** and bonding description according to extended Hückel calculations carried out in the As analog [147].

15.3

Complexes with M–Sb and M–Bi Bonds (M = d-Block Metal)

The chemistry of complexes featuring antimony and bismuth–metal bonds has garnered increased interest with their involvement in catalysis and use as single-source precursors, among other applications. For the past few decades, the field has continued to develop and now includes a large collection of complexes involving both main group elements and transition metals. In the preceding sections we have described a few complexes such as **28** and **29** which feature a main group metal bound to antimony or bismuth. We also note that this research area has been treated in a series of recent reviews which do not need to be duplicated here [4, 5, 16]. For this reason, we have chosen to focus this section on the chemistry of complexes featuring a bond between a transition metal and antimony or bismuth. Currently, transition metal complexes featuring an antimony or

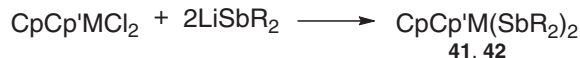
bismuth–metal bond are known for Groups 4–11. A few reviews on this topic are available in the literature [6, 148], one of which covers the chemistry of inorganic bismuthide compounds and bismuth-containing clusters in greater detail [148].

15.3.1

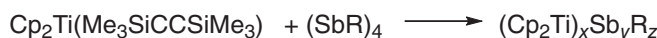
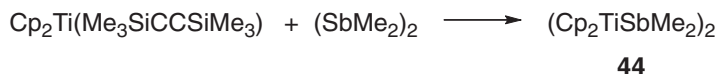
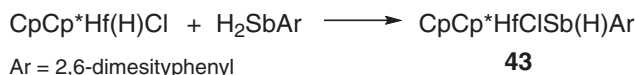
Complexes Containing R_2Pn Fragments as Ligands ($Pn = Sb$ or Bi)

15.3.1.1 Group 4 and 5 Complexes

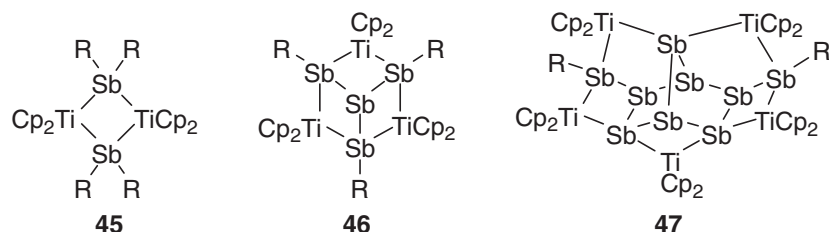
The chemistry of organoantimony–Group 4 metal complexes consists entirely of their metallocene derivatives. The first organoantimonide Group 4 metal complex, $Cp_2Zr(SbPh_2)_2$ (**41-Me**) was reported in 1984 by reaction of the corresponding lithium stibide with Cp_2ZrCl_2 , a method that has been extended to other zirconium and hafnium complexes (see compounds of types **41**, **42**, Scheme 15.12) [29, 149]. Other approaches to such complexes include the dehydrogenative coupling of a primary stibine and a metallocene hydride as in the case of $CpCp^*HfCl(Sb(H)(2,6-Mes_2C_6H_3))$ (**43**), which has been structurally characterized (Scheme 15.12) [150]. Other examples of such complexes include the titanium complex **44** as well as the polynuclear clusters **45–47** which are obtained by addition of a distibine or *cyclo*-tetrastibine to the titanocene alkyne complex $Cp_2Ti(Me_3SiCCSiMe_3)$ (Scheme 15.12) [140, 151].



$M = Zr$: **41** ($Cp' = Cp$) with $R = Ph$
 $M = Hf$: **42** ($Cp' = Cp^*$) with $R = Mes$



$R = Et$ $x = 2$ $y = 2$ $z = 4$ (**45**)
 $R = 2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4$ $x = 3$ $y = 4$ $z = 3$ (**46**)
 $R = Me_3SiCH_2$ $x = 5$ $y = 9$ $z = 2$ (**47**)



Scheme 15.12

Bridging organostibides, such as those seen in **44** [140], feature distorted tetrahedral geometries at the antimony centers (Figure 15.15). Terminal organostibides have been shown to adopt both pyramidal and trigonal planar geometries, with $CpCp^*Hf(SbMes_2)_2$ (**42**^{*}-Mes) providing an interesting

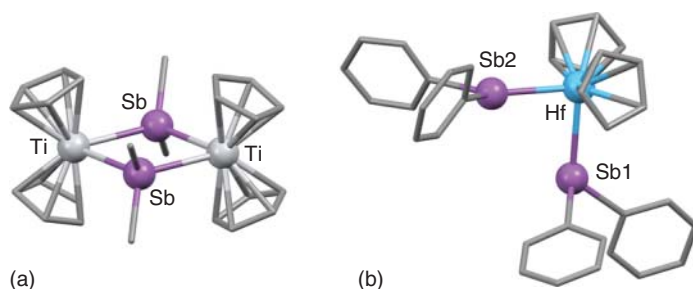
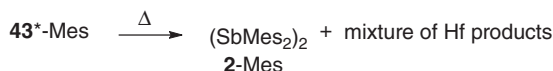
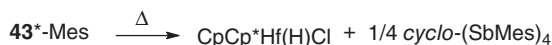
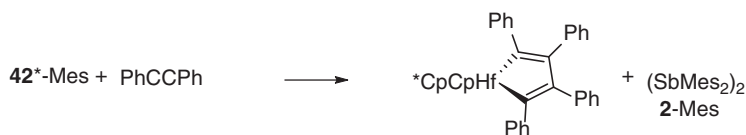
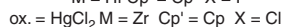
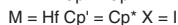


Figure 15.15 Structure of **44** (a) and **42**^{*}-Mes (b). Hydrogen atoms and methyl groups on the mesityl rings and the Cp^{*} methyl groups are omitted for clarity.

example of both geometries being present in the same structure (Figure 15.15). In **42**^{*}-Mes, the sum of angles about the pyramidal stibide ligand (Sb1) is equal to 330.4°, and the Hf–Sb1 distance of 3.014(1) Å is similar to the Hf–Sb distance of 3.0035(8) Å observed in the related **43**. The second stibide ligand (Sb2), however, attains a trigonal planar geometry, with the sum of angles about antimony equal to 358.4°. The Hf–Sb2 distance of 2.782(1) Å is considerably shorter than the Hf–Sb1 distance. These geometric parameters suggest that the second stibide ligand engages in considerable π bonding with the hafnium center and thus possesses multiple-bond character, while the first stibide ligand may be considered singly bonded. A similar bonding situation has been observed in related hafnium organophosphide complexes [152]. The reactivity of organoantimony–Group 4 metal complexes is marked by the considerable lability of the Sb–Group 4 metal bonds, especially with respect to net elimination of distibines. The exact mechanism of distibine formation remains uncertain. Several selected reactions are shown in Scheme 15.13 [29, 149, 150]. The reaction of **42**^{*}-Mes with HCl which produces Mes₂SbH and the corresponding hafnocene dichloride attests to the polarization of the Hf–Sb bond toward antimony.



Scheme 15.13

15.3.1.2 Group 5 Complexes

Compared to the chemistry of organoantimony Group 4 complexes, reports concerning complexes containing organoantimony- or organobismuth–Group 5 bonds are notably scarcer. $\text{Cp}_2\text{VSbPh}_2$ (**48**) and $(^t\text{BuO})_2\text{VSbPh}_2$ (**49**) were prepared from LiSbPh_2 and the corresponding vanadium halides [153]. Stibide-bismuthide-substituted niobocenes of the form $\text{Cp}_2\text{NbH}_2\text{PnPh}_2$ (**50** for $\text{Pn} = \text{Sb}$ and **51** for $\text{Pn} = \text{Bi}$) have also been prepared from treatment of Cp_2NbH_3 with Ph_2PnCl in the presence of NEt_3 [141, 154] $\text{Cp}_2\text{NbH}_2\text{SbPh}_2$ (**50**), which is to date the only structurally characterized complex containing an antimony- or bismuth–Group 5 metal bond, features a pyramidal antimony center and an Sb–Nb bond length of 2.8929(4) Å, which is slightly smaller than the sum of their covalent radii (3.03 Å) (Figure 15.16) [155]. Information on the reactivity of the heavy pnictogen–Group 5 complexes is also scarce. The antimony–vanadium complexes **48** and **49** are reported to form distibines when heated in solution, and undergo antimony–vanadium bond cleavage when treated with excess HCl or Br_2 [153]. Complex **50** is reported to be thermally stable at room temperature under inert atmosphere, whereas the bismuth analog **51** is both thermally unstable and light sensitive.

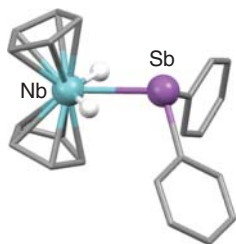
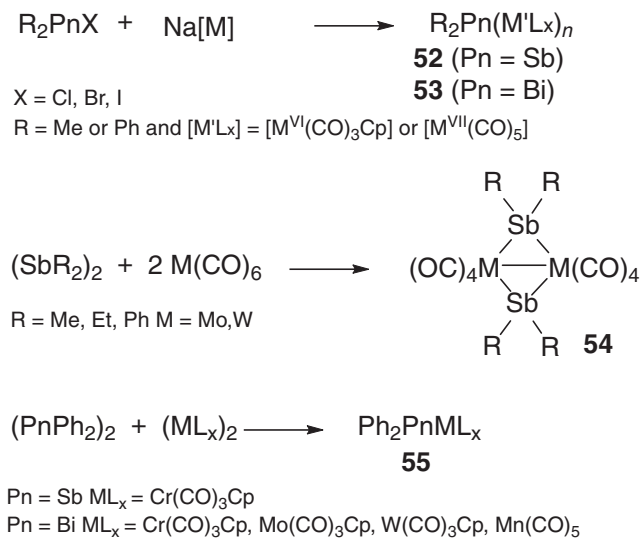


Figure 15.16 Structure of **50**. Cp and phenyl hydrogen atoms are omitted for clarity.

15.3.1.3 Group 6 and 7 Complexes

A large family of complexes of type **52** and **53** (Scheme 15.14) are accessible via simple metathesis reactions between anionic Group 6 and 7 complexes and antimony or bismuth halides [156–162]. Reactions of *in situ*-generated alkali organostibides and bismuthides with Group 6 and 7 halides have



Scheme 15.14

also been reported as an effective method to access these compounds [159, 163, 164]. Another strategy which exploits the weakness of Pn–Pn bonds is based on the direct reaction of metal carbonyls with triaryl pnictines [165–169] or dipnictines. Two examples of such reactions are presented in Scheme 15.14. Reaction of distibines with molybdenum or tungsten hexacarbonyl produces dinuclear complexes with bridging stibides of type **54** [109]. Another illustration is found in the reaction of Ph_4Pn_2 (**1-Ph**, **2-Ph**) with dinuclear metal carbonyls such as $\text{Mn}_2(\text{CO})_{10}$. Such reactions proceed by exchange to produce the corresponding terminal organopnictide complexes of type **55** [170].

In stibide and bismuthide metal carbonyl complexes, the carbonyl stretching frequencies provide insight into the nature of the pnictogen–transition metal σ bonds. A representative series of organopnictogenide chromium complexes and their respective carbonyl stretching frequencies are presented in Table 15.3. With respect to the coordinated pnictogenide, the stretching frequencies of the chromium-bound carbonyl ligands decrease in the order $\text{P} > \text{As} > \text{Sb} > \text{Bi}$, indicating that the σ -donicity of the pnictogenide fragment increases upon descending the group. This trend, which reflects the increasing electropositivity and electron releasing properties of the pnictogen atom as the group is descended, has also been documented in chalcogen/chalcogenide [172, 173] and halide [174] complexes of metal carbonyls.

Structures have been reported for several terminal and bridging Group 6 and 7 organostibide and bismuthide complexes. Structural features from selected complexes (**52b**, **52c**, **53a**) are shown in Table 15.4. In terminal organostibide and bismuthide complexes, the pnictogen center remains strongly pyramidalized, indicating that the pnictogen lone pair remains largely uninvolved with bonding to the Group 6/7 metal center. Compared to organobismuthide complexes, the corresponding organostibide complexes have a much higher propensity for bridging behavior, with only two monomeric, terminal organostibide complexes having been characterized to date (Figure 15.17) [175]. These complexes, which feature the bis(trifluoromethyl)stibide ligand, are also unusual in that they display Sb–M bonds significantly shorter than the distance predicted based on their respective atomic radii (3.01 Å for **52b** and 2.78 Å **52c**) [155]. These short distances are attributed to significant back-bonding from the metal centers. The accepting orbital of these back-bonding interactions are most likely the σ^* Sb–C orbitals, whose energy is significantly lowered by the electronegative trifluoromethyl substituents (Figure 15.17) [177].

Table 15.3 IR spectra of pnictide complexes of the formula $\text{Ph}_2\text{PnCr}(\text{CO})_3\text{Cp}$.

Complex	ν_{CO} (cm^{-1})	References
$\text{Ph}_2\text{PCr}(\text{CO})_3\text{Cp}^{\text{a}}$	2005, 1976, 1922	[171]
$\text{Ph}_2\text{AsCr}(\text{CO})_3\text{Cp}^{\text{b}}$	1998, 1934, 1929	[170]
$\text{Ph}_2\text{SbCr}(\text{CO})_3\text{Cp}^{\text{b}}$ (52a)	1990, 1931, 1915	[170]
$\text{Ph}_2\text{BiCr}(\text{CO})_3\text{Cp}^{\text{b}}$ (53a)	1983, 1926, 1904	[170]

a) Benzene solution.

b) Heptane solution.

Table 15.4 Selected geometric data from Group 6/7 stibide and bismuthide complexes.

Complex	Sum of Pn angles ($^\circ$)	Pn–M bond length (Å)	Sum of Pn–M covalent radii [155] (Å)	References
$(\text{F}_3\text{C})_2\text{SbW}(\text{CO})_3\text{Cp}$ (52b)	300.7	2.8058(7)	3.01	[175]
$(\text{F}_3\text{C})_2\text{SbMn}(\text{CO})_5$ (52c)	292.4	2.6630(12)	2.78	[175]
$\text{Ph}_2\text{BiMn}(\text{CO})_5$ (53a)	297.0	2.842(2)	2.87	[176]

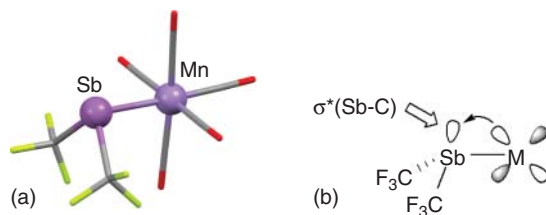
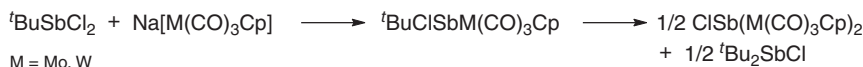


Figure 15.17 Structure of **52b** (a) and drawing (b) showing the back-bonding interaction involving the metal d-orbital to the σ^* Sb–C orbitals.

Stibide and bismuthide complexes of Group 6 and 7 metals have been reported to undergo ligand redistribution in solution as illustrated in Scheme 15.15 [158, 160]. Reactions with halogens, as illustrated for complexes of type **52** and **53** in Scheme 15.16, readily induce cleavage of the pnictogen–metal bond [159, 170, 178, 179]. This process has been reported to proceed with oxidation at the pnictogen center, followed by reductive elimination of a metal halide fragment [178]. Alkylation is reported to proceed in a similar fashion for stibide complexes to afford the corresponding cationic stibine complexes, which are reported in some instances to decompose/dissociate to a stibine and a metal halide [156, 157, 160, 179].



M = Mo, W



M = Cr, Mo, W

Scheme 15.15



X = Cl, Br, I

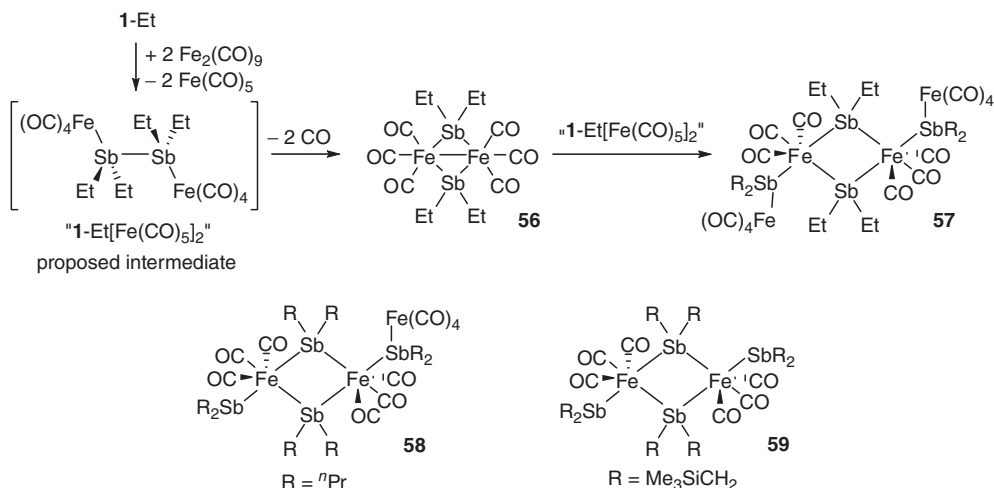
Pn = Sb, Bi R = Me, Ph $\text{ML}_x = \text{MVI}(\text{CO})_3\text{Cp}$

Scheme 15.16

15.3.1.4 Group 8 Complexes

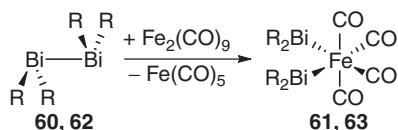
Group 8 stibides and bismuthides, in particular the iron derivatives, are perhaps the best studied group of complexes containing antimony- and bismuth–transition metal bonds. Iron-substituted complexes are the most prevalent, with $[\text{Fe}(\text{CO})_n]$ and $[\text{Fe}(\text{CO})_2\text{Cp}]$ fragments being the most common substituents. The first Group 8 organostibide complexes were reported in the 1970s [156, 180, 181], while the first of their bismuth analogs were reported in the early 1980s [182, 183]. Synthesis of Group 8 stibides and bismuthides is in many cases analogous to that of their Group 6 and 7 analogs, with salt metathesis as the main synthetic route [156, 159, 162, 182, 184–190].

Group 8 stibides and bismuthides may also be prepared from the reaction of dipnictines with low-valent Group 8 complexes [110, 180, 191, 192]. Reactions of distibines and dibismuthines with zerovalent homoleptic iron carbonyl species are among the best studied of these processes. Such an approach is illustrated in Scheme 15.17 with the reaction of **1-Et** with $\text{Fe}_2(\text{CO})_9$. The reaction is proposed to proceed via initial coordination of the antimony centers to $\text{Fe}(\text{CO})_4$ fragments, followed by cleavage of the Sb–Sb bond to afford a bridging bis-organostibide complex (**56**), which has been spectroscopically observed (Scheme 15.17) [110]. This bridged complex is proposed to then undergo further additions of free or coordinated distibines to furnish **57** [192]. The nature of the



Scheme 15.17

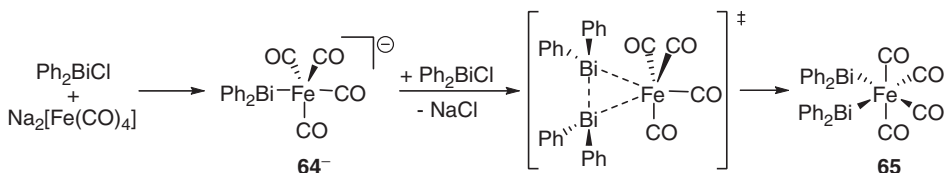
distibine substituent affects the fate of these reactions as illustrated by compounds **58** and **59**, which are obtained when starting from (ⁿPr)₄Sb₂ or (Me₃SiCH₂)₄Sb₂, respectively [192]. Analogous reactions with dibismuthines proceed via insertion of an Fe(CO)₄ fragment into the Bi–Bi bond, as illustrated by the reactions of dibismuthines **60** and **61** with Fe₂(CO)₉ to yield the bis-bismuthide products **62** and **63** (Scheme 15.18) [191].



60, 62 (R = ^tBuCH₂); **61, 63** (R = Me₃SiCH₂)

Scheme 15.18

Similar bismuthide complexes have also been observed in the stepwise addition of Ph₂BiCl to the [Fe(CO)₄]^{2−} anion (Scheme 15.19) [162, 193]. Sequential addition of Ph₂BiCl affords the mono- (**64**) and bis-bismuthide (**65**) complexes. Based on the ability of the [Ph₂BiFe(CO)₄][−] anion to coordinate unsaturated metal centers via the bismuthide ligand's lone pair [193], formation of the bis-bismuthide complex is proposed to proceed through a disbismuthine-like transition state.



Scheme 15.19

Examples of Group 8 bismuthides that have been structurally characterized include [PPN][Ph₂BiFe(CO)₄] (PPN = bis(triphenylphosphine)iminium, **64**[−]) and (Ph₂Bi)₂Fe(CO)₄ (**65**). The pyramidal (sum of angles = 300.5°) bismuth center in [PPN][Ph₂BiFe(CO)₄] (Figure 15.18) occupies an axial

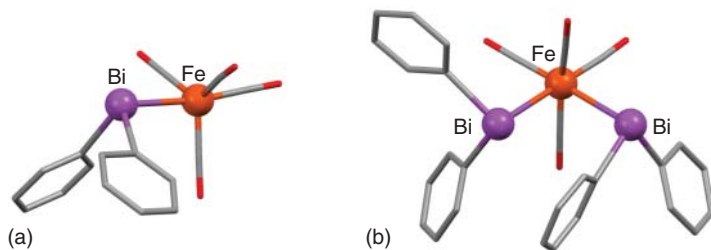


Figure 15.18 Structures of **64[−]** in the PPN⁺ salt (a) and **65** (b). Hydrogen atoms are omitted for clarity.

Table 15.5 IR spectra of metallopnictine complexes of the formula R₂PnFe(CO)₂Cp.

Complex	ν_{CO} (cm ^{−1})	References
Mes(Me)PFe(CO) ₂ Cp ^{a)}	1998, 1954	[194]
Me ₂ AsFe(CO) ₂ Cp ^{b)}	1997, 1949	[195]
Me ₂ SbFe(CO) ₂ Cp ^{b)}	1997, 1949	[156]
Me ₂ BiFe(CO) ₂ Cp ^{c)}	1972, 1924	[182]

- a) Pentane.
b) Cyclohexane.
c) Benzene.

position of the trigonal bipyramidal iron center, and features a Bi–Fe bond length of 2.676(4) Å. Complex **65** features Bi–Fe bond distances of 2.823(2) and 2.832(2) Å that are considerably longer than found in [PPN][Ph₂BiFe(CO)₄], a feature which is attributed to steric crowding at the pseudo-octahedral iron center. The distance between the two pyramidalized bismuth centers is about 4 Å, suggesting that they are not bonded to each other.

Similar to their Group 6/7 analogs, Group 8 stibides and bismuthides complexes with carbonyl ligands can be studied by IR spectroscopy. As observed for Group 6/7 analogs, the stretching frequencies observed in iron carbonyl substituted organopnictines tend to decrease in the order P > As > Sb > Bi, indicating that heavier and more electron-releasing pnictogens serve as stronger σ donors toward the transition metal center. A representative series of iron-substituted pnictines are shown in Table 15.5.

As seen in Scheme 15.13, reaction of the hafnium complex **42⁺**-Mes with HCl suggests polarization of the Hf–Sb bond toward antimony. As the transition metal becomes more electronegative and the pnictogen more electropositive, the M–Pn bond is expected to become more polarized toward the transition metal center. Although no calculations are available for the diorganostibide and diorganobismuthide complexes described in this chapter, a series of calculations on complexes such as Cl₂BiFe(CO)₂Cp shows that Fe–Bi bond is indeed polarized toward the iron center [196].

15.3.1.5 Group 9 Complexes

The majority of Group 9 stibide and bismuthide complexes reported to date are cobalt derivatives [113, 197, 198]. Calderazzo and coworkers demonstrated that Co₂(CO)₈ undergoes facile insertion into distibines and dibismuthines to afford their corresponding organostibide (**66**) and bismuthide (**67**) complexes (Scheme 15.20) [199]. Based on spectral data and parallel gas volumetric experiments, it was proposed that the antimony derivative is oligomeric, whereas the bismuth derivative is



Scheme 15.20

monomeric in nature. A triphenylphosphine-substituted derivative (**68**) of the bismuthide complex **67** was structurally characterized (Figure 15.19), revealing a pyramidalized bismuth center (sum of angles = 295.1°) and a Bi–Co bond distance of 2.692(5) Å, which is close to the distance predicted based on covalent radii (2.74 Å) [155].

An unusual rhodium complex (**69**) was prepared by the reaction of 2 equiv. of LiSbPh_2 with $[(\text{COD})\text{Rh}(\mu\text{-Cl})]_2$ ((COD = 1,5-cyclooctadiene), Scheme 15.21) [113]. This complex, which was formulated as a bis-distibine complex by the authors, features a $[(\mu\text{-Ph}_2\text{Sb}-\text{Rh}(\text{COD}))_2]$ motif with an Sb(1)–Sb(1a) distance of 3.155(1) and Sb–Rh bond lengths of 2.630(1) and 2.678(1) Å (Figure 15.20). The long separation between the Sb(1) and Sb(1a) centers of this unit suggests that there is little interaction between the two atoms. A distibine moiety with an Sb(2)–Sb(2a) bond of 2.926(2) Å in an unusual *cis* configuration bridges the $[(\mu\text{-Ph}_2\text{Sb}-\text{Rh}(\text{COD}))_2]$ unit, completing the coordination sphere at rhodium.

Another unique series of compounds containing rhodium and a heavy pnictogen element are hetero-bimetallic carboxylate bridged species [200, 201] such as **70** (Scheme 15.22) [202]. This compound is prepared by combining $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]$ with $[\text{Bi}_2(\text{O}_2\text{CCF}_3)_4]$, an unusual Bi–Bi bonded derivative, and heating the resulting mixture in an evacuated ampule. A structure of this complex shows formation of a Bi–Rh bond of 2.5493(3) Å [202], a distance significantly shorter than the sum of the covalent radii of the two elements (2.90 Å) [155]. A bonding analysis of this complex shows that the sole bonding interaction between the two central atoms is a σ -bond, which results from the overlap of the bismuth $6p_z$ orbital with the Rh $4d_{z^2}$ orbital (see inset in Scheme 15.22) [201].

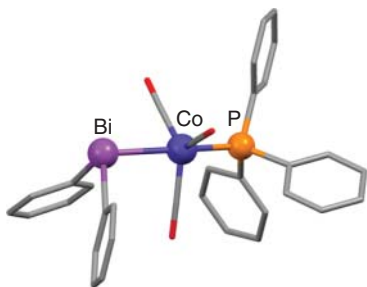
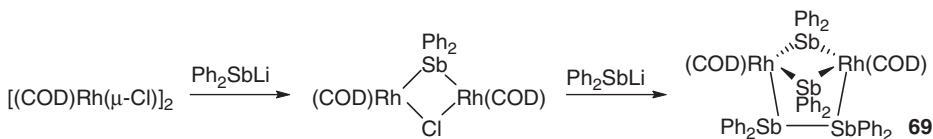


Figure 15.19 Structure of **68**. Hydrogen atoms are omitted for clarity.



Scheme 15.21

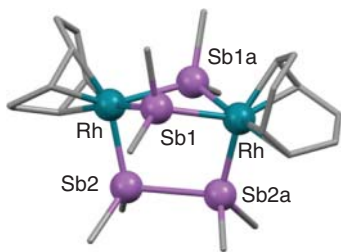
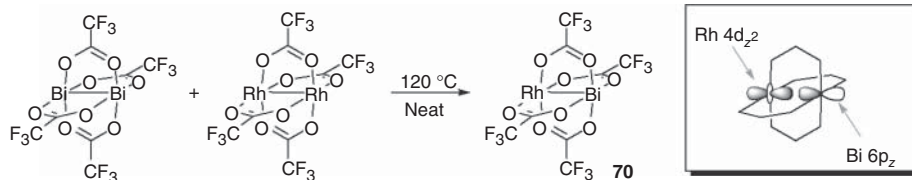


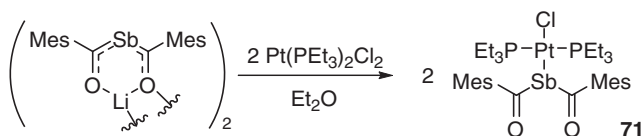
Figure 15.20 Structure of **69**. Phenyl rings are truncated and hydrogen atoms are omitted for clarity.



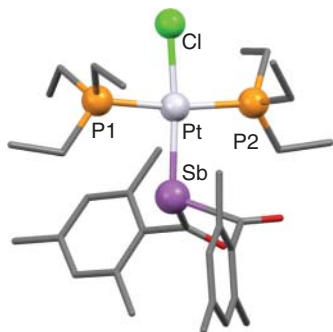
Scheme 15.22

15.3.1.6 Group 10 and 11 Complexes

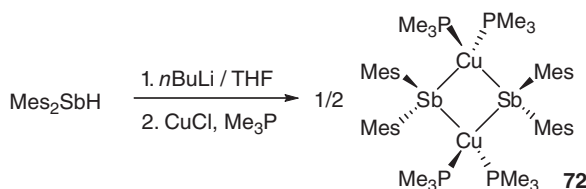
While diorganobismuthide complexes of Group 10 or 11 transition metals are not known, a few anti-mony derivatives have been described, many of which exist as clusters [165–169, 203–208]. The only monometallic Group 10 complex known is the platinum complex **71**, obtained by the reaction of $(\text{Li}(\text{Sb}[\text{C}(\text{O})\text{Mes}]_2))_2$ with $\text{cis-}[\text{PtCl}_2(\text{PEt}_3)_2]$ (Scheme 15.23) [184]. In the solid state structure, the platinum center of **71** has a slightly distorted square planar coordination environment, with *trans*-phosphine ligands and the organostibide ligand *trans* to a chloride (Figure 15.21). In addition, the antimony center has distorted pyramidal geometry. The antimony center of the organostibide ligand adopts a pyramidal geometry, indicating that the antimony lone pair does not engage strongly with the platinum center.



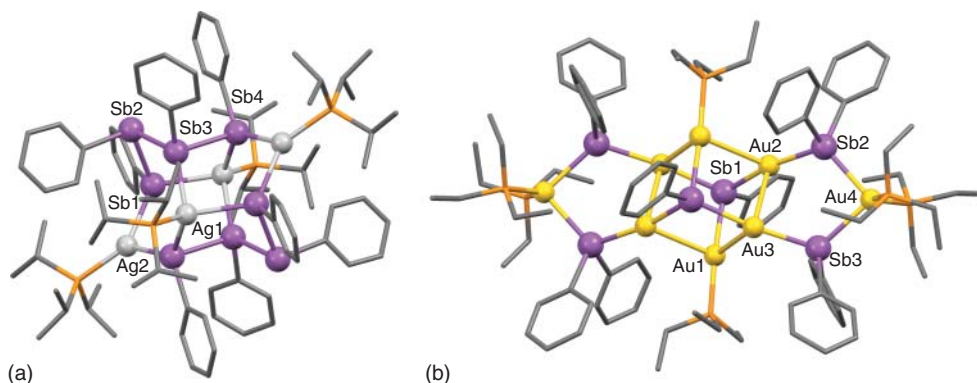
Scheme 15.23

Figure 15.21 Structure of **71**. Hydrogen atoms are omitted for clarity.

One of the simplest Group 11 stibide complexes (**72**) can be obtained by reaction of Mes_2SbLi with CuCl in the presence of PMe_3 (Scheme 15.24) [209]. The crystal structure of **72** features a planar Cu_2Sb_2 core with the average $\text{Sb}-\text{Cu}$ and $\text{Cu}-\text{Sb}-\text{Cu}$ angles of $95.11(5)^\circ$ and $84.89(5)^\circ$, respectively. The geometry at both the antimony and copper centers is distorted tetrahedral. In agreement with the bridging behavior of the stibide ligand, the average $\text{Cu}-\text{Sb}$ distance of $2.669(2) \text{ \AA}$ is close to the sum of the covalent radii for these elements ($2.71 \text{ \AA}$) [155]. It is also longer than the value of $2.554(2) \text{ \AA}$ reported for the $\text{Sb}-\text{Cu}$ bond of $[\text{Cu}(\text{SbPh}_3)_3\text{Cl}]$ [210]. Other higher nuclearity Group 11 stibide complexes have also been described. These include the silver and gold complexes $([\text{Ag}_4(\text{Sb}_4\text{Ph}_4)_2(\text{P}^i\text{Pr}_3)_4])$ (**73**) and $[\text{Au}_8(\text{SbPh})_2(\text{SbPh}_2)_4(\text{PEt}_3)_6]$ (**74**) shown in Figure 15.22. While **74** contains both stibide and formally monovalent stibinidene ligands, the silver complex **73** features a unique catenated $(\text{PhSb})_4$ unit that is stabilized by coordination to the coinage metal.



Scheme 15.24

Figure 15.22 Structures of **73** (a) and **74** (b). Hydrogen atoms are omitted for clarity.

15.3.2

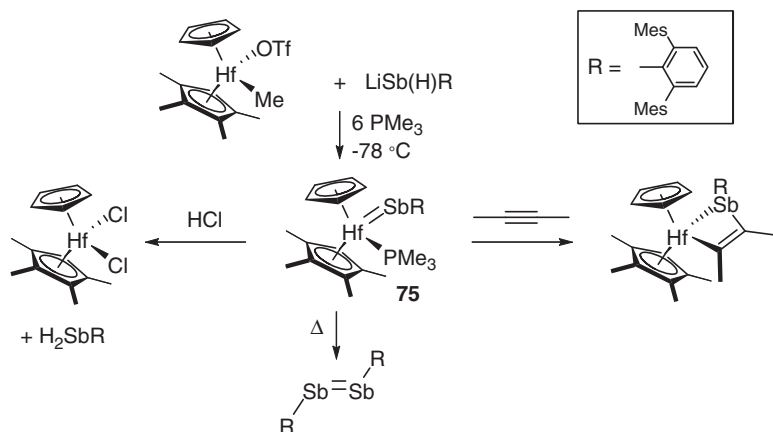
Complexes Containing RPN Fragments as Ligands (Pn = Sb or Bi)

RPN fragments, referred to as stibinidenes and bismuthinidenes, are monovalent species featuring only six electrons in their valence shell. Due to their coordinative unsaturation, these species are not stable and are typically chemically trapped by reactions with organic substrates [211] or as ligands in coordination complexes. When acting as ligand in transition complexes, the RPN fragment may act as a two- or four-electron donor, thereby influencing the nature of the metal–pnictogen bond. In this section, we will review selected complexes that fall in either of these categories.

15.3.2.1 Complexes Containing a RPN Fragment as a Two Electron Donor

A hafnium complex featuring a terminal stibinidene (**75**) has been reported from treatment of a methyl hafnocene complex with a primary stibide in the presence of PMe_3 , which acts to trap the otherwise unstable resultant stibinidene complex (Scheme 15.25) [212]. Complex **75** reacts with excess 2-butyne to afford the formal [2+2] cycloaddition product. Treating **75** with HCl affords the dichlorohafnocene and the corresponding primary stibine, suggesting a polarization of the $\text{Sb}=\text{Hf}$ bond toward antimony. Additionally, **75** undergoes thermolysis to afford the corresponding distibene and a mixture of hafnium-containing species.

Group 6 transition metal complexes with two electron donor organostibinidene and organobismuthinidene fragments are most conveniently prepared by metathesis reactions analogous to those employed to make the diorganostibide or bismuthide complexes (Scheme 15.26) [179, 193, 213]. These reactions produce complexes that are characterized by a pyramidal pnictogen element. This characteristic indicates that the organostibinidene and organobismuthinidene fragments in these complexes act as a two-electron donor. In turn, an alternative formulation for these complexes is that of dimetallated stibines or bismuthines.



Scheme 15.25

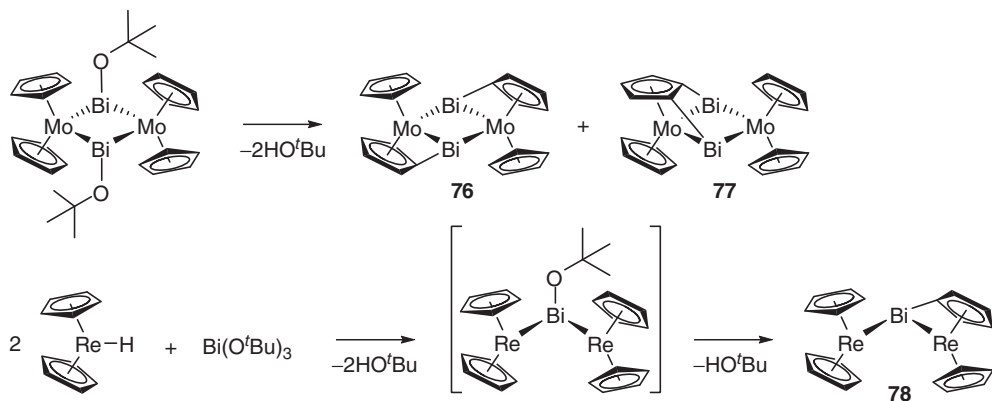


Pn = Sb, Bi X = Cl, Br, I

R = Me, Ph $\text{M}[\text{M}'\text{L}_x] = \text{Na}[\text{M}^{\text{VI}}(\text{CO})_3\text{Cp}]$

Scheme 15.26

Additional synthetic strategies include the reduction of organoantimony(V) precursors [161, 214], and dehydroalkylation of stibines and bismuthines with Group 6 or 7 metal hydrides [158, 175]. A large catalog of heterobimetallic clusters featuring bridging arylstibides and bismuthides have been derived from the reaction of rhenium carbonyl and hydride species with the corresponding triaryl-stibines and bismuthines [166, 168, 203, 205]. Limberg *et al.*, have demonstrated that Group 6 or 7 metallocene-substituted bismuth alkoxides eliminate an equivalent of alcohol to afford the unusual complexes **76**, **77**, and **78** (Scheme 15.27) [215–218]. In the case of the molybdenum complex **76**, the resulting “bent” bismuth–carbon bonds are labile and may be cleaved by addition of silanols.



Scheme 15.27

Bridging pnictinidenes have also been incorporated in several Group 8 and 9 complexes [161, 219, 220]. Examples of such complexes include $((\text{Me}_3\text{Si})_2\text{CH})\text{Sb}(\text{Fe}(\text{CO})_4)_2$ (**79**), which is obtained from $((\text{Me}_3\text{Si})_2\text{CH})\text{SbCl}_2$ and $\text{Na}_2(\text{Fe}(\text{CO})_4)$ [124, 221], and $[(\text{Me}_3\text{Si})_2\text{CHSbCo}(\text{CO})_3]_2$ (**80**)

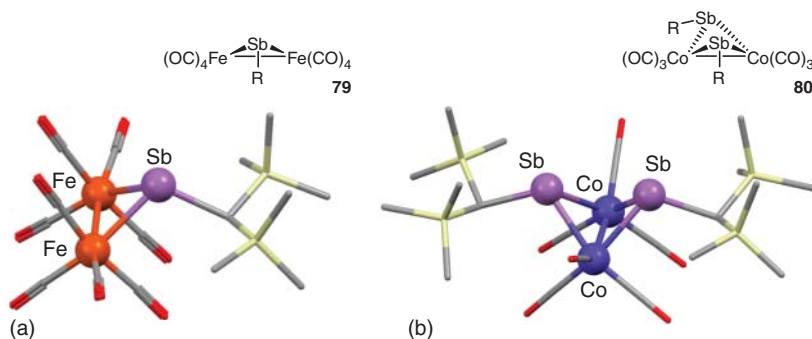
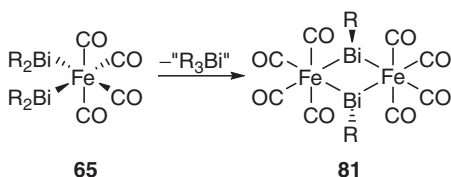


Figure 15.23 Structures of **79** (a) and **80** (b). R = ((Me₃Si)₂CH). Hydrogen atoms are omitted for clarity.

which is obtained from the reaction of *cyclo*-((Me₃Si)₂CHSb)₃ (**13**) with Co₂(CO)₈ (Figure 15.23) [119]. These complexes feature bridging stibinidene units whose strong pyramidalization (Sum of bond angles at antimony = 287.1° for **79** and 283.24° and 283.76° for **80**) support their role as two-electron donors. For **80**, the Sb–Sb separation of 3.1510(7) Å is consistent with the absence of a bond between the two centers. The Sb–Co distances in **80** range from 2.5812(7) to 2.5928(6) Å, shorter than those observed in Sb(Co(CO)₃P(OR)₃)₃ [222] (2.667(2) Å), and slightly shorter than the sum of the covalent radii of antimony and cobalt (2.74 Å) [155]. Related structures are also known for bismuthinidenes as in the case of **81** which is obtained by loss of a Ph₃Bi equivalent from **65** (Scheme 15.28) [162, 191, 193].

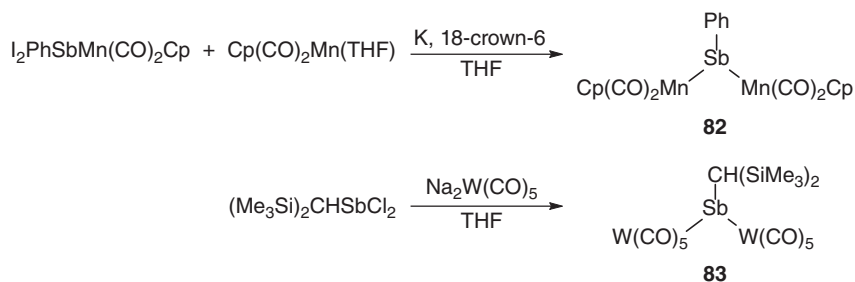


Scheme 15.28

15.3.2.2 Complexes Containing a RPN Fragment as a Four Electron Donor

The first transition metal stibinidene, PhSb(Mn(CO)₂Cp)₂ (**82**) was reported by Huttner from the reduction of a coordinated dihalostibine with potassium (Scheme 15.29). This methodology, along with the reduction of halopnictines with an anionic or zerovalent metal fragment (Scheme 15.29), has been extended to a variety of transition metal/pnictine combinations to prepare a diverse catalog of complexes such as (Me₃Si)₂CHSb(W(CO)₅)₂ (**83**) featuring RPN fragments as four-electron donors [123, 124, 221, 223–230]. In addition to acting as donors toward transition metal centers, stibinidenes and bismuthinidenes may act as Lewis acids, forming complexes with donor ligands and accepting electron density from coordinated metals via their vacant orbital. Four-electron donor stibinidene and bismuthidene complexes have been previously reviewed [231–233].

Several examples of transition metal stibinidenes and bismuthinidenes in which the inidene fragment acts as a four-electron donor have been structurally characterized. The most prominent feature of these structures is the trigonal planar coordination of the heavy pnictogen center, as seen in (Me₃Si)₂C(H)Sb(Mn(CO)₂Cp')₂ (**84**, Figure 15.24) [119]. Another notable feature of these complexes is the unusually short pnictogen–transition metal bonds, which is indicative of the partial multiple-bond character due to strong backbonding from the low-valent metal centers to the vacant orbital of the pnictogen center (Table 15.6). Similar to their lighter congeners, transition metal stibinidene and bismuthinidene complexes tend to be strongly colored with strong absorption bands at long wavelength; a property attributed to a transition from the ψ_1 and ψ_2 to the antibonding ψ_3 orbital within



Scheme 15.29

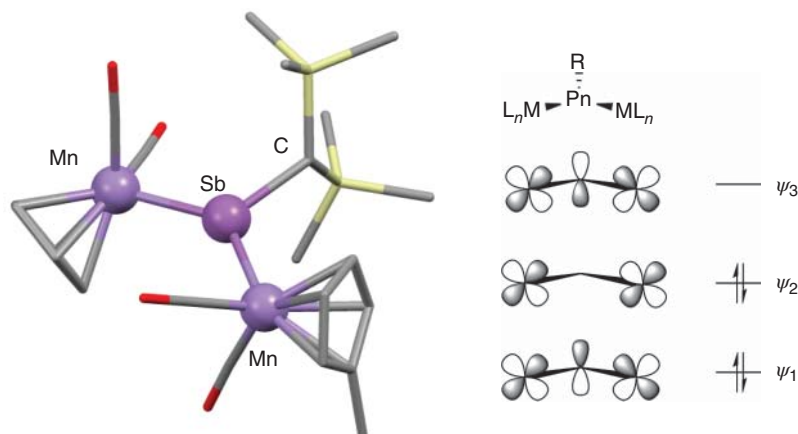


Figure 15.24 Structure of **84** (a) and generic molecular orbital depiction of the three center four electron π system proposed for pnictinidene complexes (b). Hydrogens are omitted for clarity.

Table 15.6 Geometric parameters of selected structurally characterized stibinidene and bismuthinidene complexes.

Compound	Sum of Pn angles(°)	Pn–M bond length (Å)	Sum of Pn–Sb covalent radii [155]	References
$\text{PhSb(Mn(CO)}_2\text{Cp)}_2$	360	2.457 ^{a)}	2.78	[223]
$(\text{Me}_3\text{Si})_2\text{C(H)Sb(Mn(CO)}_2\text{Cp}')_2$	359.99	2.4509 ^{a)}	2.78	[119]
$(\text{Me}_3\text{Si})_2\text{C(H)Sb(W(CO)}_5)_2$	359.98	2.687	3.01	[228]
$\text{ClBi(Mn(CO)}_2\text{Cp}')_2$	357.9	2.479 ^{a)}	2.87	[234]

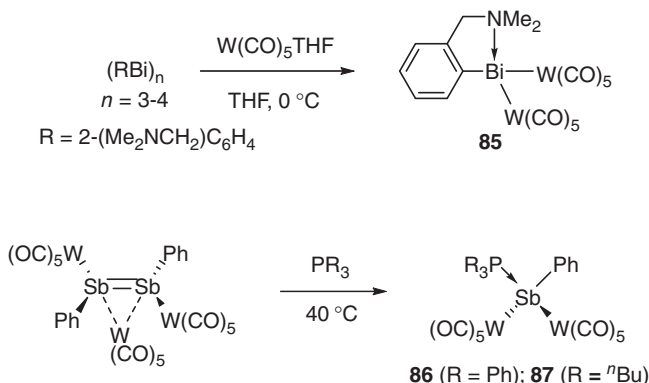
Cp' = Methylcyclopentadienyl.

a) Average.

the postulated three-center four-electron π system between the two metal centers and the main group element (see molecular orbital diagram in Figure 15.24) [231, 232].

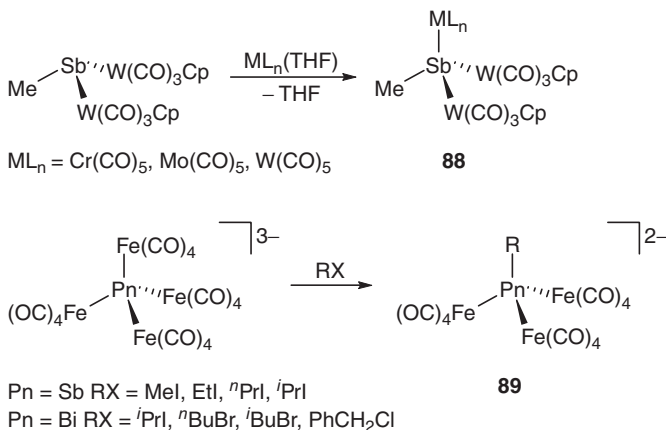
As coordinatively unsaturated species, four-electron donor stibinidenes and bismuthinidenes readily form adducts with neutral and anionic donors. The stabilizing effect of these interactions has been exploited to prepare otherwise unisolable pnictinidene complexes by addition of Lewis bases [227]. This Lewis base stabilization can also originate from a pendant donor group [30, 62, 233]. This last

approach is illustrated by the reaction in Scheme 15.30 with the formation of a bismuthinidene complex (**85**) stabilized intramolecularly by a pendant dimethylamino group [30]. In some cases, coordinated dipnictenes may be converted to pnictinidenes by treatment with an appropriate donor ligand, as in the case of the phosphine-stabilized stibinidene complexes **86** and **87** (Scheme 15.30) [123].



Scheme 15.30

Neutral and cationic complexes of type **88**, which feature RPn fragments coordinated to three metal centers, may be prepared by treatment of dimetallated $\text{RPn}(\text{ML}_n)_n$ complexes with an additional equivalent of an unsaturated metal complex [123, 235, 236] or by generation of an RPn fragment in the presence of a threefold or greater excess of the corresponding metal reagent (Scheme 15.31) [180, 237]. Shieh and coworkers have investigated a series of anionic, triply coordinated RPn complexes of type **89** derived from the alkylation of the highly charged “open cluster” anions $[\text{Sb}(\text{Fe}(\text{CO})_4)_4]^{3-}$, $[\text{Bi}(\text{Fe}(\text{CO})_4)_4]^{3-}$, and $[\text{Bi}(\text{Cr}(\text{CO})_5)_4]^{3-}$ (Scheme 15.31) [214, 238–242]. For $[\text{Sb}(\text{Fe}(\text{CO})_4)_4]^{3-}$, extended reaction times with an excess of less sterically demanding alkylating reagents ($R = \text{Me}$, Et) leads to dialkylated, bridging stibido anions of the form $[\text{R}_2\text{Sb}(\text{Fe}(\text{CO})_4)_2]^-$. Treating $[\text{Bi}(\text{Fe}(\text{CO})_4)_4]^{3-}$ under similar conditions results in bridging bismuthinidene complexes of type **81**, with monoalkylated products unobserved when MeI or EtI are used as the alkylating reagent. Complexes of type **81** may also be accessed by treating the monoalkylated bismuth derivatives of type **89** with acetic acid.

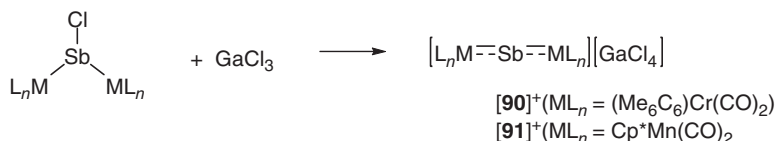


Scheme 15.31

15.3.3

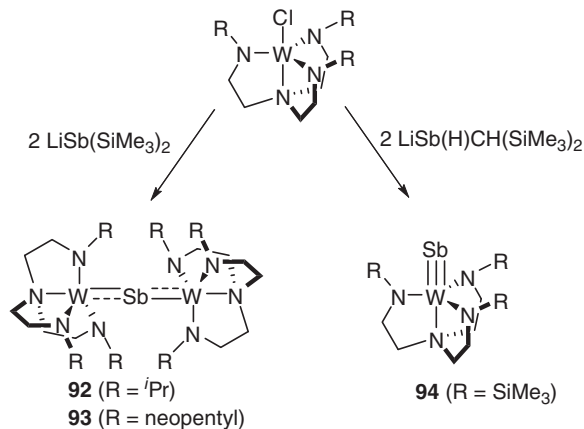
Complexes Containing Bridging or Terminal Pn Atoms as Ligands (Pn = Sb or Bi)

A number of complexes featuring a bridging or terminal Pn atom as ligands have been investigated [214, 220, 222, 243–246]. Examples include derivatives such as $\text{Pn}(\text{Mn}(\text{CO})_5)_3$ (Pn = Sb, Bi), which can be obtained from the pnictogen trihalide and $\text{NaMn}(\text{CO})_5$ [50, 247]. The structure of these complexes shows that the pnictogen is pyramidal. Because of the bulk of the $(\text{Mn}(\text{CO})_5)_3$ units, the Pn–Mn distances (av. 2.8030(23) Å for Pn = Sb and av. 2.904(3) Å for Pn = Bi) are significantly longer than the distance derived from their covalent radii (2.78 Å Sb–Mn and 2.87 Å for Bi–Mn) [155]. Another bonding situation is encountered in cationic complexes such as **[90]**⁺ and **[91]**⁺, which are prepared by halide abstraction from halostibinidenes (Scheme 15.32) [248, 249]. Such complexes have been described as heterometallic cumulenes. This classification is supported by the structure of **[90]** $[\text{GaCl}_4]$, which features an almost linear environment about antimony (Cr–Sb–Cr = 161.6(1)°). Moreover, the Cr–Sb bond length (2.387(2) Å) is shorter than that in the related stibinidene $\text{ClSb}(\text{Cr}(\text{CO})_2\text{Mes})_2$ (2.449(2) Å), indicating the presence of stronger Sb–Cr multiple bonding [250].



Scheme 15.32

Neutral complexes featuring an antimony center bridging two tungsten tris(2-amidoethyl) amine-based units have been prepared and structurally characterized by Scheer and coworkers (Scheme 15.33 and Figure 15.25) [251, 252]. These complexes feature strictly linear geometry about the antimony center, as well as W–Sb distances (2.5275(5) Å for **92** and 2.5738(8) Å for **93**) that are considerably shorter than those observed in the four-electron donor stibinidene $(\text{Me}_3\text{Si})_2\text{C}(\text{H})\text{Sb}(\text{W}(\text{CO})_5)_2$ (2.687 Å) [228]. By using a different combination of steric bulk on the amide donors of the tris(2-amidoethyl)amine ligand and as well as the antimony reagent, the first terminal stibide complex was isolated (**94**, Scheme 15.33) [253]. At 2.5255(17) Å, this complex features the shortest known W–Sb bond length. Theoretical studies carried out by the authors suggest that the bonding between tungsten and antimony is strongly covalent, and calculated molecular orbitals corresponding to a discrete σ bond and two degenerate π bonds were obtained (Figure 15.25c).



Scheme 15.33

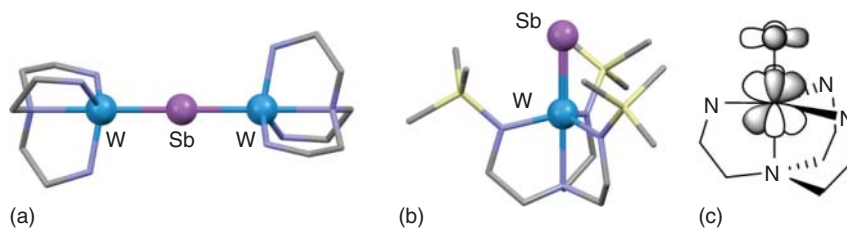
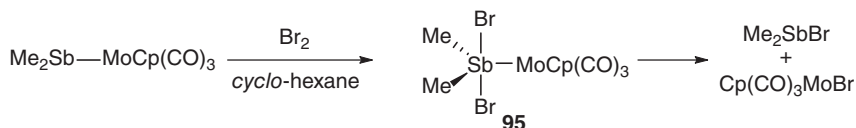


Figure 15.25 Structure of the core of **92** (left) and **94** (center) and simplified depiction of the orbitals involved in the formation of the two π -bonds in **94** (right). Hydrogen atoms are omitted for clarity. For **92**, the amide substituents are also omitted.

15.4

Metal–Antimony Bonds Involving High-Valent Antimony Fragments

Metal–antimony bonds can also be formed between a metal and a high-valent antimony fragment such as a stiboranyl (R_4Sb) unit. Such complexes were first prepared by oxidation of stibido-transition metal complexes with halogens. While such reactions sometimes proceed with cleavage of the antimony–metal bond, Malisch showed that the halogen addition product can in some instances be isolated and characterized [254, 255]. This is the case for the molybdenum complex **95** shown in Scheme 15.34. Over time, the complex **95** undergoes decomposition via cleavage of the Sb–Mo bond and formation of the corresponding bromide derivatives. This elimination reaction, which has been observed with other examples of such complexes, suggests that the oxidative cleavage reactions occur via an addition elimination sequence.



Scheme 15.34

A family of related stiboranyl complexes of type **96** has also been accessed starting from an unusual stiboranide 10-Sb-4 anion [256], which can be introduced via nucleophilic pathways in a variety of Group 6 and 8 complexes (Figure 15.26) [257–260]. X-ray crystallographic analysis of these complexes show that the geometry around the antimony atom is that of a distorted trigonal bipyramid, with the transition metal fragment in an equatorial position. While it can be safely assumed that the metal–antimony bond is strongly covalent, an interesting characteristic of these complexes pertains to the stability of the antimony coordination environment with respect to pseudorotation.

In the past few years, additional examples of stiboranyl complexes have been described. While it is usually assumed that stibines act as simple two-electron donor ligands, the Gabbai group has

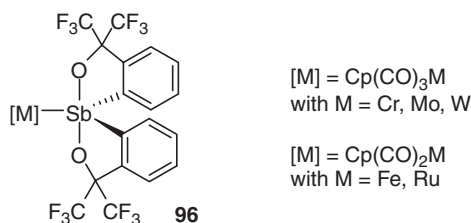
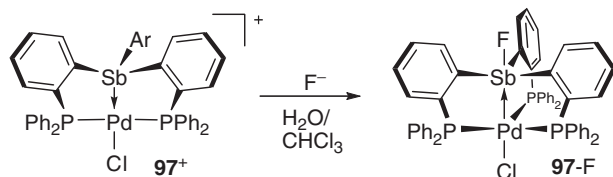


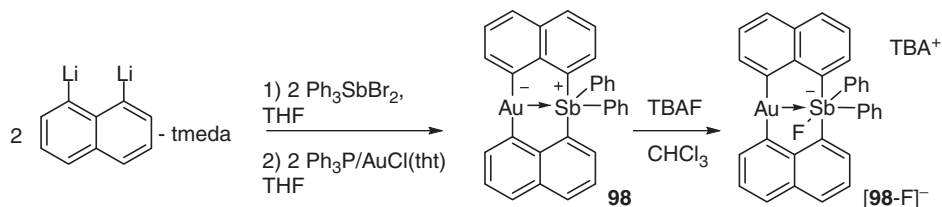
Figure 15.26 General structure of Group 6 and 8 complexes based on the bis-hexafluoroacetylalkoxide 10-Sb-4 stiboranyl ligand.

observed that such ligands are coordinatively non-innocent and can undergo addition of nucleophilic species. This, for example, the case for the cationic palladium complex **97**⁺, which reacts with fluoride to afford the corresponding fluorostiboranyl–palladium species (Scheme 15.35) [261]. An interesting aspect of this transformation is the change in the denticity of the triphosphine unit, leading to a bright-orange trigonal bipyramidal d⁸ lantern complex (**97-F**). From a bonding perspective, fluoride addition to the antimony atom induces an umpolung of the dative Sb–Pd bond, the directionality of which changes from Sb → Pd in **97**⁺ to Sb ← Pd in **97-F**. This umpolung is accompanied by a lengthening of the Sb–Pd bond from 2.4689(5) Å in **97** to 2.5721(7) Å in **97-F**. This lengthening can be assigned to the hypervalent configuration of the antimony atom in **97-F**.



Scheme 15.35

Another recent addition to the family of stiboranyl complexes is the gold derivative **98** [262]. This complex could be obtained by the reaction of dilithionaphthalene with Ph₃SbBr₂, followed by treatment with AuCl(tht)/PPh₃ (Scheme 15.36). The gold atom of this complex adopts a T-shaped geometry, and is separated from the antimony center by only 2.7486(7) Å. Despite this short Sb–Au distance, which is close to the sum of the covalent radii of the two elements (2.75 Å) [155], the bond appears to be weak and strongly polarized toward gold. This view is supported by density functional theory (DFT) calculations as well as Au L₃- and Sb K-edge X-ray absorption near edge structure (XANES) spectra, which suggest that **98** may also be described as an aurate-stibonium derivative. Further support for this description comes from the observation that the gold atom of **98** is involved in an aurophilic interaction, a phenomenon that is typically observed only for monovalent gold complexes (Figure 15.27).



Scheme 15.36

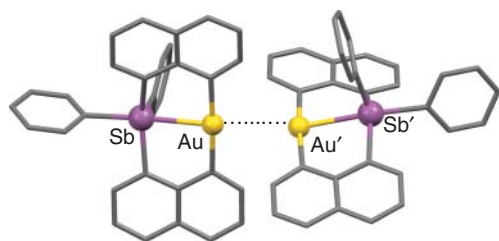
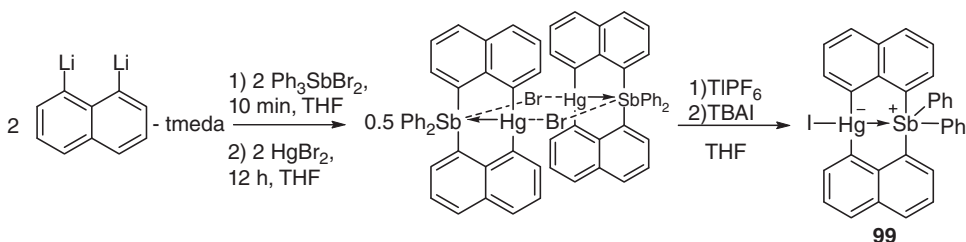


Figure 15.27 Crystal structure of **98** showing the presence of the aurophilic contact. Hydrogen atoms are omitted for clarity.

A mercury analog (**99**) of the gold complex **98** has also been studied (Scheme 15.37) [263, 264]. This complex was obtained by reaction of 1,8-dilithionaphthalene with Ph_3SbBr_2 and HgBr_2 in THF, followed by the exchange of the bromide by an iodide ligand. The crystal structure of **99** indicates the presence of a dinuclear core, characterized by a short transannular Hg–Sb separation of 3.073(1) Å (Figure 15.28). With the sum of the metallic radii at 3.17 Å and that of the covalent radii at 2.71 Å [155], this short separation suggests that the two atoms are within bonding distance. The mercury ion adopts a distorted square planar coordination geometry with a very short Hg–I bond of 2.991(1) Å. While XANES studies at the mercury L_3 -edge show that the mercury atom does not appear to be more oxidized than in Ph_2Hg , theoretical studies suggest that the Hg–Sb interaction in **99** is the result of a unique iodide push – stibonium pull effect, leading to delocalization of density from mercury into a $\sigma^*(\text{Sb}–\text{C})$ orbital (Figure 15.28).



Scheme 15.37

Finally, complexes in which an electron-rich metal is bound to a stiborane (R_5Sb) ligand have also been described. Such complexes can be obtained by oxidation of coordinated stibine ligands, as in the case of **101**, which is produced by the reaction of the stibine-gold chloride complex **100** with PhICl_2 [265], or **102** which is produced from **102** by reaction with *o*-chloranil (Scheme 15.38) [266]. In both cases, the dinuclear core of the structure shows a clear response to the oxidation of the antimony center. In particular, the Au–Sb distances (2.7086(9) Å for **101**; 2.6833(3) Å for **103**) are shorter than those measured for the reduced complexes (2.8374(4) Å for **100** and 2.8669(4) for **102**). Changes are also observed in the coordination sphere of the metals, which adopt a distorted octahedral and square planar geometry for antimony and gold, respectively. These changes, and in particular the square planar geometry of the gold atom, indicate that the latter is affected by oxidation as it transitions from a monovalent form in **100** and **102** to trivalent form in **101** and **103**. DFT calculations confirm this view, and indicate that the gold atom is oxidized by partial electron donation to the antimony center (Figure 15.29). In particular, a Natural Bond Orbital (NBO) analysis of **101** shows that the gold $d_{x^2-y^2}$ orbital acts as a donor toward a $\sigma^*(\text{Sb}–\text{Cl})$ orbital [265]. Altogether, these results show that addition of oxidation of the antimony center induces an umpolung of the Sb–Au dative bond, which switches from $\text{Sb} \rightarrow \text{Au}$ in the reduced state to $\text{Au} \rightarrow \text{Sb}$ in the oxidized state. A last method which can be used

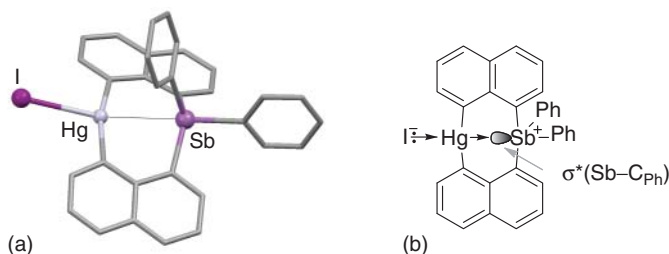
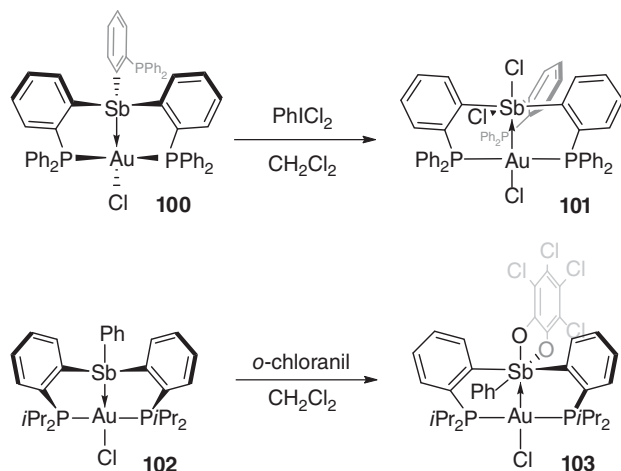


Figure 15.28 Crystal structure of **99** (a) and simplified representation of the Hg–Sb bonding interaction (b). Hydrogen atoms are omitted for clarity.



Scheme 15.38

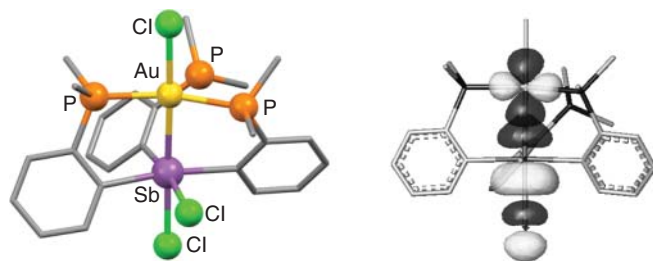


Figure 15.29 Structure of **94** and representation of some of the NBOs involved in the Au $\rightarrow$ Sb interaction (right). Selected phenyl rings are truncated and hydrogen atoms omitted for clarity.

to access metal $\rightarrow$ stiborane complexes is by addition of an anion to metal–stiboranyl complexes. This is illustrated by the reaction of **98** with fluoride, which affords the anionic aurate–fluorostiborane complex $[\mathbf{98}\text{-F}]^-$ (Scheme 15.36) [262].

15.5

Concluding Remarks

The chemistry of metal–metal bonded systems involving antimony and bismuth has continued to mature over the years. Without being exhaustive, this book chapter depicts some of the exiting developments that this field of research has witnessed. One of the main outcomes of this review is the realization that this field of research has for the most part remained quite traditional, with a large fraction of the contributions focusing solely on the synthesis and structure of the metal–metal bonded compounds. What may be lacking from this area of chemistry is a more systematic description and understanding of the metal–metal bonds. In particular, few investigations comment on the nature of the Pn–M bonds, their polarity, and their ability to support multiple bonding interactions. Given the large electronic property differences in electronic properties that antimony and bismuth display when compared to their lighter Group 15 analogs, we believe that such studies may help formulate new research problems as well as new applications. Finally, given the importance of electron transfer processes in energy research, we envision further developments in the chemistry of complexes for which the two-electron redox properties of antimony or bismuth can be harnessed.

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