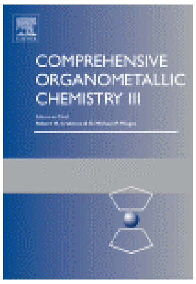

Comprehensive Organometallic Chemistry III

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7.01
Cobalt Organometallics

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7.01.1 Introduction

Since COMC (1995) has appeared, the organometallic chemistry of cobalt has witnessed a dramatic evolution. Indeed, all the basic structures of organometallic chemistry involving this metal have been described in COMC (1982) and COMC (1995). However, organocobalt chemistry remained an active part of the organometallic chemistry, as most of the work that was performed was aimed at improving known processes or finding new reactivities or new applications for the known organometallic chemistry. One important aspect of organocobalt chemistry is that very often its chemistry is elaborated by comparison with either rhodium or iridium or with the other first row transition metals. One consequence of this situation is that we have had to make some selection among the vast literature covering the field since 1993. We shall thus present here those articles dealing with novel aspects of organometallic chemistry favoring reactivity studies over purely structural studies for instance.

One significant example of such evolution is highlighted in the cobalt cluster chemistry. Whereas in the 1970s and 1980s a great deal of effort has been made to increase the number of such clusters, the last decade has seen only very limited progress in this direction. Most of the studies we have found in this area have been performed, not to add other examples to a large class of compounds, but rather to find the way to how such clusters could be useful for improving known reactions. We hope that the reported examples illustrate this important evolution.

Whereas the organization of this chapter is somewhat similar to that of the two previous issues, here the basic organometallic chemistry will not be the subject of lengthy discussions. The various items that are described refer mainly to the reactivity of the compounds.

Warning. Several aspects of the organometallic chemistry of cobalt will not be covered in detail here, as we believe that readers might find this information in chapters 10 and 11 of this monograph and companion monograph reviews.[1] Thus, readers interested in the organic chemistry induced by the cobalt complexes such as the Pauson–Khand reaction or any related C–C bond formation via alkyne–alkyne or alkene–alkyne coupling for instance should consult the corresponding volume of COMC and a recent review[2] on organometallic compounds in organic synthesis. We have also not covered those cobalt complexes in which the cobalt served simply as a protection of organic functions such as the coordination of alkynes η^2-bound to $Co_2(CO)_6$ units, as we considered that this part of the organometallic chemistry was well developed in the cobalt chapters of COMC (1982) and COMC (1995). Another aspect of organometallic chemistry of cobalt that the reader will not find here is all that refers to the biologic activity of co-enzyme B12 and it derivatives. Volume 8 of *Comprehensive Coordination Chemistry* should be consulted for this.[3,4] Finally, the carborane complexes of cobalt will not be described in any detail here either, as these complexes are better described in Volume 1 of this work.

7.01.2 Hydridocobalt Complexes

Cobalt hydride complexes have been intensively studied during the last decade. Improvements in the knowledge of the organometallic chemistry of cobalt hydride complexes have allowed a better understanding of the hydroformylation process (oxo process) through many additional mechanistic contributions. We describe a few aspects of these contributions in the first part of this section. The same period has also witnessed the synthesis of new hydrido complexes. Some of them are extensions of well-known structures described previously in COMC (1982) and COMC (1995), but some of them may present new perspectives for future organocobalt chemistry. These compounds will be presented in the second part of this section. In order to clarify this presentation, the nitrogen macrocycle hydridocobalt complexes will not be presented in this section but in Section 7.01.3.5.2.

7.01.2.1 Hydridocobalt Complexes in the Hydroformylation Reaction

Hydroformylation process is the most important application of organocobalt complexes in catalysis. During the last decade, the accumulation of thermodynamic and kinetic information has allowed a significative increase of the knowledge of this reaction. Due to its industrial importance, hydroformylation has attracted considerable importance during the past decade through both a combination of experimental improvements[5–19] and the increased computational possibilities for theoretical studies.[20–28] A two-phase system[5] and the use of supercritical carbon dioxide[6–8] as reaction medium have resulted in improving the product separation.

The hydridocarbonylcobalt active species formed in the first step of the Heck and Breslow hydroformylation mechanism[29] is the 16-electron $HCo(CO)_3$ complex, obtained via dissociation of CO from $HCo(CO)_4$, **1**. The most recent theoretical studies indicated that the stable singlet state is a C_{2v}-planar structure, which resulted from the loss of the equatorial CO from $HCo(CO)_4$, **1**.[30] In an earlier study, Ziegler's group found that the Cs structure was the most stable.[31]

This $HCo(CO)_4$ species is formed *in situ* from the reaction between $Co_2(CO)_8$ and H_2 (Equation (1)).

$$Co_2(CO)_8 + H_2 \rightleftharpoons \underset{\mathbf{1}}{2HCo(CO)_4} \qquad (1)$$

The rapid equilibrium between $HCo(CO)_4$ and $Co_2(CO)_8$ is one of the important key steps in hydroformylation reactions. A critical review of the existing data on this equilibrium has been made in parallel with new infrared spectroscopic measurements under semi-*in-situ* conditions. Thermodynamic parameters obtained were: $\Delta H = 4.054 \pm 0.175$ kcal mol^{-1} and $\Delta S = -3.067 \pm 0.488$ cal mol^{-1} K^{-1}. Values have been obtained in the 50.7–117.0 °C temperature range in hexane as solvent.[32]

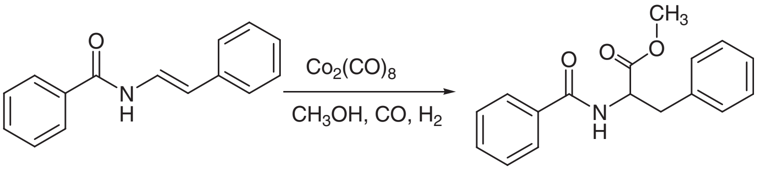
The study by Klinger and Rathke established the formation of radical $^{\cdot}Co(CO)_4$, which is involved in the equilibrium. Their observation was based on high-pressure NMR studies of hydrogen transfer and related dynamic process in oxo catalysis.[33] They have determined the Co–Co and Co–H bond-dissociation enthalpies (19 and 59 kcal mol^{-1}, respectively), which have been previously obtained by Ziegler and Folga (148 and 283 kJ mol^{-1}, respectively).[34]

$HCo(CO)_4$ is an unstable precursor, which decomposes rapidly below ca. 22 °C with a half-time of 10 min. Aylett *et al.* studied the effect of the decomposition of $DCo(CO)_4$ in porous silicon by chemical vapor infiltration and deposition. They have determined that this precursor was decomposed to afford mainly $DCo_3(CO)_9$, while above this temperature $Co_2(CO)_8$ was the main product.[35] A detailed analysis of the infrared spectra of $HCo(CO)_4$ and $DCo(CO)_4$ has provided good agreement between experiment and theory.[36]

The $HCo(CO)_4$ complex is also formed by β-elimination, from an alkylcobalt derivative ([$R_2CH–CR_2–Co$]). This reversible reaction led to an equilibrium, which is believed to play an important role in the olefin-isomerization process occurring in hydroformylation. In order to obtain kinetic information about the β-elimination mechanism, Ungváry's research group studied the reactivity of (1,2-bis(methoxycarbonyl)ethyl)cobalt tetracarbonyl. They suggested a modified β-elimination mechanism in this case, including a pre-equilibrium CO dissociation from $MeO_2CCH_2CH(CO_2Me)Co(CO)_4$, a fast intramolecular transformation of the resulting intermediate into a carbonylhydridoolefin cobalt species, which may transfer a hydrogen atom to the radical $Co(CO)_4$ (formed by the homolytic cleavage of $Co_2(CO)_8$ species) in a rate-determining step, yielding $HCo(CO)_4$.[37]

More difficult hydroformylation processes such as the hydroformylation of acetylene[38] (to form propenal) have been studied theoretically. It has been demonstrated that the hydrogenation of acetylene to yield ethane is not a concurrent reaction to hydroformylation under stoichiometric conditions. The propenal hydrogenation under $HCo(CO)_3$-catalyzed hydroformylation conditions was also studied.[39] Phenylacetylene led to 2-phenylpropanal under mild carbonylation conditions (hexane or benzene as solvent, 1 atm of CO, RT). This reaction needed an excess of $HCo(CO)_4$ to be realized. The authors found that a radical mechanism was involved.[40]

Using the hydroformylation reaction conditions, the hydroalkoxycarbonylation of enamides to amino acid esters has also been studied recently (see Equation (2)).[41] Using these conditions, it has been possible to obtain α-amino acid derivatives via an aminocarbonylation process with catalytic amounts of $Co_2(CO)_8$.[42–44]



(2)

7.01.2.2 Hydridocobalt Complexes with Phosphine Ligands

Two different crystal structures (square pyramidal and trigonal bipyramidal) have been obtained for single crystals of $HCo(CO)_2(PPh_3)_2$, **3**. Neither structure contained a solvent of crystallization. The authors suggested that the force packing is sufficient to favor one or the other geometry. In solution, an equilibrium exists between the two isomers which interconvert rapidly.[45]

Recently, a fluoroalkyl phosphine(hydrido)cobalt complex has been synthesized (Figure 1).[46]

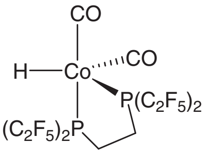
A reinvestigation of the complex **4** was undertaken because of the ambiguity of the formulation of dihydride versus η^2-dihydrogen form (Figure 2).

The characterization of η^2-H_2 coordinated to cobalt complex is not an easy feature. A careful NMR study reinvestigation by Heinekey *et al.*, based on $T_{1\mathrm{min}}$ measurement and the lack of resolvable H–D coupling in the monodeuterated form of the complex, led to a reformulation of the cobalt complex **4** as a highly dynamic dihydride species instead of an H_2 adduct η^2-coordinated to the cobalt atom.[47,48] Bianchini and co-workers have confirmed this observation and interpretation.[49]

A detailed structural and thermodynamic study of a series of cobalt complexes has been reported.[50] The complexes studied, **5**–**8**, are presented in Figure 3.

Equilibria are reported for the transfer of a hydride, a proton, or a hydrogen atom. The measurements and the determinations of various electrochemical potentials were used to determine 11 possible homolytic and heterolytic Co–H bond-dissociation free energies of **5** and its monohydride derivatives **6**. These data are reported in Scheme 1.

A new acylphenolato(hydrido)cobalt(III) complex **9** has been obtained by Klein *et al.*[51] Its reactivity toward 2-nitrophenol was investigated. This reaction involved the elimination of H_2 leading to the formation of 2-nitrophenolatocobalt(III) compounds (Figure 4).[52]



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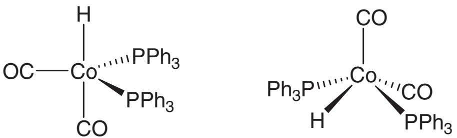

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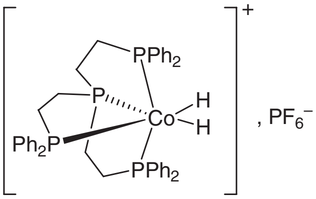

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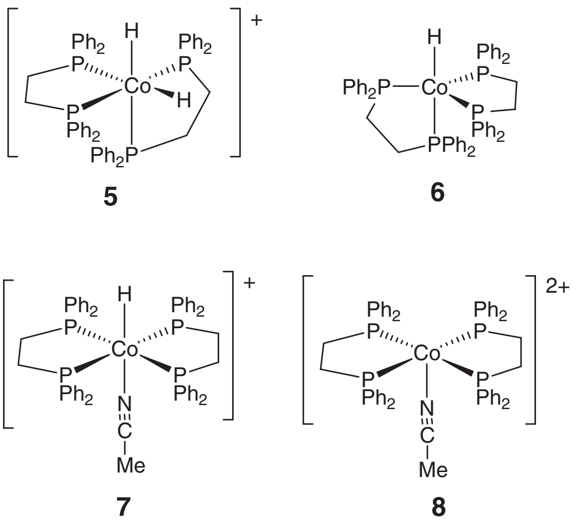
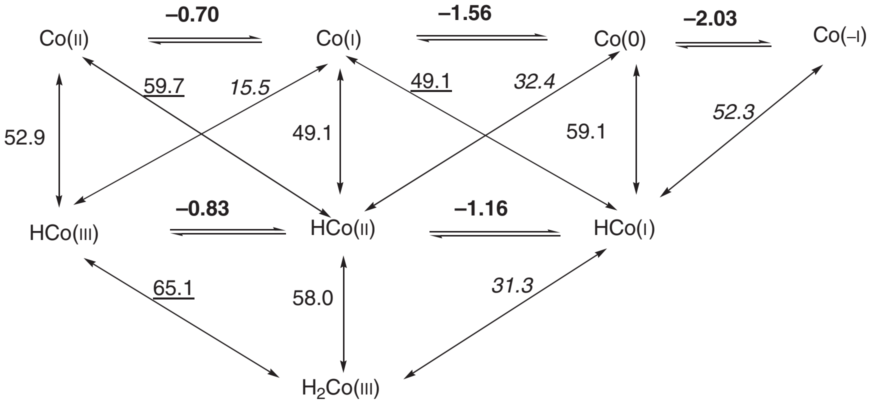
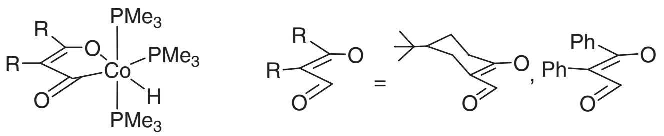


Figure 3 Reproduced with permission from Elsevier.



Scheme 1 Thermodynamic relationship between $[Co(dppe)_2]^{n+}$ and $[H_xCo(dppe)_2]^{m+}$ where $n = -1, 0, 1, 2$, $x = 1, 2$, and $m = 0, 1, 2$. Numbers in bold are reductive potentials in volts versus ferrocene. Numbers in italic are $\Delta G°$ values for proton transfer in kcal mol^{-1}. Numbers underlined are $\Delta G°$ values for hydride transfer in kcal mol^{-1}. The other numbers are $\Delta G°$ values for hydrogen transfer in kcal mol^{-1}.



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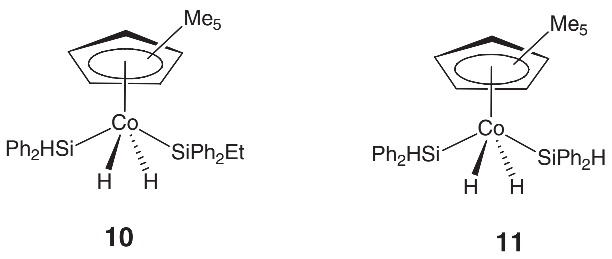
7.01.2.3 Hydridocobalt Complexes with Co–E Bonds (E = Si, Ge, Sn)

Brookhart's group has discovered a new hydrido organocobalt complex in which the cobalt atom is in a high oxidation state. They thus reported a rare example of an organometallic cobalt derivative with a +V formal oxidation state for the cobalt center **10**. This species contained additional silyl ligands that stabilized such high oxidation state complexes. These species were remarkably resistant toward reductive elimination.[53] The 2.28 Å H–H and the



10

11

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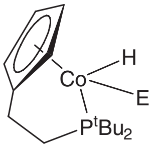
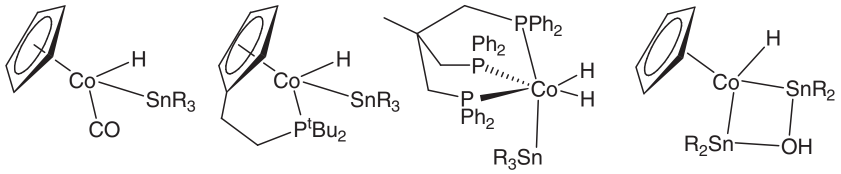


12: E = $SiPh_3$, $SiHPh_2$, SiH_2Ph

13: E = $GeHPh_2$

14: E = $SnBu_3$

Figure 6 Reproduced with permission from ACS Publications.



15: R = Ph

16: R = Bu

17a: R = Ph

17b: R = Bu

18: R = $CH(SiMe_3)_2$

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2.24–2.25 Å Si–H (H on cobalt) distances calculated by DFT methods for complex **11** were consistent with the formulation of a Co(V) complex (Figure 5).

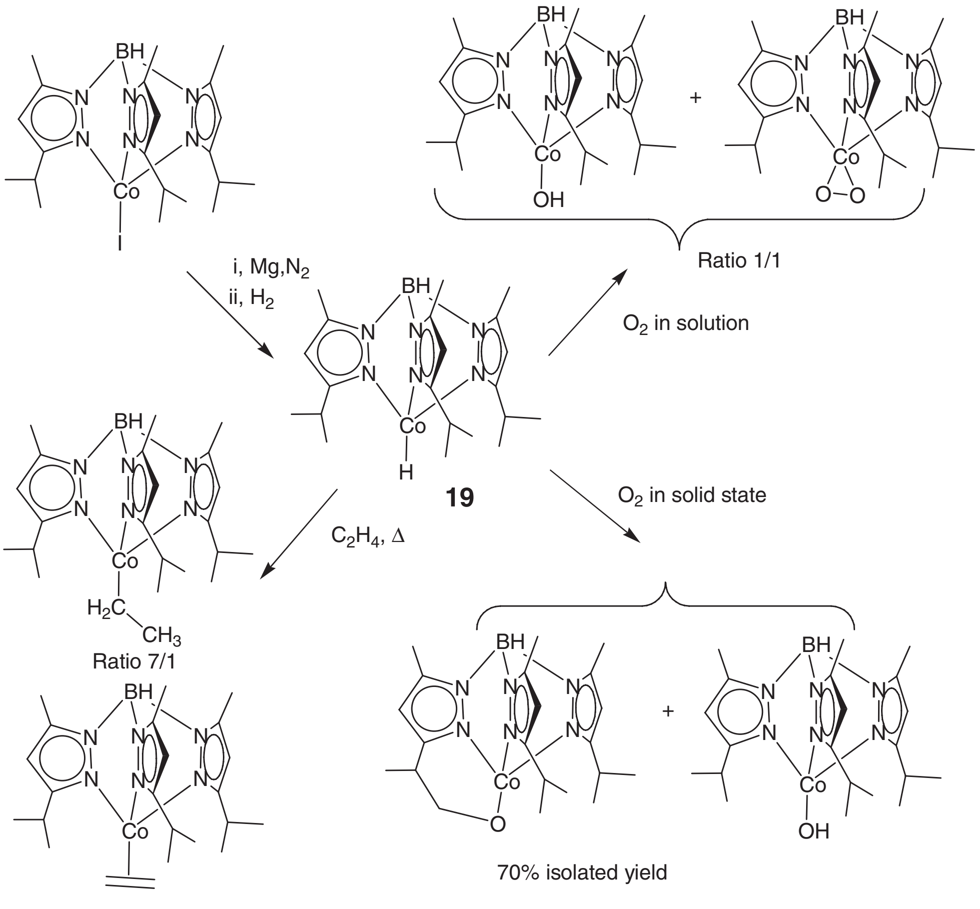
Oxidative addition of hydrosilane, hydrogermane, and hydrostannane to a cyclopentadienylcobalt(I) bearing a pendant phosphane ligand led to a complete series of hydridocobalt(III) complexes containing the same ligand environment around the metal center. Only the nature of E ligand is different on going from **12** to **14** (Figure 6).[54]

Few formal cobalt(III) hydridostannane complexes have been obtained, and all of these complexes present an Sn–H secondary interaction in solution. This has been established by the measurement of the coupling constant $J_{(\mathrm{Sn-H})} = 162$ Hz for **15**,[55] 49.4 Hz for **16**,[54] 170 Hz for **17**,[56] and 593 Hz for **18**.[57]

The complex **17a** underwent a reversible one-electron oxidation, which was assumed by the authors to be ligand-centered, producing Co(II) species ($[L_3Co(\eta^2\text{-}H_2)SnPh_3]^+$ (L_3 = the phosphine tripod ligand). Unfortunately, this species has not been isolated (Figure 7).

7.01.2.4 Hydridocobalt Complexes with Nitrogen Ligands

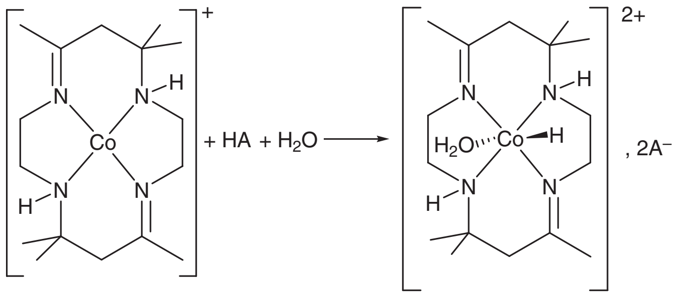
The use of the anionic tris(pyrazolyl)borate ligand afforded the possibility to obtain the neutral unsatured 15-electron cobalt(II) complex **19**. This compound was able to react with CO leading to a carbonyl derivative, or with ethylene (at elevated temperature, however) to give a 7 : 1 mixture of the alkyl and an η^2-ethene cobalt complexes.[58] The



Scheme 2

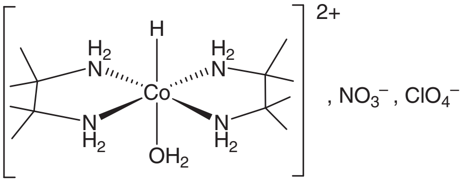
reaction with dioxygen led to a different mixture, depending upon whether the reaction was carried out in solution or in the solid.[59] (see Scheme 2).

A recent reinvestigation of the proton transfer to cobalt(I) macrocycle (*rac*-LCo(I), see Equation (3)) using a high-pressure pulse radiolysis technique led to observed accelerated reaction forming **20** when the pressure was increased.[60]



rac-LCo(I) **20** (3)

A simple nitrogen equatorial ligand system has been isolated and characterized by X-ray diffraction. This complex **21** is photosensitive, and it decomposes slowly in water or DMSO solution but also at RT in the dark (Figure 8).[61]



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7.01.2.5 Hydridocobalt Complexes with Bridging Hydrides

The neutron-diffraction structure analysis of the paramagnetic triply bridged binuclear cobalt hydride complex 22 has been realized (Figure 9).[62] This neutron analysis allowed the completion of the Co–H distance series: Co–H terminal (1.56 Å), $Co_2(\mu_2\text{-}H)$ (1.64 Å) 4, $Co_3(\mu_3\text{-}H)$, $Co_6(\mu_6\text{-}H)$ (1.82 Å).

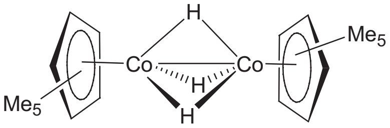
Several homopolymetallic cobalt clusters contain μ-hydrido ligands (see Section 7.01.5.1.4 of this chapter).

7.01.3 Cobalt Complexes With η^1-Hydrocarbyl Units

7.01.3.1 Organocobalt(−I) Complexes

An important study has been made by Brammer's group, aimed at the comprehension of the intermolecular and intramolecular interaction of hydrogen atom between $Co(CO)_3L$ (L = CO or phosphine) and an amine. This interaction has to be considered as an ammonium fragment with a Co(−I) fragment versus HCo(I) with an amine. The examples studied, 23 and 24, are in Figure 10.[63–66]

In the case of the aminophosphine ligand 25, the complex was a zwitterionic compound with an intramolecular interaction between the ammonium and the $[Co(CO)_3P]^-$ fragments.[67] This compound has been characterized by X-ray diffraction structure. In solution, it decomposed to give the Co(0) complex 26 as a byproduct (Figure 11). This latter compound has also been characterized by an X-ray diffraction study.



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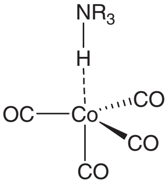
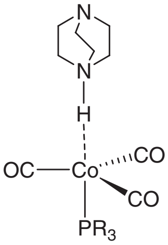


NR3 = NEt3, NH(C2H4)2NMe, N(C2H4)3N

23



PR3 = P(*p*-tol)3, PPh2(*p*-tol), PPh3

24

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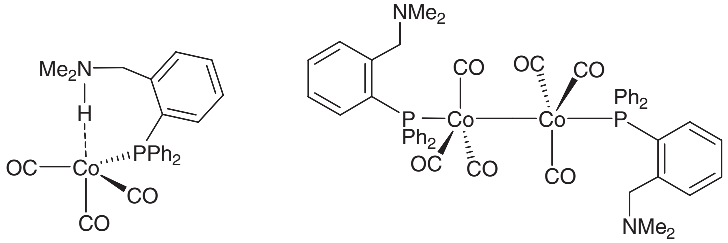

25 **26**

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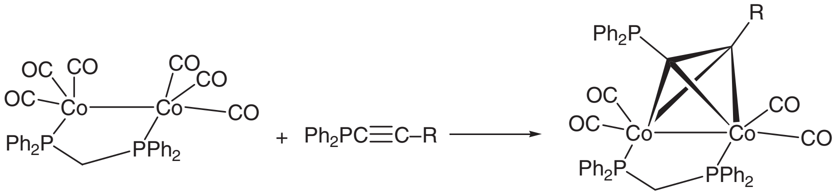
7.01.3.2 Organocobalt(0) Complexes

The first synthesis of the cobalt carbonyl carbene dimer 27 has been achieved recently via a phosphine exchange by IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) onto the dimer: $Co_2(CO)_6(PCyPh_2)_2$ (Figure 12).[68] This compound was found to be unstable under hydroformylation conditions.

The decomposition of 27 had led to the product $[Co(CO)_3(IMes)_2][Co(CO)_4]$, which has not been unambiguously identified.

In order to better understand this reaction and to be able to perform the hydroformylation and hydrogenation catalysis by cobalt complexes in supercritical carbon dioxide medium, $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ has been synthesized and *in situ* high-pressure NMR studies have been performed. The dimeric cobalt complex reacted with H_2 to give the following hydridocobalt compounds $HCo(CO)_3[P(p\text{-}CF_3C_6H_4)_3]$ and $HCo(CO)_2[P(p\text{-}CF_3C_6H_4)_3]_2$. They have been detected during the hydroformylation process monitored *in situ*.[69]

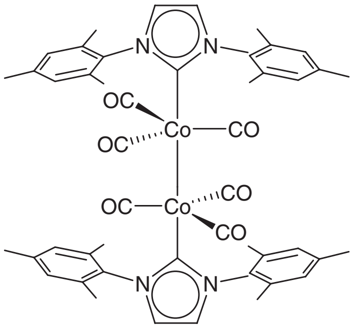
$Co_2(CO)_2$dppm (dppm = bisdiphenylphosphinomethane) has been used as a starting material for building the so-called Co_2C_2 clusters; the first step of the construction of such species is represented in Equation (4).[70] The $Co_2(CO)_6$dppm complex has thus been used as an alternative to $Co_2(CO)_8$, whose reactions with alkynes to afford similar products such as 28 are well known.[71]



R = CMe_3, $SiMe_3$

28

(4)



27

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7.01.3.3 Organocobalt(I) Complexes

A new tetracarbonyl cation $[Co(CO)_4]^+_{(solv)}$ has been formed by dissolving $Co_2(CO)_8$ in superacid media under CO atmosphere. The IR and Raman spectra suggested a trigonal-bipyramidal structure for $[Co(CO)_4]^+_{(solv)}$ with two CO and a solvent ligand in the equatorial plane.[72] $[Co(CO)_5]^+[(CF_3)_3BF]^-$, a stable salt of homoleptic metal carbonyl cation, was obtained through the reaction of $(CF_3)_3BCO$ with $Co_2(CO)_8$ in anhydrous HF. A crystal structure determination showed the $[Co(CO)_5]$ cation to have the structure of a regular trigonal bipyramid (D_{3h}).[73]

Other cationic pentacoordinate organocobalt complexes have been investigated, such as those obtained with water-soluble phosphines $P[(CH_2)_nC_6H_4\text{–}p\text{-}SO_3Na]_3$ ($n = 1, 2, 3,$ and 6). This type of phosphines reacted rapidly with $Co_2(CO)_8$ in two-phase reaction conditions to yield the disproportionation products $[Co(CO)_3(P[(CH_2)_nC_6H_4\text{-}p\text{-}SO_3Na]_3)_2][Co(CO)_4]$. This series of complexes has been used as precursors to water-soluble cobalt hydroformylation catalyst.[74]

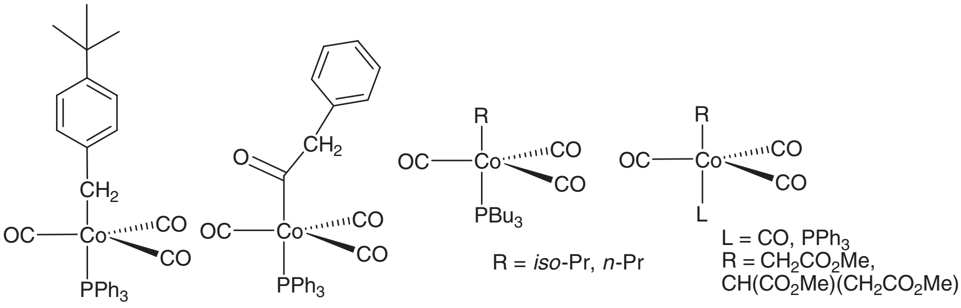
The new compounds of the form $RCo(CO)_3PR^1{}_3$, with R = benzyl and phenylacetyl, have been characterized.[75] The carbonylation–decarbonylation reactions of alkyl–acyl cobalt(I) tricarbonyl phosphine or tetracarbonyl complexes **29–32** have been studied by Ungváry's group (Figure 13). They detected the formation of the $CH_3O_2CCH_2Co(CO)_3PPh_3$ intermediate **32** during the decarbonylation reaction by multinuclear NMR spectroscopy, providing the first direct evidence for alkyl migration in cobalt carbonyl complexes.[76] The detailed carbonylation of $CH_3Co(CO)_4$ model has been reported with the determination of the transition state for CO association with each intermediates.[27] The $RCo(CO)_3PBu_3$ complexes (R = ^{i}Pr, ^{n}Pr) have been prepared and tested under hydroformylation conditions. The expected alcohol isomers have been obtained with a selectivity higher than 95%.[77]

Klein *et al.*[78–83] have investigated the selective C–H bond activation of many trialkylarylphosphanes, pyridines, or imines via an irreversible C–H activation process. Using **33** as starting material, the reaction with a selection of alkylphosphanes led to organocobalt complexes with four-, five-, or six-membered cobaltacyclic units **34–36** (Figure 14). All the structures displayed a trigonal-bipyramidal configuration in which the carbon coordinated to cobalt is in an axial position, a PMe_3 ligand being the other *trans*-ligand in the axial position. The reaction of the five- and six-membered cobaltacyclic rings with ethylene or CO induced only an exchange of ligands with one trimethylphosphine. The four-membered cobaltacycle can be expanded to five-membered ring via CO insertion. The formal insertion of an alkyne (dimethyl acetylenedicarboxylate) into the *ortho*-C–H bond of triphenyl phosphine to afford **37** occurred very likely via the formation of the corresponding cyclometallated derivative, which was then followed by the insertion of the alkyne into the Co–C bond thus formed.[84]

The Co(I) carbonyl derivatives **38** and **39** (Figure 15) have been obtained with $Tp^{i\text{-}Pr,Me}$ (isoelectronic to Cp).[85] The addition of CO was rapid (3×10^9 mol^{-1} l s^{-1}) and it was apparently spin forbidden, but this was well explained by theoretical studies (DFT).[86]

7.01.3.3.1 Organocobalt(I) complexes with isocycanide ligands

The reaction of isocyanide with electron-rich cyclopentadienyl cobalt(I) complexes has led to the formation of the substitution products **40**, **43**, and **46**, which even at RT underwent oxidative addition to give the compound **41**. This study showed that the choice of the isocyanide ligand is important to induce this reaction. The *para*-tolylisocyanide did not react by C–N bond cleavage. The complexes formed from the substitution of one phosphine by an isocyanide reacted with diphenyldiazomethane to give the *C*,*C*-bound ketenimine complexes **42**, and **44**. The *p*-tolylisocyanide



29 **30** **31** **32**

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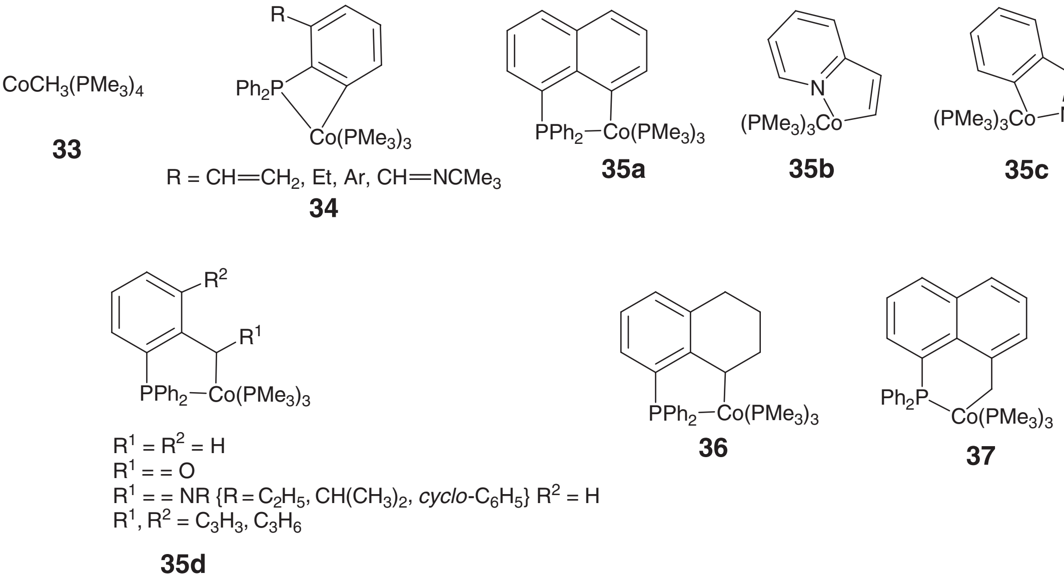


Figure 14 Reproduced with permission from Elsevier.

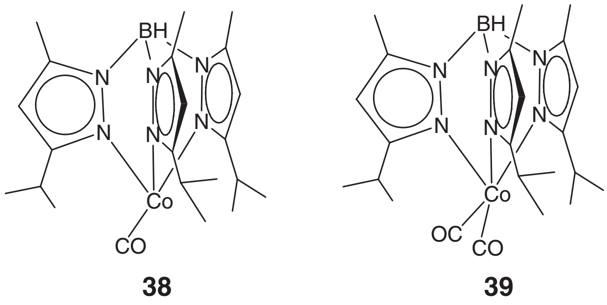
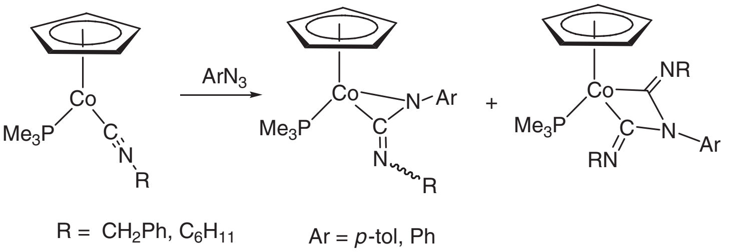


Figure 15 Reproduced with permission from Wiley.

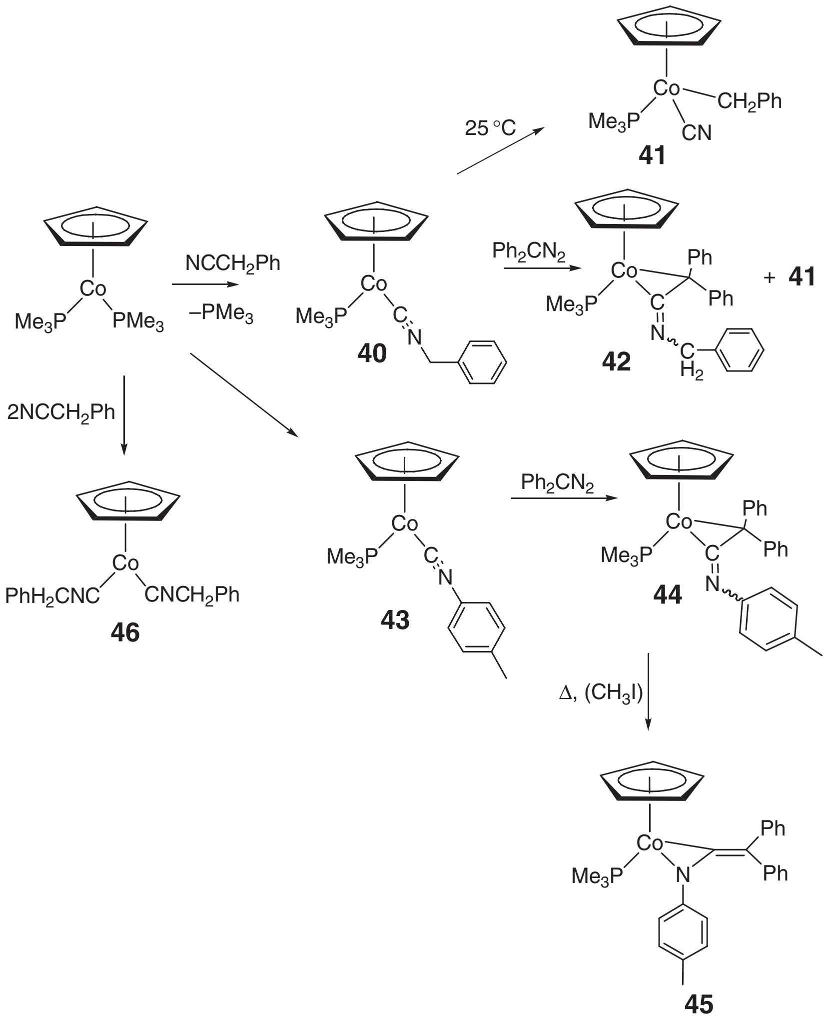
complex has led to a rearrangement to the more stable *N*,*C*-bond isomer **45** (Scheme 3). This publication reported a fully detailed characterization of previously reported compounds by the same group. The kinetic data of the formation of **41** were discussed.[87]

The same group reported the characterization of metallacycles formed via the reaction between azide onto CpCo(CNR)(PMe$_3$) (Equation (5)).[88] In benzene solution, the compound **47** rearranged slowly into the isomer **48**. After 45 days at RT, the equilibrium **47** : **48** (45 : 55) has been obtained. The equilibrium took place via the zwitterionic species **49** (Scheme 4).[89]

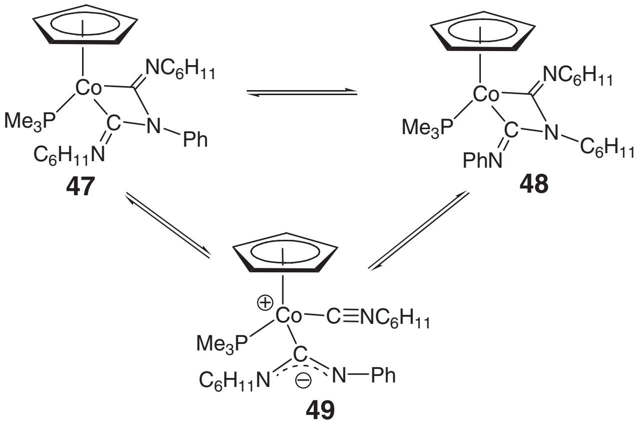


(5)

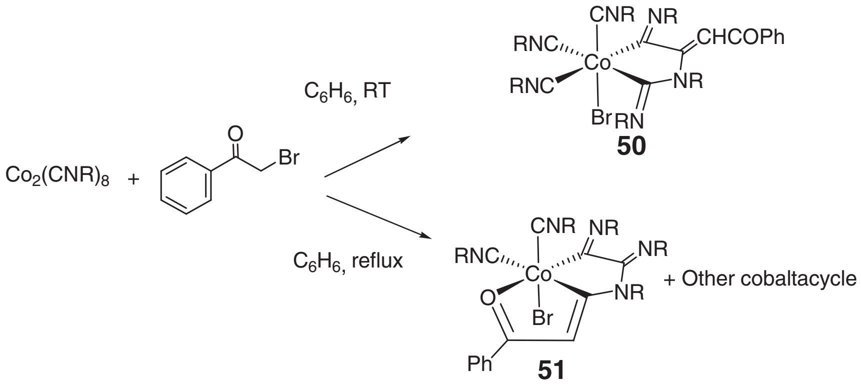
In order to complete the reactivity of isocyanide in this section, the reactivity of a well-known Co(0) isocyanide cobalt dimer is described. Yamamoto's group has also reported the reactivity of the Co(0) complex, Co$_2$(CNXyl)$_8$,



Scheme 3



Scheme 4



Scheme 5

with 2-bromoacetophenone. The formation of cobaltacyclic compound through multiple insertion of isoyanide leading to cobalt(III) organometallic species **50 and 51** was described (Scheme 5).[90]

7.01.3.3.2 Organocobalt(I) complexes with carbene ligands

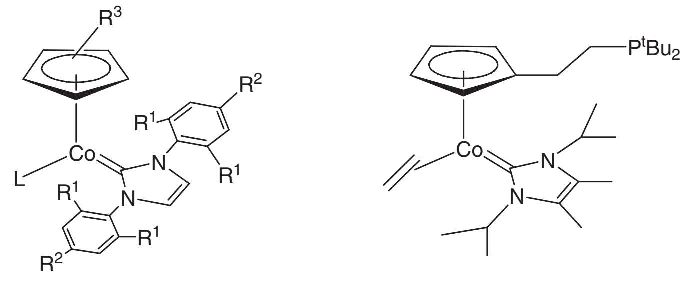
The huge interest in the chemistry of organometallic carbene complexes that emerged during the last decade has also inspired chemists to produce new organocobalt complexes with this type of ligand (see Section 7.01.3.5.1). Cobalt(I) carbene complexes **52** have been prepared by carbonyl substitution (Figure 16).[91] However, the substitution of ethylene by the carbene ligand was considerably faster.[92,93]

The chelating ligand $CpCH_2CH_2P(^tBu)_2$ allowed the synthesis of a few new vinylidenes **53–55** (Figure 17).[93,94] The first X-ray structure analysis of neutral cobalt vinylidene has thus been realized ($R^1 = R^2 = SiMe_3$).

Compound **54** has only been characterized in solution and is very unstable. Compound **55** is formed via ring opening of 3,3-diphenylcyclopropene with the η^2-ethene(di-*tert*-butylphosphanyl-*P*-ethyl)cyclopentadienylcobalt(I). Unfortunately, this compound has not been isolated.[95] It is worth mentioning that, by reaction with the same cobalt(I) precursor, diphenylcyclopropenone gave a cyclobutenone cobalt compound **56** (characterized by X-ray) in very good yields (91%) (Figure 18).[96]

The first Co(I) *N*-heterocyclic "pincer" dicarbene **57** has been recently synthesized by Danopoulos *et al.* (Figure 19).[97]

This complex has been obtained by adding an excess of MeLi onto the corresponding dibromide cobalt derivative with the same tridentate ligand, or more cleanly onto the monobromide cobalt *N*-heterocyclic "pincer" dicarbene derivative. The complex displayed a square-planar structure. This seems to be the first example of a Co(I)–alkyl complex stabilized by a CNC pincer ligand and lacking any π-acceptor coligands.

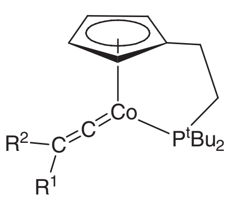


$R^1 = {}^iPr$; $R^2 = H$; $R^3 = H$; L = CO
$R^1 = Me$; $R^2 = Me$; $R^3 = H$ or CH_3, L = CO or C_2H_4

52a

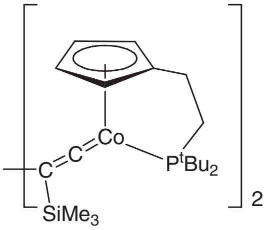
52b

Figure 16 Reproduced with permission from Wiley.

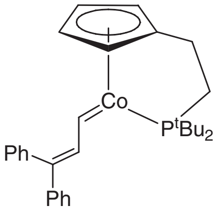


R^1 = R^2 = H
R^1 = H; R^2 = $SiMe_3$
R^1 = R^2 = $SiMe_3$

53

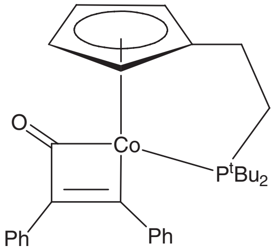


54



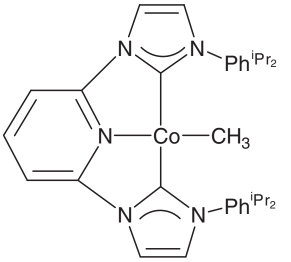
55

Figure 17



56

Figure 18



Ph^{iPr_2} = 2,6-diisopropylphenyl

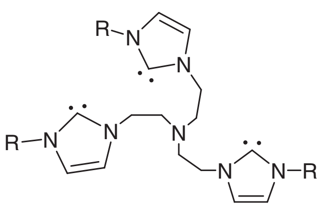
57

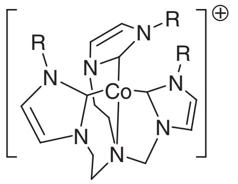
Figure 19

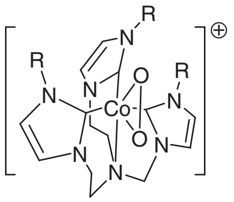
Using a new tetradendate ligand, Meyer *et al.* obtained a tris-carbene complex **57a**, which reacted with CO, one-electron oxidizers such as CH_2Cl_2 and O_2 to afford complexes **57b**–**d** (Figure 20).[98,99]

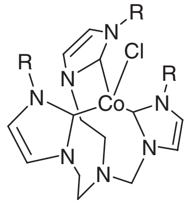
Complexes related to **57** described above were prepared with the diimino pyridine ligands with the benefit that a larger set of R groups could be linked to Co. The compounds **58** were made by reaction between the dihalide or monohalide cobalt complexes with magnesium or lithium reagents (Figure 21).[97,100–104]

β-H transfers between the alkyl ligand and the 1-alkene were observed. Rzepa and Gibson established experimentally and by theoretical calculation the mechanism of this β-H transfer, and they found that path A was preferred over path B (Scheme 6).[101,105]


R = 2,6-dimethylphenyl


57a


57d


57c

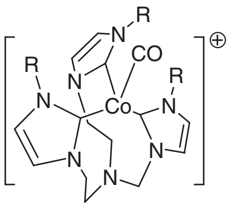
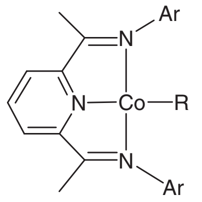

57b

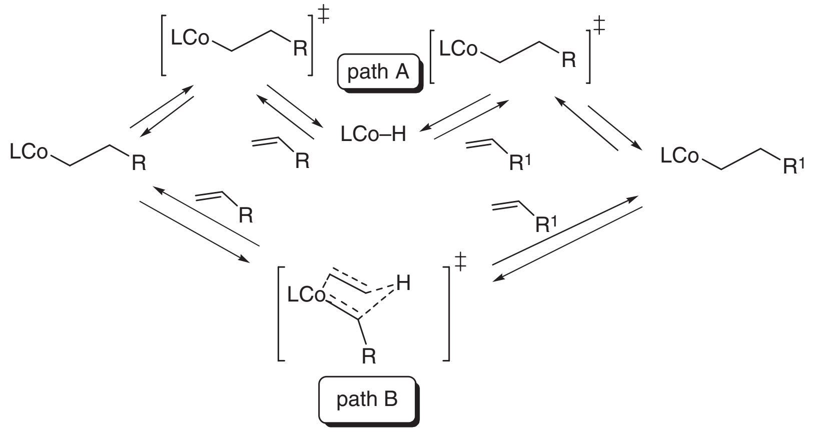
Figure 20


R = Me, Et, *n*-Pr, *n*-Bu, *n*-hexyl, CH_2Ph, C_2H_4Ph, CH_2SiMe_3

Ar = 2,6-diisopropylphenyl or 2,4,6-trimethylphenyl

58

Figure 21



L = bis(imino)pyridine

Scheme 6

7.01.3.4 Organocobalt(II) Complexes

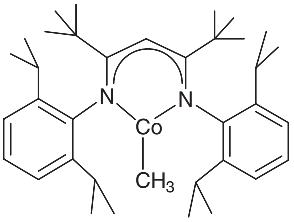
Holland *et al.*[106] have used for the first time bulky β-diketimininates to synthesize three-coordinate 13-electron organocobalt(II) complexes. Most noteworthy is a methylcobalt complex obtained from a (β-diketimininate)Co(μ-Cl)$_2$Li(ether)$_2$. The stability of the (β-diketimininate)CoCH$_3$ complex **59** is greater than that conventionally expected for an odd electronically unsaturated organometallic complex. The benzene solutions of this complex were stable for a long period of time at RT, as they decomposed slowly after several days at 80 °C. All hydrogen atoms of the ligand are at least 2.8 Å away from the cobalt atom, indicating that no direct electronic interaction between the C–H bonds and the metal should be invoked (Figure 22).

In an attempt to synthesize low-coordination 15-electron organocobalt(II) complexes, few complexes containing either one bulky σ-aryl[107] or bulky σ-alkyl units[108,109] have been obtained. All these complexes presented a tetrahedral coordination around the cobalt atoms, and they were all dimeric **60–62** (Figure 23). They displayed two halogen bridges, the fourth coordination site being occupied by an intramolecular nitrogen atom or by an oxygen atom of a solvent (THF).

Other 15-electron Co(II) complexes have been synthesized, and their X-ray diffraction analyses showed a planar geometry for the cobalt atom of the monomeric compounds **63** and **64a**. The formation of complexes with a little less sterically hindered pyridyl-substituted ligands led to a binuclear complex **64b**, with, however, a tetrahedral geometry around the cobalt atom.[110–112] A dianionic derivative with four alkyl groups having one SiR$_3$ unit on the α-carbon **65** was used as a stoichiometric reagent for the coupling of a CH$_2$SiR$_3$ unit with dibromodisilylmethanes to afford 1,1,2-trisilylethenes (Figure 24).[113]

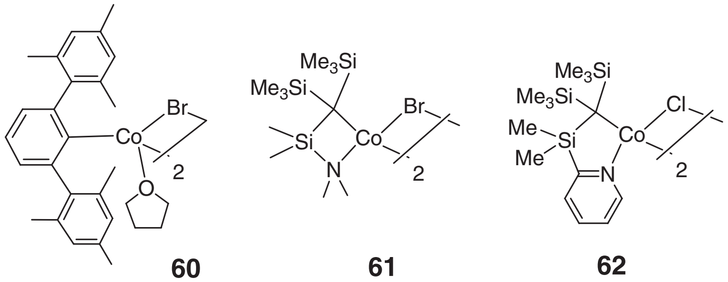
7.01.3.4.1 Trispyrazolyl boratocobalt(II) complexes

The use of a hydrotris(pyrazolyl)borato (Tp) ligand represents another possibility to create low-coordination 15-electron organocobalt(II) complexes **66** (Figure 25).[58,114] Since the Tp ligand blocks three coordination sites at the cobalt atom, this situation allows σ-aryl or σ-alkyl groups to bind the cobalt atom at the fourth coordination center. All these compounds are thermally stable under inert atmosphere, and they do not present β-hydride elimination (i.e., when R = Et, *n*-Bu, see (Figure 25). This feature is remarkable for such unsaturated complexes. Akita's group explained this high stability by a high spin configuration of the complexes where all the frontier orbitals are occupied by an electron pair or an unpaired electron.[115]



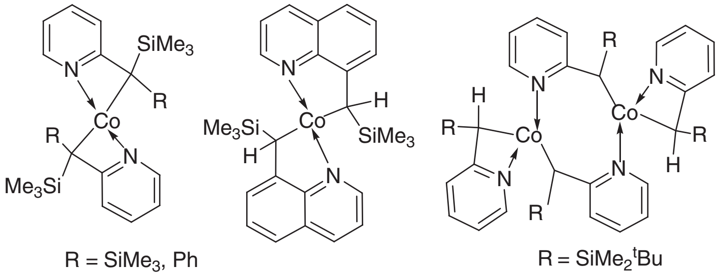
59

Figure 22



60 **61** **62**

Figure 23

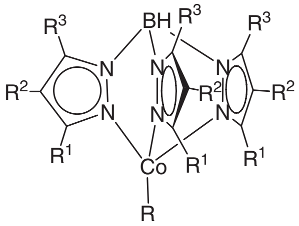


$[(R^3{}_3SiCH_2)_4Co(MgCl)_2]$

$R^3{}_3Si = Me_3Si, Me_2PhSi,$
$(iPrO)Me_2Si,(CH_2{=}CHCH_2)Me_2Si$

63 **64a** **64b** **65**

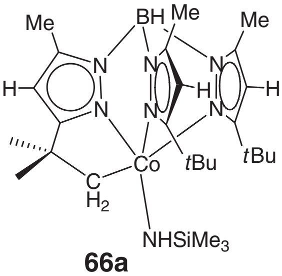
Figure 24



$R^1 = {}^tBu; R^2 = H; R^3 = H; R = CH_3$
$R^1 = {}^tBu; R^2 = H; R^3 = Me; R = CH_3$, Et, *n*-Bu, ethylene, propene, $NHSiMe_3$
$R^1 = {}^tBu; R^2 = H; R^3 = H; R = CH_3$
$R^1 = {}^iPr; R^2 = H; R^3 = {}^iPr$; R = *p*-methylbenzyl, α-naphthylmethyl, ethyl, η^3-allyl, Ph
$R^1 = Me; R^2 = Me; R^3 = Me$; R = *p*-methylbenzyl

66

Figure 25

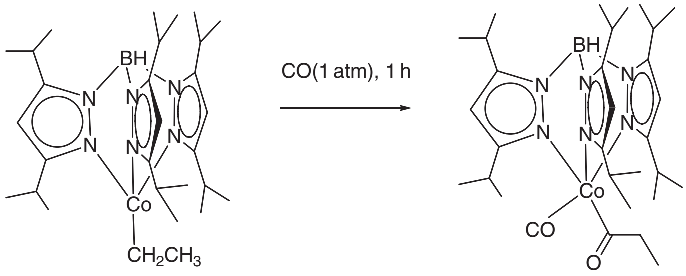


66a

Figure 25a

When R was a trimethylsilylamido unit and R^1 a *tert*-butyl substituent, a rare case of intramolecular CH activation took place on a *tert*-butyl group leading to a paramagnetic Co(III) derivative, displaying a distorted trigonal-bipyramidal geometry (Figure 25a).[116]

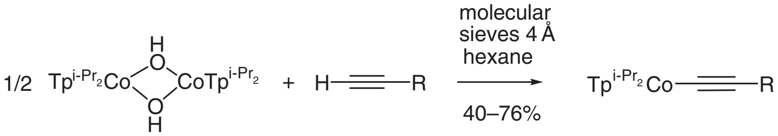
These β-elimination-resistant alkyl complexes **66** present an interesting reactivity toward insertion reaction such as with CO, leading to a 17-electron acyl(carbonyl) complex **68** (see Equation (6)). Other small unsaturated organic molecules have been used by Akita's group, but only phenylacetylene has led to C–C bond formation, affording, after hydrolysis of the solution, a mixture of *cis–trans*-1-phenyl-1-butene with 68% yield.



67 **68**

(6)

The alkynyl TpCo derivatives have been prepared via an original route of dehydrative condensation of the hydroxo complex $[\mathrm{Tp}^{i\text{-}\mathrm{Pr}_2}\mathrm{Co}(\mu\text{-OH})]_2$ with alkynes (Equation (7)).[117] The complexes formed **70** have a high spin configuration ($S = 3/2$).



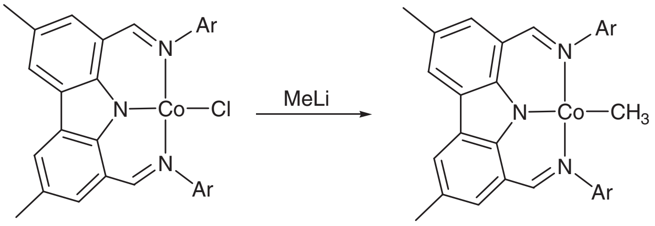
69 **70**

R = CO_2Me, CO_2Et, COMe, $SiMe_3$, $SiEt_3$, H, Ph, *t*-Bu

(7)

A phenyltris(*tert*-butylthio)methylborato ligand has been used to obtain a tetrahedral methyl organocobalt compound **71** (Figure 26).[118] The coordination environment is similar to that of the Tp complexes (see above). The synthesis has been performed by the reaction of MeLi with the chloro[phenyltris(*tert*-butylthio)methylborato]cobalt(II) derivative.

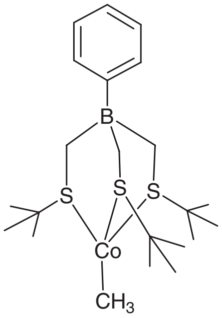
Gibson *et al.*[119] have obtained a methyl[bis(imino)carbazolide]cobalt(II) complex **73** from the chloride derivative **72** (Equation (8)). The chloride complex in the presence of MAO was expected to produce oligomerization or polymerization of ethylene but no reaction has been observed, which is in marked contrast to the high polymerization activity of related bis(imino)pyridine complexes of Co.[120]



Ar = 2,4,6-trimethylphenyl

72 **73**

(8)



71

Figure 26

7.01.3.5 Organocobalt(III) Complexes

7.01.3.5.1 Organocobalt(III) complexes with non-macrocyclic ligands

Kofod *et al.* have synthesized a huge series of methylcobaltamine complexes **74–77** with ammonia and other saturated polyamine (see Figure 27).[121,122] The mechanism of substitution of four ammonia ligands by two ethylenediamine (en) chelates was followed by a slow *cis*- to *trans*-rearrangement of the bis(en)(amine)methylcobalt complex.[123] The mechanism is strictly dissociative.

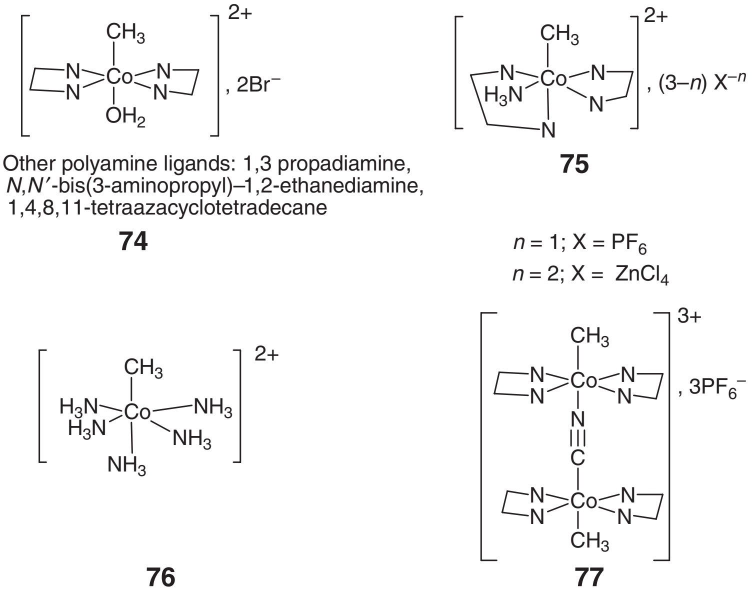
The kinetics of formation of complexes with Co–C bonds in the reaction between $[Co(NH_3)_5H_2O]^{2+}$ or $[Co(NH_3)_6]^{2+}$ with different aliphatic radicals ($R = CH_3$, $CH_2CO_2^-$, CH_2OH) was studied in aqueous solutions using the pulse radiolysis technique. The formation of $((NH_3)_5Co^{III}–R)^{n+}$ obeys pseudo-first-order rate laws.[124]

The preparation of pentacyano(iminiumacetyl)cobaltate(III) anion **79** and its *N*-methyl and *N*,*N*-dimethyl derivatives has been reported by Kofod *et al.* The iminium acetyl group is formed by migratory insertion into the Co–Me bond of hydrogen isocyanide located at the *cis*-position with respect to the methyl group in the pentacyano(methyl)cobaltate(III) anion. These new compounds have been characterized by ^1H, ^{13}C, ^{15}N, and ^{59}Co NMR spectroscopy, and by absorption spectroscopy.[125] By isotope labeling, it has been possible to demonstrate that insertion migration of the methyl to cyano group occurred via the formation of a *cis*-hydrogen isocyanide (Scheme 7).

An interesting study of tris-orthometallated 1-phenylpyrazolato (ppz) and 2-phenylpyridinato (ppy) cobalt complexes employed as hole transporting layer (HTL) in organic light emitting diode (OLED) was recently published.[126] However, only poor yields (7%) of pure *fac*-$(Co(ppz)_3)$ compounds were obtained, whereas yields were not mentioned for the synthesis of $Co(ppy)_3$. One of the reasons for this was that the first step of the synthesis gave mixtures of *fac*- and *mer*-isomers in poor yields (<20%). While *fac*-$Co(ppy)_3$ **81** gave stable OLEDs, the *fac*-$Co(ppz)_3$-based devices **80** had a very short lifetime. It was also concluded that weak absorption bands for Co(III) due to *d*–*d* transition can lead to exciton loss from the emissive layer; therefore, the use of first row transition metal complexes as hole transporting materials in efficient devices is being problematic (Figure 28).

Homoleptic hexacoordinate carbenecobalt(III) has been recently obtained. The preparation of the tris-carbene tris-(imidazolin-2-ylidene)borate **82**, which is the *C*-isomer analog of Trofimenko's well-known tris(pyrazolyl)borate, has been reported. Two of these tris-carbene ligands have been coordinated onto the cobalt atom (Figure 29).[127]

A one-pot route has also been described in the same paper, providing an easy access to hexacarbene cobalt(III) complex **83**, with oxazolidin-2-ylidene ligands from 2-hydroxyalkylisocyanides (Equation (9)).



Other polyamine ligands: 1,3 propadiamine, *N*,*N*′-bis(3-aminopropyl)–1,2-ethanediamine, 1,4,8,11-tetraazacyclotetradecane

74

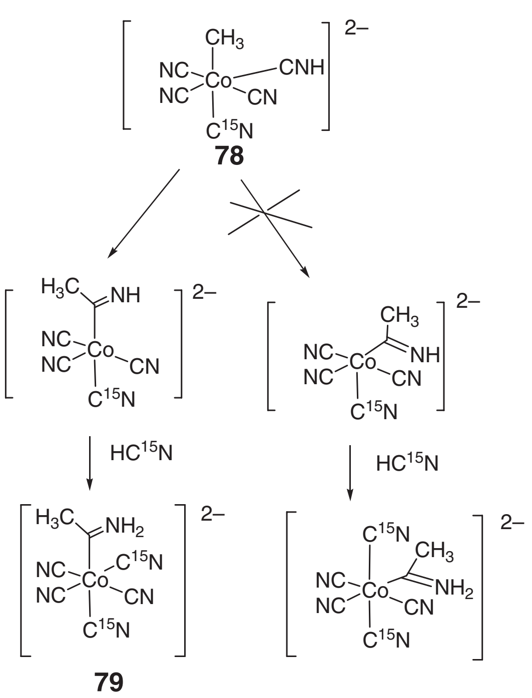
75

$n = 1$; $X = PF_6$
$n = 2$; $X = ZnCl_4$

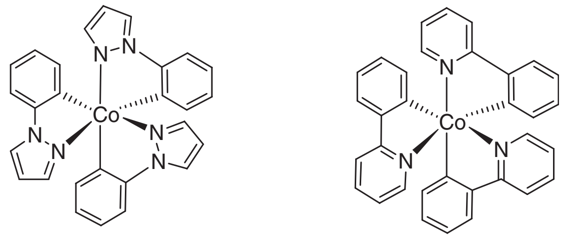
76

77

Figure 27



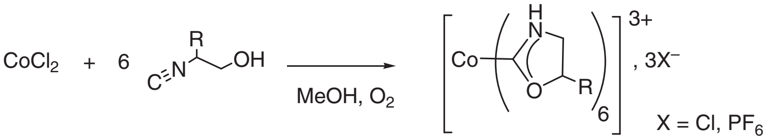
Scheme 7



fac-Co(ppz)$_3$
80

fac-Co(ppy)$_3$
81

Figure 28

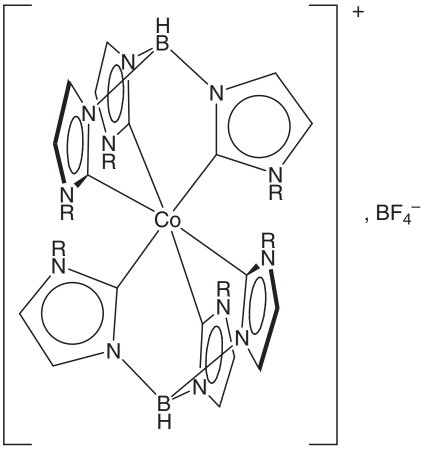


83

(9)

Brookhart *et al.* have described the synthesis of various tetramethyl(2-methylthioethyl)cyclopentadienyl cobalt complexes 84–86, and tested them in ethylene polymerization. The activity of the catalyst has been improved as compared to the previously described catalyst containing the $[Cp^*CoPR_3]^+$ unit (see Sections 7.01.4.4.1 and 7.01.4.4.3). In order to prepare a stable cationic precursor, the complexes 86 have been synthesized (Scheme 8).[128]

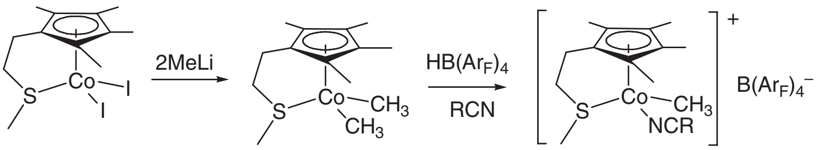
Long fluoroalkyl chain ligands have been coordinated onto the metal center of indenyl[129] and cyclopentadienyl[130] cobalt complexes 88, in order to improve the solubility of these complexes (Scheme 9).



R = Me, Et

82

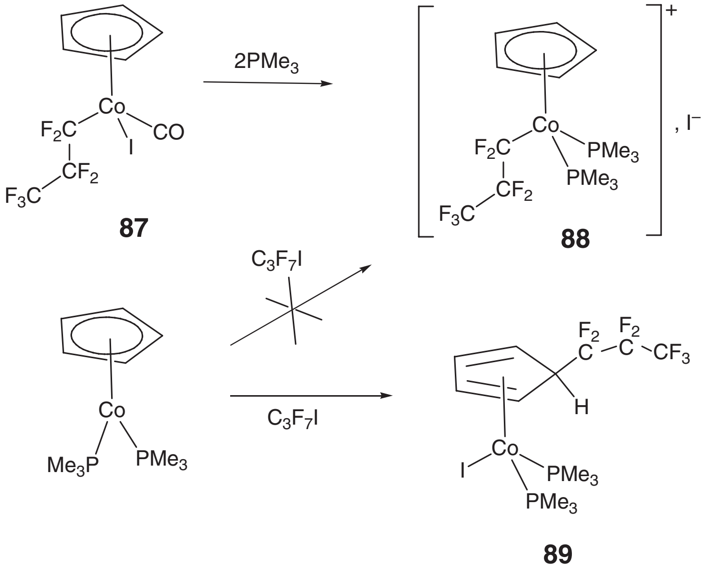
Figure 29



84 **85** **86**

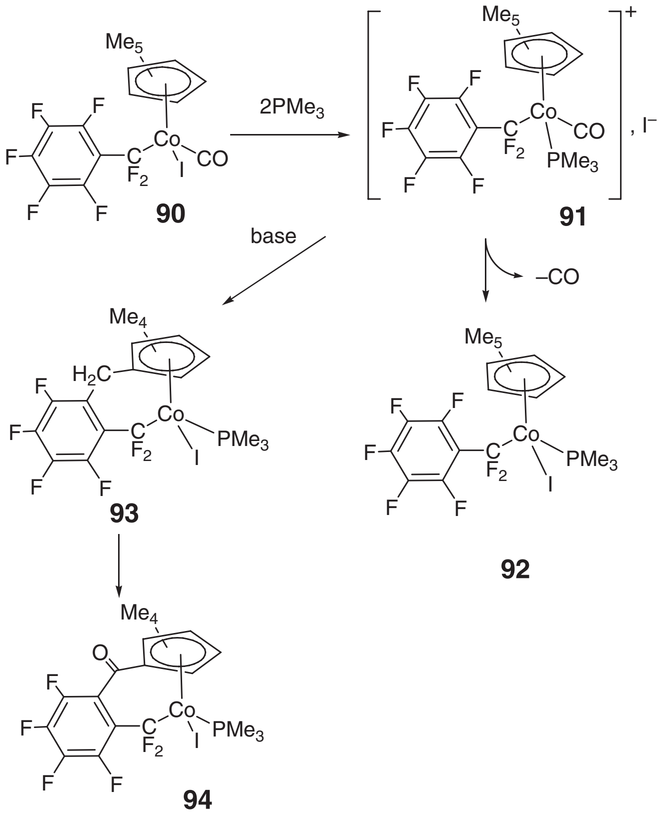
R = CH_3, 3,5-$(CF_3)_2C_6H_3$

Scheme 8



87 **88** **89**

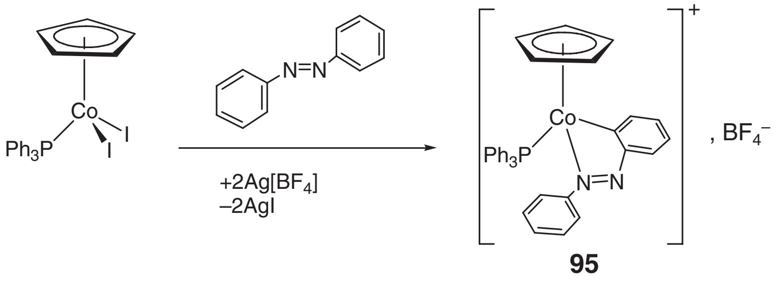
Scheme 9



Scheme 10

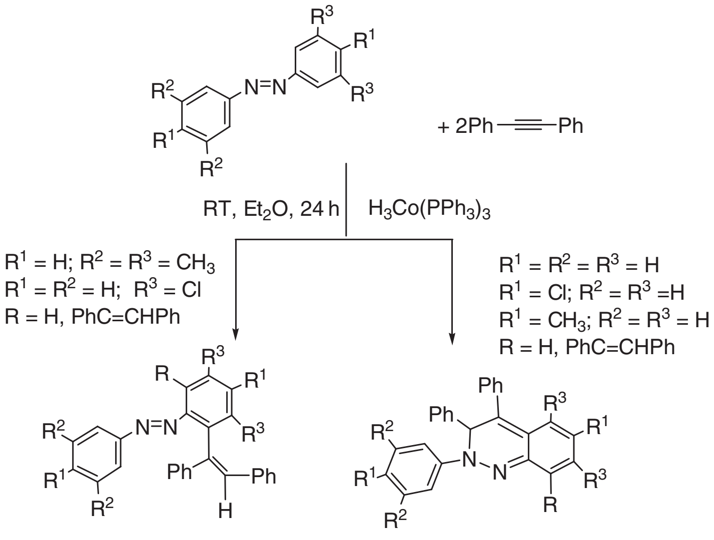
In the case of perfluroro benzyl ligand **90**, a coupling between the pentamethylcyclopentadienyl ligand and the *ortho*-carbon of the perfluoro benzyl ligand was observed, which involved the formation of HF = fluorhydric acid.[131] The authors have proposed a mechanism where traces of a base (not defined) could induce the reaction by deprotonating a methyl of the pentamethylcyclopentyl ring in **91**. The carbanion thus formed could play the role of a nucleophile toward the aromatic C–F bond to afford **93**. The arm thus obtained presented a high sensitivity toward hydrolysis (on the CH_2 moiety). The resulting hydrolysis led to a compound **94** with a pendant arm bearing an acyl function coordinated to cobalt (see Scheme 10).

The first direct orthometallation products of *trans*-azobenzene with Co(III) **95** were observed and fully characterized (Equation (10)).[132]

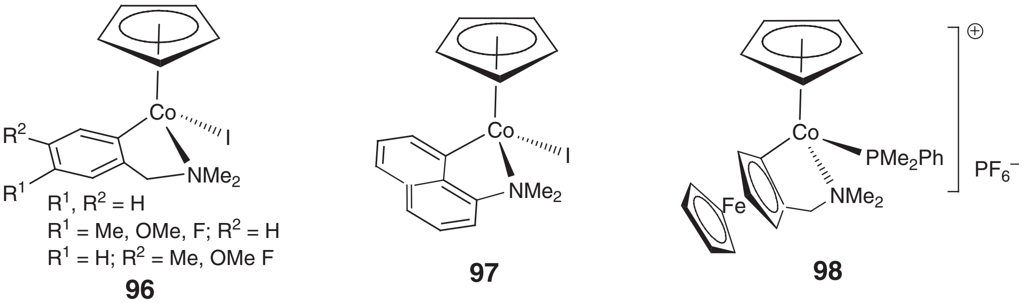


(10)

Previously, it has been reported that diphenylacetylene could be inserted into the *ortho*-C–H bond of *trans*-azobenzene. This reaction was catalyzed by $H_3Co(PPh_3)_3$ at RT. The orthometallation has been proposed to occur in the catalytic cycle (Scheme 11).[133]



Scheme 11

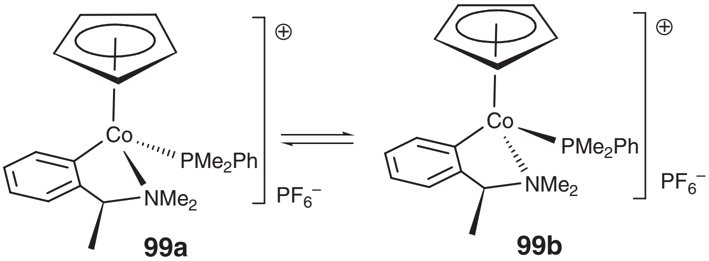


96 **97** **98**

Figure 30

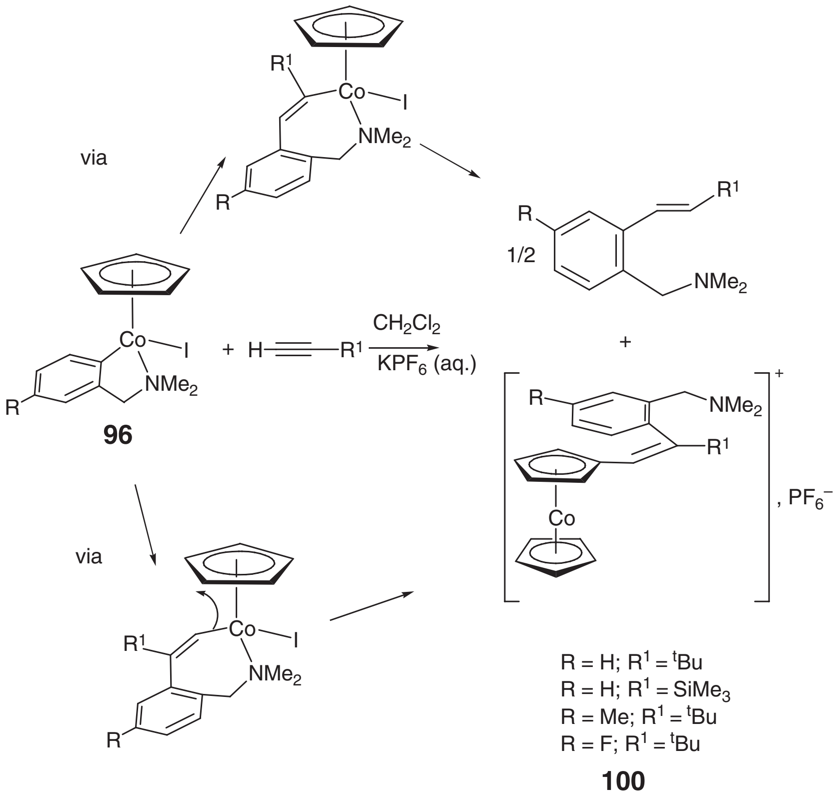
A series of cyclometallated cobalt(III) complexes with substituted *N*,*N*-dimethylbenzylamines, 1-*N*,*N*-dimethylnaphthylamine, and *N*,*N*-dimethylferrocenylmethylamine **96–98** has been synthesized by a transmetallation reaction, using the corresponding lithium derivatives with $[CpCoI_2]_2$. When the NMe_2 group was attached to a chiral benzylic unit with a given configuration, such as in (*S* or *R*) *N*,*N*-dimethyl-1-phenylethylamine, this reaction led to the formation of two diastereoisomers with a diastereoselectivity of up to 92%.[134] The configuration at the cobalt center was however not stable as it has been shown that the diastereoisomeric mixture (whose composition did not vary once it has been established in a given solvent) was in fact the result of an equilibrium whose thermodynamic constants have been determined by ^1H NMR (Figure 30). [135,136]

It was found moreover that the fourth ligand on the cobalt atom could play a decisive role upon the stability of the diastereoisomers. Thus, the cationic derivative **99b** obtained with a phosphine ligand was unstable as it isomerized slowly (within one week at RT) to the less congested compound **99a** (Equation (11)).



99a **99b**

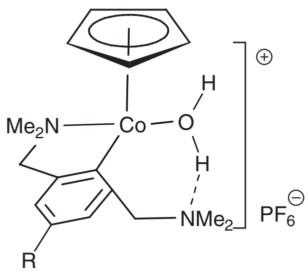
(11)



Scheme 12

The insertion of alkynes into the carbon–cobalt bond of cyclometallated compounds has also been reported for *N*,*N*-dimethylbenzylamine cobalt derivatives **96** leading to organic products and new organometallic cobalt(III) complexes. The reaction was unfortunately limited to terminal alkynes bearing one bulky substituent, for example, $SiMe_3$ or ^{t}Bu. The reaction pathway was dependent upon the regioselectivity of the alkyne insertion into the Co–C bond, the selectivity of the product obtained being mainly a result of the steric interactions between the alkyne substituents and the CoCp unit (Scheme 12).[137]

A cyclometallated cobalt(III) complex with an N–C–N pincer ligand **101** was synthesized following the same transmetallation reaction as that used for obtaining the compounds **96**–**98**, that is, via the reaction of the lithiated pincer on $[CpCoI_2]_2$.[138] However, this procedure proved not to be very useful for the synthesis of the pincer compounds substituted at *para*-position by either OMe or COMe as it led to very low yields of products whose purification was moreover not possible. The transmetallation reaction using gold derivatives on the same dimeric cobalt complex proved to be the method of choice as it led to the expected clean products in fair to good yields (Figure 31).[139]

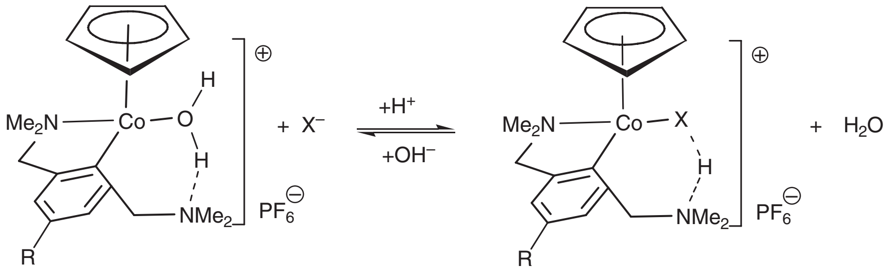


R = H, OMe, COMe

101

Figure 31

These aquo derivatives were stabilized by an extra hydrogen bond with the non-bonded dimethylamino group. The pK_a of this "free" amine was measured by ^{1}H NMR in the presence of variable amounts of HPF_6 (R = H, pK_a = 6.1; R = OMe, pK_a = 6.2; R = COMe, pK_a = 5.6). These compounds proved to be interesting anion receptors as in slightly acidic media, the water molecule could be reversibly displaced by several anions as those depicted in (Equation (12)).[140]



101

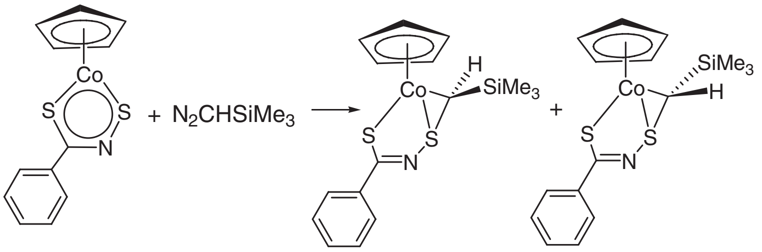
X = F, Cl, Br, I, OAc, H_2PO_4

102

(12)

The stability constants of the various anion supercomplexes **102** have been determined. They showed that these complexes show significantly higher affinity for oxygen-containing anions such as carboxylates in water.[139,140]

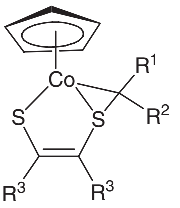
The reaction of trimethylsilyldiazomethane with dithiazolecobalt(III) complexes **103** led to the formation of heterometallacycles **104** and **105** with the three-membered ring (Equation (13)). Two diastereoisomers, **106**, (figure 32) have been obtained while reacting a series of diazomethane with dithiloene ligands bound to a CoCp unit.[141–143]



103 **104** **105**

(13)

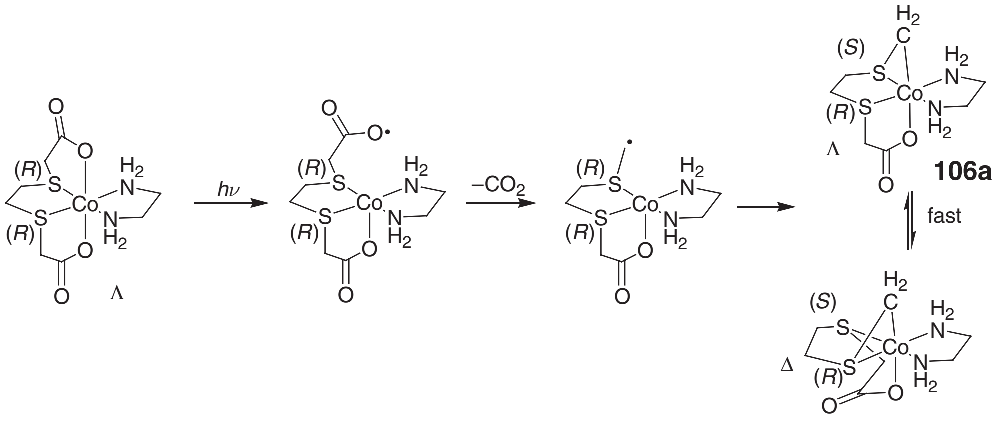
A three-membered Co–SCH_2 chelate ring was obtained via photodecarboxylation reaction of a dithiodicarboxylatocobalt(III) complex.[144] The product **106a** and **106b** was obtained as a racemate mixture (Figure 32). The racemization was presumed to be the result of the rapid chiral inversion on the two chiral thioether S atoms (Equation (14)).



R^1 = H; R^2 = CO_2Et; R^3 = CO_2Me or CN
R^1 = H; R^2 = $SiMe_3$; R^3 = CO_2Me or CN
R^1 = R^2 = R^3 = CO_2Me
R^1 = R^2 = Ph; R^3 = CO_2Me
R^1 = R^2 = H; R^3 = CO_2Me or CN or Ph

106

Figure 32

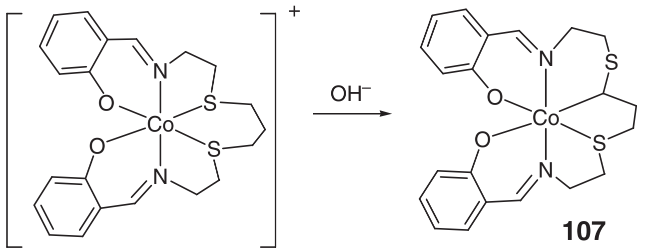


106a

106b

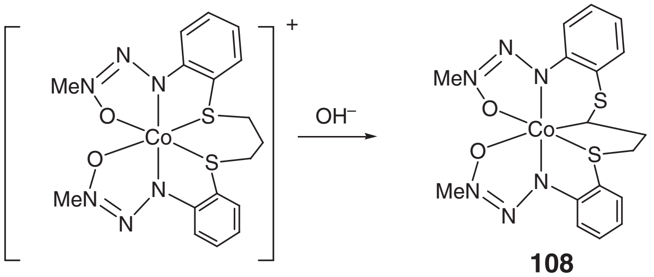
(14)

A specific ring-size transformation has been observed for the family of compound salicylaldimine-substituted dithiaalkanes or dithiaalkyl-substituted triazene 1-oxide bonded to a trivalent cobalt. When the spacer between the two sulfur atoms was a propyl group, then a C–H activation was observed leading to an organocobalt complex **107** and **108** (Equations (15) and (15a)).[145–147]



107

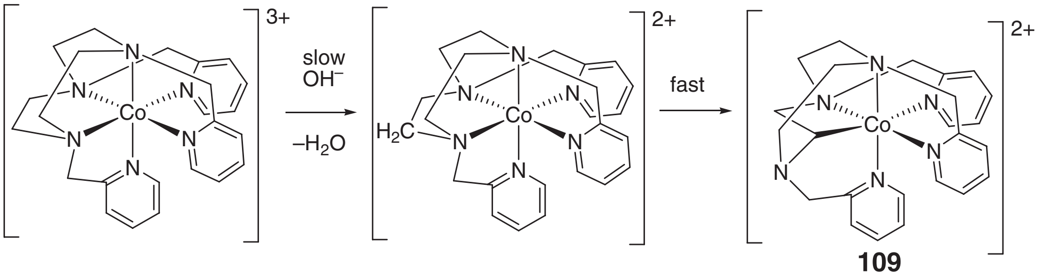
(15)



108

(15a)

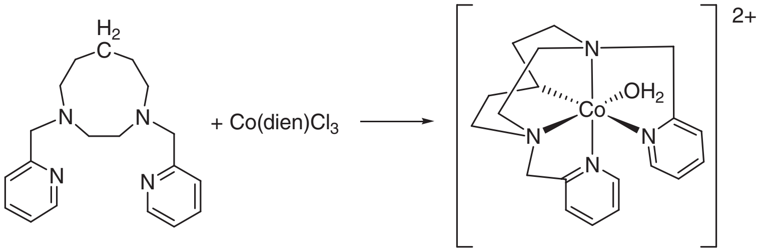
A similar process has been recently reported with 1,4-bis(2-pyridylmethyl)–1,4,7-triazacyclononane (dmptacn). The reaction proceeded rapidly and completely ($t_{1/2}$ = ca. 15 min in 1M NaOH at 25 °C), leading to a strained four-membered ring **109** (Scheme 13).[148] This reaction was reversible in acidic solution. The 1,4-bis(2-pyridylmethyl)-



109

Scheme 13

1,4-diazacyclononane ligand can give directly the intramolecular cobalt alkyl complex **110** resulting from the CH activation (Equation (16)).

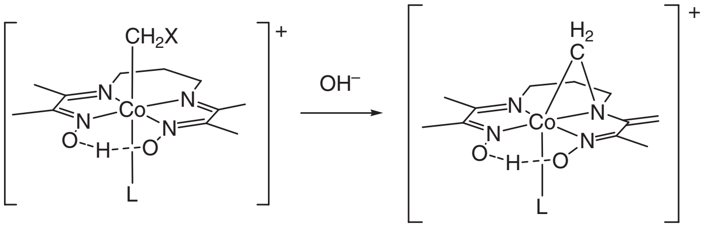


110

(16)

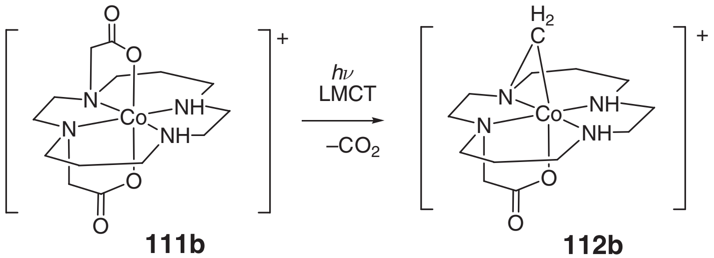
[$CoR_2(N–N)_2X$] (R = Me, $PhCH_2$; N–N = 2,2′-bipyridine, 1,10-phenanthroline; X = BF_4^-, PF_6^-) were obtained through the addition of the appropriate organic halide on $CoCl_2$ with $NaBH_4$ in MeOH. These compounds are efficient catalysts for the polymerization of polar olefins such as acrylonitrile in the dark and with no addition of radical traps. Molecular weight and polydispersities determination suggest a catalytic controlled radical mechanism.[149]

Rare CoNC three-membered rings in **112a** and **112b** have been formed either by a novel pathway involving a facile interligand nucleophilic addition of an equatorial nitrogen donor to a ligated axial carbon or via decarboxylatrion of an α-amino acid coordinated to Co(III) (Equations (17) and (17a)).[150–152]



111a **112a**

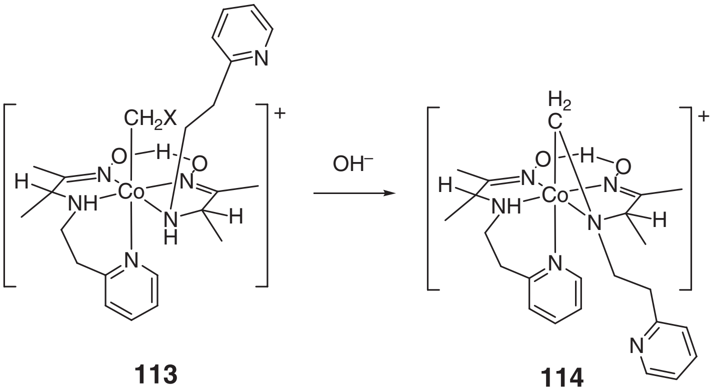
(17)



111b **112b**

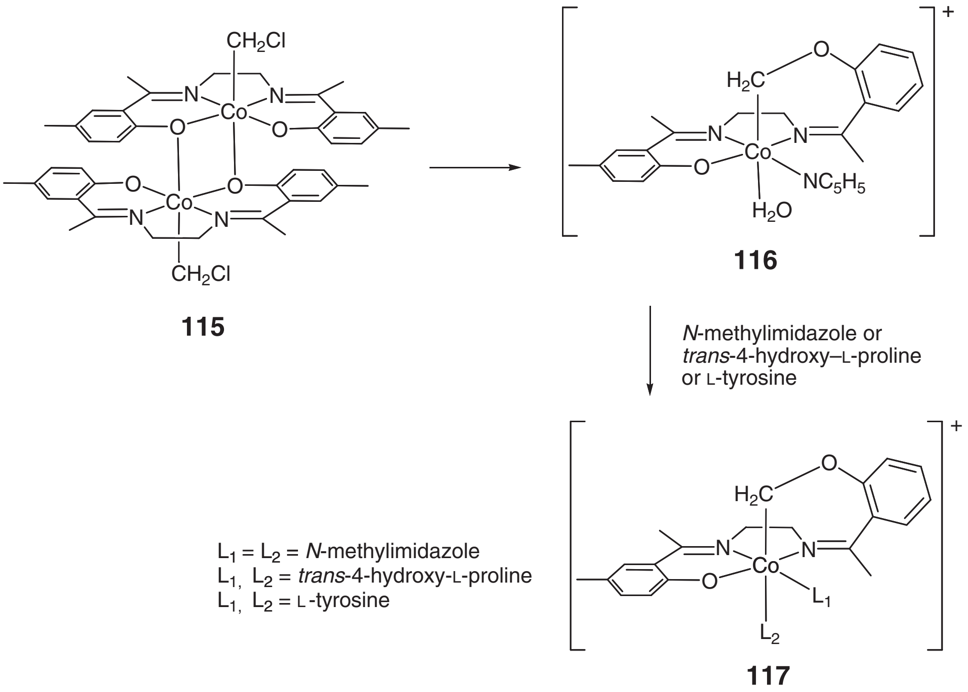
(17a)

The analogous three-membered ring has been obtained with the cobalt complex containing the tridentate ligand 2-((2-pyridylmethyl)amino)-3-butanone oxime. It has been notified that intramolecular process forming the metallacycle **114** is quite rapid, whereas the carbon bonded to cobalt is inert toward intermolecular nucleophilic attack (Equation (18)).[153,154]



113 **114**

(18)



Scheme 14

Another type of reaction leading to the incorporation of the Co–C alkyl chain inside the salen ligand set has been developed by Dreos *et al.* If the dimer **115** was left for a longer time in contact with the reaction mixture, an intramolecular reaction occurred between the chloromethyl group and the equatorial chelate. The unidentate ligands on cobalt can be replaced quantitatively by *N*-MeIm, leading to a complex **116** in which the *β*-*cis*-geometry was maintained.[155] If chiral amino acids were used, the diastereoisomers **117** could be separated (Scheme 14).[156]

7.01.3.5.2 Organocobalt(III) complexes with nitrogen-containing macrocyclic ligands

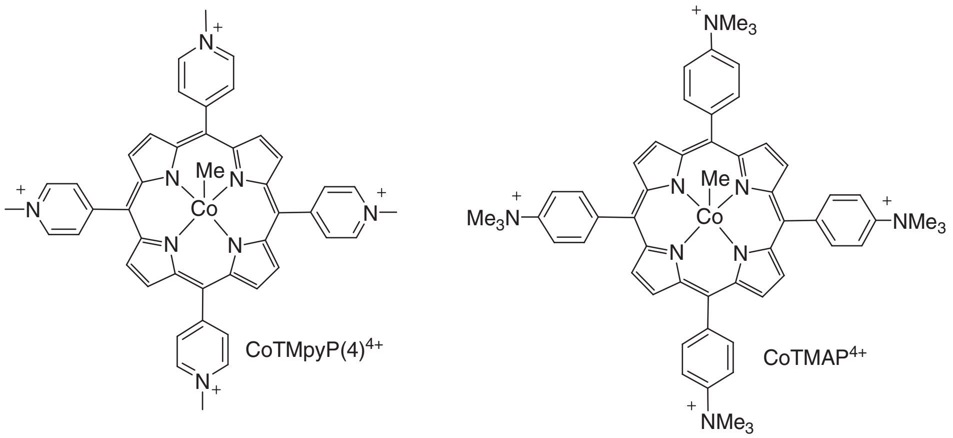
The bioorganometallic chemistry as well as the biological chemistry of cobalt has been reviewed recently in *Comprehensive Coordination Chemistry*.[1,3]

We shall report here the synthesis of cobalt–carbon bond involved in coenzyme B_{12} and cobalamine, cobaloxime, and Schiff base analog models, together with some aspects of their reactivity.

Organocobalt complexes of tetrameric water-soluble porphyrins are difficult to prepare via typical reductive alkylation of the porphyrin Co(II). It has been possible to incorporate a Co(III)–CH_3 moiety directly into the porphyrin core, using $[Co(III)(NH_3)_5CH_3]^{2+}$ as the starting material.[157] The porphyrin systems are the *meso*-tetrakis(*N*-methyl-4-pyridiniumyl)porphyrin (TMyP(4)) **118** and the *meso*-tetrakis(*N*,*N*,*N*-trimethyl-aniliniumyl)porphyrin (TMAP) **119** (Figure 33). This method afforded two new $[CH_3Co(Por)]^{4+}$ compounds. The binding of each of the $[CH_3Co(Por)]^{4+}$ to DNA and polymeric DNA has been studied. Upon binding of each of the $[CH_3Co(Por)]^{4+}$ cations to all of the DNA polymers, the Soret bands displayed blue shifts, whereas the Soret bands of the corresponding $[(H_2O)_2Co(Por)]^{5+}$ cations displayed red shifts. The blue shifts strongly suggested that on DNA binding, the $[CH_3Co(Por)]^{4+}$ cations became five coordinate.

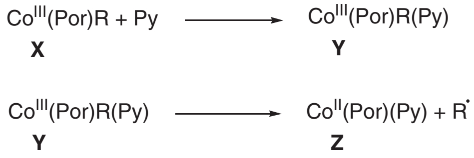
A study of ^{13}C labeled compounds derived from ethylcobalt(III) octaethylporphyrin and other porphyrins indicated that the ^{13}C NMR resonances of the carbon atoms bound to cobalt were quite broad and were upfield shifted. The anomalous features of the NMR spectra were ascribed to the quadrupolar cobalt nucleus, and to the paramagnetic contact shifts that arose from thermal population ground state instead of agostic bond.[158]

The study of several structural changes observed in (methyl)(OEP)cobalt and (methyl)(pyridine)(OEP)cobalt complex (OEP = octaethylporphyrin) led to rationalize the "base-on" effect in which the coordination of an axial ligand accelerated the homolysis of the Co–C bond. The compounds are related by a reaction sequence in which coordination of the pyridine to the five-coordinate compound **X** afforded a six-coordinate compound **Y**, which then



118 **119**

Figure 33



$$\underset{\mathbf{X}}{\mathrm{Co^{III}(Por)R}} + \mathrm{Py} \longrightarrow \underset{\mathbf{Y}}{\mathrm{Co^{III}(Por)R(Py)}}$$

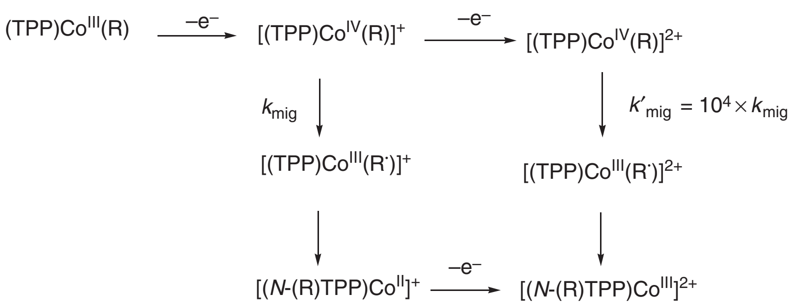
$$\underset{\mathbf{Y}}{\mathrm{Co^{III}(Por)R(Py)}} \longrightarrow \underset{\mathbf{Z}}{\mathrm{Co^{II}(Por)(Py)}} + \mathrm{R^{\cdot}}$$

Scheme 15

underwent homolysis of the alkyl bond to afford the five-coordinate Co(II) complex **Z** (Scheme 15). The significant elongation of the Co–C bond distance in the Co(Por)(CH$_3$)(py) relative to Co(Por)(CH$_3$) reflects both the electronic *trans*-influence of the pyridine and the increased steric interactions of the alkyl ligand with the porphyrin.[159]

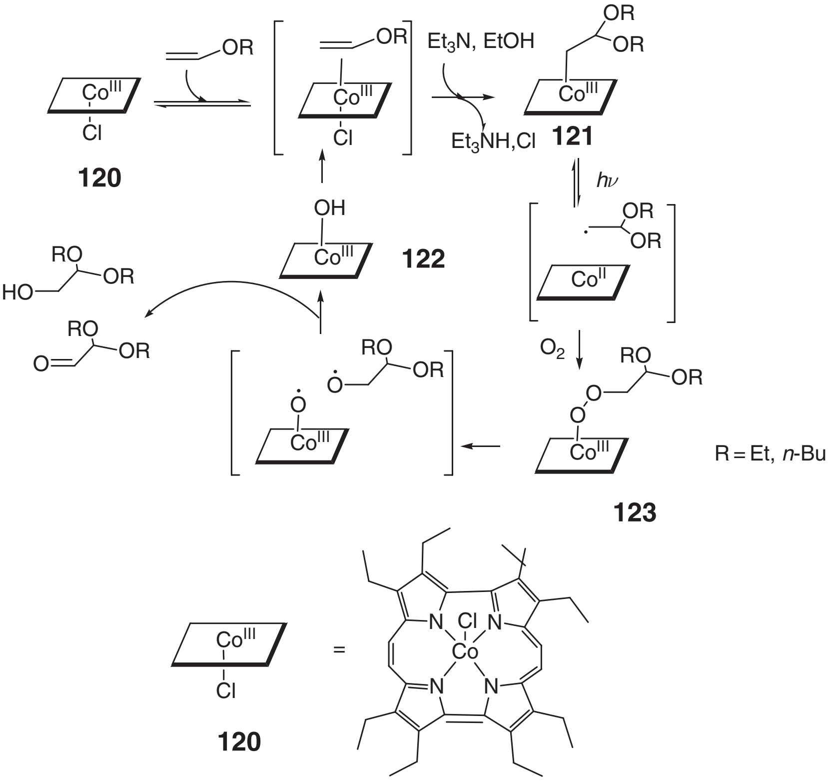
The stability constants for the coordination of pyridine or substituted pyridines to various alkylcobalt porphyrin systems have been reported. This study has been done in order to observe the *cis*-influence of hydroporphyrin macrocycles on axial position and alkyl exchange reactions.[160] The alkyl exchange reactions of organocobalt(III) porphyrins with a cobalt(II) complex of a distinguishable porphyrin or tetrapyrrole have been studied. The equilibrium constants for the alkyl transfer have been reported. The exchange of the axial ligand is reversible and it follows a bimolecular mechanism.[161] Thermodynamic and activation parameters for homolytic Co–C bond dissociation have been obtained on the (TAP)CoC(CH$_3$)$_2$CN complex (TAP = tetraanisylporphirinato).[162]

The migration reactivity of σ-bonded ligands of organocobalt porphyrin is also depending upon the oxidation states of the cobalt center (Scheme 16). The migration of the (R) group onto the macrocycle of [(TTP)Co$^{\mathrm{III}}$(R)]$^+$



$$\begin{tikzcd}
\mathrm{(TPP)Co^{III}(R)} \arrow[r, "-e^-"] & \mathrm{[(TPP)Co^{IV}(R)]^+} \arrow[r, "-e^-"] \arrow[d, "k_{\mathrm{mig}}"'] & \mathrm{[(TPP)Co^{IV}(R)]^{2+}} \arrow[d, "k'_{\mathrm{mig}} = 10^4 \times k_{\mathrm{mig}}"] \\
 & \mathrm{[(TPP)Co^{III}(R^{\cdot})]^+} \arrow[d] & \mathrm{[(TPP)Co^{III}(R^{\cdot})]^{2+}} \arrow[d] \\
 & \mathrm{[(\mathit{N}\text{-}(R)TPP)Co^{II}]^+} \arrow[r, "-e^-"] & \mathrm{[(\mathit{N}\text{-}(R)TPP)Co^{III}]^{2+}}
\end{tikzcd}$$

Scheme 16



Scheme 17

(TPP = 5,10,15,20-tetraphenylporphyrin, R = Me, Ph) has been studied. The migration rate of the σ-bonded ligand of $[(TTP)Co^{III}(R)]^+$, produced from one-electron oxidation of $[(TTP)Co^{IV}(R)]$, is 10^4 times slower than the migration rate of the R group in the corresponding two-electron oxidized species: $[(TTP)Co^{IV}(R)]^{2+}$.[163,164]

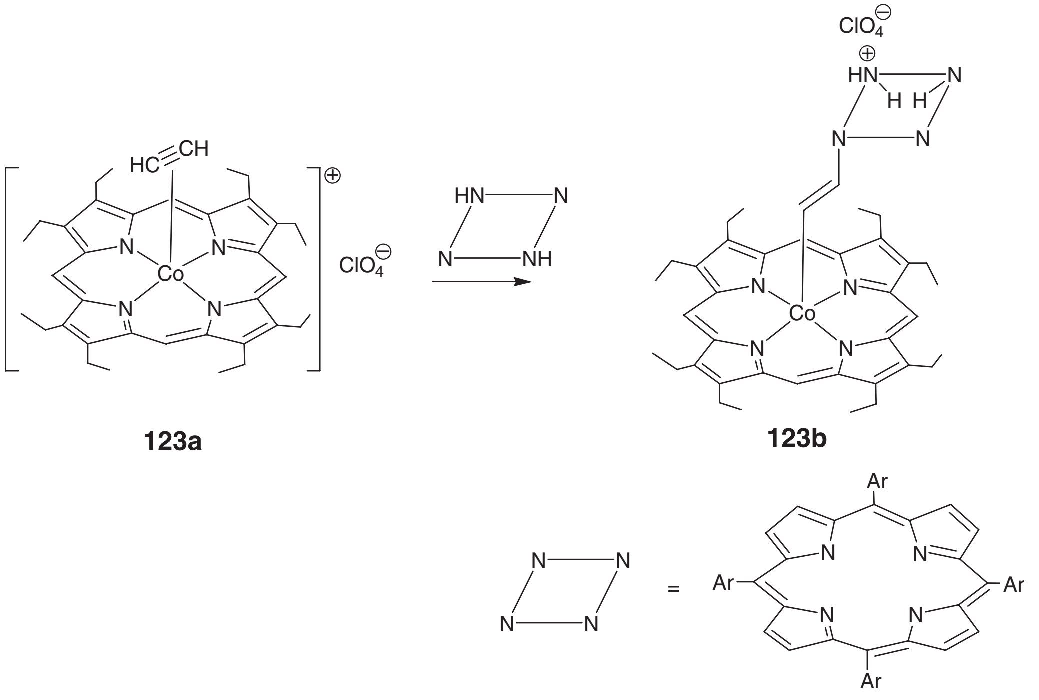
The same migration of σ-bonded cobalt porphycenes has also been investigated (Scheme 17).[165] The cobalt porphycene could now also be used in catalytic oxidation of vinyl ether via the formation and dissociation of cobalt–carbon bonds.[166,167]

N-substituted porphyrin free bases were *N*-vinylated regioselectively via a nucleophilic addition reaction of a pyrrole nitrogen to a π-complexed acetylene ligand in a cationic Co(III) porphyrin intermediate (Scheme 17a).[168]

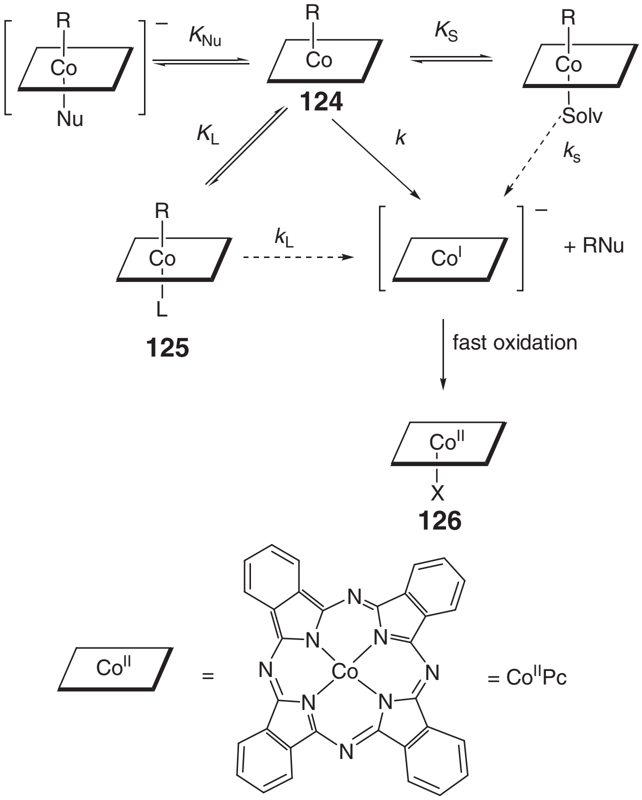
In some cases where a reaction involving a radical species occurred within cobalt porphyrin complexes, it has been possible to trap transient cobalt porphyrin hydride species. This was indeed observed during the synthesis of organocobalt porphyrin that resulted from the reaction of cobalt(II) porphyrin and dialkylcyanomethylradicals with alkenes, alkynes, alkyl halides, and epoxide.[169,170] A transient hydride porphyrin complex was also involved in the cobalt porphyrin-catalyzed chain transfer in the free-radical polymerization of methacrylate.[171] The catalytic chain transfer in free-radical polymerizations using cobalt porphyrin systems has been extensively investigated and will not be treated in this section. Gridnev and Ittel have published a comprehensive overview of the catalytic chain transfer in free-radical polymerizations.[172]

$CH_3Co^{III}Pc$ (Pc = phthalocyanine dianion) has been characterized by equilibrium studies of its *trans*-axial ligation and cyclic voltammetry as a relatively "electron-poor" model of methyl cobalamin, which, in non-coordinating solvents, remained a five-coordinate complex (Scheme 18). Axial base inhibition of methyl transfer from $CH_3Co^{III}Pc$ showed that the reaction proceeded via a reactive five-coordinate species, even in coordinating solvents. The virtual inactivity of six-coordinate $CH_3Co^{III}Pc(L)$ complexes provided a reference point for important biological processes.[173]

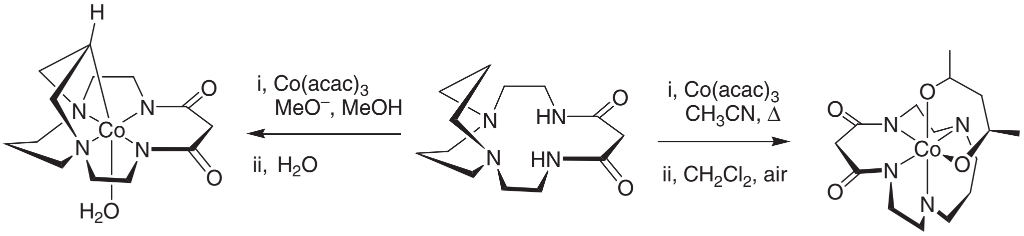
Unusual C–H activation and C–N bond cleavage were observed when treating a sterically hindered N_4 macrocyclic ligand that contained the 1,5-diazacyclooctane ring with $Co(acac)_3$ (Scheme 18a). The presence of a base led to the



Scheme 17a

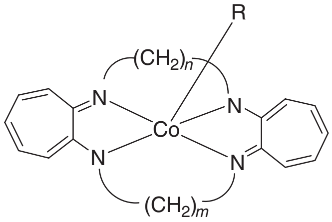


Scheme 18



126a **126b**

Scheme 18a



127

Figure 34

formation in **126a** of an axial Co–C bond via heterolytic C–H cleavage, whereas the absence of a base afforded a new ligand in **126b** after two C–N bonds have been cleaved.[174]

Some cobalt macrocycle complexes such as *trans*-RCo(H_2O) (5,7,7,12,14,14-hexamethyl-1,4,8,11-tertraazacyclotetradeca-4,11-diene)$^{2+}$ may exist as different isomers. The isomerization has been studied, and the kinetic and thermodynamic parameters were investigated.[175]

A family of Co(III) complexes has been synthesized by using the macrocyclic tropocoronand ligands [CoEt(TC-3,3)], [Co(*n*-Pr)(TC-3,3)], [CoMe(TC-4,4)], **127** (Figure 34). The geometries of the different alkyl complexes are square pyramidal. All these complexes led to homolysis to give the corresponding Co(II) complex. CO can be inserted into the Co–C bond of [CoMe(TC-4,4)], whereas this reaction was impossible with [CoEt(TC-3,3)]. The difference in reactivity was assigned to the size of the ligand that might thus provide enough flexibility to allow the *cis*-coordination of the alkyl and CO on the cobalt center.[176]

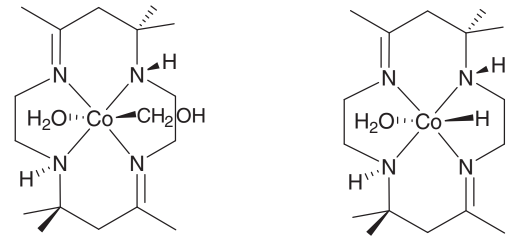
A review[177] explained the decomposition process of the complex hydroxymethylcobalt **128** in water to the hydridocobalt compound **129** and formaldehyde at a first step. In a second step, the decomposition of the hydride complex via a deprotonation of the metal hydride bond to yield the cobalt(I) complex followed by reduction of the parent hydride and rapid formation of cobalt(II) and H_2 was observed. The authors explained that while this pathway is not without precedent, its occurrence in alkaline solution is particularly striking since the thermodynamic formation becomes less and less favorable as the pH increases.

Mechanistic information from the pressure acceleration for the hydride formation via the proton binding to cobalt(I) macrocycle have been obtained (Figure 35).[60]

7.01.3.5.3 Organocobalt(III) complexes with oxime ligands

The family of cobaltoxime complexes has been the subject of many new contributions. The synthesis and characterization of a large number of axial alkyl compounds has thus been made. From these studies, few structural informations completed those obtained previously.[1,178]

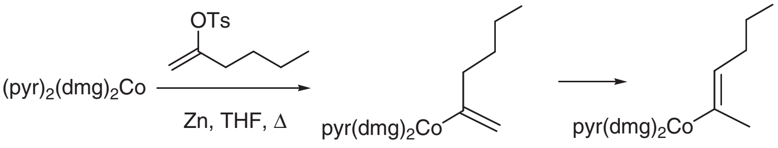
An unusual shortening of C(sp^3)–C(sp^3) bonds in *n*-propylcobaloximes has thus been observed.[179] This result was in contrast to those reported for the anhydrous [(*n*-Pr)Co(dmgH)$_2$(H_2O)] complex and its inclusion compound with



N-*meso*-CoHMD(CH_2OH)$^{2+}$ **128**

N-*meso*-CoHMD(H)$^{2+}$ **129**

Figure 35



131 **132** **133**

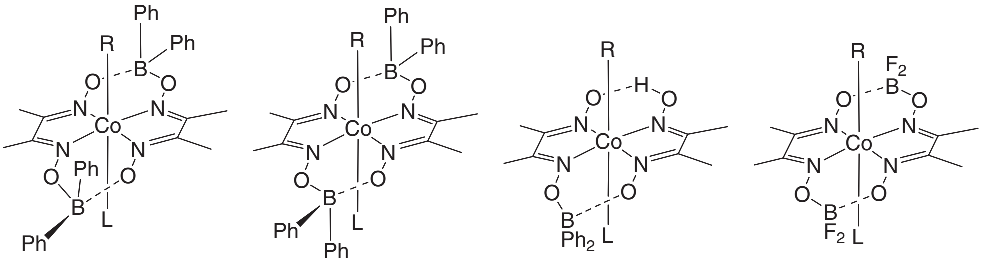
Scheme 19

α-cyclodextrin **130** = [(n-Pr)Co($dmgH)_2(H_2O$)] + cyclodextrine where a significant lengthening, by 0.16 Å, of the C_α–C_β bond of *n*-Pr in a cyclodextrin complex occurred.[180]

The methodology used for the preparation of a Co–C(sp^2) bond for dienyl cobalt complexes (see below: the Diels–Alder reactions in Section 7.01.3.5.4(i)) has been applied for the preparation of alkenylcobaloxime complexes **132** and **133** (Scheme 19). The methodology involved a zinc-mediated coupling of alkenyl halides and trifluoromethanes to $(pyr)_2(dmgH)_2$–Co **131** (pyr = pyridine; dmgH = dimethylglyoximate).[181]

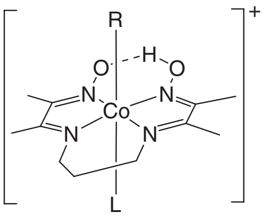
The incorporation of boron moieties in the oxime bridges has been discovered during the last decades. This modification was made in order to study the steric effect of bulky cobaloxime toward the coordination of the axial ligand and also to study the behavior of the different conformers that could occur after the introduction of the BPh_2 fragment. Mixed H and BPh_2 bridges have also been studied.[182–185]

The organocobaloxime with BF_2 bridges in dioxime ring is a convenient alternative for dimethylglyoxime system, when the presence of a proton could be a problem in the reaction studied. This was the case for the study of alkyl transfer from organocobalt to Ni(I): this latter could be oxidized rapidly in Ni(II) with production of H_2 (Figure 36).[186]



134 **135** **136** **137**

Figure 36



L = Lewis base
R = *i*Pr, *i*Bu, CH_2Ph, Me, CH_2COOMe, CH_2CF_3, etc...

138

Figure 37

The Costa model consists in using the monoanion of *N*^{2},*N*$^{2\prime}$-propanediylbis(2,3-butanedione-2-imine-3-oxime) to obtain the equatorial coordination set of ligands on the cobalt center (Figure 37).

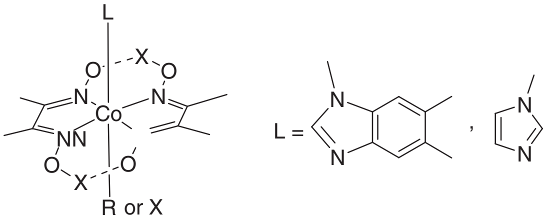
The comparison of the C–Co distances determined by EXAFS[187] and X-ray crystallography of the Costa model (R = CH_2CF_3, CH_2COOMe) has been made.[188] By EXAFS, it was found that the Co–C bond distance increased with the decrease in the R σ-donating ability, in marked contrast to the results obtained with the crystallographic data of the aquo complexes (R = Me, Et, CH_2Ph, *i*-Pr). Randaccio *et al.* thus proposed that the EXAFS conclusions should be refuted.

The Co–C bond strength in cobaloximes with various axial ligands is a function of both steric and electronic factors and, therefore, this property in related complexes with different chelates is still being intensively investigated.[189–200] Many different approaches to quantitatively rationalize the influence of the steric and electronic effects of the axial ligands in cobaloxime on thermodynamic and kinetic data, as well as on structural parameters and NMR data, have been reported.[201–204]

The *t* parameters obtained from the principal component analysis (PCA) method of cobaloxime data were used in the analysis of intraligand coupling constant.[201] These parameters led to identify steric effects on ^{13}C NMR shifts and $^1J_{CH}$ values for bulky ligand.[205] The coupling constant was also correlated to the electronic parameter (EP)[204] (a scale was elaborated where each R or X axial ligand were characterized by a numerical value) (Figure 38).[206]

The nature of the alkyl group at the axial position has an effect on the Co–C and Co–$N_{(axial)}$ bond length. They are significantly influenced by the nature of the equatorial ligand, and it has been reported that the Co–$N_{(axial)}$ bond length increased with the increasing donor properties of the σ-donor ligand.[184,207,208] The number of investigations about the *cis*–*trans*-influence has significantly increased along this period (Figure 39).[209–211]

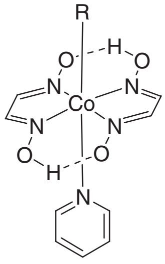
The orientation of the planar ligand (py, Me_3Bzm = 1,5,6-trimethylbenzimidazole, imidazole) with respect to the equatorial moiety on Co–L distance has been established.[198,205] The orientation close to **A** has been observed for cobaloximes with L = py and Me_3Bzm, whereas orientations close to **B** were found in iminocobaloxime.[212,213] However, cobaloximes with less bulky imidazole-type ligands exhibited both orientations. Orientation **C** has been observed for a BF_2 bridge (Figure 40).[208]



139

Figure 38

Co(gh)(gh)(R)(Py)



R = methyl through decyl

140

Figure 39

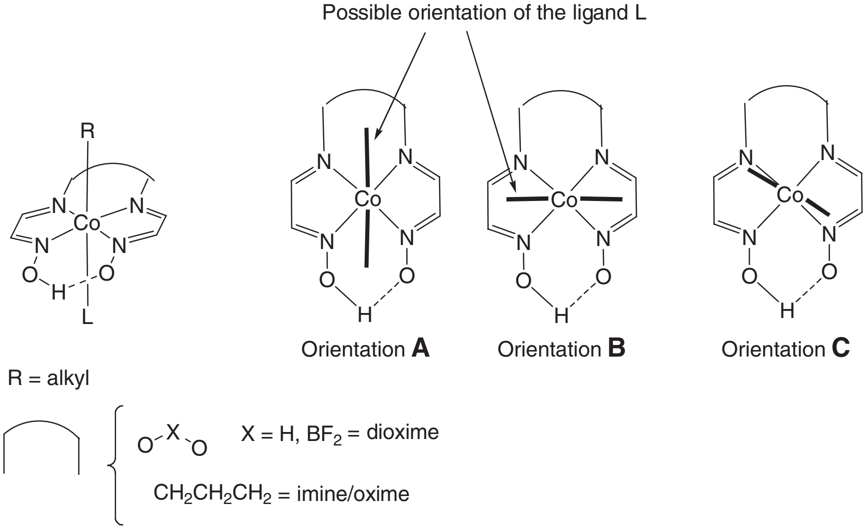


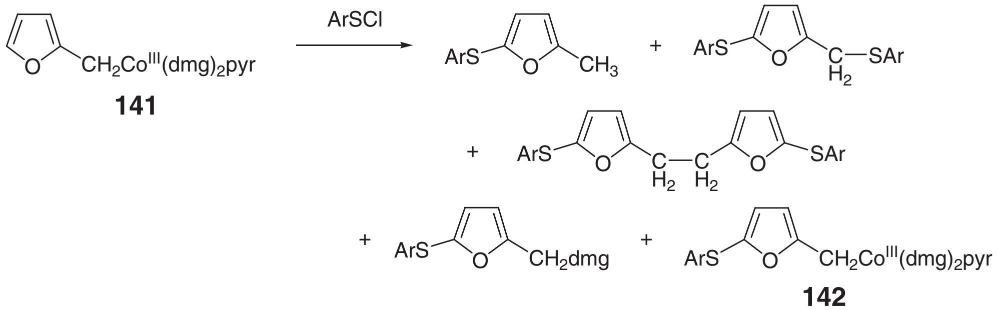
Figure 40

Since 1993, extensive investigations for determining the strength of the cobalt–carbon bond and analyzing the factors that will influence it have been carried out on both biologically active cobalamin and organocobalt model compounds. Photoacoustic calorimetry has been used to determine Co–C bond dissociation.[214]

Homolysis of the cobalt–carbon bond in naturally occurring cobalamines and in model compounds is induced by photolysis and thermolysis, and it is anticipated that the products of these reactions are identical to those found during the enzymatic processes in which cobalamines are present. Accordingly, new informations on the structure and reactions in which Co(II) species are involved have been achieved by studying photolysis and thermolysis of B12 compounds and related models.[215–220]

For B12 model compounds, several studies concerning anaerobic photolysis of alkylcobaloximes with nitrogen donor bases have been made. Recently, a work on photolysis cobaloximes and imino/oxime compounds controlled by steric hindrance imposed by the Lewis base has been investigated.[221]

The reaction of arene sulfenyl chlorides, ArSCl, with organocobaloximes RCo(dmgH)pyr (R = alkyl, benzyl, and methyl groups bearing an heteroatom) **141** were carried out under thermal and photochemical conditions. A variety of organic and organometallic products are formed depending upon the cobaloxime substrate. Bimolecular homolytic displacement is the dominant pathway for alkyl- and benzylcobaloximes with electron transfer process occurring in the latter as a competitive process (Equation (19)).[193]

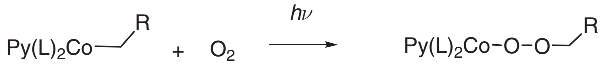


141

142

(19)

The insertion of dioxygene into the cobalt–carbon bond is a known reaction; over this last decade, it has been studied with a few other organocobaloxime complexes. The kinetic studies at ambient temperature under irradiation show that the rate of insertion depends upon the nature of all the ligands (Equation (20)).[222]



$R = Ph, 4Cl\text{-}C_6H_4, 4\text{-}NCC_6H_4, 4\text{-}MeOC_6H_4, 3\text{-}MeOC_6H_4,$
2-thienyl, 3-thienyl, furfuryl,1-napthyl

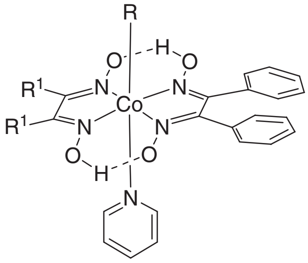
L = dmgH, chgH, dpgH

143 **144**

(20)

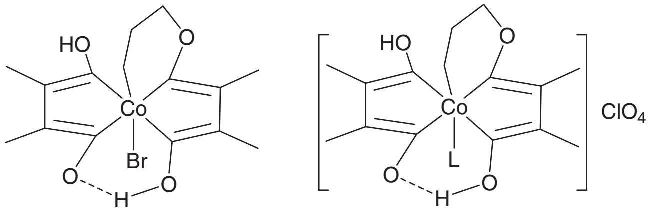
A series of alkylcobalt(III) of mixed and homodioxime complexes **145**, (Figure 41), Co(dmgH)(dgpH)(R)Py and Co(dmgH)(dgpH)(R)Py, respectively (dmgH = dimethylglyoximato, dpgH = diphenylglyoximato) was synthesized by a one-pot strategy.[223,224]

Related intramolecular-bridged alkylcobaloxime Co(II) derivatives **146** were obtained through an intramolecular nucleophilic substitution of a –$(CH_2)_3$–Br group bound to Co on an OH unit (Figure 42).[225]



R = alkyl
R^1 = Me, Ph
145

Figure 41



L = H_2O, py, Bzm, Im

146a **146b**

Figure 42

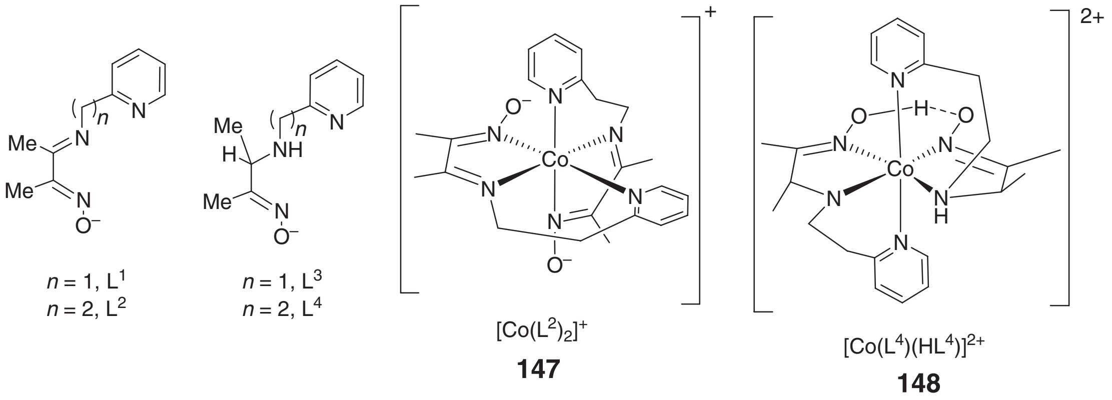
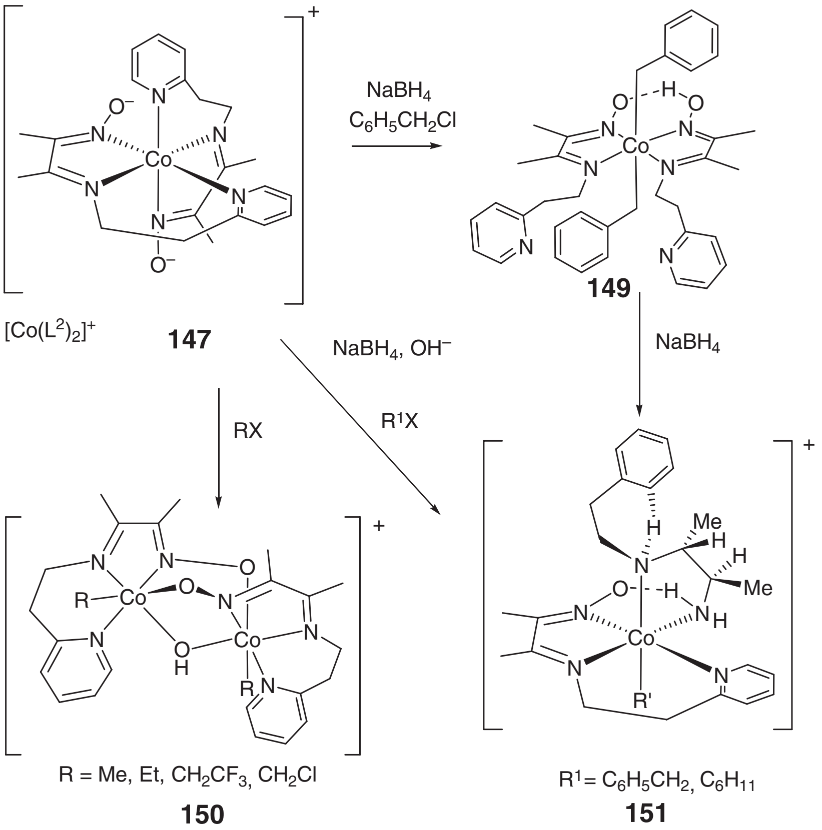


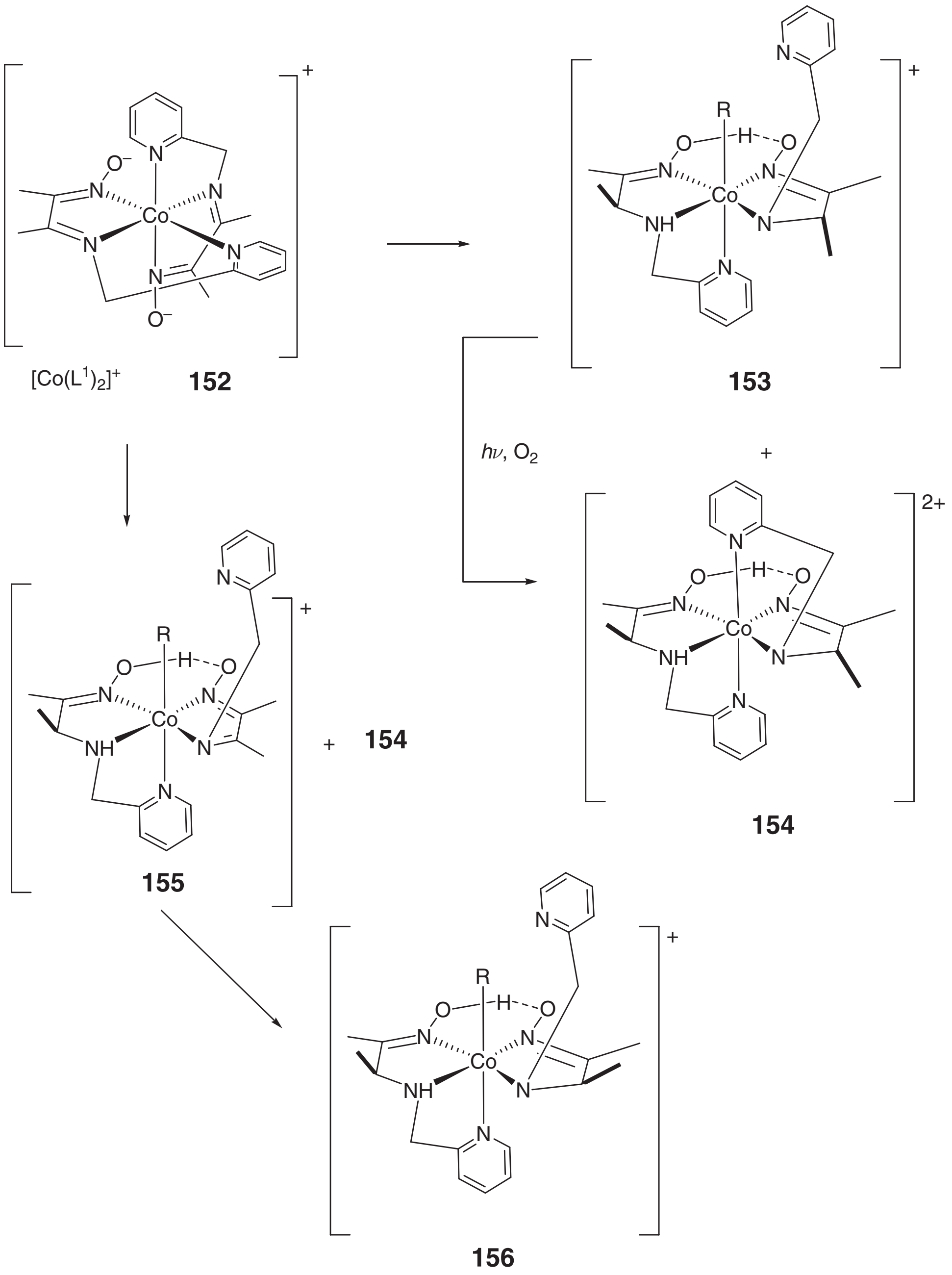
Figure 43

Another type of oximes, amino–oxime ligands, has been developed by the condensation of biacetyl monooxime with 2-(aminomethyl)pyridine and 2-(2-aminoethyl)pyridine. This tridendate ligand led to different stereoisomers. The stability of the various possible isomers of cobalt complexes **147** and **148** has been calculated.[226] The minimum strain energy is observed for a *mer*-configuration for imino complexes $[Co(L^{1,2})_2]^+$ and amino complex $[Co(L^{3,4})(HL^{3,4})]^{2+}$ (Figure 43).

These compounds are the starting materials for numerous organocobalt complexes. From **147**, by reaction with $NaBH_4$ and an alkyl halide, it has been possible to obtain a mononuclear **149** and **151** or a dinuclear complex **150** depending on the nature of the halide compound (Scheme 20).[227–230]



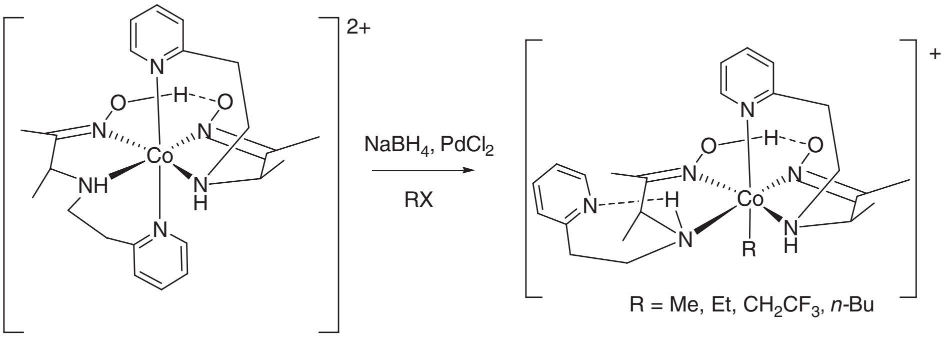
Scheme 20



Scheme 21

The reduction of $[Co(L^1)_2]^+$ by $NaBH_4$ and alkyl halide led not only to the synthesis of $[Co(L^3)(HL^3)]^{2+}$ compounds but also to the synthesis of alkylcobalt compounds (Scheme 21).[231]

From compound **148**, the reduction with $NaBH_4$ led also to a Co(I) intermediate. This intermediate, in the presence of alkyl halide, gave a cobalt(III) complex **157** where the coordination of one pyridine fragment was broken and replaced by the alkyl incoming fragment. The non-coordinated pyridine fragment was found to be part of an intramolecular hydrogen bonding (Equation (21)).[153,232]



148 **157** (21)

Over the past few years, Van Eldik and co-workers have developed a systematic tuning of the substitution behavior of alkylcobalt(III) complexes to explain the mechanism behavior of coenzyme B12. The introduction of a single Co–C bond in Co(III) complexes has a profound influence on their substitution lability. These complexes allow a systematic adjustment of their reactivity via steric hindrance and electron donor/acceptor effects of spectator ligands and the coordinated alkyl or aryl group. Different Co(III) systems have been studied: *trans*-[Co(LNHpy)(HLNHpy)(R)]$^+$ (HLNHPy = 2-(2-pyridinylethyl)amino-3-butanone oxime; R = Et, Me, CF_3CH_2, bridging CH_2),[233] *trans*-[Co(Hdmg)$_2$(R)S] (Hdmg = dimethylglyoximate; R = *cyclo*-C_5H_9, Et, Me, Ph, $PhCH_2$, CF_3CH_2; S = H_2O, MeOH),[234–236] *trans*-[Co(en)(Me)H_2O]$^{2+}$,[237] *trans*-[Co(en)(Me)NH_3]$^{2+}$,[238] as well as modified cobalamins with R = Et, Pr, Me, CF_3CH_2, $NCCH_2$, CF_3, and CN.[235] In these studies, detailed kinetics investigations enabled the determination of rate and activation parameters, on which basic detailed mechanistic assignments could be made. For instance, for the reaction of cyanide with different cobalamins, it was found that the nature of the alkyl group has a marked influence on the thermodynamic stability constants and the kinetics and mechanism of the substitution reactions of the axial ligand *trans* to alkyl group.[235,239,240]

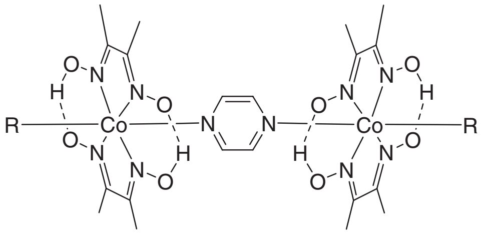
Organobridged dicobaloximes have been described earlier but not fully characterized until recently. The old procedure led to a mixture of halocobaloximes and the organobridged species. The synthesis and the characterization of dicobaloxime complexes by ^{1}H NMR with various alkyl-bridged chains **159** has been published (Scheme 22).[241]

Another possibility is to form a bridge with other axial ligands by using pyrazine instead of pyridine (Figure 44).[242–244]

$$\mathrm{ClCo(III)(L)_2Py} \xrightarrow{\mathrm{NaBH_4}} \mathrm{ClCo(I)(L)_2Py} \xrightarrow{+\,\mathrm{X(CH_2)}_n\mathrm{X}} \begin{array}{c} \mathrm{X(CH_2)}_n\mathrm{Co(III)(L)_2Py} \\ \mathbf{158} \\ + \\ \mathrm{Py(L)_2Co(III)(CH_2)}_n\mathrm{Co(III)(L)_2Py} \\ \mathbf{159} \end{array}$$

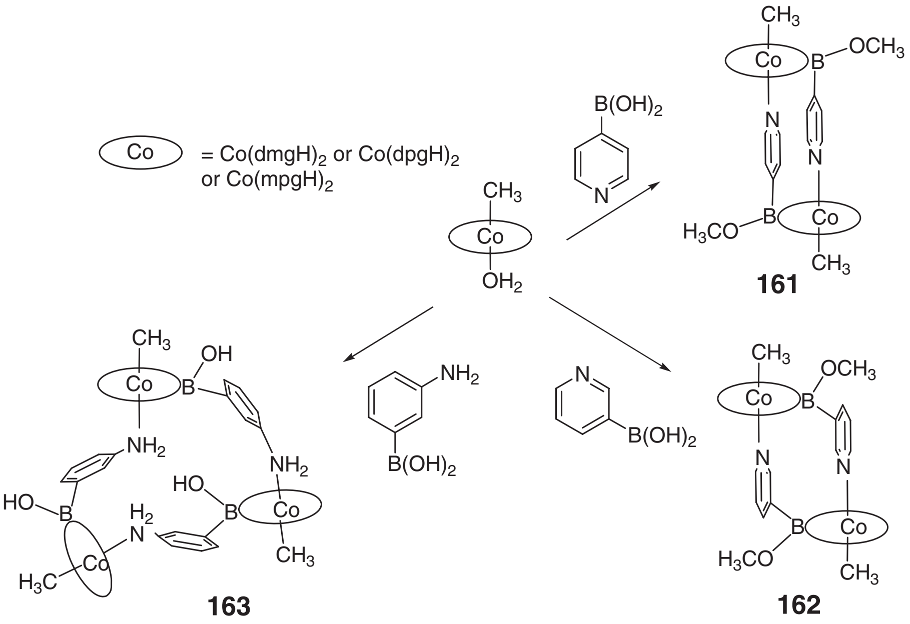
L = dmgH or dpgH

Scheme 22



160

Figure 44



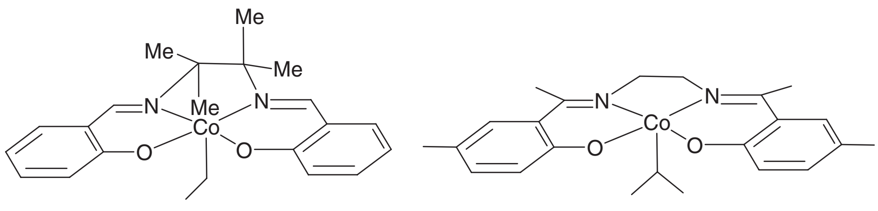
Scheme 23

The 4-pyridylboronic acid and the 3-pyridylboronic acids led to dimeric cobaloximes **161 and 162** by a reaction with cobaloxime compounds. The bridges consisted in the axial pyridyl fragment and the boron inserted inside the dioxime macrocycles. In the case of 3-aminophenylboronic acid, a trinuclear arrangement **163** was observed (Scheme 23).[245–249]

7.01.3.5.4 Organocobalt(III) complexes with Schiff base ligands

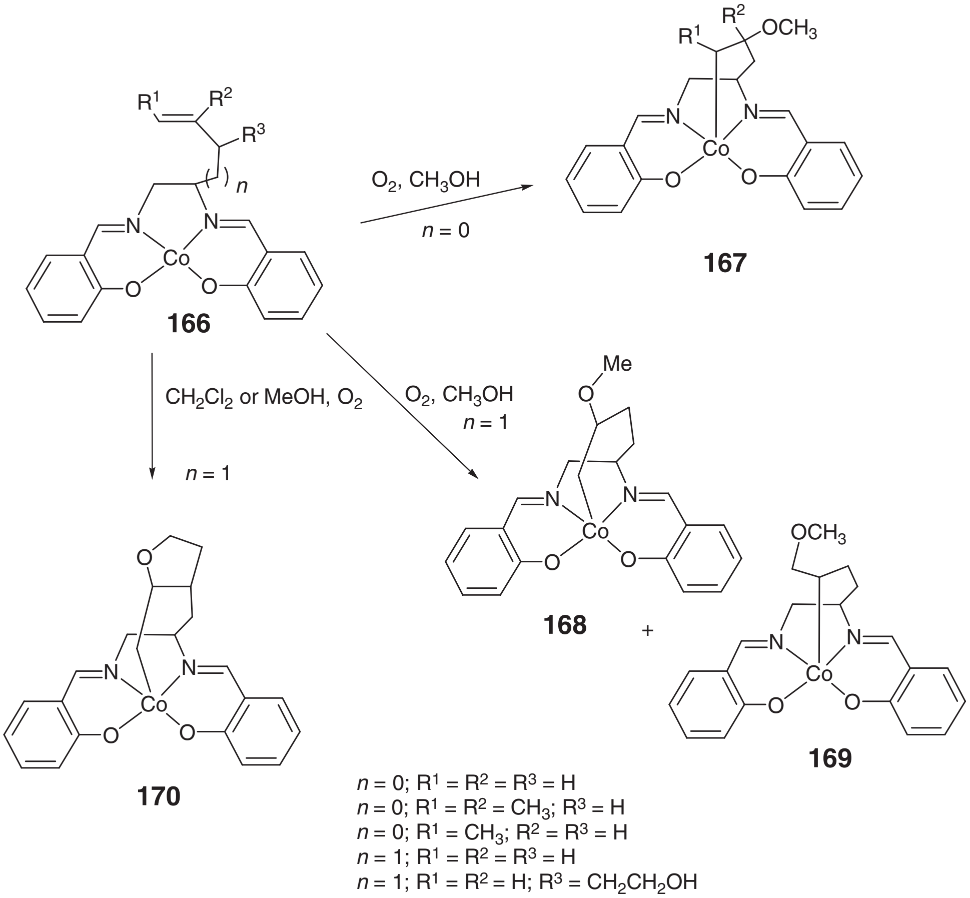
Another series of coenzyme B_{12} model has attracted a lot of attention both for their syntheses and their characterization.[250] For example, an organocobalt(III) complex with a bulky Schiff base on the equatorial positions or with secondary alkyl ligands led to a rarely observed five-coordinate organocobalt(III) complexes **164 and 165** (Figure 45).[251,252] These studies also gave many examples of more conventional six-coordinate organocobalt complexes.

Intramolecularly bridged (β-alkoxyalkyl)Co^{III}(salen) complexes **167–170** are formed when Co^{II}(salen) derivatives carrying an alkenyl side chain are oxidized in alcoholic media. Mechanistic studies indicate that this reaction has three main separate stages: (i) fast oxidation of cobalt(II) to give an (alkoxo)Co^{III}(salen) derivative, (ii) acid-catalyzed dissociation of the alkoxo ligand enabling intramolecular interaction of Co(III) with the alkenyl double bond to yield a carbocationic intermediate, and (iii) nucleophilic attack by alcohol. Whether the intermediate in the second stage is better described as a Co(salen) π-cation than as a β-cobaltoethyl cation stabilized by cobalt–carbon hyperconjugation depends on the substitution pattern of the C=C bond (Scheme 24).[253,254] The thermolysis and photolysis of intramolecular-alkylated Co salen complexes have also been studied.[255]



164 **165**

Figure 45



Scheme 24

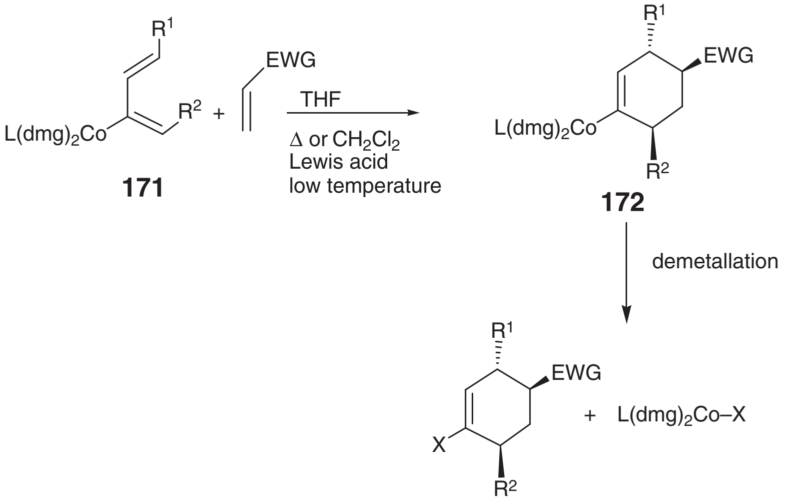
To achieve a deeper understanding of the behavior of coenzyme B_{12} by studying *cis*- and *trans*-effects that significantly influence the physical and chemical properties of vitamin B_{12} and its chemical models, the ligand-substitution reactions of *trans*-$[(R)Co^{III}(LNHpy)(HLNHpy)]^+$ (where R = Et, Me, CF_3CH_2, bridging CH_2, and LNHpy is 2-(2-pyridylethyl)amino–3-butanone oxime) by CN^- were investigated.[256] The reaction followed a dissociative mechanism whose nature can vary from limiting dissociative to interchange (I_d) depending upon the σ-donor and steric properties of the alkyl group.

7.01.3.5.5 Applications of organocobalt(III) complexes

7.01.3.5.5.(i) Diels–Alder reactions

During the last decade, numerous cobalt-substituted 1,3-dienes have been synthesized and the rates, regioselectivities, and stereoselectivities of their reactions with dienophiles in [4 + 2]-cycloaddition reactions were examined (Scheme 25).[191,257–264] Few reviews gave an overview of the results obtained in this field.[265,266] The dienylcobalt complexes were able to react with a variety of dienophiles. High regio- and stereoselectivity has been observed to produce air stable cobalt-substituted cyclohexenes in good yields. It has been rationalized that the *exo*-diastereoselectivity observed was based on steric interactions between the dienophile and the cobaloxime ligand set. The demetallation reaction has led to an organic product as well as to a cobalt complex, which could be recycled into the synthesis of the starting dienyl complexes. The reaction could be performed in organic media or in water when L is H_2O.[267]

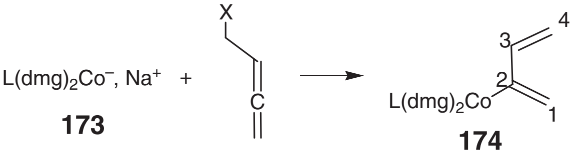
The ease of synthesis of diene–cobalt complexes depends on the position of the cobalt on the dienyl fragment (position 1 or 2) and it also depends on the substituent on the carbon atoms (1–3). Various synthetic routes are shown



171 **172**

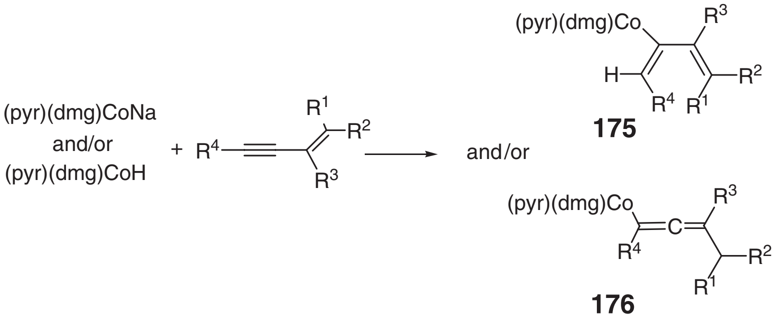
Scheme 25

in Equations (22) and (23). The reaction of anionic cobaloxime complex **173** with allenic or enyne compounds afforded, after protonation, the expected complexes **174–176** via an S_N2'-type mechanism.[258,268]



173 **174**

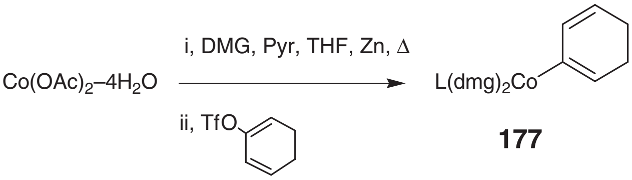
(22)



175 **176**

(23)

An alternative route using dienyl triflate ligands with a zinc-mediated cobaloxime reduction has also been used for simple cobaloxime-substituted alkenes **177** (Equation (24)).[269]

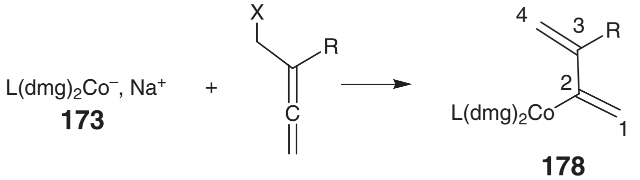


177

(24)

Vinylallenes can be hydrometallated to produce 1-cobaloxime-substituted dienyl complexes (Equation (25)).[270] Cobaloxime-substitued 1,3-diene without a substituent in the 3-position will participate in thermal and Lewis acid-catalyzed Diels–Alder reactions, but the resulting cycloadducts apparently rearrange and give products with regiochemistries that are identical to the ones seen for Diels–Alder cycloadducts of 2-cobaloxime-substituted 1,3-dienes. The authors suggest that the driving force for this rearrangement is presumably the relief of steric strain at the quaternary carbon that would be formed initially in these Diels–Alder reactions.

The 2-cobaloxime dienyl complexes substituted in 3-position could not effect Diels–Alder reactions. To circumvent this synthetic limitation, 3-subtituted 1-cobaloximes have been synthesized (Equation (25)).

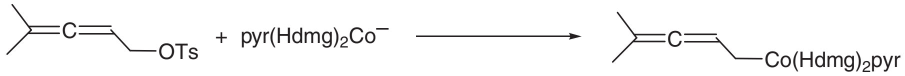


173 **178** (25)

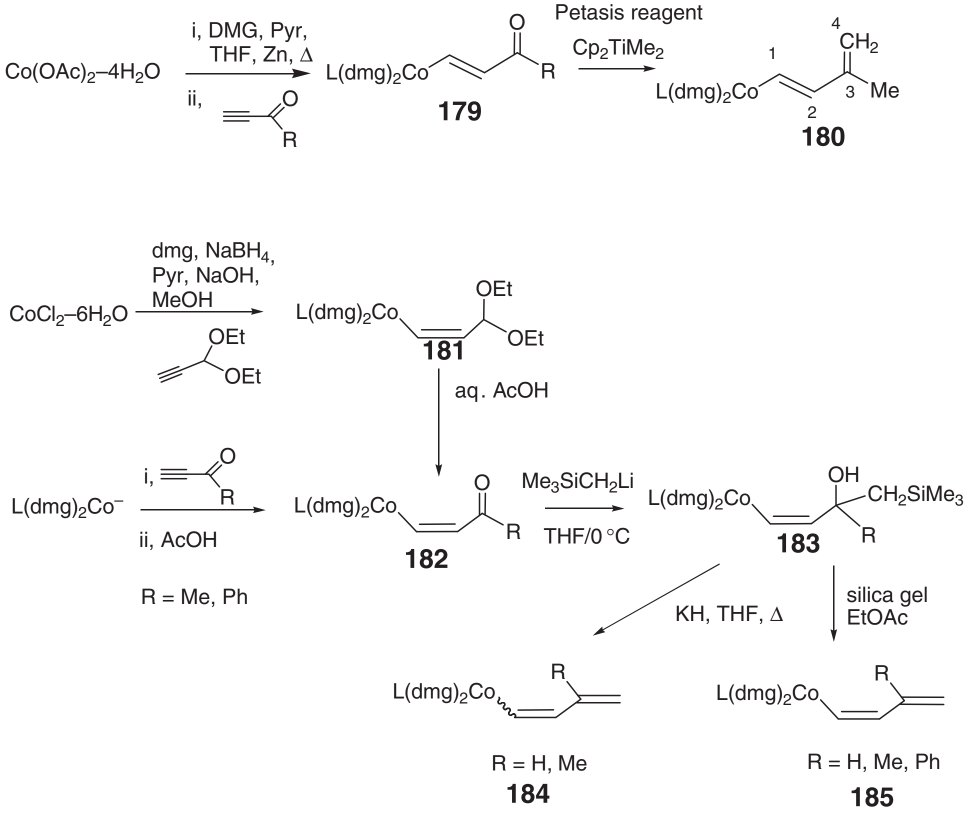
Another route via hydrocobaltation of ynone and ynoate led easily to 1-cobaloxime enone or enoate.[271] 1-cobaloxime diene **180** was obtained after Peterson or Petasis olefination (Scheme 26).[272]

The reaction of the 1,1-disubstituted allenic tosylate with cobaloxime anion afforded the S_N2-product **187** rather than the S_N2'-product (Equations (26) and (27)).[268,272]

186 (26)

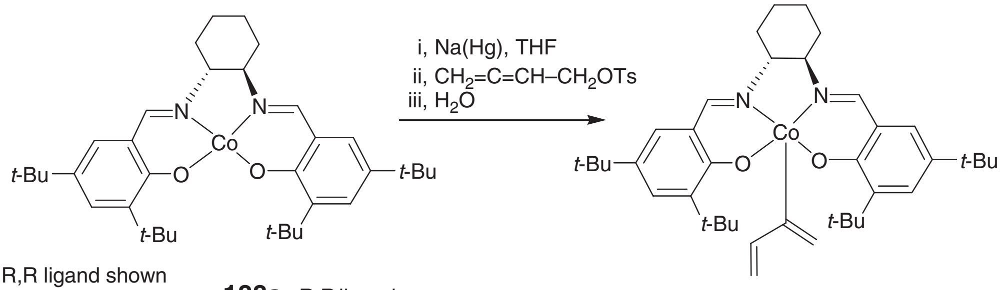


187 (27)



Scheme 26

The attempts to achieve enantioselective synthesis of cycloadduct compounds by using a chiral Lewis acid associated with achiral cobaltoxime resulted in moderate ee.[273] Another approach is to replace the dimethylglyoxime ligand set by salen ligands. Cobalt(II) salen complexes synthesized in achiral form showed good results in Diels–Alder reactivity. In the chiral salen complex, the corresponding optically active dienylcobalt complexes **189** have been obtained by the reaction of optically active cobalt(II) salen complexes **188** with allenic compounds (Equation (28)).



R,R ligand shown

188a: *R*,*R* ligand
188b: *S*,*S* ligand

189a: *R*,*R* ligand
189b: *S*,*S* ligand

(28)

The reactivity of these dienylcobalt complexes **189** toward fumarate have been tested to afford **190**, which led, after treatment with $NaBH_4$, to high ee of the organic cycloadduct and regeneration of the starting optically active cobalt(II) salen complexes **188** (Scheme 27).[274–276]

In order to obtain a catalytic reaction, a strategy, presented in Scheme 28, has been investigated.

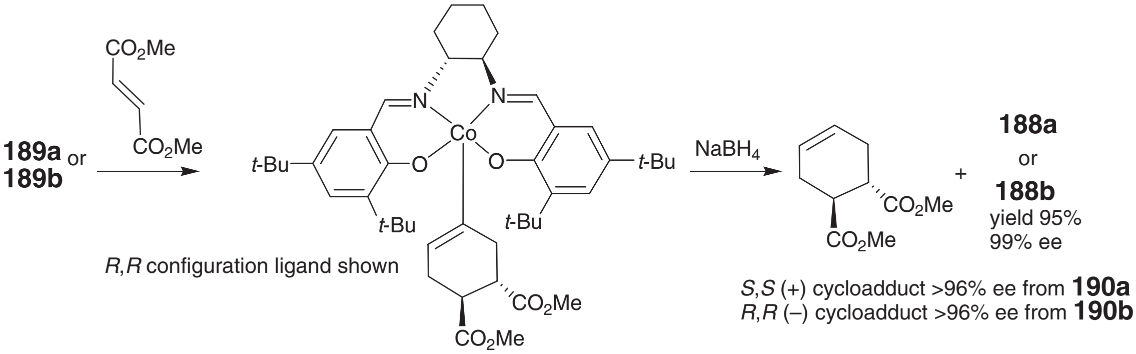
While all the three steps of the cycle can be performed without performing the purification of the intermediates, in practice, the chemical yields are higher if only the first two steps of the cycle are run in this manner. The cobaloxime cycloadduct **192** had to be isolated prior to the obtention of the silane-mediated demetallation reaction (Scheme 29).[277]

7.01.3.5.5.(ii) Hetero-Diels–Alder reactions

Dienylcobalt complexes such as **193** react as well with aldehydes in hetero-Diels–Alders reactions, providing dihydropyrans after demetallation of **194** (Scheme 30).[278] The relative stereochemistry of the R and R_1 substituent is *anti*. This was explained by the fact that the reaction proceeds through a transition state where the aldehyde R group is *exo* to the metal's ligand set.

7.01.3.5.5.(iii) Dechlorination reactions

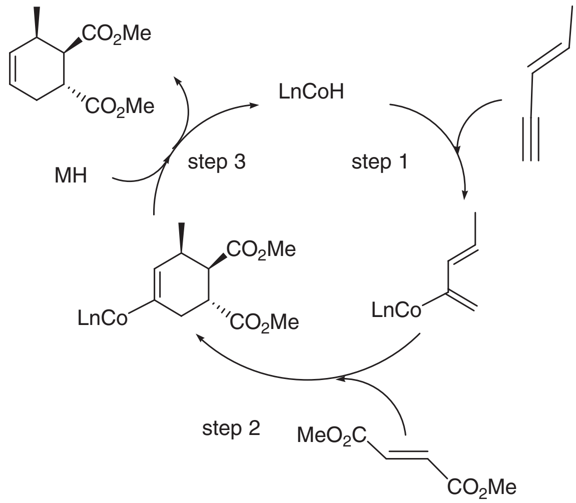
Vitamin B_{12} **195** has also been used as a catalyst for the abiotic dechlorination of perchloroethylene (PCE) to trichloroethylene (TCE) in the presence of titanium(III) citrate (Scheme 31).[279,280] Mechanistic studies on this latter process suggested that the conversion of PCE to TCE occurred via electron transfer from cobalt(I) alamin to PCE,[281]



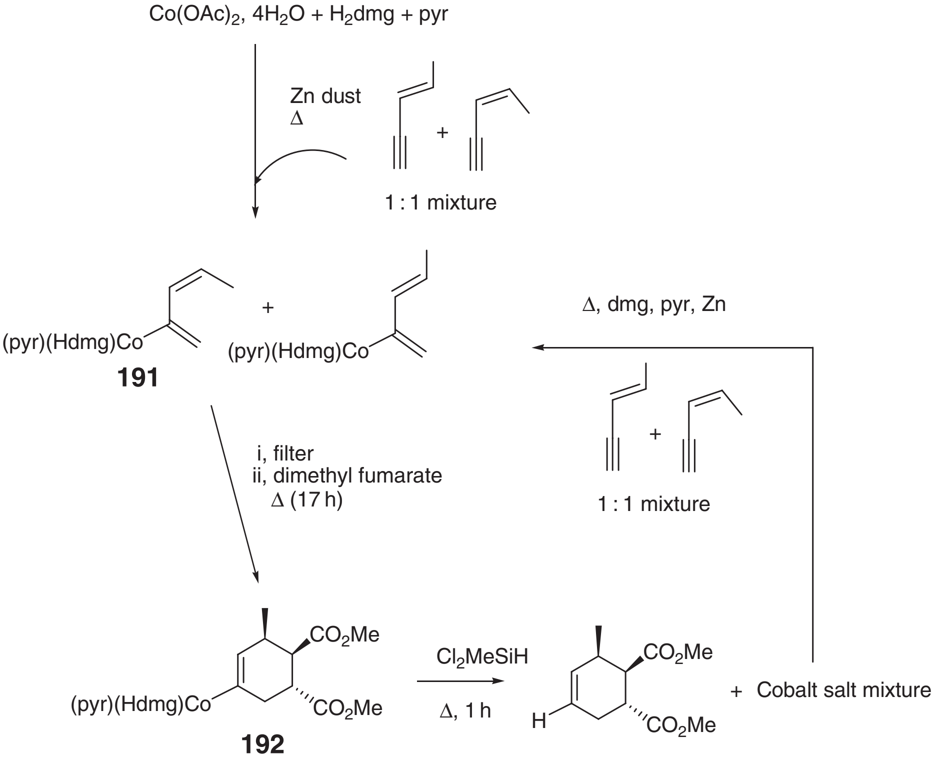
S,S (+) cycloadduct >96% ee from **190a**
R,R (–) cycloadduct >96% ee from **190b**

190a *R*,*R* ligand
190b *S*,*S* ligand

Scheme 27



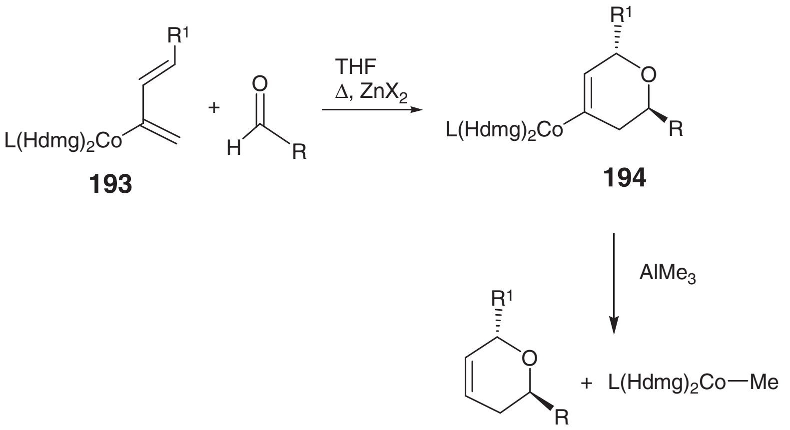
Scheme 28



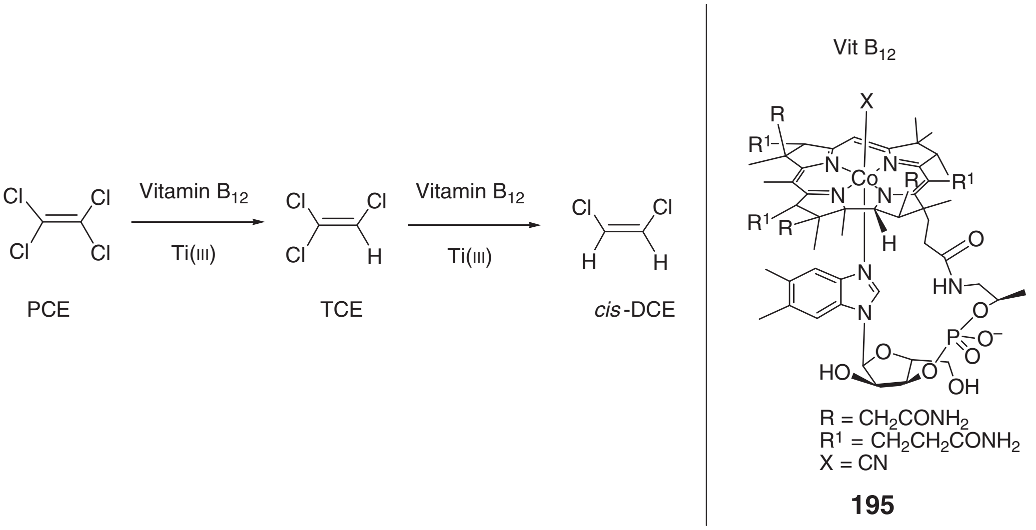
Scheme 29

whereas further transformation of TCE to di- and monochlorinated ethylenes, acetylene, and ethene involved organocobalamins.[282]

It was recently found that chlorovinylcobalamin is, however, readily reduced under the conditions of reductive dechlorination. The chlorovinylcobalamin and vinylcobalamin show a strong resistance toward photolysis. Reduction of vinylcobalamin is difficult, but reduction of chlorovinylcobalamin occurs readily and it produces vinylcobalamin. The mechanism of this reaction involves acetylene as an intermediate.[283]



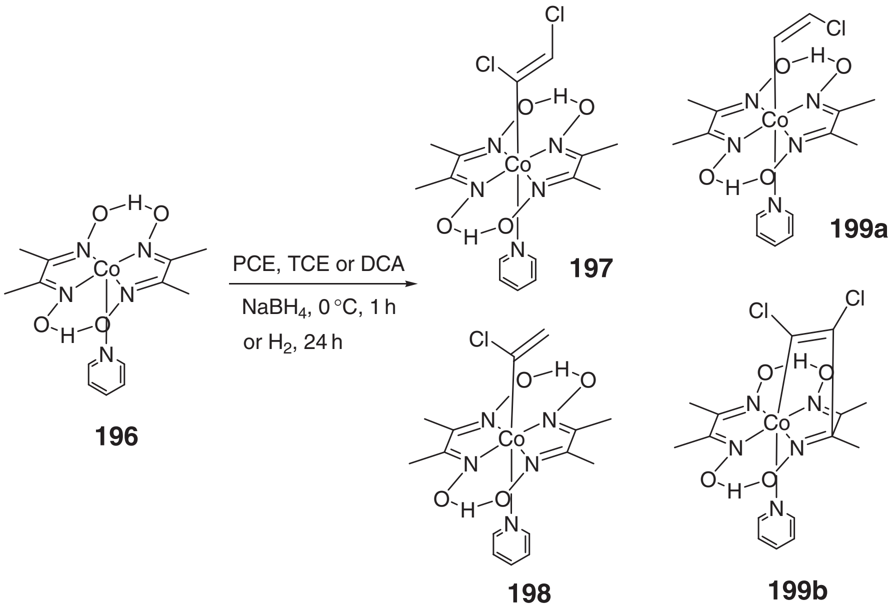
Scheme 30



Scheme 31

The transformation of the chlorinated vinylcobalamins to the active form of the catalyst is achieved via a reductive dealkylation promoted by Co(I)alamin. This reaction is particularly facile for multichlorinated vinylcobalamins, but not for non-chlorinated vinylcobalamins.

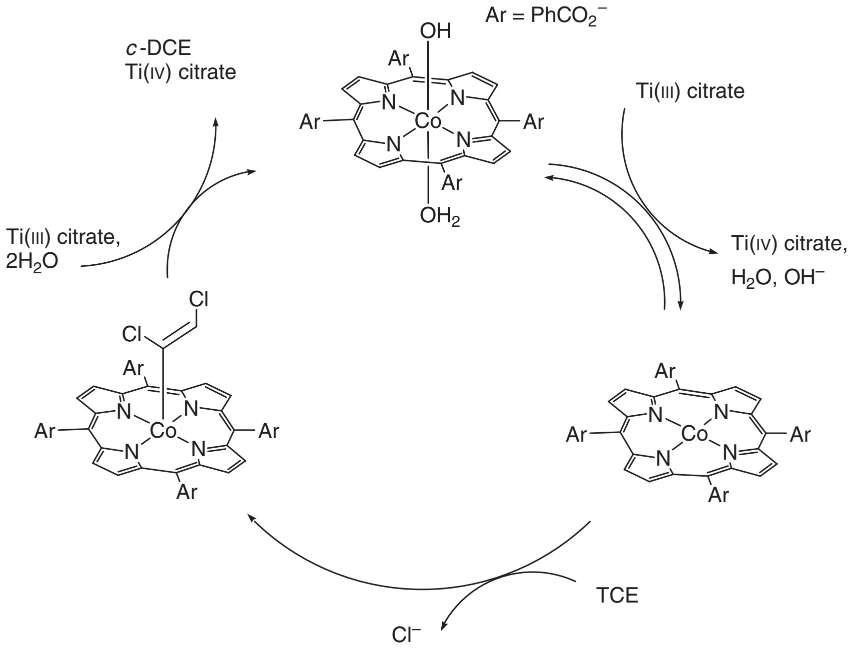
Vitamin B12 catalyzed the reductive dechlorination of PCE and TCE, thus suggesting that vitamin B12 may be useful for dechlorination of polluted environments.[284–288] In order to obtain information on the mechanism involved in these processes, the synthesis of chloroethenylcobaloxime has been performed. The products have been made via a reduction by $NaBH_4$ or by H_2 of *in situ*-generated Co^{II}(dmgH)$_2$py in the presence of TCE or PCE. The isolation of chlorinated vinylcobaloximes has been achieved in low yields as a mixture of products. These complexes were stable in the presence of ethanolic $NaBH_4$ medium unless external cobaloximes were added. If these latter reagents were added, less chlorinated compounds could be obtained. The reaction product obtained from the reaction under H_2 with 2 equiv. of TCE (Scheme 32) led only to the *cis*-dichlorinated complex **197** in 18% yield. The authors found that chlorinated ethenylcobaloximes are stable compounds that are unlikely to undergo homolytic Co–C bond cleavage at a sufficient rate to support dechlorination of chlorinated alkenes.[289] Mechanistic studies indicated that the reaction took place via the formation of chloroacetylene, but dichloroacetylene seemed not to be an intermediate to dichlorovinylcobaloxime or dichlorovinylcobalamine, as the reaction with dichloroacetylene (DCA) led to an unexpected cobalt complex **199b**.[290]



Scheme 32

At the same time, a similar synthetic approach has been made by McNeill *et al.*, who found that using Zn instead of H_2 or $NaBH_4$ afforded an increased isolate yield (45%).[291] The reactivity of chlorovinylcobaloxime toward reducing agents was examined. The formation of the volatile chloroacetylene depends on the nature of the reducing agent.

The dechlorination of chlorinated alkenes could also be performed by porphyrin cobalt complex such as 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin cobalt ((TCPP)-Co). This cobalt complex, structurally similar to vitamin B_{12}, was found to have superior aqueous-phase dechlorination activity on chlorinated ethylenes relative to vitamin B_{12}.[283] Based on fully detailed parameters dependence, the authors suggest the catalytic cycle below.[292] This methodology has been used to synthesize ^{14}C-labeled *cis*-DCE from TCE (Scheme 33).[293]



Scheme 33

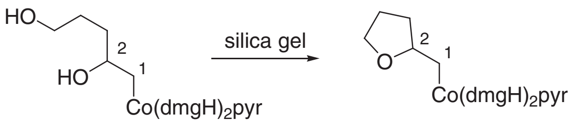
Dechlorination of alkyl chlorides such as chloroacetonitrile by vitamin B_{12} has also been observed to take place.[294]

7.01.3.5.5.(iv) Miscellaneous applications

7.01.3.5.5.(iv).(a) Cobaloxime π-cations

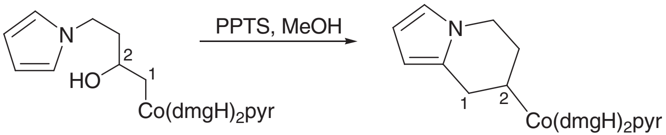
The cobaloxime π-cations **200** have been known since the early 1970s, but they have only been used extensively for carbon–heteroatom and carbon–carbon bond-forming reactions since 1996 (Scheme 34).[195,295,296]

These π-cations have been used to form five- and six-membered ring heterocycles (Equations (29) and (30)).



201 **202**

(29)



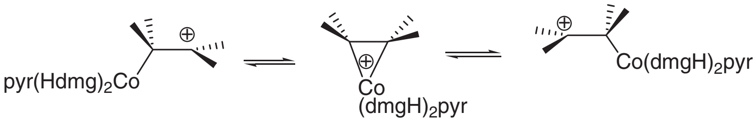
203 **204**

(30)

The reaction was enantioselective when starting with chiral β-hydroxyl fragment.[196,297,298]

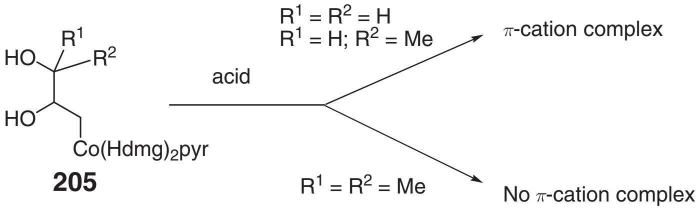
It was not possible to obtain seven-membered ring heterocycles with a longer chain, and the cationic complex was unstable.[299] The limit to the formation of the π-cation intermediate is related to the steric hindrance of the substituents on the γ-carbon (Scheme 35).[300]

Cobaloxime allyl complexes **206** can be prepared by three different methods: (i) *in situ* generation and allylation of $[L(dmgH)_2Co]_2$ dimer, (ii) generation and allylation of $L(dmgH)_2Co$ anion from $L(dmgH)_2CoCl$, and (iii) 1,4-hydrocobaltation of 1,3-dienes. The reaction of these allyl complexes with tetracyanoethylene gives a mixture of cyclized and uncyclized products **207** and **208** (Equation (31)). The ratio of cyclized/uncyclized is influenced by the allyl complex substitution pattern as well as by the nature of the axial ligand present in the allyl complex.[301]



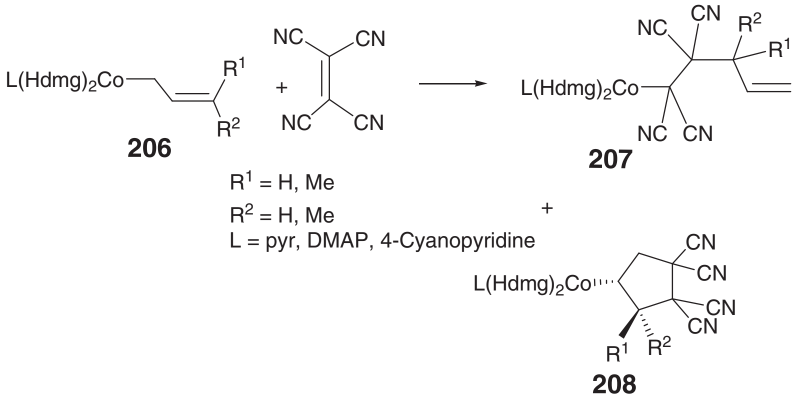
200

Scheme 34



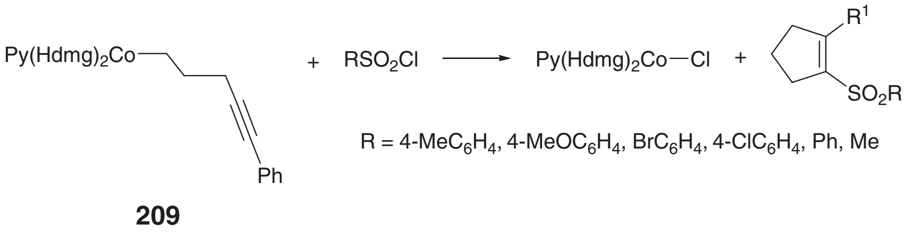
205

Scheme 35



(31)

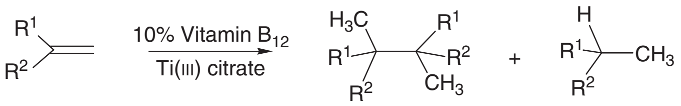
The formation of a five-membered ring via alkynylcobaloxime derivatives 209 by a radical process led to the formation of cyclopentene derivatives (Equation (32)).[302]



(32)

7.01.3.5.5.(iv).(b) Olefin dimerization via coenzyme B12

In the presence of catalytic amounts of vitamin B12, it has been possible to couple 1,1-disubstituted alkenes with defined regiochemistry under mild conditions in environmentally benign solvent system such as ethanol/water (Table 1). The mechanistic studies led the authors to conclude that organic free radicals are formed in this reaction. In the current process, the rate of combination of two radicals is increased by removing the persistent Co(II) radical with Ti(III) or Zn. This is in contrast to cobalt-catalyzed free-radical chain transfer and cobalt-mediated living radical polymerization in which the cobalt macrocycle's role is to reduce the steady-state concentration of free radicals (Equation (33)).[303]

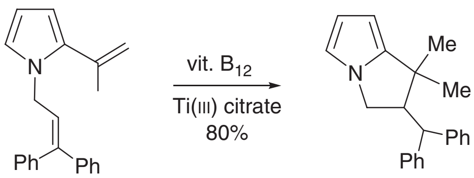


(33)

Table 1 Vitamin B$_{12}$-catalyzed dimerization of 1,1-disubstituted alkenes. Reprinted with permission from Shey, J.; McGinley, C. M.; McCauley, K. M.; Dearth, A. S.; Young, B. T.; van der Donk, W. A. *J. Org. Chem.* 2002, 67, 837–846.[a] 2002 American Chemical Society

	Alkene		*Yield (%)*	
Entry	*R$_1$*	*R$_2$*	*Dimer*	*Reduction product*
1	Ph	H	50	4
2	4MeC$_6$H$_4$	H	80	13
3	2,5-(Me)$_2$C$_6$H$_3$	H	56	7
4	Ph	Me	85	7
5	4-ClC$_6$H$_4$	Me	80	3
6	4-FC$_6$H$_4$	Me	70	0
7	Ph	Ph	90	5

This reaction can be used with diene to produce intramolecular coupling reactions (see Equation (34)).[303]



(34)

7.01.3.5.5.(iv).(c) About some organometallic aspects of coenzyme B12

The B_{12} cofactors[304] known so far are alkylcobalamins (RCbl) consisting of a cobaltcorrinoid with a pendant nucleotide (with different purine base), which occupies five or six coordination sites of an octahedral Co(III). The sixth position is occupied by the R group or by a CN ligand in the cyanocobalamin (CNCbl), the vitamin B12 (Figure 46).

CNCbl is not a biologically active species, whereas the cobalamins MeCbl and coenzyme B_{12} (AdoCbl) are cofactors for several different enzymatic systems.[305–308] All the currently known reactions of the B_{12}-dependent enzymes involve the making and breaking of the Co–C bond.[309,310]

The MeCbl-based enzymes (methyltransferases) catalyze the transfer of methyl groups, and the overall mechanistic scheme requires a reversible heterolytic cleavage of the Co–Me bond.[311] The process catalyzed by AdoCbl-based enzymes (isomerase and eliminase) proceeds through a stepwise process initiated by the homolytic cleavage of the Co–C bond.[312,313]

Adenosylcobinamide ($AdoCbi^+$) is an analog of (AdoCbl), where the a-axial 5,6-Me_2–benzimidazole ligand has been removed. ($AdoCbi^+$) plus exogenous, sterically hindered, putative, axial bases have been reinvestigated in order to understand the cause of record levels of Co–C bond heterolysis.[314] This reinvestigation has listed the different problems, which have caused incorrect conclusions.

Brown *et al.* and Van Eldik *et al.* have studied in detail the structure and the kinetics of the thermolysis of neopentylcobalamin and parent derivatives.[315–319] Two homologs of coenzyme B_{12}, in which respectively one and two CH_2 units have been incorporated between the cobalt atom and the 5′-deoxy–5′-adenosyl–methyl group

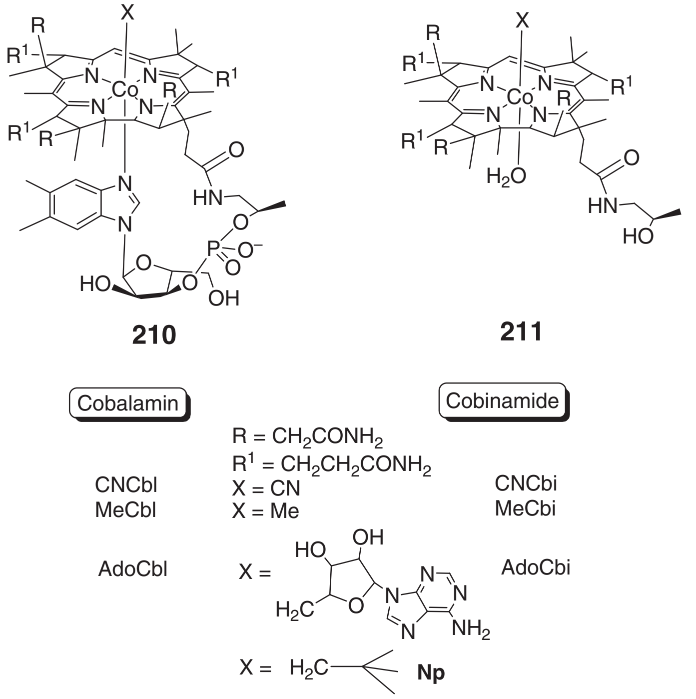


Figure 46

(see Figure 46), have recently been found to function as covalent structural mimics of the hypothetical enzyme bond "activated" state of the B_{12} cofactor.[320]

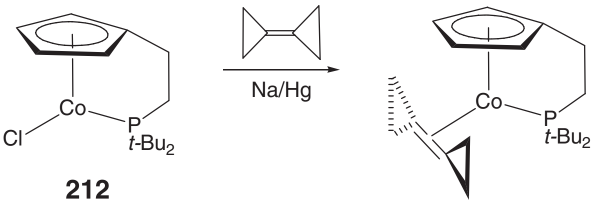
7.01.4 Organocobalt Complexes of η^n-Bonded Hydrocarbyl Ligands and Related Examples

7.01.4.1 Organocobalt Complexes with η^2-Ligands

7.01.4.1.1 Alkene compounds

The η^2-interaction of alkenes to a cobalt center has been well described in the previous issues of COMC (see COMC (1982) and COMC (1995) for reviews). Several theoretical and gas-phase studies have been performed on organocobalt compounds containing $Co(\eta^2\text{-}C_2H_4)$ or $Co(\eta^2\text{-}C_nH_{2n})$ units.[321–323] Besides these physical studies, a few compounds displaying novel type of η^2-interactions with cobalt have been reported.

The stabilization of highly reactive bicyclopropylidene through coordination to a metal center was possible via reductive complexation to a cobalt(II) compound to which a chelating "phosphine–Cp" ligand **213a** was attached (Equation (35)).[324]



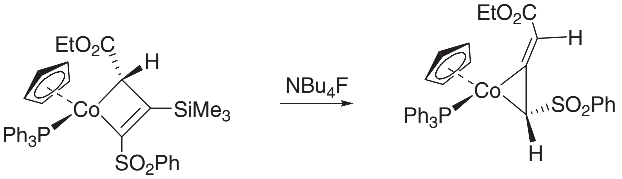
212

213a

(35)

The η^2-coordination of the C═C bond of tropylidene phosphanes has been found to occur both on Co(0) **213b** and Co(I) **213c** species (Figure 46a). The cobalt(0) complex displayed rather large g anisotropies ($g_{\text{parallel}} = 2.320$ and $g_{\text{perp}} = 2.080$).[325]

Allene complexes η^2-bound to Co **213d** were obtained from cobaltacyclobutene compounds (Equation (35a)).[326]

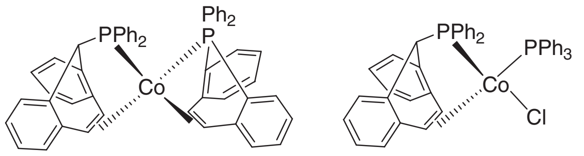


213d

(35a)

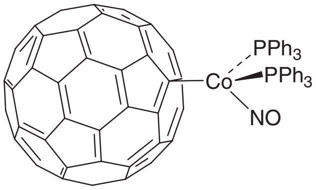
7.01.4.1.2 Fullerene-containing compounds

While performing the synthesis of several C_{60} adducts of transition metals, Green *et al.* reported the easy synthesis of $(C_{60})Co(PPh_3)_2NO$ **214** (Figure 47) via the substitution of a PPh_3 ligand by C_{60}. ^{13}C NMR studies showed that for similarly related Ru and Rh compounds, these Co species display fluxional processes at 50 °C, the equivalence of the carbon atoms arising via a 1,3-shift process.[327,328]



213b **213c**

Figure 46a



214

Figure 47

No X-ray diffraction studies on structure were performed; however, the NMR studies provided evidence that the Co species should have a structure closely related to that of analogous Ru or Rh derivatives whose X-ray structures are known, that is, the C_{60} unit being η^2-bonded to the metal center via one of its C=C units. Electrochemical reduction has been performed to afford the dianion species. The fullerene unit was shown to be weakly coordinated to Co as it could be easily displaced by smooth electrophiles such as I_2, maleic anhydride, or PPh_3, regenerating the free C_{60}. At approximately the same time, Baird *et al.* studied the electron transfer between C_{60} and $NaCo(CO)_4$. This reaction led to a transient compound $NaCo(CO)_3[C_{60}]$, which was unstable and led in refluxing THF solution to $NaCo[C_{60}]\cdot 3THF$ **215**.[329,330] Unfortunately, this carbonyl-free compound could not be analyzed by X-ray diffraction studies. However, infrared studies of the unstable $NaCo(CO)_3[C_{60}]$ species provided some indirect evidence that the C_{60} moiety should behave like an electron-withdrawing alkene for the cobalt center. Related $[\eta^5\text{-(R–Cp)}]\text{-}Co(PPh_3)(\eta^2\text{-}C_{60})$ **216** were synthesized recently.[331] These compounds were very air sensitive and thermally unstable as they lost the C_{60} ligand at RT under an argon atmosphere. These compounds displayed interesting non-linear optical (NLO) properties.

The Co(II)(tetraphenylporphyrine)$(C_{60}(CN)_2)^-$ anion, **217** (Figure 48), the X-ray structure of which showed that the C_{60} unit was indeed interacting in the η^2-fashion with Co,[332] was found to be part of a multi-component electron-transfer salt containing Co(II)(TPP), $Cr(PhH)_2$, and $C_{60}(CN)_2$ (TPP = tetraphenylporphyrine).

A triple scission of a six-membered ring on the surface of C_{60} leading to one of the most remarkable transformations in metal–fullerene chemistry has been observed in **219**.[333] This reaction occurred via addition of $CpCo(CO)_2$ on the bis-methano annulene **218** (Equation (36)).

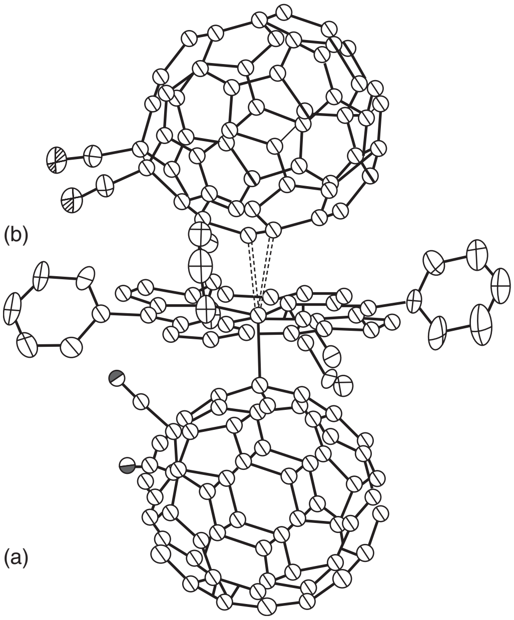
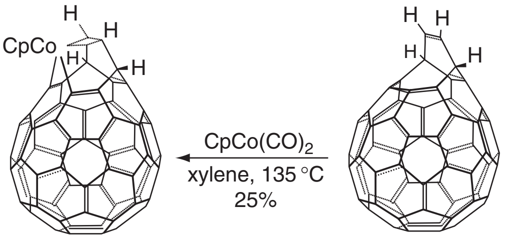


Figure 48 ORTEP drawing of $CoTPPC_{60}(CN)_2$ **217**. Reprinted with permission from Konarev, D. V.; Khasanov, S. S.; Otsuka, A.; Yoshida, Y.; Saito, G. *J. Am. Chem. Soc.* **2002**, *124*, 7648. © 2002 American Chemical Society.



219 **218**

(36)

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An X-ray crystal structure analysis on **219** showed that the ethylene bridge acted as an η^2-handle to the cobalt and, more interestingly, that the cobalt has oxidatively inserted into the C–C bond of a six-membered ring of the C_{60}, thus giving rise to a rare "opened" fullerene derivative (Figure 49).

7.01.4.1.3 η^2-Alkyne complexes of cobalt

Similar to the alkene complexes, the alkyne complexes of cobalt were amply described in COMC (1982) and COMC (1995). We shall therefore report in this section the most remarkable examples that have been published since 1993.

Interactions of alkynes with $CpCo(CO)_2$ led to cyclobutadiene or cyclopentadienone complexes or benzene derivatives. Despite the fact that the mono-adduct of cobalt is most likely to be the first intermediate to exist in this alkyne di- or trimerization, such an intermediate has only seldom been isolated.[334] The use of an alkyne substituted by strong electron-withdrawing groups such as $^tBuSO_2$– allowed Gleiter *et al.* to isolate this key compound **220** (Figure 50).[335]

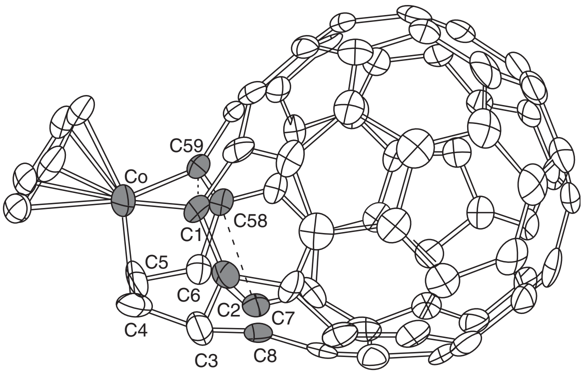
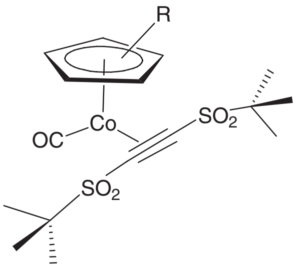


Figure 49 ORTEP drawing of **219**. Reprinted with permission from Arce, M.-J.; Viado, A. L.; An, Y.-Z.; Khan, S. I.; Rubin, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3775. © 1996 American Chemical Society.

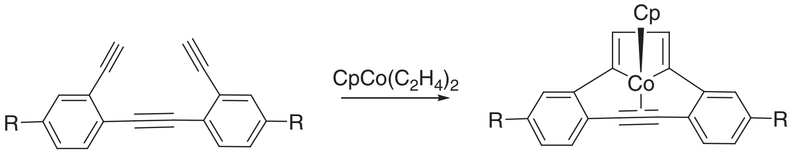


R = H, Me, $SiMe_3$, CO_2CH_3, Me_4Et, (*n*-allyl)$_5$

220

Figure 50

Another important intermediate in the trimerization of alkynes that was never isolated is the cobaltacyclopentadiene unit to which an alkyne is η^2- bound to Co. Vollhardt *et al.*[336] succeeded in obtaining a series of such compounds **221** by treating $CpCo(C_2H_4)_2$ with a triyne as depicted in Equation (37).

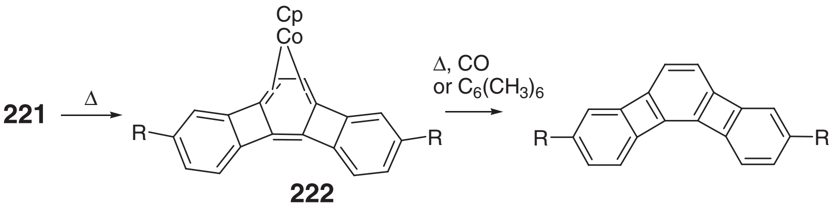


R = H, *i*-Pr
Cp = C_5H_5, C_5Me_5, $C_5H_4CH_3$, indenyl
221

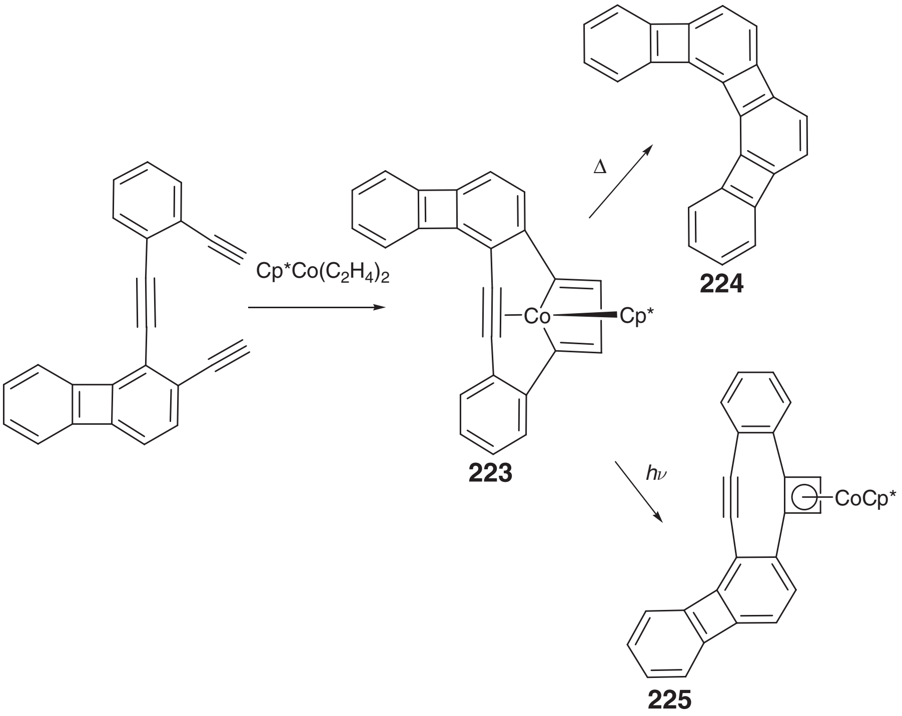
(37)

Rather good yields (72–91%) of **221** were obtained, and their relevance to the mechanism of the CpCo-catalyzed cyclization of the triyne to the angular [3]-phenylene was established by allowing **221** to rearrange thermally to **222** (see Scheme 36).

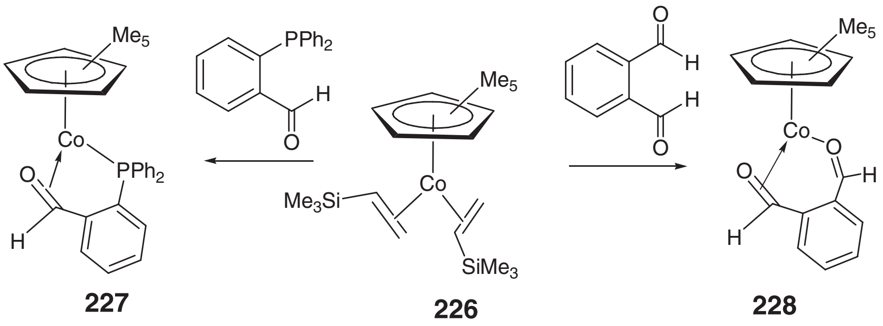
Definite proofs of the structure of **221** were given more recently,[337] when the same authors depicted the reaction of a closely related triyne with $Cp^*Co(C_2H_4)_2$, forming **223** that led to compounds **224** and **225** (Scheme 37).



Scheme 36



Scheme 37



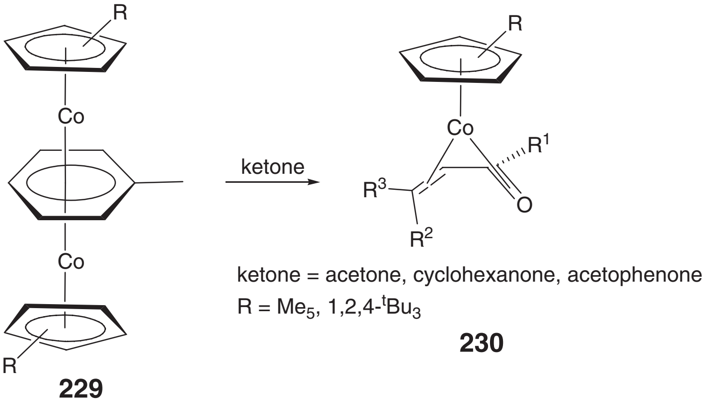
Scheme 38

The structure of compound **223** was ascertained by a crystal structure analysis. Whereas the thermal treatment of **223** afforded the expected phenylene **224**, under UV irradiation, a cyclobutadiene ring was formed, **225**. The UV light was most probably responsible for the dissociation of the alkyne η^2-bound to Co in **223**, thus producing a coordinatively unsaturated Co derivative which is well known to lead to such cyclobutene compounds via reductive elimination (see Section 7.01.4.3).

7.01.4.1.4 η^2-C=O complexes of cobalt

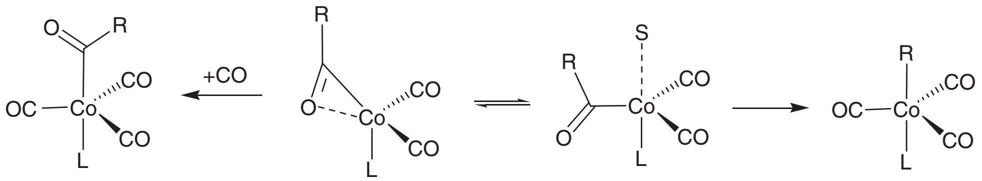
Aldehydes or ketones are known to be able to coordinate side-on to metals. Genuine such bonding modes in **227** and **228** have been identified while treating (η^5-C_5Me_5)Co(η^2-CH_2=$CHSiMe_3$)$_2$ **226** with phthalaldehyde or a phosphine ligand (Scheme 38).[338]

In complex **228**, the phthalaldehyde ligand is behaving as a non-symmetrical ligand, one aldehyde group interacting with Co via a σ-bond, whereas the second aldehyde unit forms a π-interaction with the metal. The crystal structure of **228** revealed that the two C=O bond lengths differ considerably: 1.26 Å versus 1.33 Å for the σ-bonded and the π-bonded carbonyl function respectively. The important elongation observed for the η^2-C=O group indicated considerable backbonding from a filled *d*-orbital of the cobalt(I), the bond order of the carbonyl function being thus dramatically reduced. Cobalt-catalyzed intermolecular hydroacylation of trimethylvinylsilane with isovaleraldehyde was proposed to take place via side-on coordination of the C=O unit to cobalt.[339] A compound **227** closely related to **228** which displays a side-on-bonded aldehyde function was obtained using a phosphine derivative. That the side-on coordination of the carbonyl function to Co led to improved reactivity of the C=O function was illustrated by Schneider *et al.*,[340] who observed the stoichiometric homoaldol coupling of ketones **230** that involved the C_{sp^3}–H activation of the ketone by the 14-electron fragments (η^5-CpR)Co(I) generated from the triple-decker complexes **229** (Equation (38)).



(38)

Based on time-resolved spectroscopic techniques, the existence of an intermediate having an η^2-carbonyl ligand was proposed to occur during the carbon monoxide "migratory insertion" into metal–alkyl bonds (Scheme 38a).[13,341]



Scheme 38a

7.01.4.2 Organocobalt Complexes with η^3-Ligands

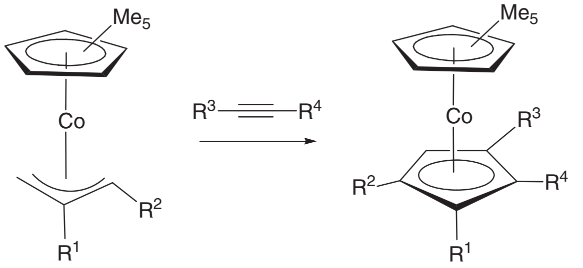
There have been relatively few studies on either η^3-cyclopropenyl- or allylcobalt derivatives during the last decade as compared with the η^4- or η^5-hydrocarbyl–Co complexes.

Basolo *et al.* studied the kinetics of the CO substitution in η^3-cyclopropenyl complexes of Co with phosphine ligands.[342] They showed that the reaction occurred via a dissociation of the CO ligand rather than via association of the phosphine to the Co center. This would have led to the slippage of the cyclopropenyl unit, leading thus to a transient η^1-cyclopropenyl unit of a 16-electron Co species.

A study involving Co(η^3-C_3H_5)(CO)$_2$PCy$_3$, *para*-hydrogen, and NMR spectroscopy provided direct evidence for the mechanism of hydroformylation catalysis as it allowed the detection of linear and branched cobalt acyl intermediates in conjunction to the corresponding alhedydes.[343]

Co(II)(η^5-C_5Me_5)(η^3-allyl) were obtained via the transmetallation reaction of lithium or Grignard allyl derivatives onto [(Cp*)CoCl]$_2$, **231**.[344] These compounds are easily reduced or oxidized. With lithium they led to [Cp*Co(I)(η^3-allyl)]$^-$, Li$^+$(THF)$_2$, whereas a Co(III) derivative was obtained by oxidative addition of a methyl group through reaction with acetonitrile affording [Cp*Co(η^3-allyl)Me]. Compounds **231** have been shown to be selective catalysts for the co-cyclotrimerization of two alkynes and nitrile compounds to afford pyridines.[345] The reaction was selective, affording only small amounts of benzenes (0.5–14%, depending upon the reagents used).

With alkynes, a cyclopentadienyl moiety is being formed **233** via insertion of the C–C triple bond into the allyl–Co unit of **232** followed by ring closure (Equation (39)).



232

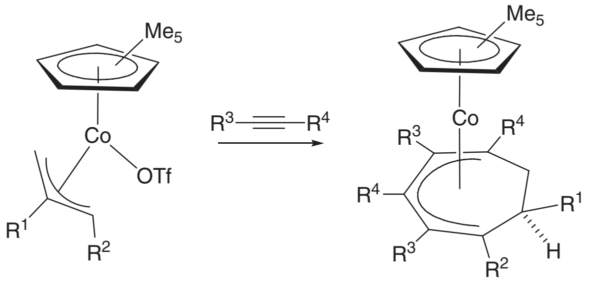
R^1	R^2
H	H
H	Me
Ph	H

233

R^1	R^2	R^3	R^4
H	H	Ph	Ph
H	H	H	Ph
H	H	Me	Me
H	Me	Ph	Ph
Ph	H	Ph	Ph

(39)

A complementary set of reactions has been found to take place when starting with [(η^5-C_5Me_5)Co(III)(η^3-allyl)OTf] derivatives **234** as η^5-cycloheptadienyl complexes **235** were obtained via a [3 + 2 + 2]-cycloaddition (Equation (40)).[346]



234

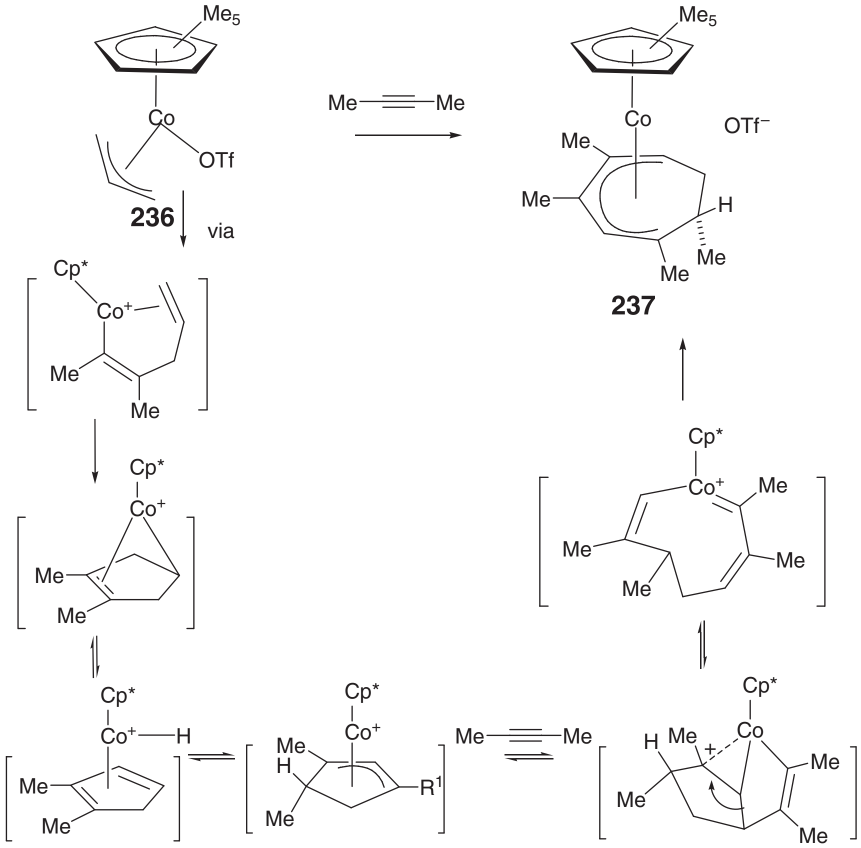
R^1	R^2
H	H
H	Me
Me	Me

235

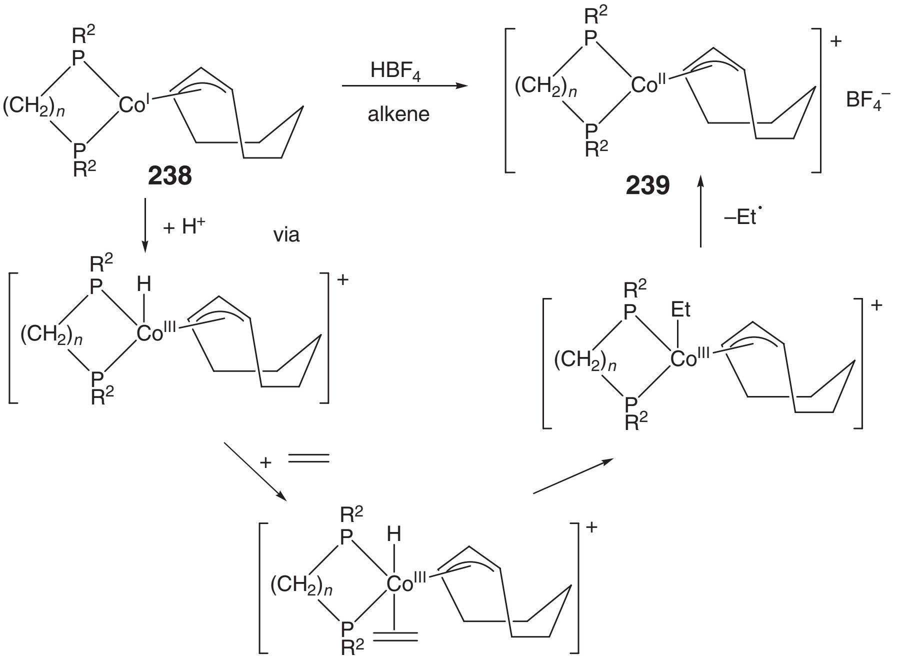
R^1	R^2	R^3	R^4
H	H	H	H
H	Me	H	H
Me	Me	H	H
H	H	H	Ph
H	H	^{t}Bu	H

(40)

However, this reaction led to more complicated products as analyzed at first sight, since several C–C bond activations could be observed during the formation of the products.[347] For instance (Scheme 39), the reaction between excess of 2-butyne and the Co(allyl) group led to a scrambling of the substituents that could be explained by the occurrence of C–C bond cleavage induced by the cobalt atom.



Scheme 39



Scheme 40

Support to the mechanism depicted in Scheme 39 was brought about recently as alkynes could be added to *in situ*-generated C5 rings η^3-bound to CoCp, leading to the formation of η^5-cycloheptadienyl rings.[348]

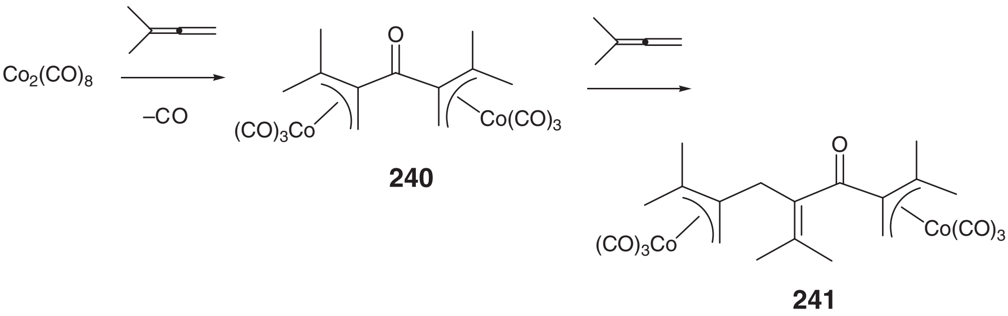
Cobalt(II)(η^3-allyl) derivatives **239** were obtained by reacting (η^3-cyclooctenyl)Co(I)(bisphosphine) compounds **238** with HBF_4 in the presence of alkenes.[349]

One likely mechanism for this reaction is depicted in Scheme 40.

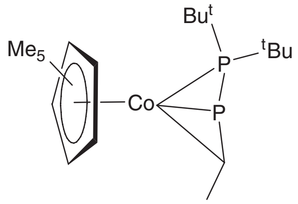
This oxidation reaction was also extended to acyclic (η^3-allyl)Co complexes. The Co(II) derivatives could be easily reduced to the starting material or oxidized to Co(III) through reaction with NO.

Reaction of $Co_2(CO)_8$ with dimethylallene afforded a polymeric material that displays π-allyl-to-Co interactions.[350,351] The polymeric chain was obtained via stepwise insertion of the allene moiety into one Co–CO bond of cobaltooctacarbonyl **240**. The further insertion of allene in the η^3-allyl–Co unit formed gave rise to a helical structure of a living polymer containing a ketonic carbonyl group and C═C bonds suitable for further chemical modifications (Scheme 41).

Combining the odd-electron Co(0)(η^2-cyclopentene)(PMe_3)$_3$ complex **242** with the electron-accepting π ligand, 6,6-diarylfulvene, led to bimetallic species **243** in which a *C*,*C*-coupling has occurred via a radical reaction (Equation (41)).[352]

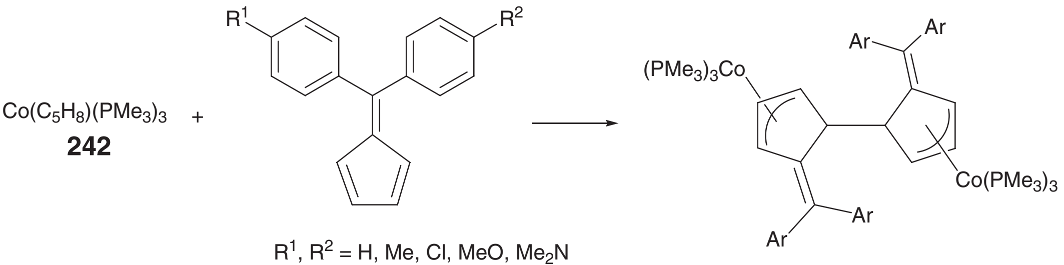


Scheme 41



244

Figure 51



243

(41)

A heteroatom containing η^3-ligand in **244** was obtained while treating Cp*Co(C$_2$H$_4$)$_2$ with the P-rich ^{t}Bu$_2$P–P=P(Me)^{t}Bu$_2$ ligand (Figure 51).[353]

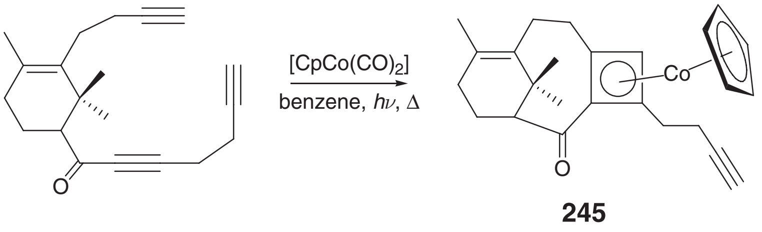
7.01.4.3 Organocobalt Complexes with η^4-Ligands

The examples that will be found in this section are those that provide new structures or new reactivity as compared with those reported in the corresponding chapter of COMC (1995). Simple compounds having η^4-COD ligands, for instance, will not be described here. Many types of η^4-ligands have been described in the previous issues of COMC, especially in COMC (1982). Until then, most of the achievements in this area of organocobalt compounds (and this is even more obvious for Section 7.01.4.4.) have been made in order to use the peculiar advantages of the η^4- or η^5-ligands bound to a cobalt center.

A vast majority of the compounds having η^4-hydrocarbyl ligands have been obtained via the [2+2]-cycloaddition of alkynes on cobalt. It is indeed well known that the cyclotrimerization of alkynes to produce arenes or the co-cyclotrimerization of alkynes and nitriles to form pyridines[354] occurs via the formation of cobaltacyclobutadienes. At this step, reductive elimination leads to a cyclobutadiene unit that can be trapped by the Co(I) unit thus formed. This reaction has been used to synthesize several types of compounds having the η^4-(cyclobutadiene)cobalt unit present. Several sections will be devoted to these compounds according to their relevance to special areas of chemistry (supramolecular chemistry, superphane complexes, synthesis, etc.). Besides this, many papers have been published on several types of η^4-bound hydrocarbyl ligands of four-, five-, six-, or seven-membered rings, all of which are in fact variants of ligands found in the complexes described already in COMC (1982) and COMC (1995). Thus, a large selection of cyclobutadiene moieties substituted by various thioether groups or carbocyclic units,[355,356] azulene units,[357,358] boron-containing substituents[359] or phosphoryl units,[360,361] fluorenones or diazafluorenones,[362] azepines,[363] cyclopentadienes,[364] quinones,[365] iminocyclopentadienes[366] has been obtained via this route. A selection of such reactions is reported below, together with some reactivity studies of relevant examples of cobalt cyclobutadiene-containing compounds.

7.01.4.3.1 η^4-(Cyclobutadiene) cobalt compounds formed by [2+2]-cycloaddition of alkynes

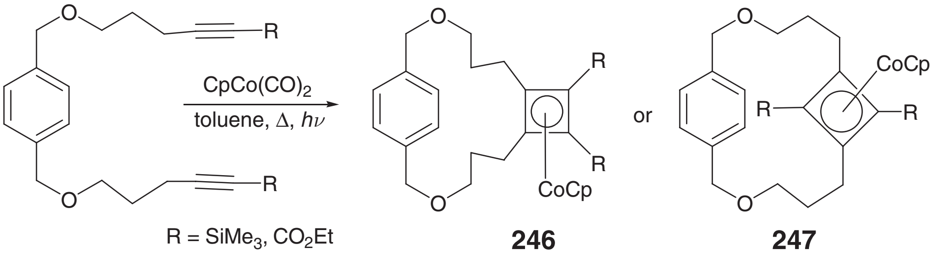
While trying to synthesize the ABCD taxane framework by using a [2+2+2]-cycloaddition reaction mediated by Co(I), the intramolecular variants of the [2+2]-cycloaddition of two alkynes have been shown to occur,[367] affording a cyclobutene adduct **245** stabilized by a CoCp unit (Equation (42)).



245

(42)

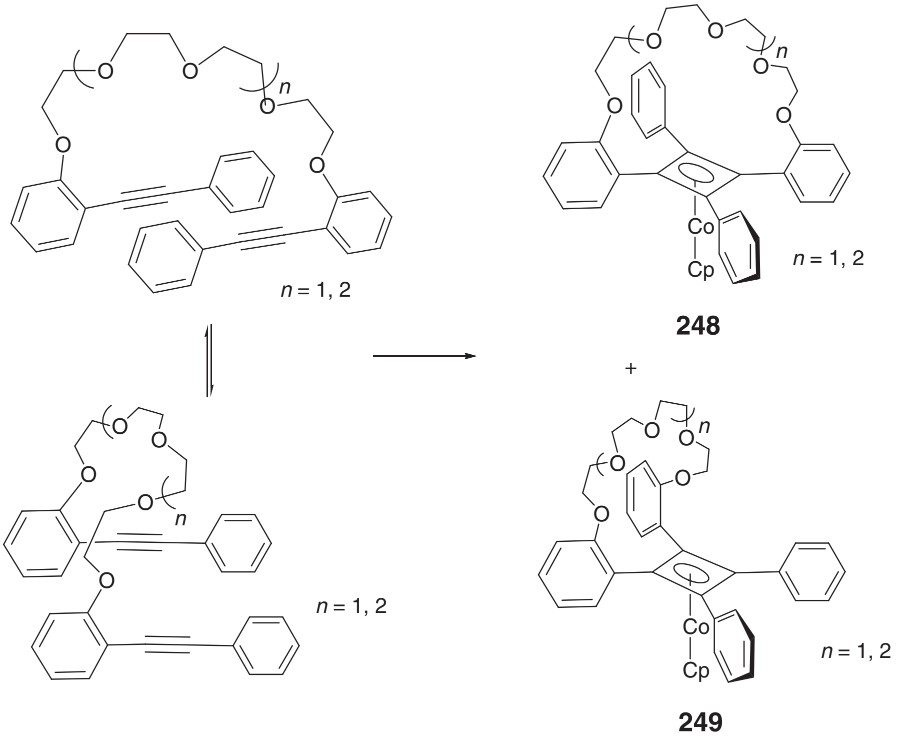
A somewhat related constrained cyclization occurred with an aryl unit 1,4-substituted by acyclic alkynes. Depending upon the nature of the alkyne substituents, 1,2-**246** or 1,3-tethered products **247** were formed regioselectively (Equation (43)).[368]



246 **247**

(43)

Polyether macrocycles containing a η^4-cyclobutadiene cobalt unit **248** and **249** were obtained in a related way (Equation (44)).[369]



248

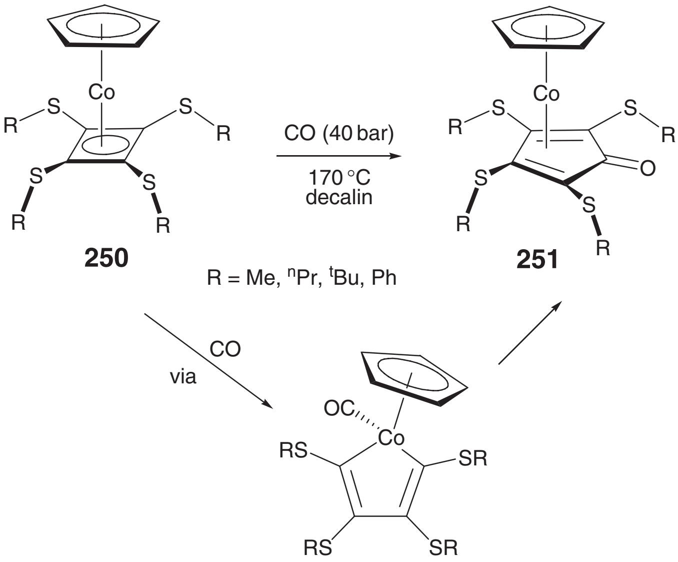
249

(44)

Various superphanes related to those reported above have been synthesized by Gleiter *et al.* via similar procedures; these compounds will be described in Section 7.01.4.3.2.

7.01.4.3.1.(i) Ring enlargements of cyclobutadiene cobalt units

Carbon monoxide could be inserted into a C–C bond of electron-rich Cp–Co-stabilized cyclobutadienes **251**. The reaction occurred, however, under rather harsh reaction conditions, and this reaction was only observed with sulfur-substituted cyclobutadienes **250** (Equation (45)).[370] DFT calculations showed that electron-donating substituents favor the formation of an intermediate in which the cobalt atom inserts into a C–C bond of the cyclobutadiene leading to a cobaltacyclopentadiene unit from which the insertion of CO into a Co–C bond can take place.

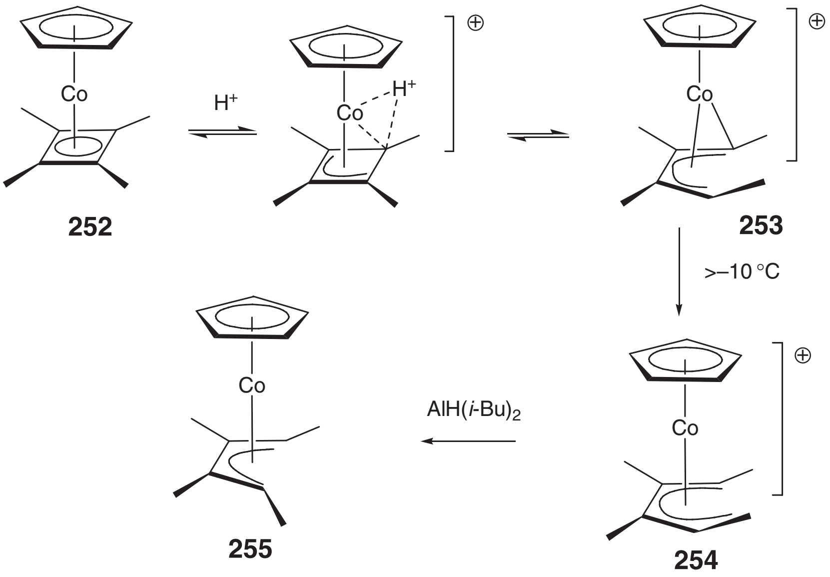


(45)

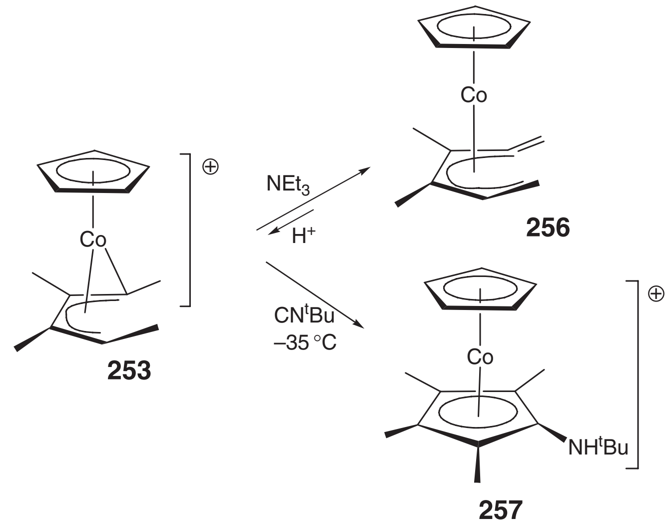
Ring opening of tetramethylcyclobutadiene–Co unit can occur upon protonation. The species thus formed rearranged to a half-opened cobalticinium species that could be reduced by DIBAL-H to a neutral compound (Scheme 42).[371]

The butadienyl compound **253** obtained above was deprotonated with Net$_3$ leading to a hexatriene complex. It also afforded another interesting ring-enlargement reaction when it was reacted with *t*-butylisocyanide to afford **257** (Scheme 43).[372]

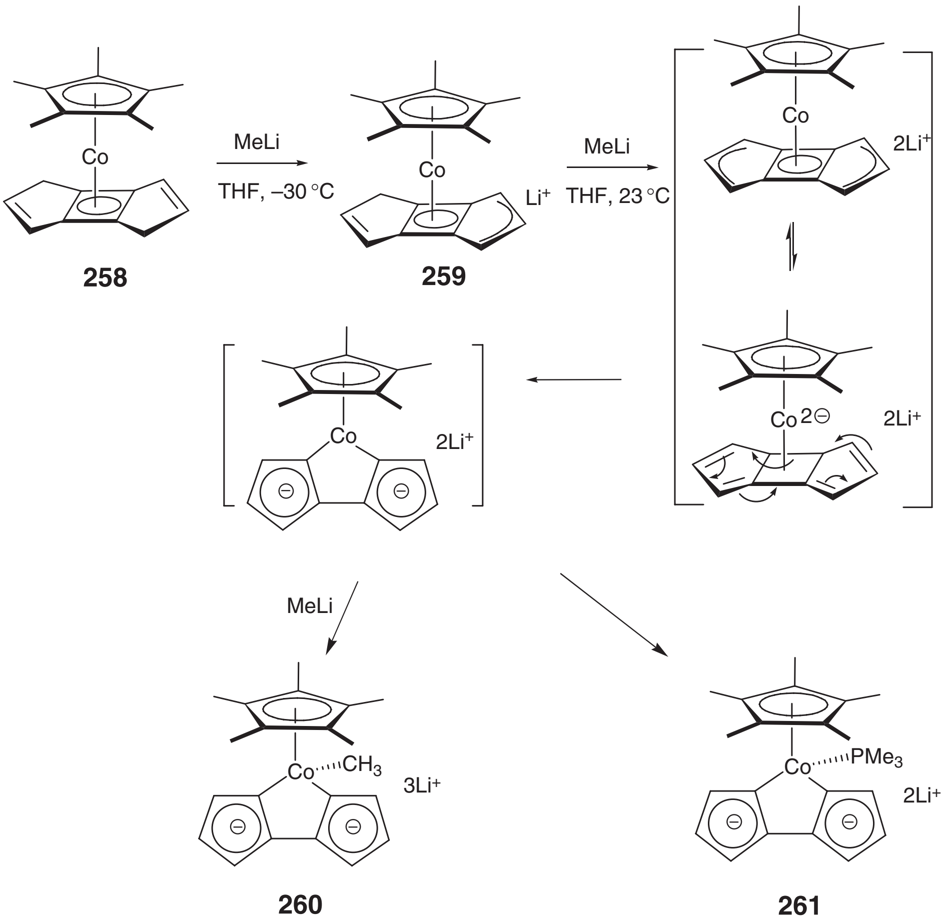
Mono- and polyanionic species were obtained through deprotonation reactions of cyclobutadienes by excesses of methyllithium. The dianionic complex readily rearranged to a cobaltacyclopentadienyl unit (Scheme 44).[373]



Scheme 42



Scheme 43



Scheme 44

7.01.4.3.2 Superphane complexes stabilized with CpCo units

In superphanes, two π-units are connected with each other by the maximum number of chains. Thus, two benzene units form a superphane structure when they are linked by six bridges, for example, in the following example (Figure 52).

Gleiter and his group contributed to expand the large family of phanes by developing a general way of synthesis of superphanes of the 4π-systems. This was partly achieved when studying the intermolecular dimerization of carbo- or heterocyclic diynes with Co derivatives. An archetypal reaction that leads to such a complex is described in Scheme 45.[374]

Several variations on this theme have been performed by the same researchers leading to aesthetically attractive molecules.[375] These compounds can lead to cage compounds such as tricycle[4.2.0.0]-octa-3,7-diene and the cubane derivative.[376]

Many modifications have been made on the diyne derivatives used for the cyclobutadiene units that led to a large library of superphane molecules **264–274**, a few examples of which are represented in Figure 53.[375–379]

The same or two different CoCp units can be found in the dinuclear compounds depicted above in which the cyclopentadienyl ring can be substituted by electron-donating or electron-withdrawing groups.

These metal-capped cyclobutadiene superphanes can be considered as intervalence compounds. Depending upon the nature of the Cp ligands,[380] a low barrier to intramolecular electron transfer might occur between the metal centers; thus, these compounds have attracted considerable interest. Depending upon the distances between the cyclopentadienone or cyclobutadiene rings,[381] the first oxidation potentials of these compounds gave evidence for a partial charge delocalization over both CpCoCb fragments of the superphanes (Cb = cyclobutadiene).[377]

When using more strained cyclodiynes with Cp rings less congested than Cp^* (i.e., RCp = C_5H_5, $CO_2MeC_5H_4$), Gleiter *et al.* observed the intermolecular reaction between the alkyne units, thus leading to higher oligomers **276a and 276b**, such as those described in Scheme 46.[382] The X-ray structure analysis of the trimer **276a** having the silyl bridges on one side of the ring revealed that the tube formed by the three units had a conical shape, the widest diameter in the tube being 6.9 Å, the narrowest one being 4.5 Å.

More symmetrical "belt-like cyclophane" molecules have been obtained more recently, which involved respectively four, **277a**, and eight, **277b**, cobalt cyclobutadiene units (Scheme 46a).[383]

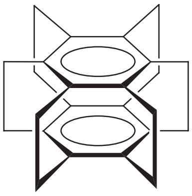
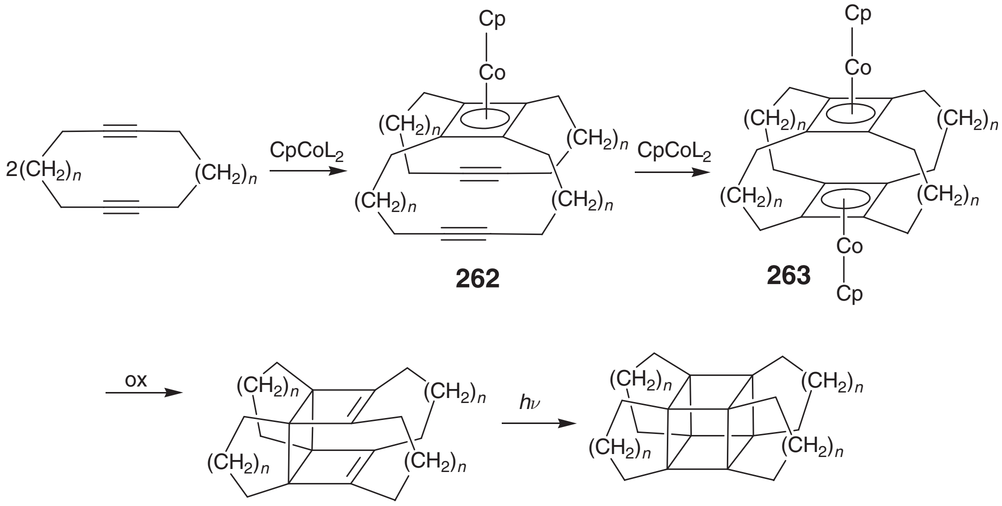
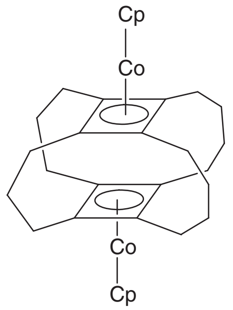


Figure 52



Scheme 45



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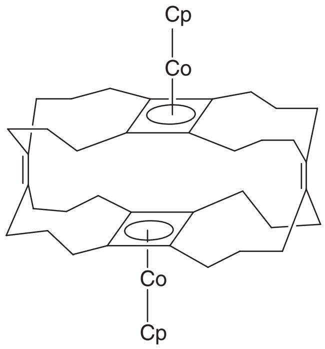

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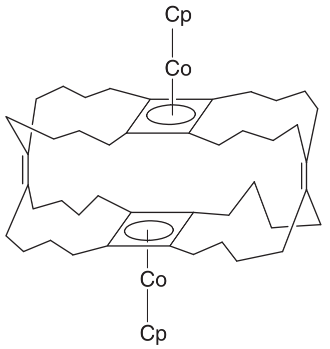

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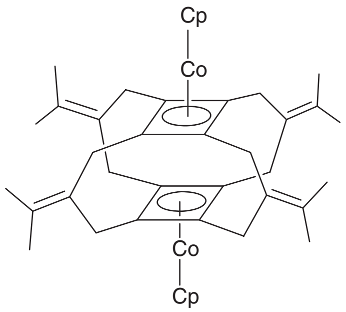

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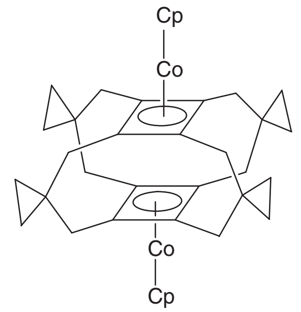

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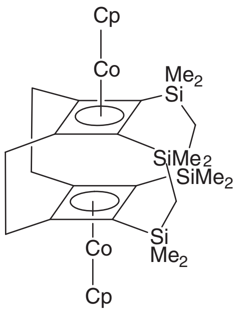

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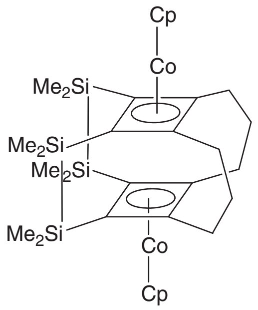

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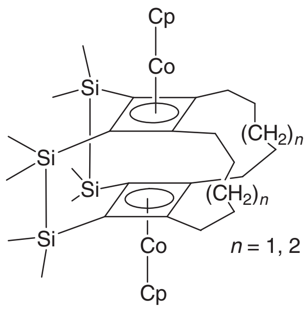

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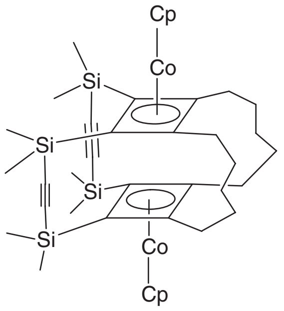

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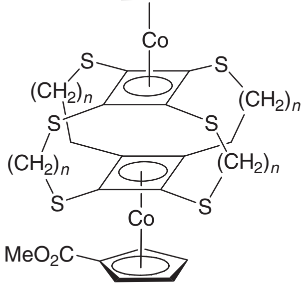

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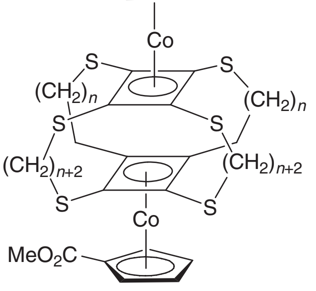

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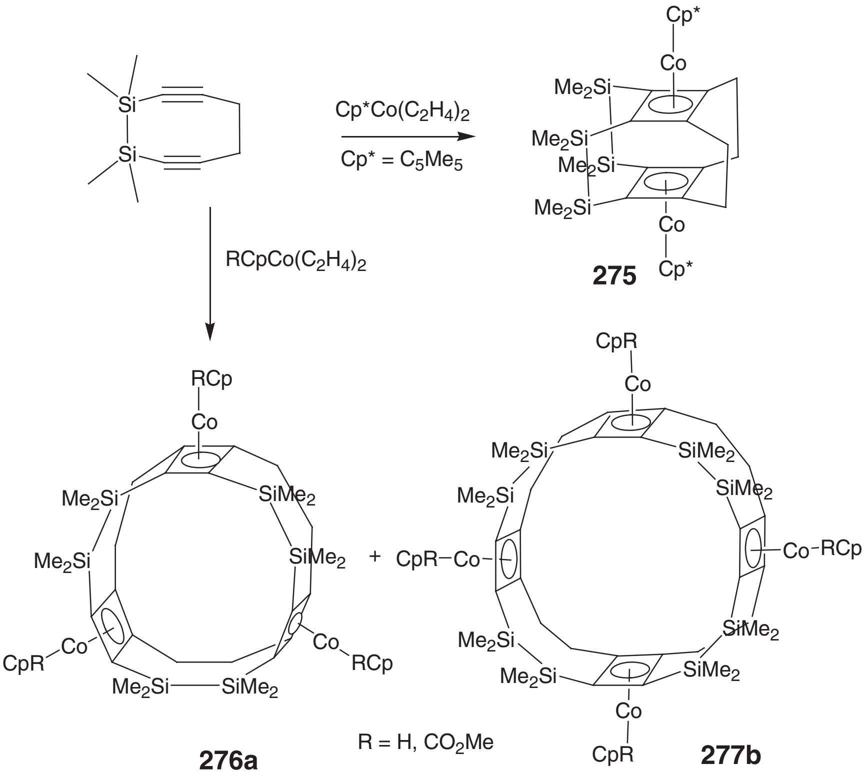
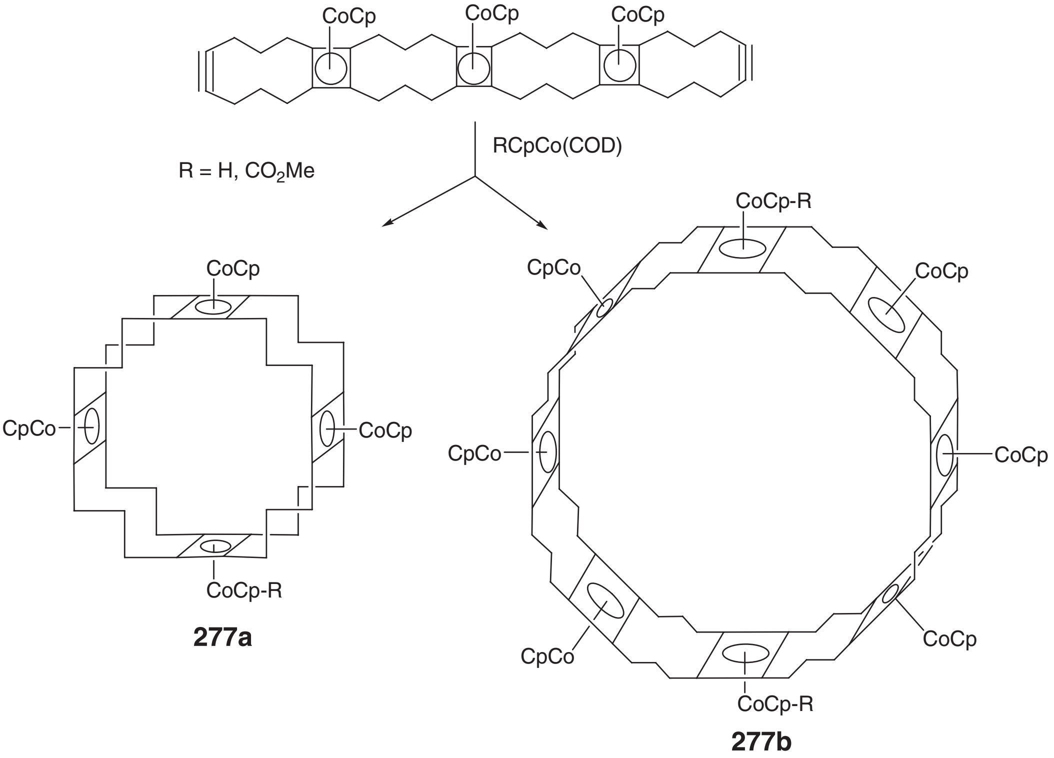
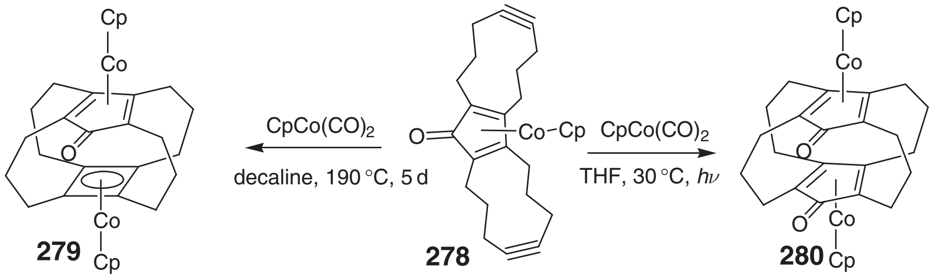
Figure 53



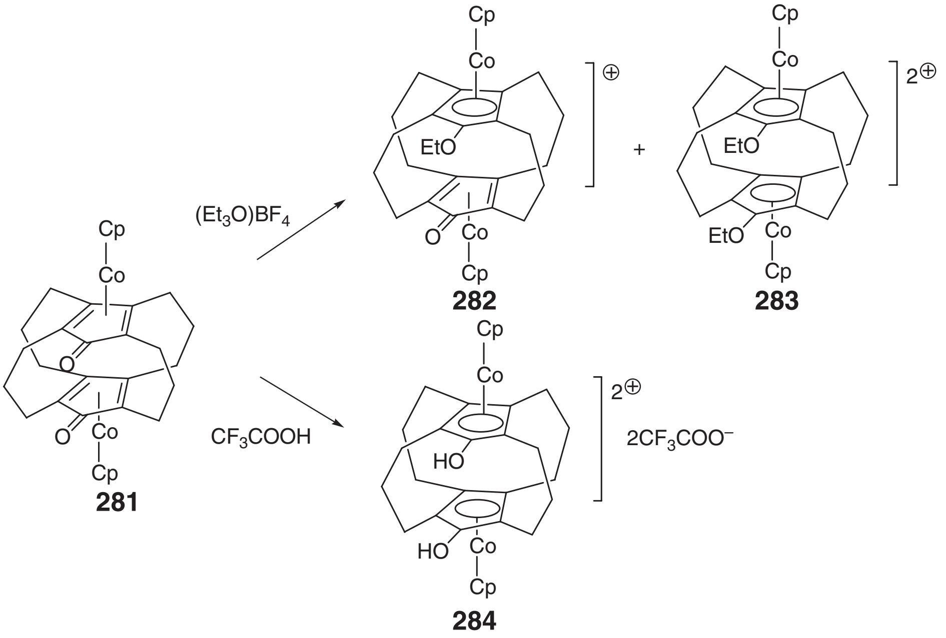
Scheme 46



Scheme 46a



Scheme 47



Scheme 48

Related superphane molecules **279 and 280** having cyclopentadienone rings stabilized by CoCp units have been obtained in analogous reactions in the presence of CO-containing cobalt complexes (Scheme 47).[384–386]

Alkylation or protonation of the ketone unit has been performed, leading to dicobalticinium superphanes **282–284** (Scheme 48).[387]

7.01.4.3.3 η^4-Cyclobutadiene cobalt units as building blocks for the elaboration of supramolecular architectures

The ease with which the formation of (η^4-cyclobutadiene)Co can be formed by coupling of two alkyne reagents with Co(I) derivatives has inspired several groups who wished to use these units as building blocks for nanoscale organometallic topologies and unusual conjugated organometallic polymers.

Carbon-rich molecules such as alkynylated π-systems are among those molecules that attract significant attention. These molecules are related to dendrimers, fullerenes, and carbon nanotubes. They can be used as precursors to novel aromatic systems, molecular wires, or NLO active materials.

Bunz *et al.* have made an interesting contribution to this field as they developed the area of highly alkynylated cyclobutadienes stabilized by η^4-bonding to CoCp moiety.

Using Vollhardt's cyclobutadiene **285**,[388–390] this group described the synthesis of organometallic dehydro[14]-annulenes such as **287** (Scheme 49), and suggested that the aromaticity of fused cyclobutadiene complex might be stronger than that of benzene according to ring current criterion.[391,392]

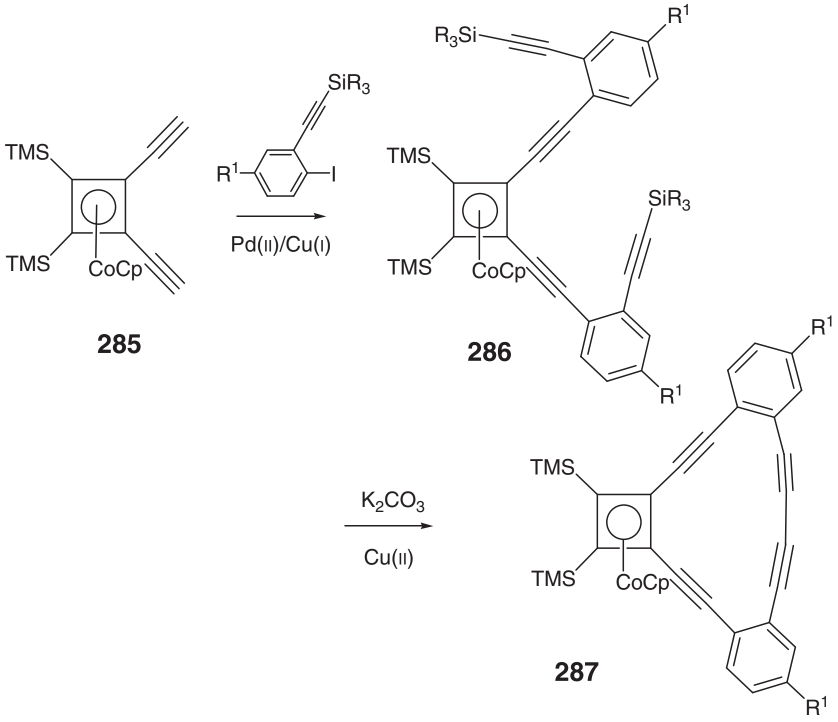
Some of these carbon-rich complexes exploded at temperatures from 196 to 293 °C and formed insoluble carbon materials with no discerning features on the nanoscale.[393]

Based on the preceding procedure, the same group investigated the synthesis of novel organometallic cyclynes with expanded bicyclo[1.1.0]-butane and tricyclo[2.1.0.0]-pentane topology (Figure 54).[394–397]

In **A–D** structures, the C–C single bonds of the small rings are replaced by alkyne or butadiyne bridges while the carbon atoms at the centers are substituted by (η^4-cyclobutadiene)CoCp units.

A model for molecule of type **A** is given in Equation (46).

Models for **B** and **C** **290** and **291** have been obtained in a closely related procedure involving selective orthometallation of organometallic acetals, the conversion of aldehydes into alkynes by the Ohira method and Cu-catalyzed dimerization of terminal alkynes (Figure 55).



Scheme 49

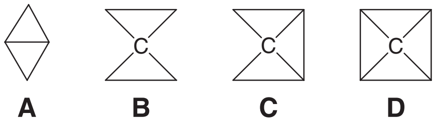
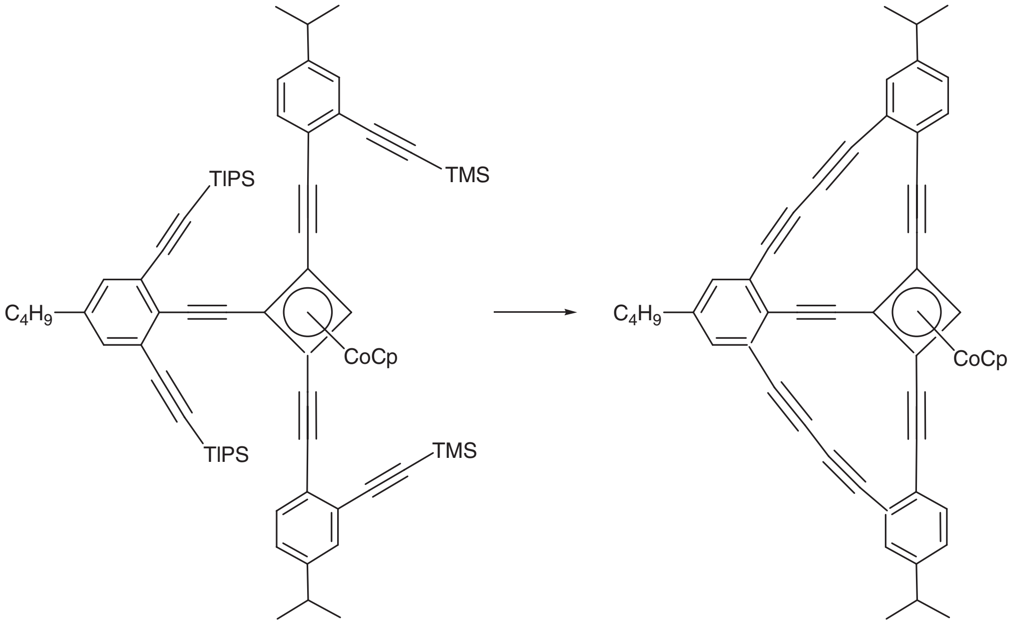


Figure 54



288 **289**

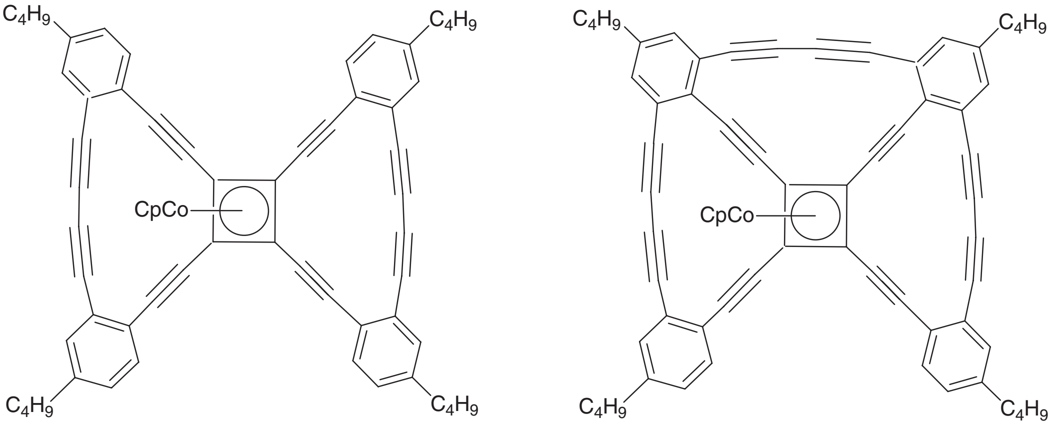
(46)

The X-ray structure analysis of these compounds showed a small bending to planarity. Similar compounds were obtained with ferrocene units in place of the cyclobutadiene unit. The former compounds displayed more pronounced deformations toward planarity than the latter, as can be seen in Figure 56.

Using related synthetic tools as above, Bunz *et al.* also performed the synthesis of polyphenylene dendrimers containing a cyclobutadiene CoCP at the core of the dendrimers. The necessary ethynyl phenyl starting materials **292** were prepared using a Pd-catalyzed Sonogashira-type coupling reaction in good yields. The Co-initiated [2+2]-cycloaddition of the ethynyl units with $CpCo(CO)_2$ proceeded exclusively between the desired internal alkynes to afford **293** (Scheme 50).[398]

The chemistry of alkynylated cyclobutadiene(cyclopentadienyl) cobalt complexes has been reviewed recently.[399]

The synthesis of the polyphenylene then followed a procedure exploited by Müllen *et al.* for the obtention of its dendrimers.[400] This procedure provided the access of extremely large ligands around the metal center that may alter the reactivity of the organometallic unit.



290 **291**

Figure 55

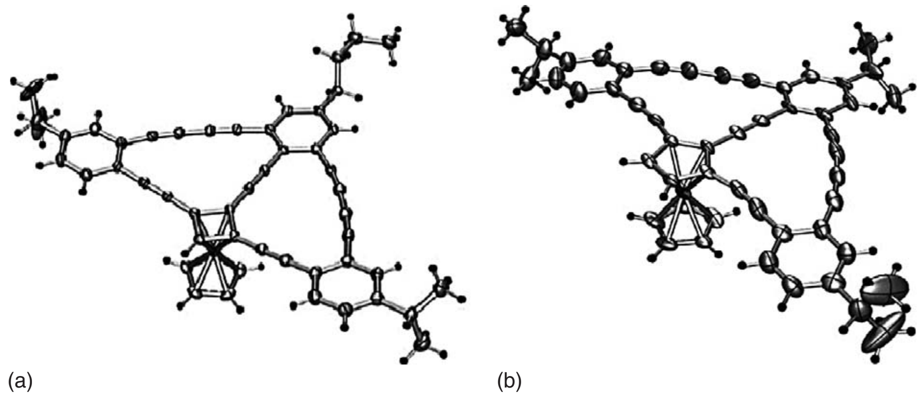
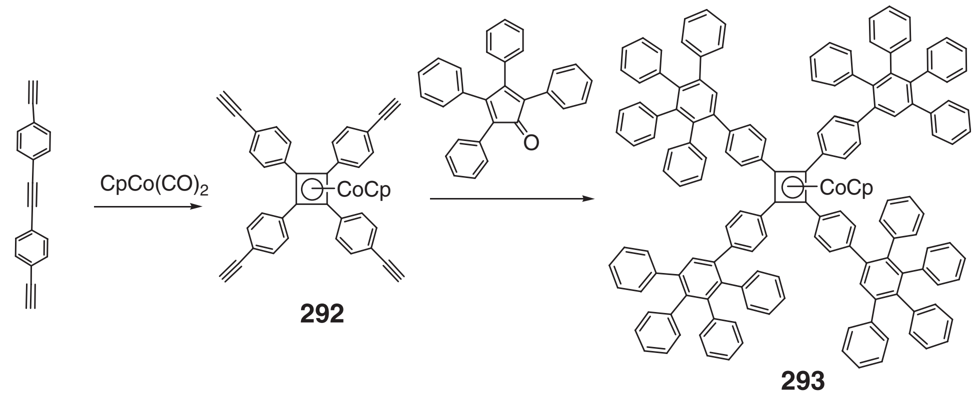


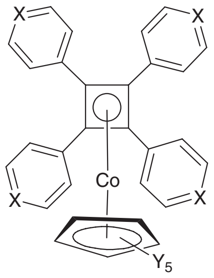
Figure 56 ORTEP view of **289** (a) and its ferrocene analog (b). Reproduced from Laskoski, M.; Steffen, W.; Morton, J. G. M.; Smith, M. D.; Bunz, U. H. F. *J. Organomet. Chem.* **2003**, *673*, 25, with permission from Elsevier.



Scheme 50

In their search to modular chemistry, Michl *et al.* described the synthesis of (η^4-Cb)Co derivatives **294** in which the cyclobutadiene (Cb) moiety was substituted by 4-pyridine or 4-R–phenyl groups permitting the access to square-grid polymers (Figure 57).[401]

Using this and related pyridine-containing cyclobutadienes allowed, when reacted with the Pd($NH_2CH_2CH_2NH_2$) dication, the synthesis of nanoscale barrel **295** and cubes **296** is represented in Figure 58.[402]



X = N, C-Br, C-I, C-p-$CB_{10}H_{10}CH$, C-CO_2Et, C-CO_2H, C-C≡$CSiEt_3$
Y = H, CF_3CO_2Hg, CH_2OHCH_2SHg

294

Figure 57

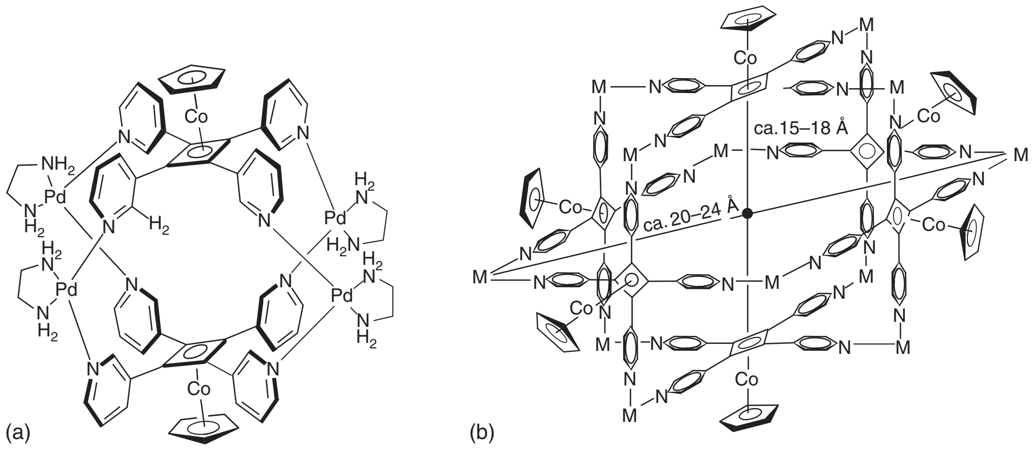
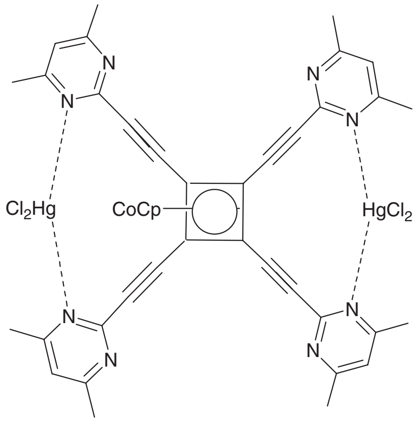


Figure 58 Representation of the supramolecular barrel **295** (a) and cube **296** (b) (M = Pd($NH_2CH_2CH_2NH_2$)$^+$). Reprinted with permission from Johannessen, S. C.; Brisbois, R. G.; Fischer, J. P.; Grieco, P. A.; Counterman, A. E.; Clemmer, D. E. *J. Am. Chem. Soc.* **2001**, *123*, 3818. © 2001 American Chemical Society.



297

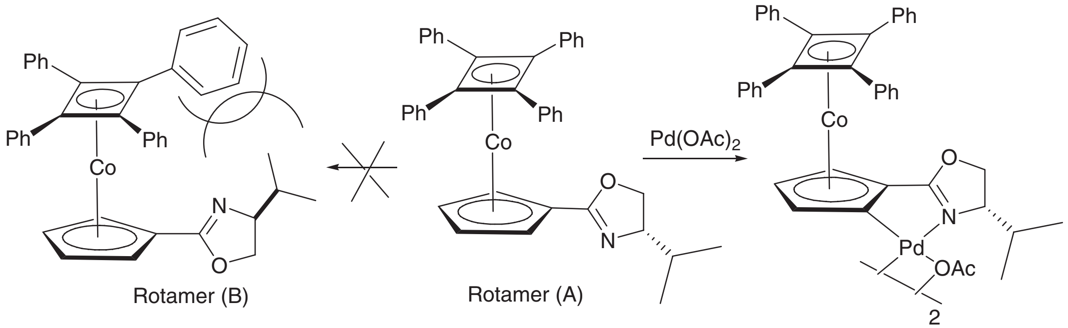
Figure 59

A metalloorganic square **297** was obtained by reacting [tetrakis(2-pyrimidinylethynyl)cyclobutadiene](cyclopentadienyl)cobalt with $HgCl_2$ (Figure 59).[403]

7.01.4.3.4 η^4-cyclobutadiene cobalt units as part of new ligands

It has been recently recognized that (η^4-tetraphenylcyclobutadiene)CoCp substituted on the Cp ring by a chiral substituent can display planar chirality properties after a second substitution of the Cp ring has occurred. The compounds thus formed might be useful catalysts for asymmetric reactions. Following a way similar to that used for related ferrocene derivatives, Richards *et al.* have found that the oxazoline derivative **298** can be orthometallated by palladium stereospecifically at the Cp ring affording **299** as a single diastereoisomer (Equation (47)).[404]

The orientation of the palladation was thought to be due to the inability of **298** to access the rotamer (B) as this situation would result in a repulsive interaction between the oxazoline isopropyl substituent and the phenyl groups of the cyclobutadienyl unit. However, when the isopropyl group was substituted by a tertiobutyl unit, the opposite configuration of the palladated compound was obtained, this being likely to be due to some increased steric interaction brought about by the extra methyl unit during the electrophilic attack of the palladium on the Cp ring.[405]



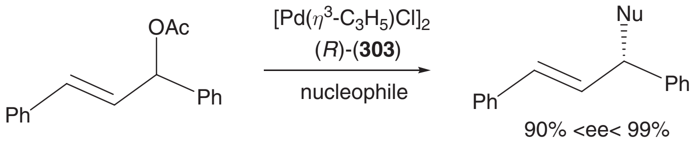
298 **299**

(47)

Several related compounds, in which either the isopropyl group of the oxazoline moiety has been modified or this latter fragment was replaced by chiral imidazole units, have been obtained following a similar procedure.[406–408] These and related compounds were found to be the most active catalysts for the rearrangement of prochiral allylic imidates to allylic amides with high enantioselectivities.[409–411]

Carretero *et al.* succeeded to functionalize twice the Cp ring of Cp(η^4-C_4Ph_4)Co, via the superbasic reagent combination of *tert*-BuLi and potassium *tert*-butoxide, to obtain a chiral *P*,*S*-bidentate ligand, **303** (Scheme 51).

This bidentate ligand provided very high enantioselectivities in Pd-catalyzed allylic substitution with both carbon and nitrogen nucleophiles (Equation (48)).[412]



(48)

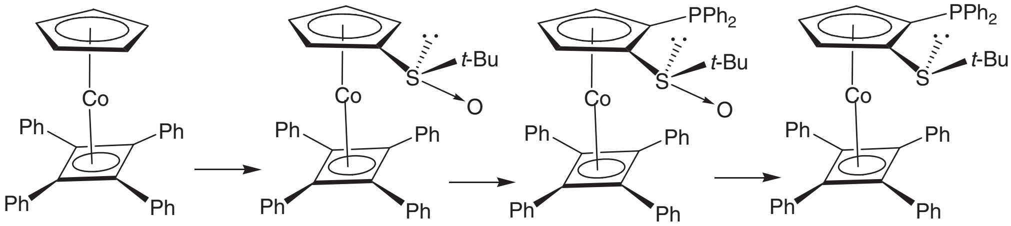
7.01.4.4 Organocobalt Complexes with η^5-Ligands

A vast majority of the organocobalt derivatives are built with the cyclopentadienyl unit. The previous issues of COMC should be consulted for reviews on this topic. In this section, we shall describe organocobalt compounds containing either a simple η^5-Cp ligand or a modified Cp unit, which show unusual reactivity or display valuable properties useful for synthetic chemists or other fields of chemistry.

7.01.4.4.1 Organocobalt complexes with new types of substituted η^5-Cp ligands

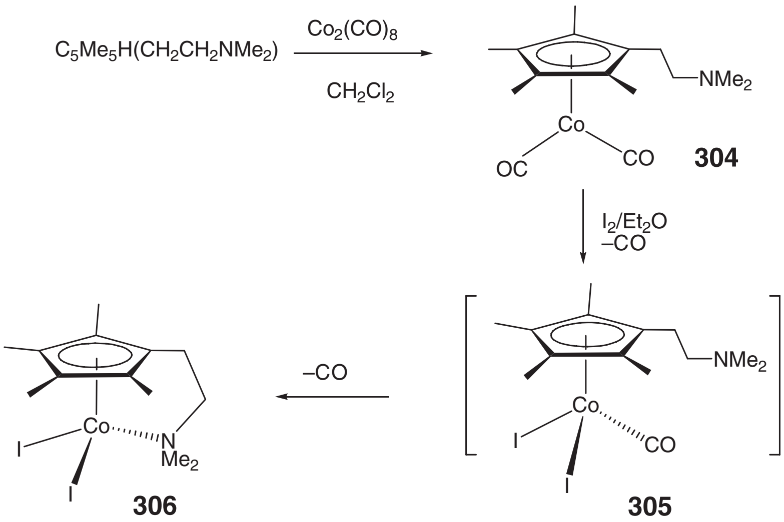
Cp ligands with additional donor atoms have attracted increasing interest in the chemistry of metal complexes as these ligands might stabilize highly reactive intermediates and/or influence the selectivity of catalytic processes. Jutzi has published a review article on this topic.[413]

Due to their poor acceptor abilities, amino groups prefer to bind metals in high oxidation states. Hence, nitrogen donors such as pyridine or amines attached on Cp rings do not coordinate to Co(I) species but they do coordinate to



300 **301** **302** **303**

Scheme 51



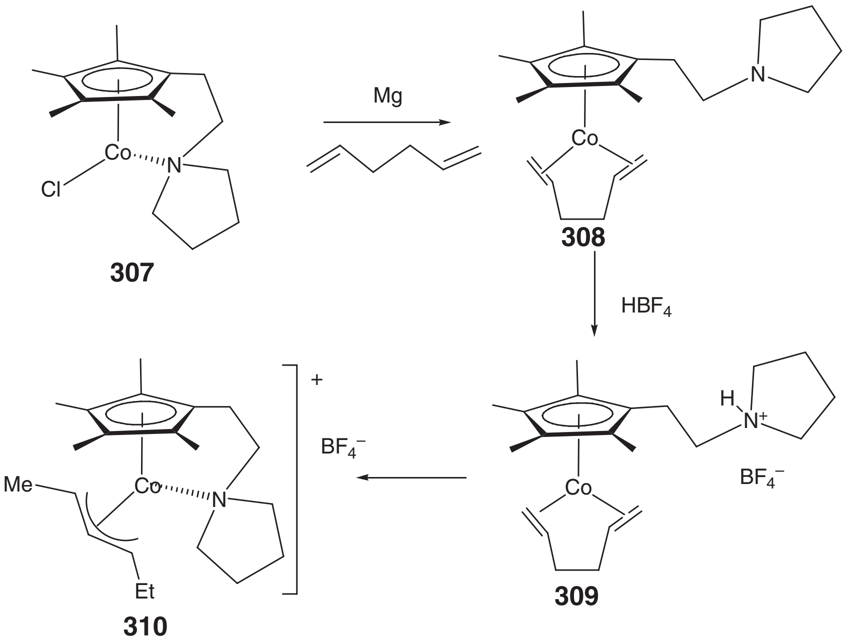
Scheme 52

Co(III). Oxidation by iodine of the thus synthesised Co(I) derivatives **304** usually leads to the desired compounds **305** and **306** (Scheme 52).[414,415]

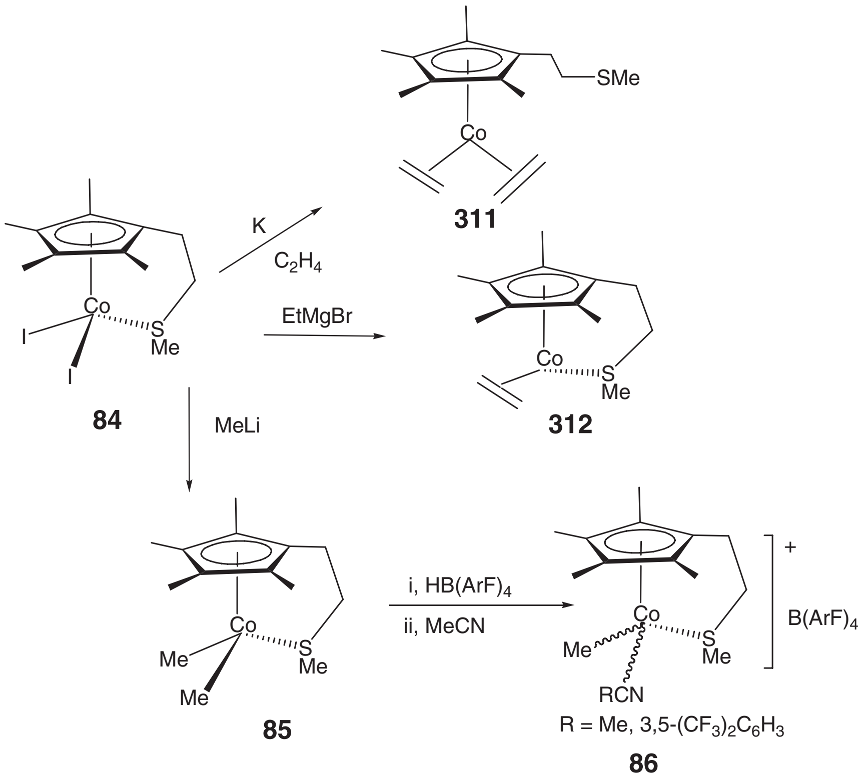
Similar results were obtained with 2-(*N*,*N*-dimethylaminophenyl)-2,3,4,5-tetramethylcyclopentadiene and $Co_2(CO)_8$.[416]

Jolly and Holle[417] found that lithium derivatives of the same type of monosubstituted Cp ligands with $CoCl_2$ led to Co(II) derivatives in which the NR_2 units and the Cp are coordinated to the cobalt center. However, reducing the latter with magnesium in the presence of alkenes or dialkenes led to Co(I) species in which the amino groupings were again non-coordinated to Co. Treating this species with HBF_4 led to the protonation of the amine, which was followed by the transfer of the proton to the diene affording a π-allylcobalt(III) salt **310** (Scheme 53).

Following similar reasoning, Brookhart *et al.* prepared a compound analog to **306** having a thioether unit instead of a NMe_2 group **84**.[128] The resulting Co(III) compound was reduced in the presence of ethylene, affording, as for the



Scheme 53



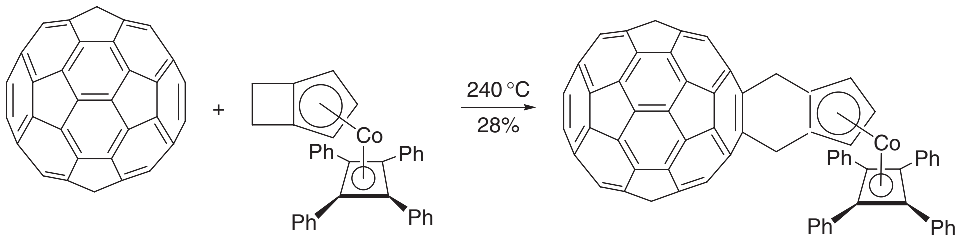
Scheme 54

related nitrogen-containing complexes, a Co(I) compound in which the thioether was not bound to Co **311**. However the reaction with EtMgBr led to the successful synthesis of the expected Co(I) **312**, presumably via decomplexation of the sulphide arm from a diethyl complex followed by β-hydride elimination, reductive elimination of ethane and recoordination of the sulphide. This latter compound was rather unstable and another synthetic procedure had to be found to obtain a cationic derivative containing one methyl group and an acetonitrile ligand **86** (Scheme 54). This compound proved to be very active for the polymerization of ethylene (see Section 7.01.4.4.3.(iii)).

Half-sandwich complexes of cobalt with intramolecular phosphorous coordination have been known for the cobalt atoms in oxidation state +I and +II (see Sections 7.01.3.3 and 7.01.3.4). Butenschön has published a comprehensive review recently on cyclopentadienyl metal complexes bearing pendant phosphorous arsenic and sulphur ligands.[418]

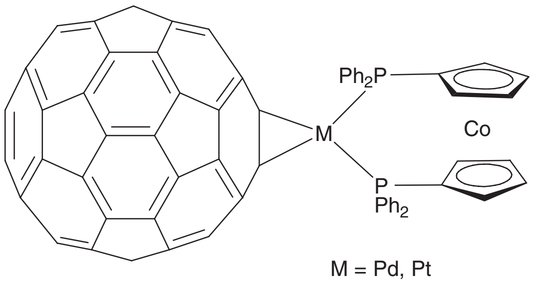
Intramolecular coordination to the cobalt center via a substituted Cp ring also occurred in a rare reaction which combined C–H and C–F activation at the same time, thus leading to the coupling between a pentafluorophenyl ring and a pentamethylcyclopentadienyl ring (see Scheme 10 above).[131]

Cyclopentadienyl rings substituted by fullerene units have been synthesized in order to obtain molecules presenting donor–acceptor interactions.[419] The synthesis involves the [4+2]-cycloaddition of a $CoCp(C_4Ph_4)$ derivative with C_{60} at rather high temperatures that led to an organocobalt compound **314** stable in air but which proved to be apparently unstable under redox conditions (Equation (49)).



313 **314**

(49)



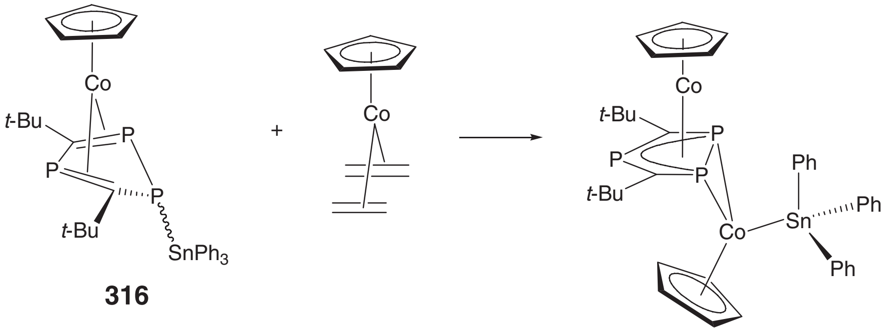
315

Figure 60

A somewhat different type of compound **315** that also contained a fullerene unit indirectly bound to a Cp ring was obtained when reacting an *o*-dichlorobenzene solution of C_{60} with $M(dba)_2$ (M = Pd, Pt) and $[(\eta^5\text{-}Ph_2PC_5H_4)_2\text{-}Co]^+(PF_6)^-$ (Figure 60).[420]

The 1,2,4-triphospholyl ring $[C_2Bu^t{}_2P_3]^-$ has been extensively studied by Nixon.[421] Co-condensation of electron beam-generated cobalt atoms with an excess of ${}^tBuCP$ produced a mixture of compounds from which the sandwich compounds $[Co(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^4\text{-}P_2C_2{}^tBu_2)]$ and $[Co(\eta^5\text{-}P_2C_3{}^tBu_3)(\eta^4\text{-}P_2C_2{}^tBu_2)]$ have been isolated.[422]

A trinuclear Co_2Sn species was obtained while treating **316** with $CpCo(C_2H_4)_2$. This compound **317** can be viewed as an extremely slipped 34 VE triple-decker sandwich compound (see COMC (1995) and COMC (1982)), as it contains a bridging 1,2,4-triphospholyl η^5-bonded to one and η^2-bonded to the other CpCo unit (Equation (50)).[423]



316

317

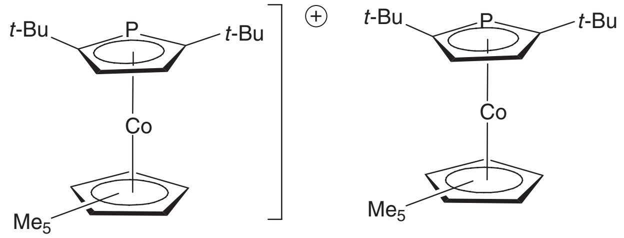
(50)

Compounds containing related polysubstituted rings such as $[C_2Bu^t{}_2P_2As]^-$ have been used as ligands for ruthenium compounds but apparently no cobalt derivatives with such a ligand have been reported.[424] However, a $[C_2Bu^t{}_2P_2Sb]^-$ ligand led to $[Co(\eta^5\text{-}C_2Bu^t{}_2P_2Sb)(\eta^4\text{-}C_2Bu^t{}_2HP_2Sb)]$, which represented the first example of diphosphastibicyclopentadiene complex.[425]

Monophosphametallocenium cations of cobalt, **318a**, were prepared through metathesis of bis(η^5-2,5-di-*tert*-butylphospholyl)lead with $[CoCp^*X_2]_2$. A reversible reduction half-wave potential occurred at –0.74 V (vs. SCE in *n*-Bu_4NBF_4–THF) and was insensitive to water.[426] The reduction of **318a** by magnesium furnished good yields of the air sensitive phosphacobaltocene, **318b** (Figure 61). A comparison of cyclovoltammograms for the latter compound and the corresponding cyclopentadienyl complex $[CoCp^*(1,3\text{-}C_5{}^tBu_2H_3)]^+[BPh_4]^-$, **318c**, showed that replacing a CH group by an *sp*^{2}-phosphorous atom results in an anodic first reduction potential shift of 0.29 V.[427]

7.01.4.4.1.(i) Chirality at Cp

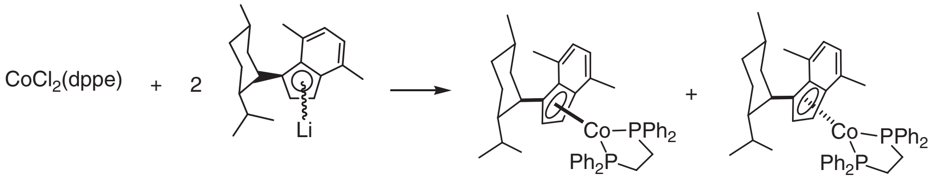
Several ways have been followed in order to induce chirality at CpCo units. The menthyl moiety attached to a cyclopentadienyl ring proved to be a powerful tool for the amplification of chiral information. Schumann's group has



318a **318b**

Figure 61

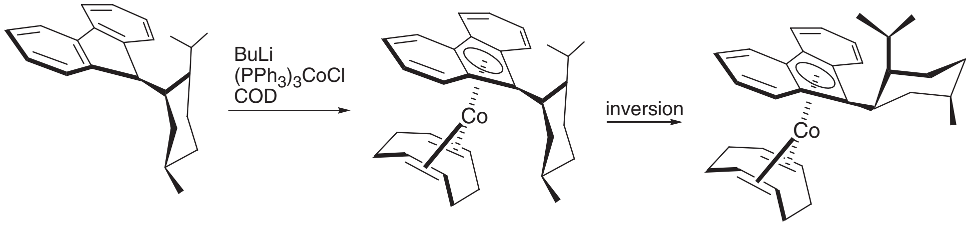
been active in this area of research, showing that menthyl-functionnalized chiral nonracemic monoindenyl complexes of the cobalt triad **319** and **320** and of molybdenum could be synthesized (Equation (51)).[428,429]



319 **320**

(51)

A related compound was obtained from the analogous fluorenyl derivatives **321** and **322**.[430] An inversion of the cyclohexyl ring of the terpene moiety occurred upon complexation to the cobalt center (Equation (52)).

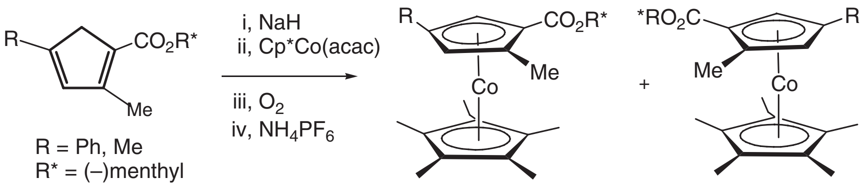


321 **322**

(52)

Chirality centered at carbon atoms was also introduced at the Cp ring by using tartrate ligands. This procedure has been known since 1986,[431] and it has been improved recently to afford better yields of both a mono- and a disubsubsituted Cp ring.[432] The cobalt derivatives **323** and **324** were formed via methatetical reaction of the lithium derivatives of these ligands (Scheme 55).

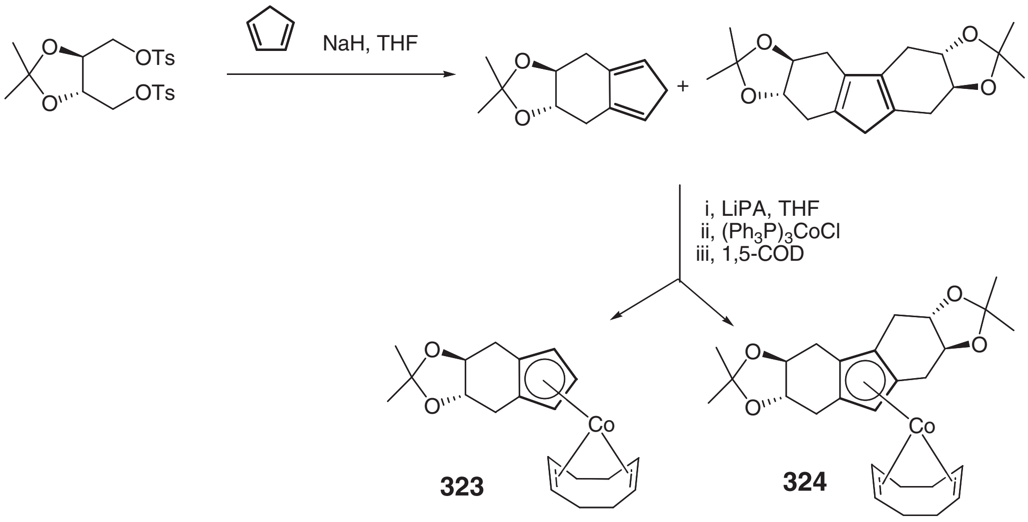
Planar chirality has been observed in cobalticinium complexes **325** and **326** via the introduction of three different substituents on one of the Cp rings, one of them carrying a chiral auxiliary such as a (–)-menthyl group (Equation (53)).[433]



325 **326**

(53)

Helical chirality on cobalt Cp units was also found while synthesizing helicene derivatives, **327**, which could be complexed by cyclopentadienyl cobalt derivatives (Figure 62).[434]



Scheme 55

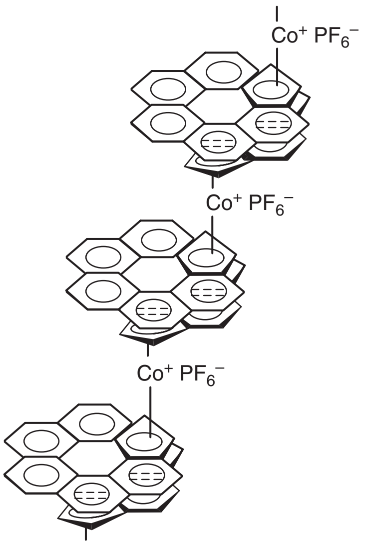


Figure 62 Oligomer of cobalt helicenes 327. Reprinted with permission from Katz, T. J.; Sudhakar, A.; Teasley, M. F.; Gilbert, A. M.; Geiger, W. E.; Robben, M. P.; Wuensch, M.; Wards, M. D. *J. Am. Chem. Soc.* **1993**, *115*, 3182. © 1993 American Chemical Society.

The optical activity of these oligomers is very high and their cyclic voltammogram showed two close cathodic waves; thus, the interaction between adjacent units is weak.

Monohelicenes, 328, with either one or two CoCp* units have also been produced by the same team (Figure 63).[435]

The X-ray diffraction analysis showed that the cobalt atoms are separated by 8.49 Å, and that the (+)-isomer has the (*P*)-configuration.

Finally, all three types of chirality were claimed to occur in the first optically pure planar-chiral cyclopentadienyl cobalt complex 329, which uniquely contained three different types of chirality, planar, carbon-centered, and helical chirality (Figure 64).[436]

The helical chirality was brought about by the relative orientation of the four phenyl units of the cyclobutadienyl fragment which were shown to form a four-blade windmill arrangement.

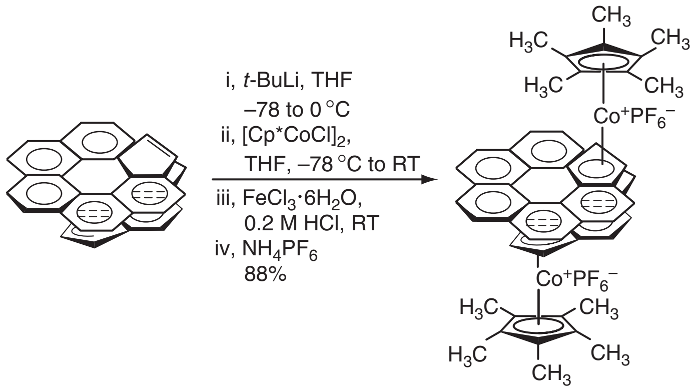
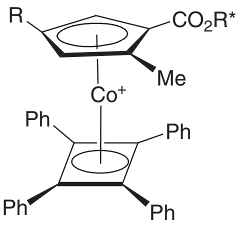


Figure 63 Dicobalthelicene **328**. Reprinted with permission from Gilbert, A. M.; Katz, T. J.; Geiger, W. E.; Robben, M. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 3199. © 1993 American Chemical Society.

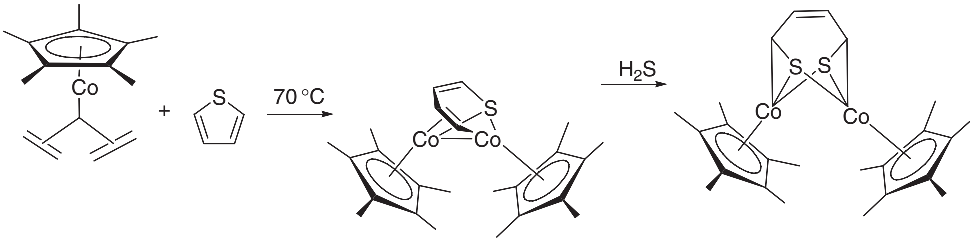


329

Figure 64

7.01.4.4.2 Organocobalt complexes with η^5-Cp ligands displaying synthetically important chemistry

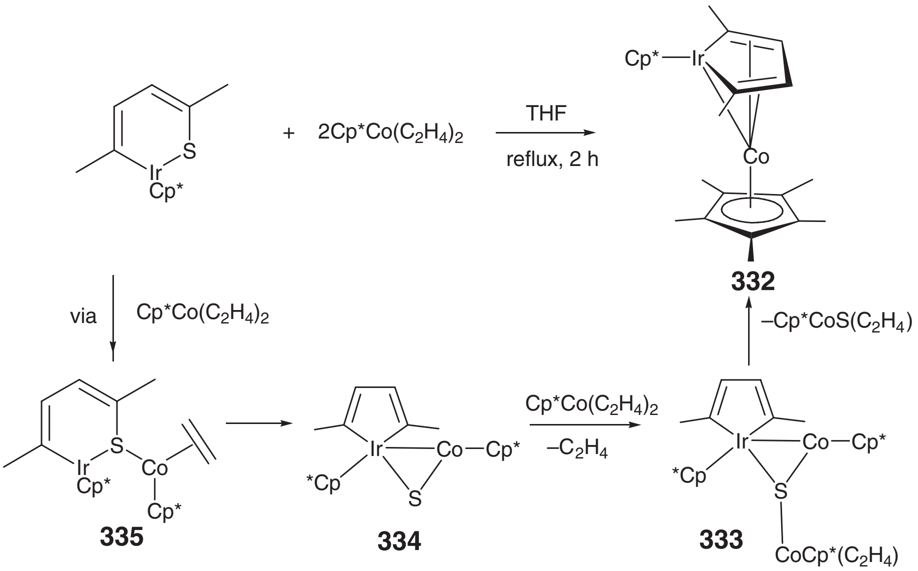
Carbon–sulfur bond breaking was observed while treating thiophene with Cp*Co(C$_2$H$_4$)$_2$ at 70 °C in benzene. A cobalt metal center had inserted into the C–S bond and a second Cp*Co unit had complexed to the cobalt, sulfur, and C–C double bond **330**. Further reaction of the resulting compound with H$_2$S produced a new butadiene dithiolate compound, in which a sulfur atom has been inserted into the metal–carbon bond **331**. Reaction with dibenzothiophene produced an analogous dinuclear C–S insertion-reaction adduct (Equation (54)).[437]



330 **331** (54)

Evidence for the desulfurization of thiophene by cobaltocene or Cp*Co(C$_2$H$_4$)$_2$ was obtained when a dimethylthiophene adduct of iridium was treated with these organocobalt compounds (Scheme 56).[438] The proposed mechanism is analogous to the one proposed earlier when the same iridium derivative was treated with iron carbonyl compounds. This type of desulfurization reactivity is consistent with the involvement of η^4- or ring-opened thiophenes in hydrodesulfuration (HDS), as proposed earlier.[439]

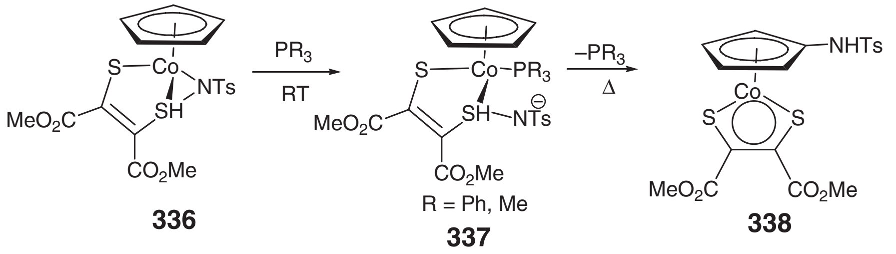
Somewhat related C–N bond cleavage was observed when reacting CpCo(PMe$_3$)$_2$ with isocyanide derivatives under very mild reaction conditions (RT) (see Scheme 3, Section 7.01.3.3.1.).[87] Surprisingly, the corresponding



Scheme 56

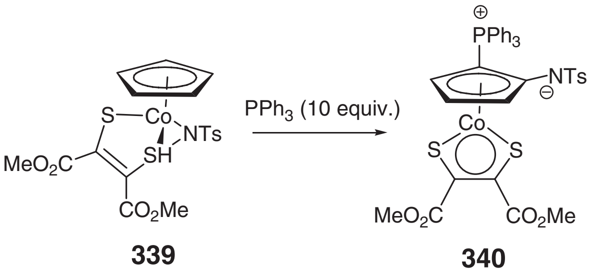
tolylisocyanide derivative was quite inert, and did not lead to the same type of rearrangement. The reaction followed first-order kinetics, and its rate did not depend upon the amount of free PMe_3.

The migrations of monodentate ligands from the central transition metal to the Cp ring are well-known reactions. They are usually induced by strong bases. Kajitani *et al.* reported what appeared to be the first example of nitrogen migration to the Cp ring in organometallic complexes **336–338**, this migration being induced by triphenylphosphine (Equation (55)).[440]



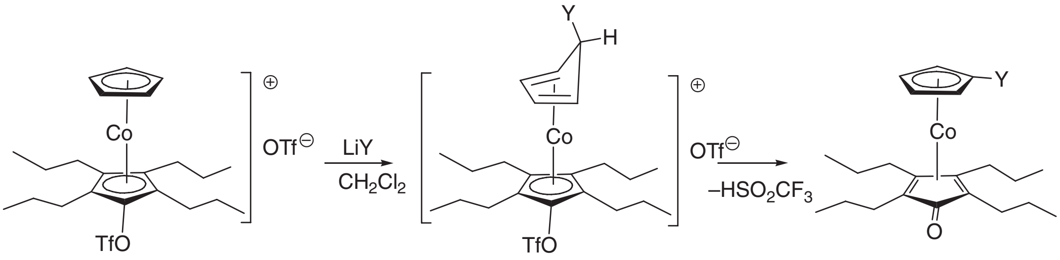
(55)

When this reaction was performed in the presence of a large excess of PPh_3 (10 equiv.), a Cp ring disubstituted with an imido and a triphenylphosphonium unit was obtained **340** (Equation (56)).[441,442]



(56)

A rare case of SN′-reaction on a cobaltocenium triflate **341**, attack of a nucleophile on one ring of the cobaltocenium ion, followed by the departure of a leaving group on the other ring has been encountered by Gleiter *et al.* (Equation (57)).[443]



341

Y = Me, Ph, *n*-Bu, *t*-Bu, ≡—$SiMe_3$ ≡—$SiEt_3$

342 **343**

(57)

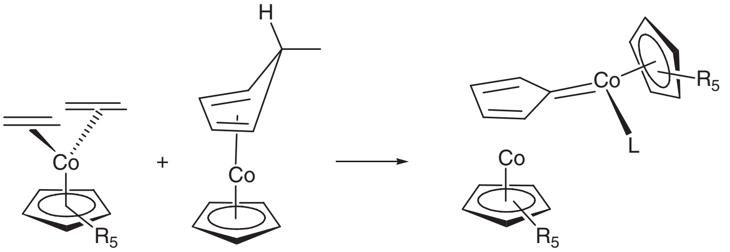
Thus, after the nucleophile Y^- had attacked the Cp ring at the *exo*-position **342**, this was followed by the elimination of triflate acid that led to the substituted cyclopentadienone complex **343**. This method afforded an easy way to the synthesis of otherwise difficult-to-obtain substituted Cp rings, such as those substituted by alkyne units. In the case of the *n*-butyl derivative, the reaction could be repeated, thus leading to the substitution of another butyl group in the β-position to the first one.

7.01.4.4.3 Important organometallic chemistry taking place at the CoCp unit

7.01.4.4.3.(i) CH activation on CoCp units

It is very well established that 16-electron species such as $[C_5R_5ML]$ (M = Rh, Ir) generated *in situ* undergo facile oxidative addition of CH bonds of saturated hydrocarbons or arenes (see COMC (1995) and COMC (1982)). This situation is likely to be due to the fact that iridium and rhodium complexes are kinetically far more stable than cobalt. However, during the last decade, some CH activations were found to take place on some typical cobalt complexes.

Wadepohl *et al.* have reported earlier the exceptional CH activating properties of $CpCo(C_2H_4)_2$, that led to the cleavage of both methylene CH bonds of $CpCo(\eta^4\text{-}C_5H_6)$ in **344** (Equation (58)).[444–447]

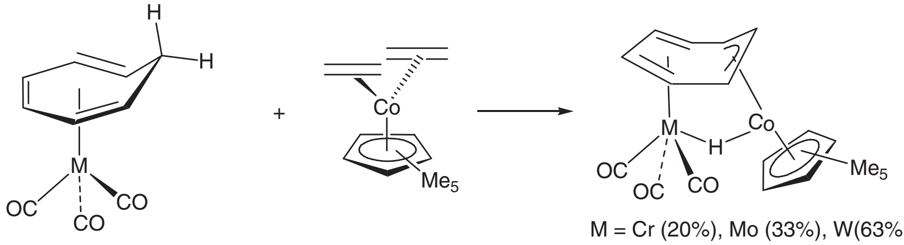


R = H, Me

344

(58)

More recently, a related reaction was found to take place to afford a heteronuclear bimetallic compound **345** (in poor yields however), when cycloheptatrienyl derivatives of Cr, Mo, and W were allowed to react with the same electron-rich cobalt complex (Equation (59)).[448]

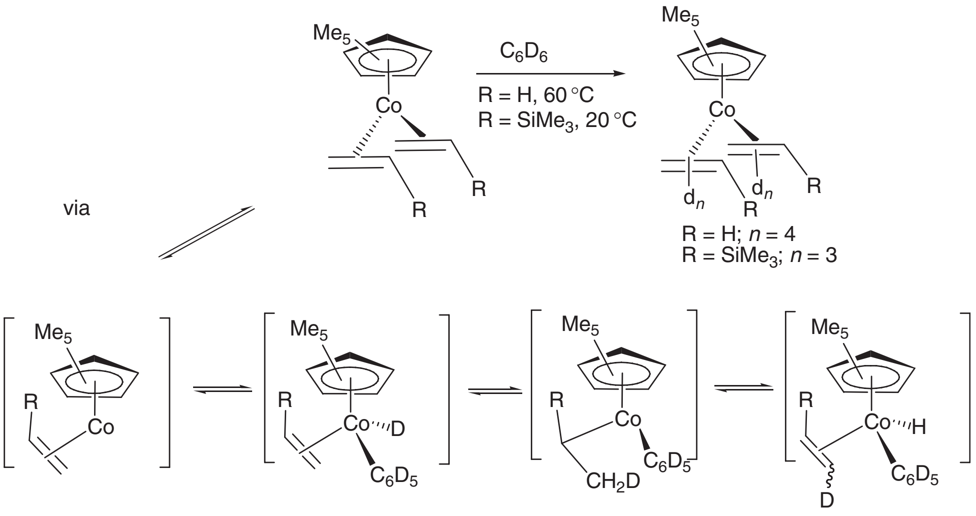


M = Cr (20%), Mo (33%), W(63%)

345

(59)

The chromium derivative led to a reversible reaction as its treatment with carbon monoxide afforded the starting compounds.



Scheme 57

H–D exchange reactions were observed between C_6D_6 and alkenes coordinated to the electron-rich $Cp^*Co(CH_2{=}CHR)_2$. This was interpreted as an evidence for the oxidative addition of C–H bonds to a 16-electron Co(I) center (Scheme 57).[449]

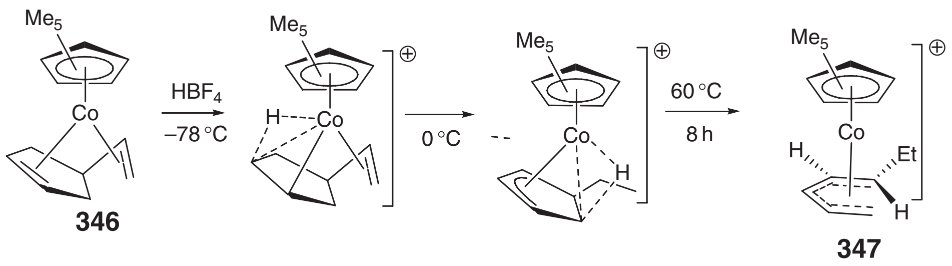
The addition of pyridine to the related $Co(I)(alkene)_2$ species did not result in the formation of the bis-pyridine adduct but the monosubstituted species Cp^*Co(alkene)(pyridine). This latter compound led also to deuterium incorporation into the coordinated olefin when it was treated with benzene-d_6. This occurred following a mechanism analogous to the one depicted above for the bis-olefin complex, that is, this emphasized the fact that the pyridine is only weakly bonded to the cobalt(I) electron-rich center.[450]

7.01.4.4.3.(ii) C–C bond activation on CoCp units

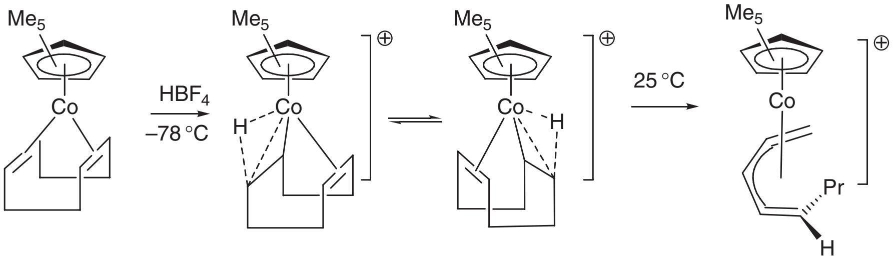
The cleavage of unreactive carbon–carbon bonds is an elusive target in organometallic chemistry. A rather rare case of such a C–C bond cleavage has been described by Spencer *et al.* The protonation of the neutral (η^4-4-vinylcyclopentene)Co(η^5-C_5R_5) **346** by non-coordinating acids such as HBF_4 led to the cationic ethylcyclopentenyl complex of cobalt, in which the metal was stabilized by a three-center, two-electron interaction (agostic interaction) (Scheme 58). Disrotatory "inwards" ring opening then occurred to afford an acyclic 5-ethylpentadienyl ligand **347**.[451]

The fact that agostic systems should show a lower energy barrier to C–C bond cleavage, as seen in the latter example, was again illustrated by the same research group through the next example (depicted in Scheme 59) using the 1,5-COD ligand.[452]

The carbon–carbon bond cleavage of biphenylene was also observed while reacting biphenylene with $Cp^*M(ethylene)_2$ (M = Rh, Co). Similar to rhodium, the cobalt analog can lose two ethylene ligands affording a reactive cobalt center. Thus, with biphenylene, a reaction somehow reminiscent of the C–S bond cleavage of

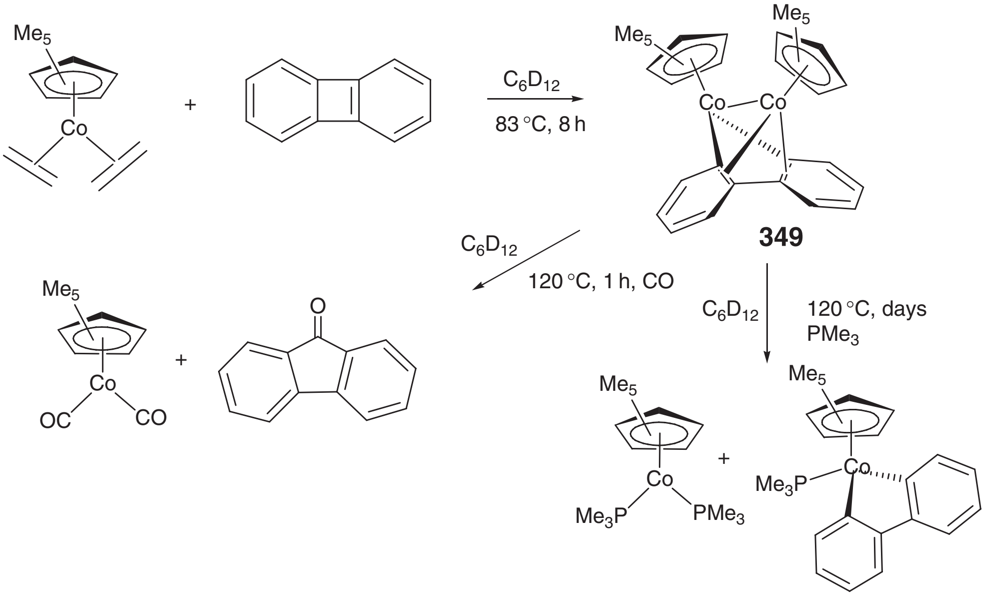


Scheme 58



348

Scheme 59



349

350

Scheme 60

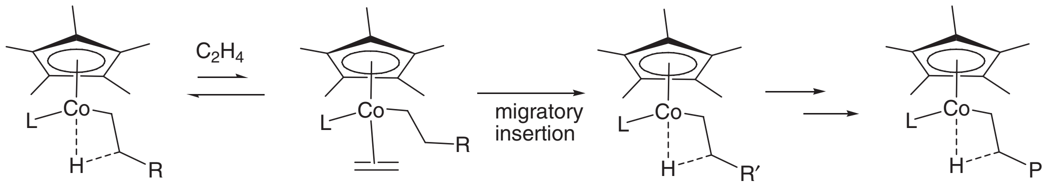
thiophene seen above occurred, affording a dinuclear species **349** in which a Cp*Co unit has formally been inserted into one C–C bond (Scheme 60).[453]

The reactivity of the dicobalt derivative **349** with nucleophiles was investigated. With carbon monoxide, it afforded fluorenone together with Cp*Co(CO)$_2$. The production of fluorenone could be rendered catalytic by reacting Cp*Co(CO)$_2$ with excesses of biphenylene under 500 torr of CO. However, as the reaction was run at 160 °C, decomposition of Cp*Co(CO)$_2$ occurred concurrently, and only three molecules of fluorenone per atom of cobalt could be obtained.

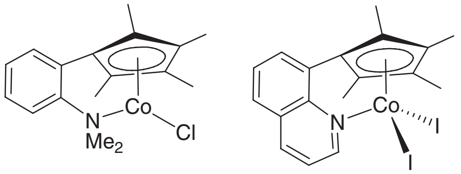
7.01.4.4.3.(iii) CpCo in polymerization of ethylene processes

The late metal d^6-Co(III) alkyl complexes are catalysts for the living polymerization of ethylene. It is generally accepted that the catalyst resting state is a β-agostic compound and that an alkyl olefin complex should be present in low equilibrium concentrations during the polymerization (Scheme 61).

Brookhart *et al.* found that an inverse kinetic isotope effect ($k_H/k_D = 0.48$) was taking place when comparing the polymerization of C_2H_4 versus C_2D_4. This is in contrast to normal isotope effect ($k_H/k_D > 1$) found in d^0-systems where agostic interactions are proposed to occur only in the transition state. This finding had mechanistic implications as this inverse isotope effect was assigned to the presence of a β-agostic Co—H—C (Co—D—C) interaction in the catalyst resting state.[454]



Scheme 61



351 **352**

Figure 65

Organocobalt complexes in which the Cp unit is intramolecularly bound to the cobalt center via extra coordination bonds such as **351** and **352** have been found to have moderate activities for the polymerization of ethylene (Figure 65).[416]

However, Brookhart showed that related sulfur-containing compounds **84** and **86** are far more active for this reaction.[128]

Thus, when the diiodide derivative was used in combination with MMAO ($300 < Al/Co < 1000$), turnover frequencies of ethylene polymerization of up to 630 TON h^{-1} were obtained, the catalyst being moreover stable for hours at RT. The analysis of the catalytic properties of this compound led to the conclusion that the catalyst resting state is a cobalt alkyl complex and not a cobalt alkyl ethylene complex. Thus, the cationic methyl acetonitrile or arylnitrile species were active for the polymerization of ethylene and, not requiring the presence of MMAO as under related reaction conditions, they led to polyethylene products with similar molecular weights and branching levels as compared to the polyethylene produced with the diiodide species.

7.01.4.4.4 Cobaltocene and cobaltocenium complexes

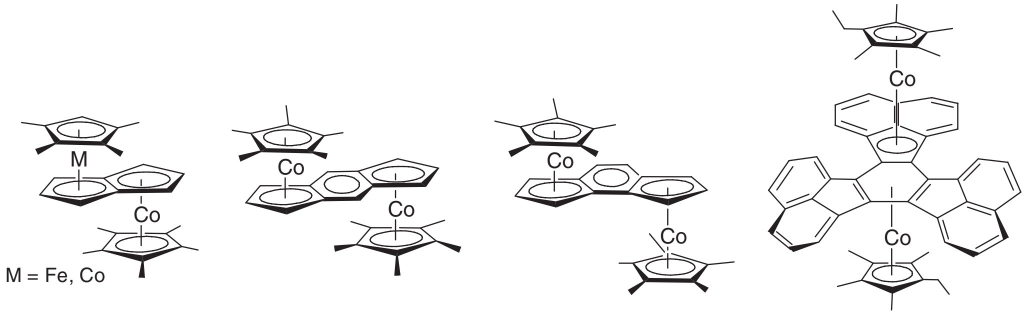
Cobaltocene compounds have been amply discussed in COMC (1982) and COMC (1995) which should be consulted for reviews. Some specific properties of cobaltocenium derivatives will be discussed in this section.

7.01.4.4.4.(i) Binuclear and polynuclear complexes

Manriquez *et al.* have investigated multi-decker complexes of the Fe, Co, and Ni triad in which intra- and intermolecular electronic interactions between the metal centers might result in interesting magnetic properties. Using pentalene, *s*-indacene, and *as*-indacene ligands, several homo-and heterobimetallic compounds **353–355a** were synthesized.[455] Recently, related dicobalt species were obtained with decacyclene hydrocarbons **355b** (Figure 66).[456]

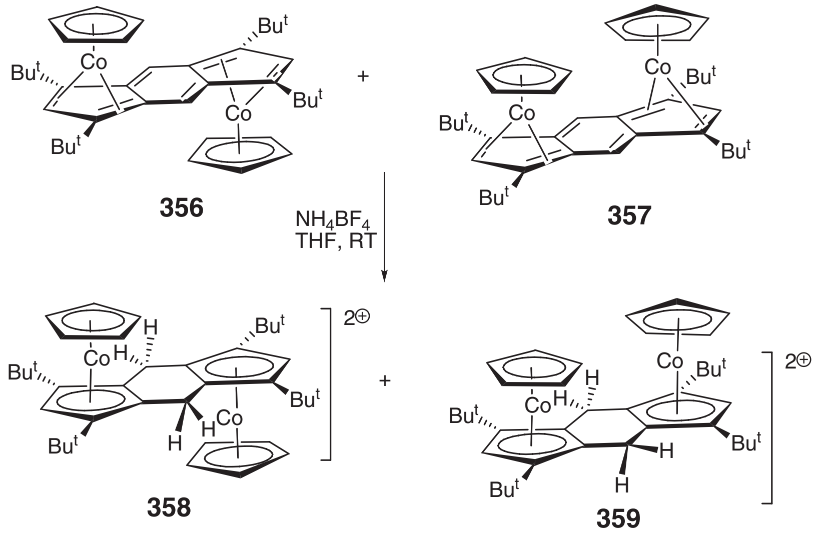
These paramagnetic complexes all exhibited Curie–Weiss behavior. The magnetic susceptibility of the dicobalt compounds **353** and **354** were consistent with intramolecular antiferromagnetic coupling of spins.

The Bu^t_4-*s*-indacene ligand afforded a mixture of *cis*- and *trans*-isomers of a di(cobalt–Cp) adduct.[457] These neutral compounds **356** and **357** interconverted in solution. The oxidation of these compounds by NH_4BF_4 afforded the corresponding dicobalticinium derivatives **358** and **359**, in which the *s*-indacene ligand has been protonated at the 4,8-positions. These new complexes did no more interconversion (Equation (60)).



353 **354** **355a** **355b**

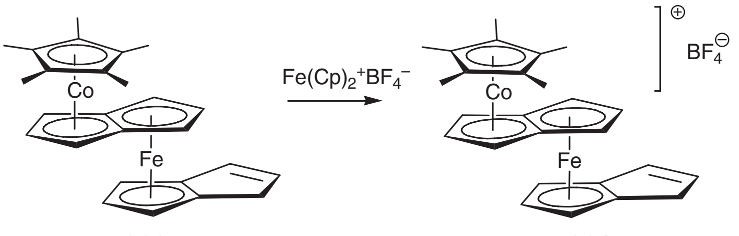
Figure 66



356 **357** **358** **359**

(60)

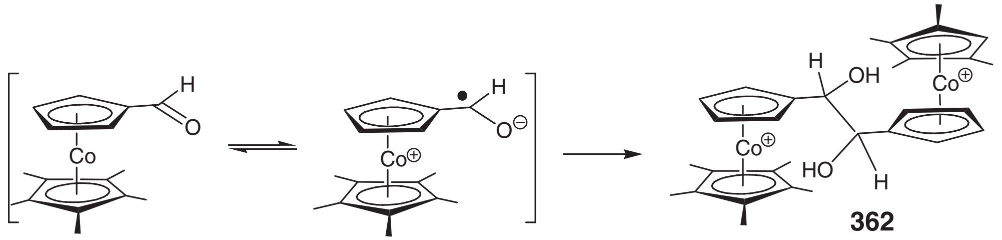
Prior to this work, Manriquez *et al.* published the synthesis of polydecker complexes **360 and 361a** that could somehow mimic one-dimensional (1D) organometallic polymers (Equation (61)).[458]



360 **361a**

(61)

Unfortunately, as a quadruple decker was obtained (which contained however only iron), no further results in this potentially very interesting area were published until then. A somewhat related dinuclear compound has been obtained while attempting the synthesis of 1-formyl-1′,2′,3′,4′,5′-pentamethylcobaltocene. This compound was only made *in situ* as it rearranged into dimeric species **362** by redox disproportionation with radical coupling (Equation (62)).[459]



(62)

The donor–acceptor heterodimetallic *Fe*,*Co*-compound **361b** displayed interesting NLO properties.[460]

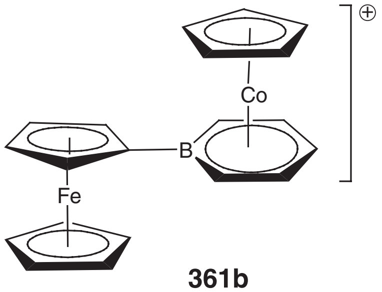
Mixed cobaltocenium ferrocene complexes **363** and **364** were synthesized in order to study their binding ability toward β-cyclodextrin (Figure 68).[461,462]

Both compounds exhibited three oxidation states. Cyclic voltammetry, in the presence of host β-cyclodextrin, revealed that the Fc^{+}–Co^{+} form is not bound to this ligand, the Fc–Co^{+} oxidation state forming a stable complex by inclusion of the ferrocene site, while the fully reduced form Fc–Co presenting two binding sites for the CD host.

A large series of heterobimetallic metallocenes in which a zirconocene moiety was associated with another metallocene (M = Rh, Mn, Ru, Fe, Co, Zr, Hf) in the same molecule were synthesized in order to check their ability to polymerize ethylene. The Zr–Co member **365** of this series was shown to be among the most active catalysts, and it also provided the most uniform polymers (Figure 69).[463]

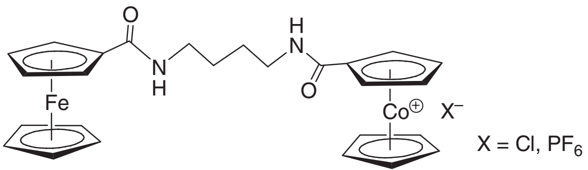
7.01.4.4.4.(ii) Anion receptors

During the last 15 years, there have been several studies dealing with the use of cobaltocenium derivatives as anion receptors. Indeed, the molecular recognition by abiotic receptors is an area of intense current interest. This is due to the known essential role played by anions in chemical and biochemical processes. Thus the design of abiotic and allosteric receptor molecules that can show binding cooperativity of guest species is a research field to which a large number of

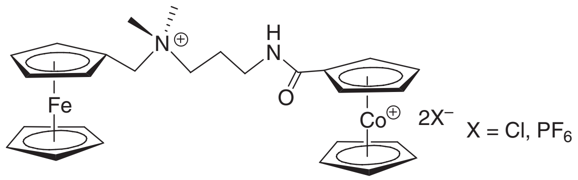


361b

Figure 67

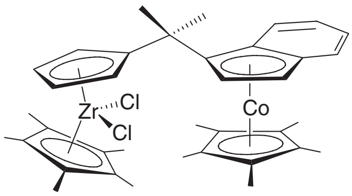


363



364

Figure 68



365

Figure 69

chemists of different backgrounds have taken part. As the recognition of anions can take place via hydrogen bonds and through the interaction with transition metals, organometallic chemistry has also been involved in this quest.

Many modifications of Cp rings of organocobaltocenium complexes have thus been performed with the aim of achieving selective anion complexations. It was anticipated that the presence of the positive charge on the cobalt atom would have a favorable effect upon the anion complexation. Beer's group has been one of the most active in this area of research as the first publications about this project were reported already in the late 1980s.[464]

The first important breakthrough was achieved with ester-linked polycobaltocenium macrocyclic ligand which bound bromide and allowed its electrochemical detection. Later on, amide-based derivatives of cobaltocenium proved not only to be easier to synthesize, but they also afforded good anion-recognition abilities. A selection of such species **366–375** is represented below (Figures 70–72). Either mono- or disubstituted Cp rings, mono-, di-, and trinuclear complexes have thus been synthesized.[465–469]

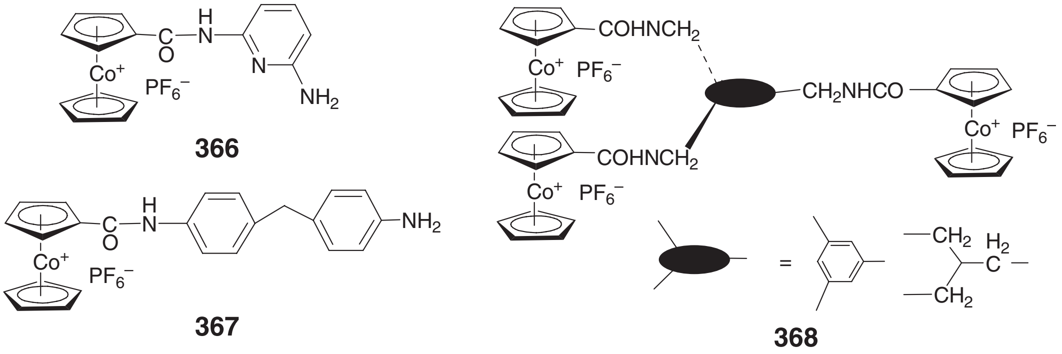
Proton NMR spectroscopy (through the perturbations of the chemical shift of the amide protons) and cyclic voltammetry (through the cathodic shift of cobaltocenium–cobaltocene reduction redox couple) were used to investigate the coordination of anions. These techniques revealed that the combination of the positively charged cobaltocenium unit together with an amide group are the essential components for the molecular and electrochemical recognition of anionic guest species. In these studies, the complexation of anions such as chloride, bromide, and dihydrogenophosphate were studied.

Crystal structure determinations of some of the compounds with guests such as chloride or bromide clearly showed the intra- and intermolecular hydrogen bonds that were involved in the halide coordination into the receptor.

Following similar reasoning, Beer *et al.* also synthesized cobaltocenium derivatives bearing macrocyclic units **376** capable of selectively recognizing cations.[470] It was expected that the presence of a cation in the macrocyclic unit would enhance the strength of anion complexation (Figure 73).

Indeed, in Figure 74, both Cl^- and Br^- would be more strongly bound to the cobaltocenium receptor in the presence of the complexed Na^+.

However, whereas the free receptor complexed and recognized electrochemically the halide anions, the introduction of sodium cations **380** had little effect on strengthening the halide anion complexing properties of the receptor.[471] The potassium complex **379** did not complex anions, because of the conformation of the rigid receptor which did not allow the access of the anion to the mid-CO–NH moiety. A novel potential molecular switch has thus been developed, whereby the binding of halide anions can be switched on and off via the absence or presence of potassium cations (Equation (63)).

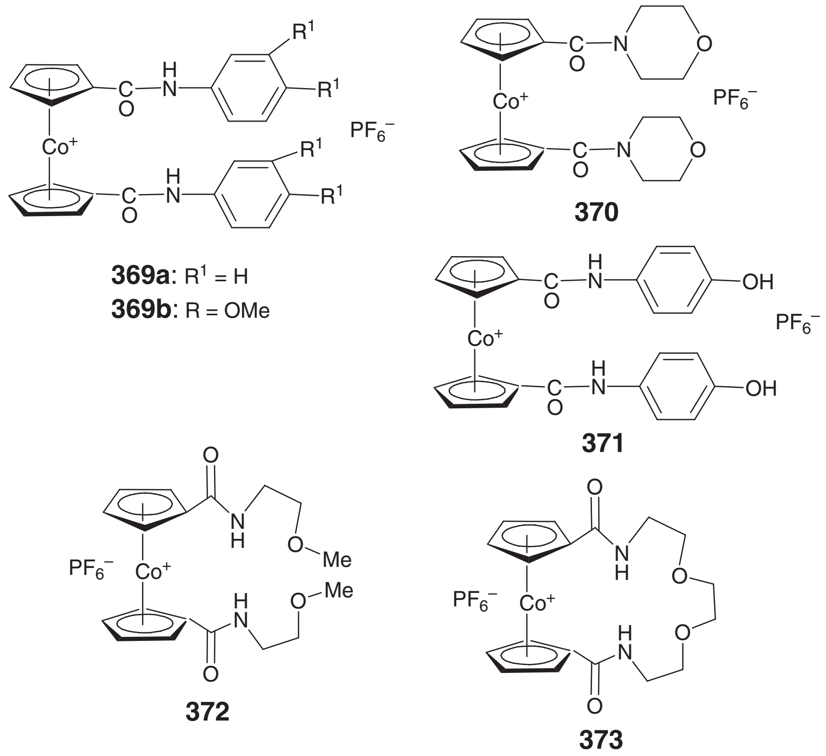


366

367

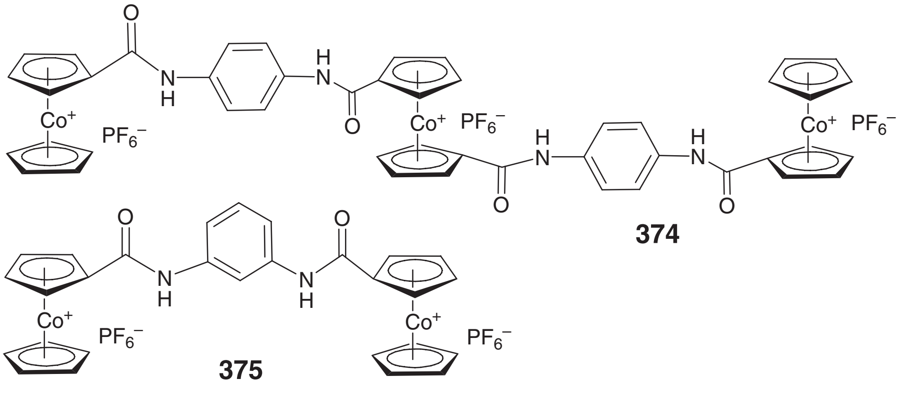
368

Figure 70



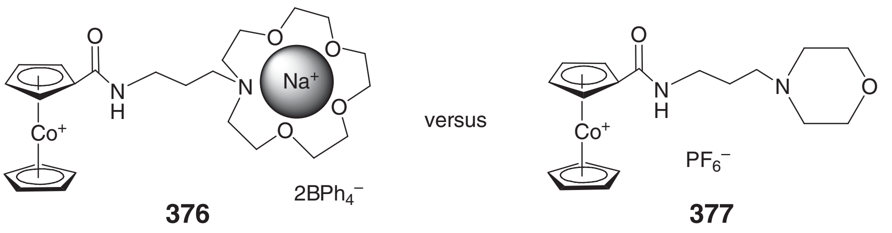
369a: R^1 = H
369b: R = OMe
370
371
372
373

Figure 71



374
375

Figure 72



376
377

Figure 73

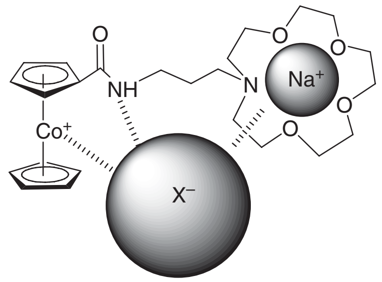
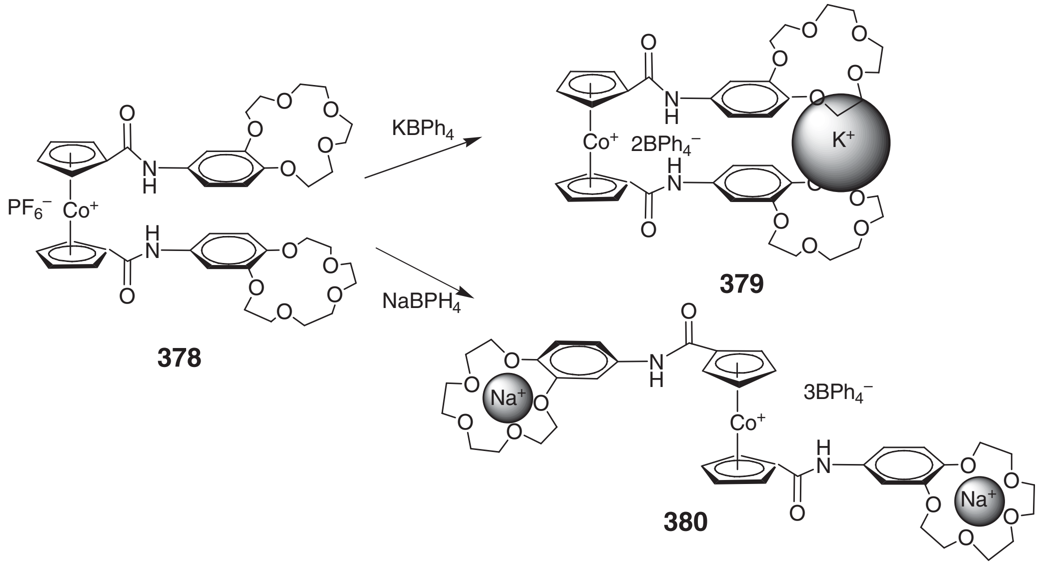


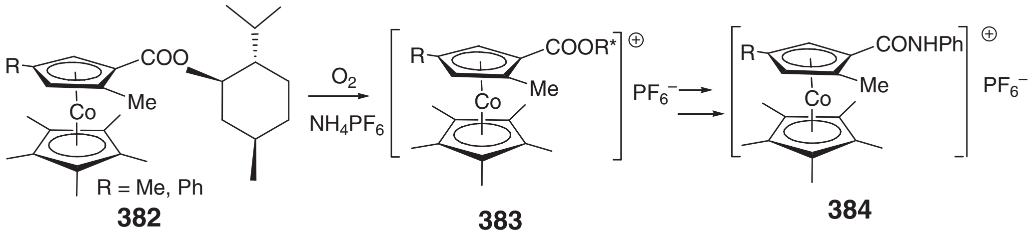
Figure 74



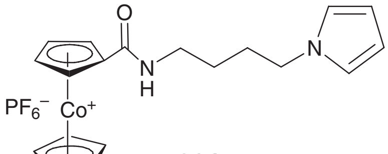
(63)

Cobaltocenium moiety covalently attached to a pyrrole group **381** also played the role of anion sensors[472] both in solution and when immobilized onto electrode surfaces by electropolymerization (Figure 75).[473]

Takahashi *et al.* obtained a chiral version of a cobaltocenium complex. This was achieved via what appeared to be the synthesis of the first examples of planar-chiral ionic metallocenes.[474] The amide cobaltocenium **384** was obtained as enantiomerically pure with the help of a (–)-menthyl group as the removable chiral auxiliary (Equation (64)).

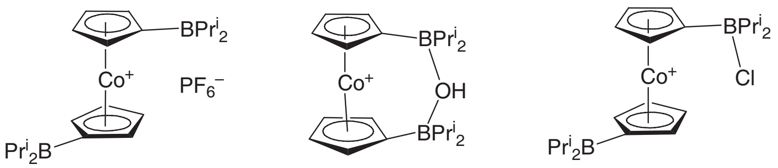


(64)



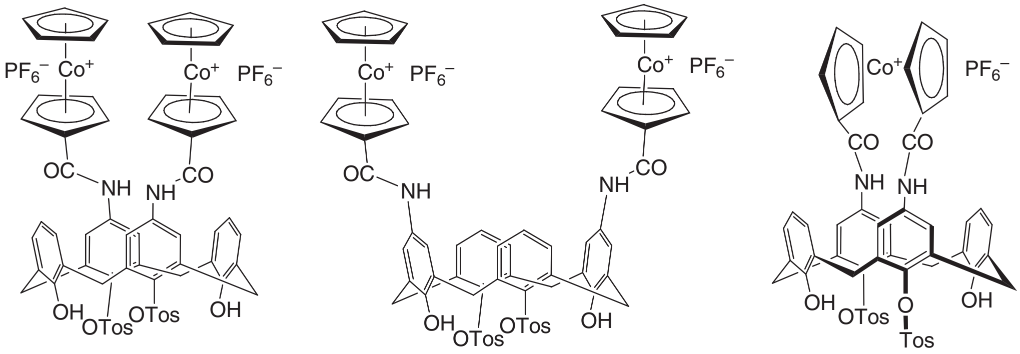
381

Figure 75



385 **386** **387**

Figure 76



388 **389** **390**

Figure 77

This latter compound behaved indeed as an anion receptor, which moreover could recognize (with modest ee however) the chirality of camphor-10-sulfonate.

1,1′-bis(dialkylboryl)cobaltocenium cations were also found to display useful behavior for anion complexation through coordination to one or both of the boron atoms.[475,476] Three situations can be encountered with these compounds: (i) a compound without specific interactions between the boron atoms and the anion, as in **385**; (ii) a case where the cobaltocenium makes an inverse chelate with an anion such as a hydroxide which was shown to be highly stable even in the presence of CF_3CO_2H **386**; and (iii) a case where the chloride anion is only bound to one boron atom **387** (Figure 76).

A further generation of anion receptors with related principles was also synthesized by Beer *et al.* They combined calix[4]-arene with cobaltocenium units **388–390** (Figure 77).[477–479]

These new systems displayed remarkable anion thermodynamic stability and selectivity trends. These were dependent upon the organization of the upper-rim anion-recognition site, the efficiency of which was dictated by the relative position of the tosyl substituents (Table 2).

These cobaltocenium calix[4]-arene receptors proved to be very efficient receptors, especially for carboxylate anions (see Table 3).

Compound **391** (in which the tosylate was substituted by methyl groups), which seemed to be less selective for carboxylate than **388** and **390**, proved however to be a good receptor for the adipate dianion. No crystal structure of the resulting host–guest molecule could be obtained. However, a likely arrangement of the dicarboxylate unit in **391** based upon ^1H NMR data is as represented in Figure 78.

7.01.4.4.4.(iii) Dendrimeric cobaltocenium derivatives

Dendrimeric structures containing cobaltocenium units have been synthesized during the last decade. This interest partly arose because of the positive charge of these species, which might attract anionic guests. Thus, Astruc *et al.* described the synthesis and the anion-receptor ability of a polycationic nonacobaltocenium dendrimer **392** (Figure 79).[480] This compound has been shown to be efficient for sensing small inorganic anions such as $H_2PO_4^-$, HSO_4^-, and Cl^- via cyclic voltammetry and ^1H NMR.[481]

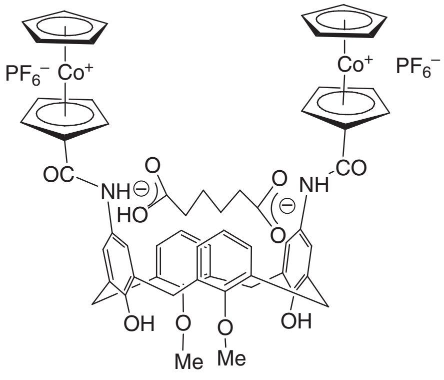
Table 2 Stability constant data for some cobaltocenium derivatives

	Association constants K_a (dm^3 mol^{-1})			
Compounds	*Cl^-*	*Br^-*	*$H_2PO_4^-$*	*References*
377	400 (CD_3CN)	270 (CD_3CN)		470
376	3200 (CD_3CN)	1600 (CD_3CN)		470
381			1190 ($(CD_3)_2SO$)	472
366	60 (CD_3CN)		250 ($(CD_3)_2SO$)	467
367	750 (CD_3CN)		No binding	467
375	30 ($(CD_3)_2SO$)		Precipitation	467
371	32 ($(CD_3)_2SO$)	60 ($(CD_3)_2SO$)		466
373	250 ($(CD_3)_2SO$)	100 ($(CD_3)_2SO$)		466
372	20 ($(CD_3)_2SO$)	15($(CD_3)_2SO$)		466
369a	35 ($(CD_3)_2SO$)	25 ($(CD_3)_2SO$)	320 ($(CD_3)_2SO$)	468
369b	30 ($(CD_3)_2SO$)	25($(CD_3)_2SO$)		468
388	weak ($(CD_3)_2SO$)	25 ($(CD_3)_2SO$)	3100 ($(CD_3)_2SO$)	479
389	400 ($(CD_3)_2SO$)	25 ($(CD_3)_2SO$)	2500 ($(CD_3)_2SO$)	479
390	70 ($(CD_3)_2SO$)	25 ($(CD_3)_2SO$)	6380 ($(CD_3)_2SO$)	479

Table 3 Anion stability constant data for cobaltocenium calix[4]-arene receptors (K_a/dm^3 mol^{-1}) in $(CD_3)_2SO$.[479] Reprinted with permission from Beer, P. D.; Hesek, D.; Nam, K. C.; Drew, M. G. B. Organometallics 1999, 18, 3933–3943. [a]2002 American Chemical Society

Anions	**388**	**389**	**390**
$MeCO_2^-$	21 000	820	41 520
$PhCO_2^-$	4025	620	38 400
$PhCH_2CO_2^-$	8100	830	22 270
β-$NfCO_2^-$	2800	610	19 750

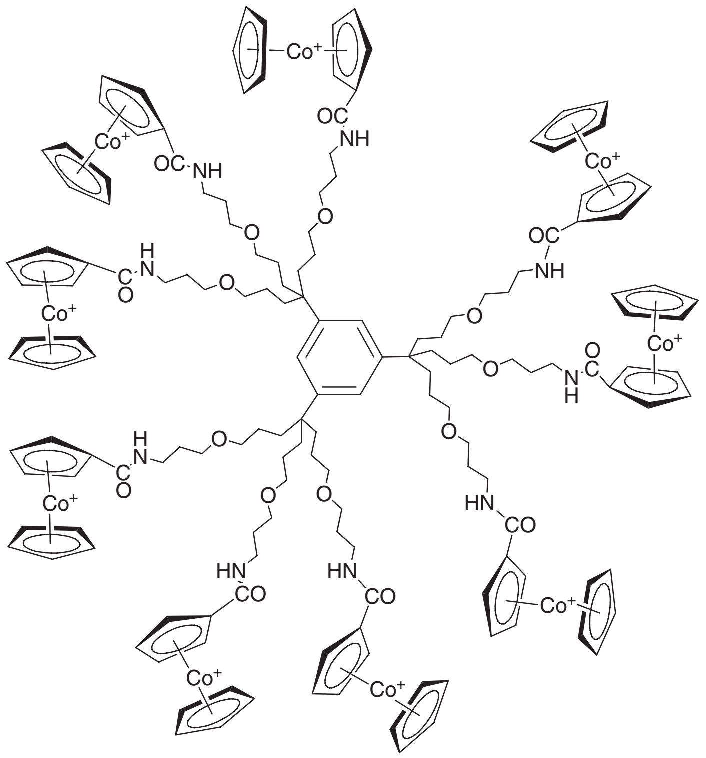
Error estimated to be <10%.



391

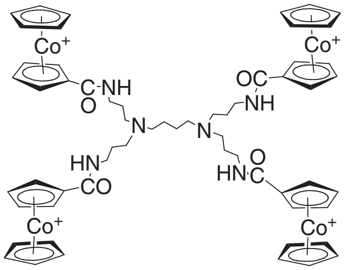
Figure 78

A series of poly(propyleneimine) dendrimers functionalized with 4, 8, 16, 32 peripheral cobaltcenium subunits was prepared. The compound with four Co nuclei, **393**, and the one with 32 cobalt atoms, **394**, are presented below (Figures 80 and 81). The reduced form of these complexes precipitated on the electrode surface.[482] In the presence of a fourfold excess of β-dextrin, the reduction of the cobaltocenium units was fully reversible, this being an indication of the formation of inclusion complexes between the cobaltocene units and β-dextrin.[483]



392

Figure 79

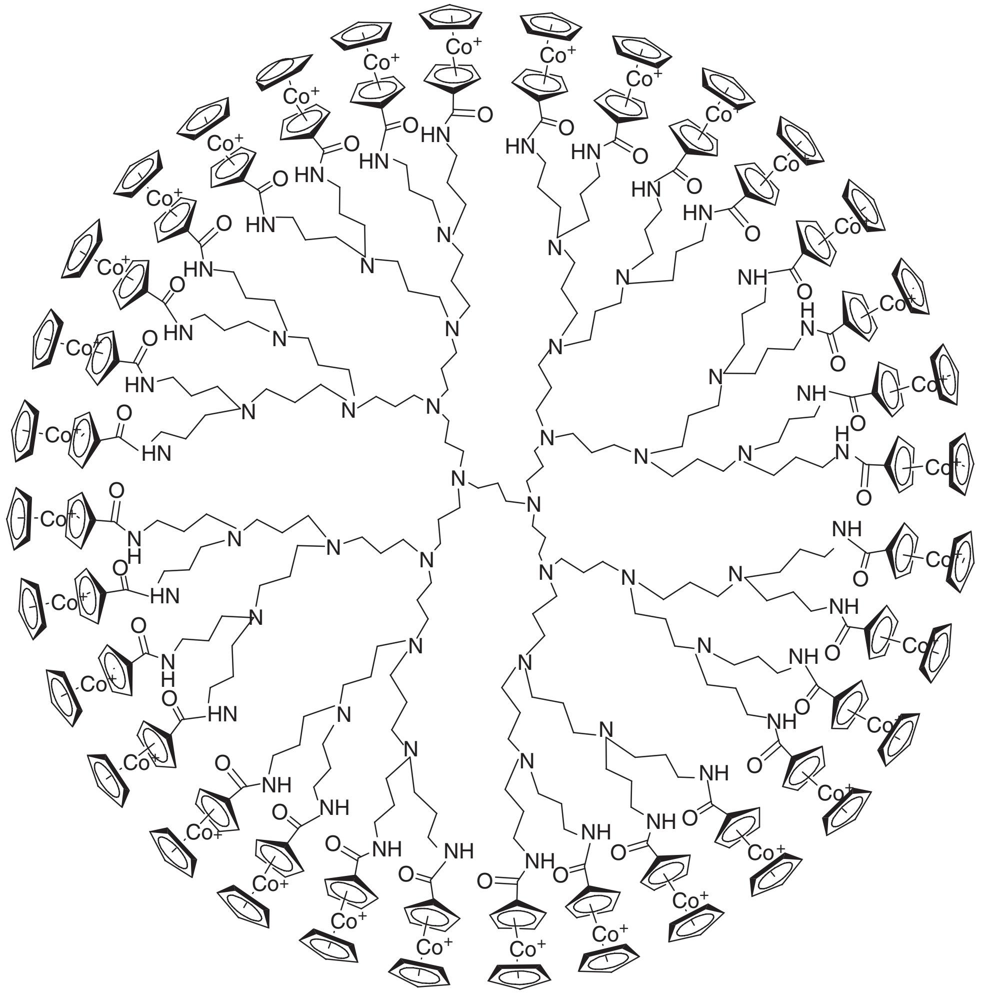


393

Figure 80

7.01.5 Cluster Complexes of Cobalt

The word "cluster" in this section will refer to complexes of cobalt containing three or more metals for which there is, moreover, evidence for the existence of metal–metal bonds in the complex. In addition, for such compounds to be reported in this section, the organometallic nature of the cluster (the direct interaction between one of the cobalt atoms and at least one carbon atom) must be present. In fact, purely inorganic cobalt clusters became more numerous until recently. Some examples will be described at the end of this section; however, these compounds will not be covered in any comprehensive fashion. Polynuclear clusters, which contain other metal atoms associated to cobalt, are the subjects of another chapter of this work.



394

Figure 81

The amount of work devoted to cobalt clusters seems to have dramatically decreased since COMC (1995) has appeared. Indeed, whereas in the previous report cobalt clusters were a wealthy research field, the number of research articles dealing with either new synthetic work involving Co clusters or various applications of these complexes has decreased significantly during the last decade. In fact, there have been relatively few reports of new types of cobalt clusters as compared to the previous period covered in COMC (1995). Most of what was achieved concerned reactions on already-described basic structures.

Some specific aspects of the cluster chemistry involving cobalt atoms have been reviewed.[484–487]

7.01.5.1 Cluster Complexes with Three Cobalt Atoms

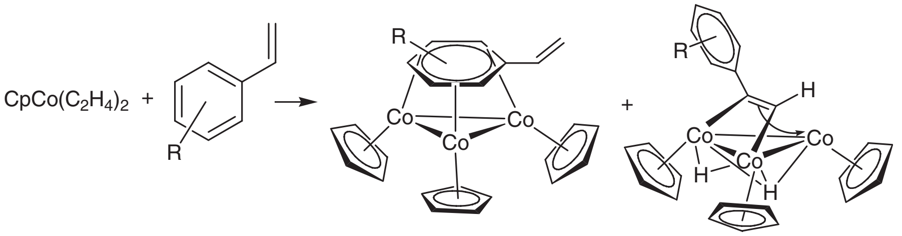
7.01.5.1.1 Synthesis of Co_3 Clusters

The isolation (in rather low yield) of the *all*-bridging CO isomer $CpCo_3(\mu_3\text{-}CO)_3$, **395**, together with the known $CpCo_3(\mu_2\text{-}CO)_2(\mu_3\text{-}CO)$ was achieved by Geiger *et al.*[488] **395** displayed near-C3 symmetry with *all*-Cp being displaced to one side of the molecule, one Co–Co bond being 1.2 pm shorter than the other two. This compound was also stable in the 49-electron form (the CO ligands were still *all*-bridging) but the 47-electron cation isomerized to the $CpCo_3(CO)(\mu_2\text{-}CO)_2^+$ cation, **396**.[489]

The reduction of $Cp^*Co(acac\text{-}O,O')$ with potassium metal in pyridine as solvent resulted in the formation of Cp^*Co(pentamethyl-η^4-cyclopentadiene) and to the trinuclear cluster: $(Cp^*Co)_3(\mu_2\text{-}(C_5H_4N)(\mu_3\text{-}H)$, **397**, containing an orthometallated pyridine ligand.[490]

Several syntheses of Co_3-based clusters have been performed via the well-known reaction of $Co_2(CO)_8$ with various reagents capable of delivering a μ_3-bridging atom. Thus, $Cl_3C\text{–}Y$ with $Y = p\text{-}(Cl_3C)_2C_6H_4$,[491] $P{=}O(OR)_2$,[492] or $C(OH)CH\text{–}C{=}O\text{–}CH_3$[493] have led to $Y\text{–}CCo_3(CO)_9$ derivatives when treated with $Co_2(CO)_8$. A silatrane derivative $(Si(OCH_2CH_2)_3N)$ was obtained also via direct reaction of the same starting material with the hydrosilatrane.[494] The reaction between $Co_2(CO)_8$ and $HC{\equiv}CR$ (where $R = CH_2NH_2$, $C_6H_4NH_2$, $CONH_2$, $COCH_3$) gave the corresponding methylidyne clusters $Co_3(CO)_9(\mu_3\text{-}CR)$, **398**.[495] With $3\text{-}Cl_3C\text{–}NC_5H_4$, $NC_5H_3\text{–}3\text{-}CCo_3(CO)_9$, a cluster functionalized with a pyridine, was obtained. Complexation with Pd(II) afforded a compound that unfortunately could not be characterized by X-ray diffraction studies.[496]

While attempting the synthesis of (μ_3-arene)Co_3 clusters (see Section 7.01.5.1.3.) through the reaction between styrenes and $CpCo(C_2H_4)_2$, Wadepohl *et al.* observed, besides the formation of the expected product **399**, the double C–H activation reaction at the vinyl unit **400** (Equation (65)).[446]

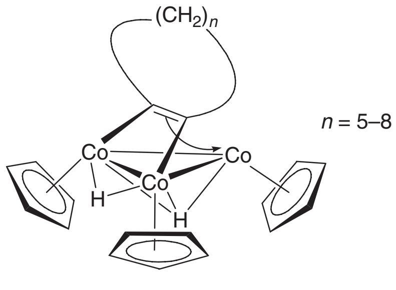


399 **400**

(65)

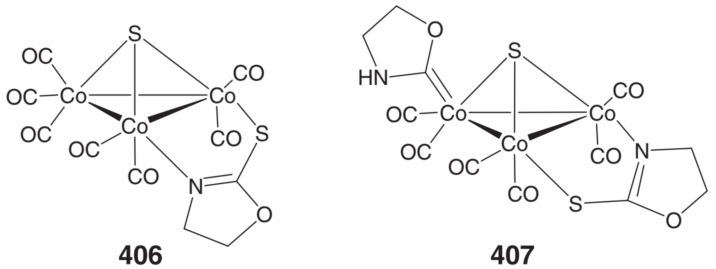
This reaction could be reproduced with several carbocyclic alkenes **401** with the same electron-rich reagent, but better results (as far as selectivity was concerned) were obtained with cobaltocene reduced with potassium, Cp_2Co/K (Figure 82).[497]

A combination of sulfur-capped Co_3 clusters was synthesized with $PPh_2(SPh)$ and $Co_2(CO)_8$, $[Co_3(\mu_3\text{-}S)(\mu_3\text{-}PPh_2)(CO)_7]$ **402**, $[Co_3(\mu_3\text{-}S)(\mu_3\text{-}PPh_2)(CO)_6(PPh_3)]$ **403**, and $[Co_3(\mu_3\text{-}S)(\mu_3\text{-}PPh_2)(CO)_5(PPh_3)_2]$ **404**. Insertion of the alkyne $PhC{\equiv}CH$ into a P–Co bond of a PPh_2 unit bridging two cobalt atoms was observed with these latter compounds.[498] With perfluorodiphenyl disulfide, $Co_3(\mu_3\text{-}S)(C_6F_5)(CO)_8$ **405** containing an aryl–metal σ-bond was obtained.[499] With the heterocyclic thioamide $S{=}COCH_2CH_2NH$, this reaction gave two products **406 and 407**, one of them containing a terminal carbene ligand **407** (Figure 83).



401

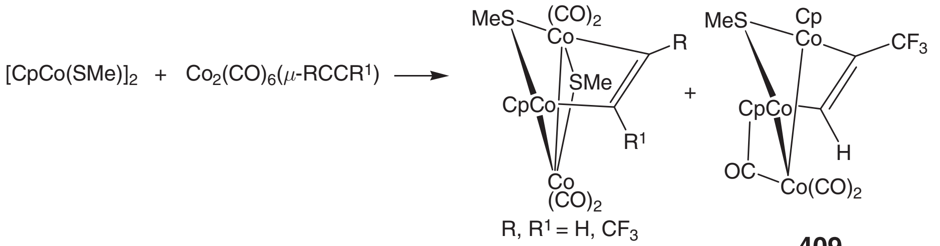
Figure 82



406 **407**

Figure 83

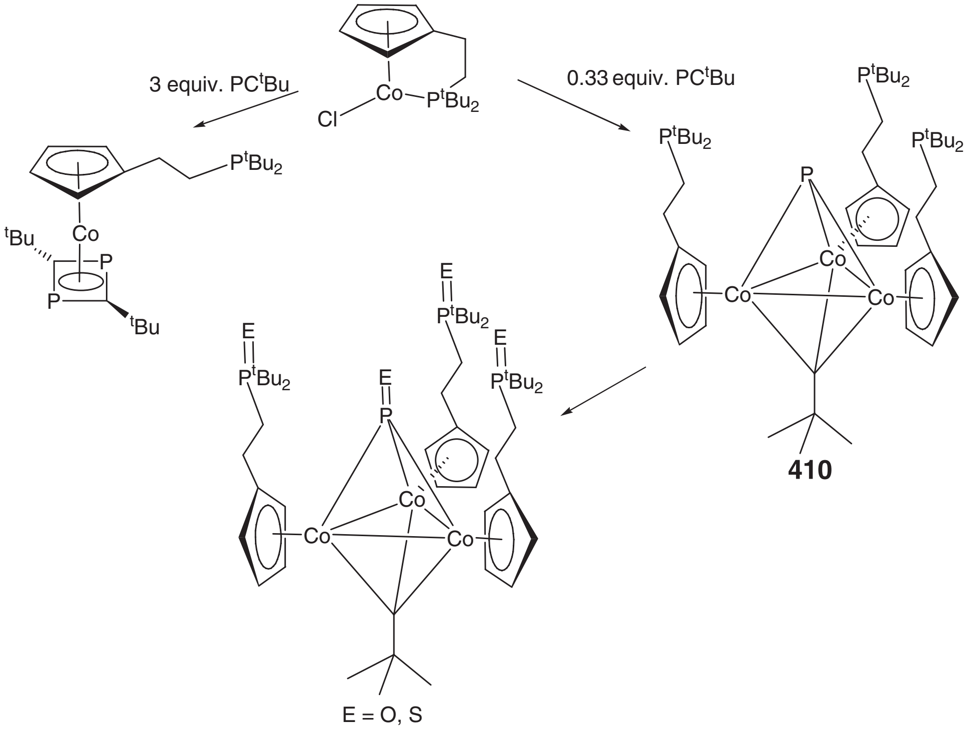
A route to new clusters 408 and 409 has been obtained through the reaction between alkynedicobalt hexacarbonyl complexes and Co dimer derivatives (Equation (66)).[500]



408 **409**

(66)

The reaction between the monometallic cobalt(II) [Cp′CoCl] (Cp′ = $C_5H_4CH_2CH_2P^tBu_2$) complex and a phosphaalkyne led to an original synthesis of a *P*-capped Co_3 cluster 410 via the cleavage of the P–C triple bond. This reaction was however very much dependent upon the stoichiometry used, as depicted in Scheme 62.[501] In the



410

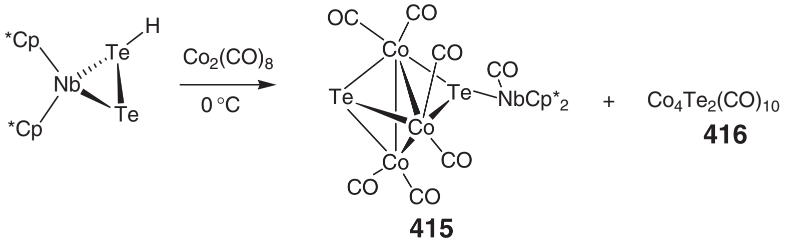
E = O, S

411

Scheme 62

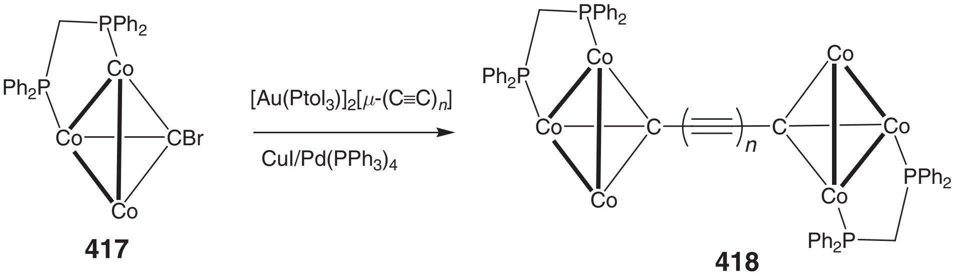
presence of molecular oxygen or elemental sulfur, the oxidation of *all*-phosphorous atom was observed, affording the correspondent molecule **411** with *all*-P atom being substituted by P=O or P=S units.

The co-thermolysis of $Cp''Co(CO)_2$ ($Cp'' = C_5H_3Bu^t{}_2$-1,3) and P_4 afforded $[(Cp''Co)_3(\mu^3\text{-}P)_2]$, **412**, together with a Co_4 cluster and a Co_2 species. The oxidation of the Co_3 cluster with gray selenium led to a mixture of two products $[(Cp''Co)_3(\mu^3\text{-}PSe)_2]$, **413**, and $[(Cp''Co)_3(\mu^3\text{-}P)(\mu^3\text{-}PSe)]$, **414**.[502] A ditelluride Co_3 cluster **415** was formed together with a known Co_4 cluster while reacting the tellurium-transfer reagent Cp^* $Nb(Te_2H)$ with $Co_2(CO)_8$ (Equation (67)).[503]



(67)

A few examples of modifying existing $RCCo_3L_n$ clusters bearing a reactive functional group at the carbyne-bridging atom have been reported. Reaction of $HCCo_3(CO)_9$ with $O(SiMe_2H)_2$ and $C_6H_4(SiMe_3H)_2$ led to products for which one or both SiH groups have reacted with the bridging carbyne CH unit, thus giving raise to mono- or dicluster complexes.[504] A somewhat similar procedure starting with $Co_3(\mu_3\text{-}CBr)(\mu\text{-}dppm)(CO)_7$, **417**, which was reacted with $[Au(P(Tol)_3]_2[\mu\text{-}(C{\equiv}C)_n]$ (n = 2–4), has given $[Co_3(\mu\text{-}dppm)(CO)_7]_2[\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_nC]$, **418**, in which the Co_3 cluster unit acts as end cap to the carbon chain (Equation (68)).[505]



(68)

The reaction of $Co_3[\mu_3\text{-}C(C{\equiv}C)_2Au(PR_3)](\mu\text{-}dppm)(CO)_7$ with $I(C{\equiv}C)_3I$ gave the bis(cluster) $[Co_3(\mu(dppm)(CO)_7]_2[\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_7C]$, **419**, which contained a C_{16} chain that was supposed to be the longest odd-numbered carbon chain linking two metal centers.[506] This C_{16} chain was close to linear, with a maximum deviation of 10.3° from linearity at C3 (see Figure 84). The C···C separation between the two Co_3 units was 19.176(8) Å, which is 0.15 Å shorter than the sum of the C–C distances.

Co_3 cluster grafted on a polyacrylate resin has been obtained through the free-radical-initiated polymerization of $Co_3(CO)_9[C(CO)OCH_2CH_2O(CO)CH{=}CH_2]$, **420**, with mixtures of methyl methacrylate and butyl acrylate. The $Co_3(CO)_9$ units remain fully intact in the thus-obtained films under ambient atmospheric conditions.[507] $[\mu_3\text{-}RC(O)OC]Co_3(CO)_9$ (R = Ph, ^{t}Bu) have been transformed to the corresponding $(\mu_3\text{-}RC)Co_3(CO)_9$ derivatives by silica-mediated decarboxylation.[508]

Complex cobalt carbonyl ligand clusters have been described in COMC (1995). In this respect, $[Co_3(CO)_9(\mu\text{-}CCO_2)]^-$, **421**, has been used to form larger metal ensembles through a template-like coordination of the carboxylate groups to the edges of a $[M_4O]^{6+}$ (M = Co, Zn) unit.[509] Some of these compounds, after partial or complete thermolysis, have been used as catalysts for selective hydrogenation of 2-butenal to afford 2-butenol.[510]

7.01.5.1.2 Ligand-substitution reactions on previously reported Co_3 clusters

Starting from $MeCCo_3(CO)_9$, **422**, the electron-transfer chain-catalyzed synthesis of Co carbonyl clusters in which one to three CO ligands have been selectively substituted by ferrocenyldiphenylphosphine ligands has been achieved using electron-reservoir complexes [Fe(I)Cp(arene)] as electrocatalysts.[511] One or two CO's of the same starting material could also be substituted by the diphenyl-2-thienylphosphine ligand; however, the ligand was coordinated to the Co atoms via the phosphorous atoms only – no coordination of the sulfur atom and, consequently, no weakening of the C–S bond being observed.[512]

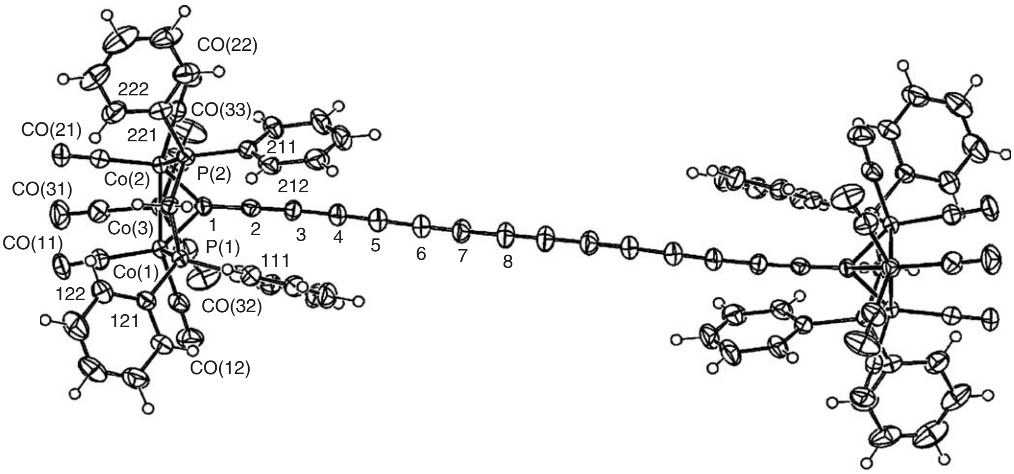
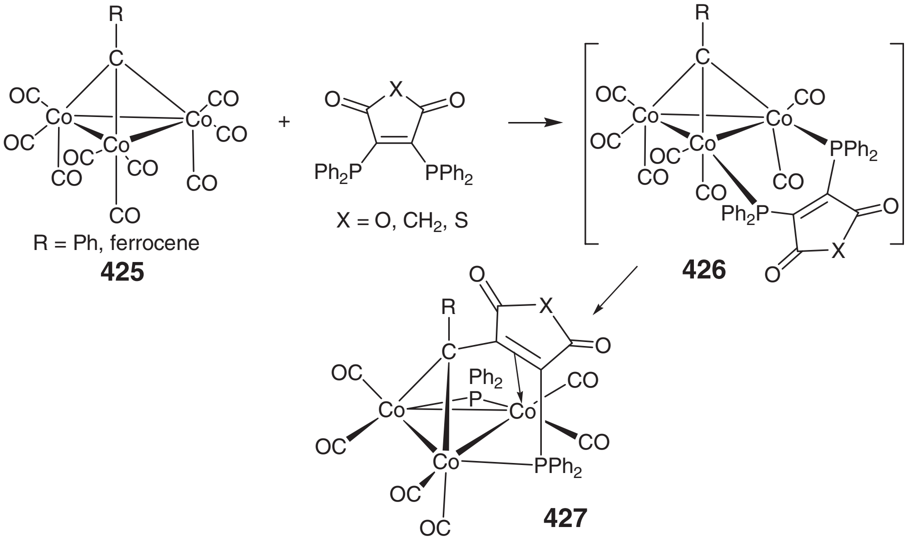


Figure 84 ORTEP view of $[Co_3(\mu\text{–}(dppm)(CO)_7]_2[\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_7C]$ **419**. Reproduced from Antonova, A. B.; Bruce, M. I.; Ellis, B. G.; Gaudio, M.; Humphrey, P. A.; Jevric, M.; Melino, G.; Nicholson, B. K.; Perkins, G. J.; Skelton, B. W., *et al*. *Chem. Commun.* **2004**, 960–961, with permission from the Royal Society of Chemistry.

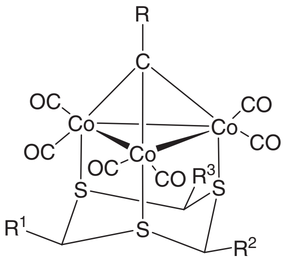
The substitution of CO ligands in various μ_3-carbido-capped tricobalt carbonyl complexes such as $XCCo_3(CO)_9$ (X = H, Br, Ph), with bidentate diphosphine ligands, such as dppm,[513–515] *cis*-$Ph_2PCH{=}CHPPh_2$[516] and 1,1′-bis(diphenylphosphinoferrocene)(dppf),[517] has been realized by thermolysis, oxidative decarbonylation with Me_3NO, and electron-transfer chain catalysis using sodium benzophenone ketyl. The bidentate ligands were found to bridge two adjacent cobalt centers via axial coordination as was found earlier for 1,2-bis(diphenylphosphino)ethane.[518] The result with dppf was markedly different from the result reported at the same time by a different group who found that the same bidentate ligand led to the formation of a hexanuclear species in which the dppf bridged two $PhCCo_3(CO)_8$ units.[491]

With tridentate crown thioethers, the same starting material led to two different substitution reactions depending upon the nature of the tridentate ligand.[519] Thus, trithiane, the smallest six-membered ring ligand, invariably occupied the axial coordination sites on the three cobalt atoms, regardless of the nature of the bridging alkylidyne ligand or the bulkiness of the substituents on the trithiane 423. Some intermolecular hydrogen bonds between axial C–H units of the trithiane and CO of neighbouring molecules might somehow explain the stability of the complexes. On the other hand, the trithiacyclononane was chelating one single cobalt atom 424 (Figure 85).

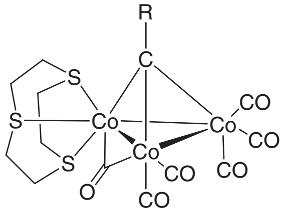
An unexpected rearrangement was observed while studying the substitution reaction between $PhCCo_3(CO)_9$, 425, and 2,3-bis(diphenylphosphine)maleic anhydride (bma), as the facile activation of the μ_3-benzylidyne-capping ligand leading to a μ_2-benzylidene bridge was observed in 427 (Equation (69)).[520–524]



425 **426** **427** (69)



423



R = Me, Ph

424

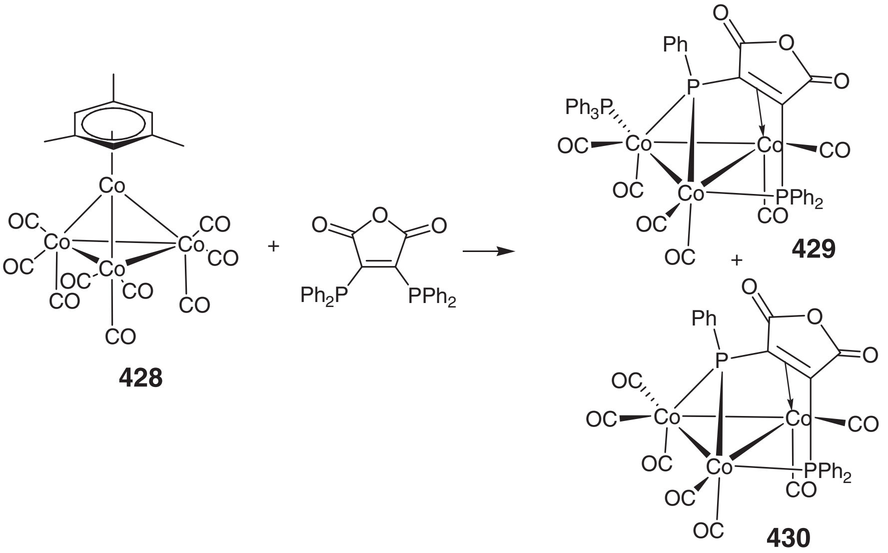
R	*R*[1]	*R*[2]	*R*[3]
Cl	H	H	H
Me	H	H	H
Ph	H	H	H
Cl	Me	H	H
Me	Me	H	H
Ph	Me	H	H
Cl	Me	H	H
Me	Me	Me	H
Ph	Me	Me	H
Cl	Me	Me	Me
Me	Me	Me	Me
Cl	CH_2Ph	H	H
Me	CH_2Ph	H	H
Ph	CH_2Ph	H	H
Cl	CH_2Ph	CH_2Ph	CH_2Ph
Me	CH_2Ph	CH_2Ph	CH_2Ph
Ph	CH_2Ph	CH_2Ph	CH_2Ph

Figure 85

Reaction of this tricobalt *arachno*-cluster with PMe_3 led ultimately to the substitution of two CO ligands, while the C═C to Co bond of the maleic anhydride was not substituted.[525,526]

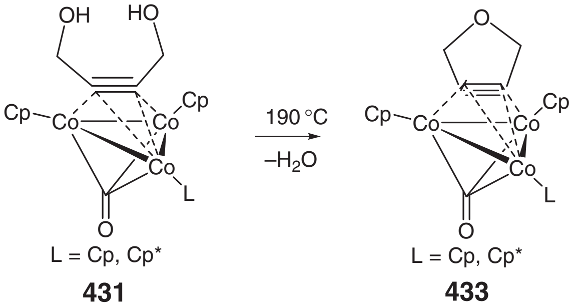
The reaction between the tetranuclear cluster $Co_4(CO)_9$(mesitylene), **428**, and the same diphosphine bma, afforded a mixture of products, two of them **429** and **430** (in low yield) being trinuclear species together with two dinuclear rearranged products. Here too, P–Ph bond cleavage and the transfer of the phenyl group to a transient μ_2-PPh_2 group evidenced the activation of the bisphosphine ligand (bma) by Co clusters (Equation (70)).

Heating the alkyne complexes $(CpCo)_3(CO)(RC{\equiv}CR)$, **431**, at 190 °C generally led to the bis(carbyne) complexes, $(CpCo)_3(\mu^3\text{-}CR)_2$, **432**. When $RC{\equiv}CR$ = 1,4-dihydroxy-2-butyne, an unusual reaction occurred as the formation of a furyne derivative was observed, the carbocyclic ring being stabilized by coordination to the Co_3 unit (Equation (71)).[527,528]



428 **429** **430**

(70)



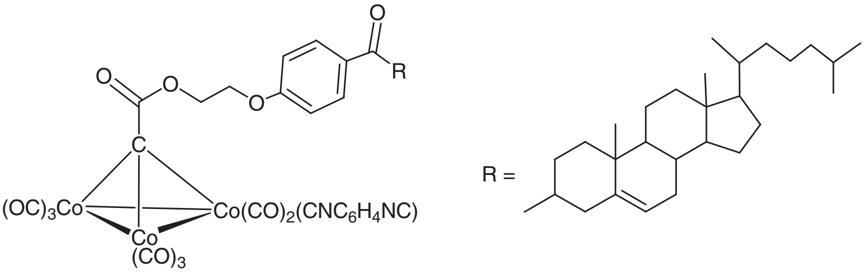
431 **433**

(71)

Electrochemical properties of the obtained complex are similar to those of non-cyclic analogs.

An amphiphilic polynuclear Co_3 cluster was synthesized by linking a $Co_3(CO)_9$ to a hydrophobic cholesterol framework to which a polar head was introduced by substituting one CO by an isocyanide derivative bearing a hydrophilic functional group **434** (Figure 86).[529]

The structure of the cluster was established by X-ray crystallography, which showed that the total length of the molecule was up to 4 nm. Organometallic-containing films on water, stable between 10 and 20 °C, were prepared. Transferred films were performed on hydrophobized solids (mica, glass, quartz, silicon wafers). Their structural characterization demonstrated the formation of stable, highly organized crystals.



434

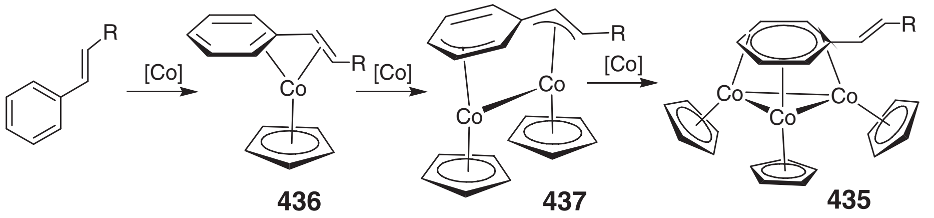
Figure 86

7.01.5.1.3 Co_3 clusters with a face-capping cyclopolyene ligand

Arene-capped trinuclear cobalt clusters have been briefly mentioned in COMC (1995) as this field of cobalt cluster chemistry started in the early 1990s.[530]

As mentioned above, the treatment of arene derivatives by electron-rich cobalt(I) complexes such as $CpCo(C_2H_4)_2$ or $CpCo(C_6Me_6)$ led generally to good yields of $[(CpCo)_3(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-arene})]$, **435**.

A mechanism of the formation of such species was proposed earlier,[531] and this hypothesis was strengthened later by the isolation of key intermediates such as a mononuclear diene complex, **436**, having a $\beta,\alpha,1,2\text{-}\eta^4$-alkenylarene ligand (Equation (72)).[532]



$[Co] = CpCo(C_2H_4)_2$ or $CpCo(C_6Me_6)$

(72)

Substitution of the arene by various groups might be detrimental to the yield of this reaction, especially when the arene rings are substituted at the *ortho*- and *para*-positions.[533]

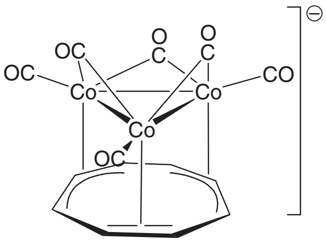
A trinuclear Co cluster with a cyclooctatetraene capping the Co_3 face, **438** (Figure 87), was obtained via the reduction of the tetranuclear cluster complex $[Co_4(CO)_3(\mu_3\text{-}CO)_3(C_8H_8)L_2]$, **439** (L = CO or cyclopolyene ligand) (see Section 7.01.5.2), with $Li[HBEt_3]$.[534]

The product was remarkably more stable than the corresponding binary carbonyl $[Co_3(CO)_{10}]^-$, this increased stability being very likely due to the capping ligand.

The effect of facial coordination of benzene to a trinuclear cluster has been studied by statistical analysis of their crystal structures and by DFT calculations. The arene ligand was thus found to be considerably expanded with respect to the free arene and it showed a small but significant Kekulé distortion. DFT calculation led to the conclusion that facial benzene exhibits substantial cyclic electron delocalization.[535]

The tricobalt clusters of the type $(CpCo)_3(\mu_3\text{-arene})$, **435**, could only be synthesized with alkenylbenzenes as the facial ligands (see the mechanism of synthesis above). The exocyclic C=C bond did however play no role in the stabilization of these complexes. Indeed, the catalytic hydrogenation of this C=C unit in the side chain was achieved and the corresponding reduced compounds were perfectly stable as was evidenced by their crystal structure analyses, which showed a very similar geometry for the new complexes. In solution, hindered rotation of the μ_3-arene was observed.[536]

Nucleophilic substitution occurred on the capping arene ring but only when using fluoride as leaving groups. Thus, the treatment of the compounds $(CpCo)_3(\mu_3\text{-arene})$, in which the arene was the $p\text{-}F_6H_4CHMe{=}CH_2$, with $LiBHEt_3$ or LiPh led to the corresponding compounds in which the fluoride ion was substituted by H and Ph, respectively.[537]



438

Figure 87

7.01.5.1.4 Polyhydride Co_3 clusters

A compound somewhat related to a polyhydride was obtained while studying the reaction between $[Cp^*CoCl]_2$ and BH_4^-, as the product was a Co_3 cluster formulated as $Cp^*{}_3Co_3(\mu_3\text{-HBH})_2$, **439a**. Its crystal structure analysis did not allow to locate the bridging hydrogens; however, there was some spectroscopic evidence that these protons should be bridging a cobalt and a boron atom (Figure 88).[538]

While investigating the chemistry of low-valent cobalt clusters, Klein *et al.* obtained triangulo cobalt hydride clusters of the form $[X\{Co(\mu\text{-CO})(PMe_3)_2\}_3]$, where X = H **439b** or H_3 **439c**. The X-ray diffraction analysis of these complexes did not allow detection of the hydride in **439b**, whereas two of the three hydride ligands in **439c** were found to occupy two symmetrically equivalent positions above and below the center of the Co_3 triangle.[539]

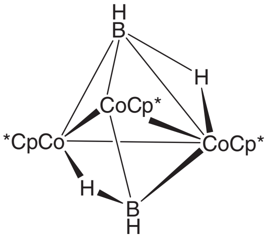
Theopold, Casey *et al.* reported in 1992 the synthesis of an unusual trinuclear tetrahydride cobalt cluster, $Cp^*{}_3Co_3(\mu_2\text{-H})_3(\mu_3\text{-H})$ **440**, together with the dinuclear complex $Cp^*{}_2Co_2(\mu\text{-H})_3$ **441** from the reaction between $(Cp^*CoCl)_2$ and $LiAlH_4$.[540] At about the same time, Schneider studied the reaction of $CpCo(C_2H_4)_2$ and $Cp^*Co(C_2H_4)_2$ with Et_2AlH. He found that the Cp^* derivatives led to a mixture of the same products together with the tetranuclear cluster $Cp^*{}_4Co_4(\mu_3\text{-H})_4$ **442**, whereas the Cp complex only afforded the corresponding tetranuclear species.[541] Schneider also showed in the same paper that the Co_4 and the Co_3 clusters could be obtained directly from the reaction of cobalt atoms with polysubsituted cyclopentadienes.

The paramagnetic 46-electron trinuclear cluster was highly reactive due to its lack of bridging ligands other than hydrogen.

With acetylene, the tetrahydride Co_3 cluster, **440**, ultimately gave the bis(μ_3-ethylidyne) complex, **445**.[542] However, performing the reaction under milder conditions afforded a trihydride, **443**, and a monohydride intermediate, **444** (Scheme 63). The bis(μ_3-ethylidyne) compound **445** was thought earlier to be the product of the pyrolysis of $Cp^*Co(C_2H_4)_2$.[543] However, Casey *et al.* were able to demonstrate that, in fact, this latter reaction afforded instead **444**.[544] The mechanism of the formation of the μ_3-ethylidyne unit was studied, and a third intermediate, $Cp^*{}_3Co_3(\mu_2\text{-H})_2(\mu_3\text{-}\eta^2\text{-CHCH})$, which rearranged exclusively to **445**, was detected by ^1H NMR. The reaction of the tetrahydride Co_3 cluster **440** with $DC{\equiv}CD$ formed $Cp^*{}_3Co_3(\mu_2\text{-H})_2(\mu_2\text{-D})(\mu_3\text{-CCH}_2D)$, which was consistent with the presence of the ethylidene dihydride $Cp^*{}_3Co_3(\mu_2\text{-H})_2(\mu_2\text{-CDCH}_2D)$ intermediate.[545] Whereas the reaction with NO afforded directly the 48-electron cluster **448**,[546] the reaction with CO gave the known 46-electron dicarbonyl cluster **447**, which was preceded by the 48-electron dihydride species **446**.[547]

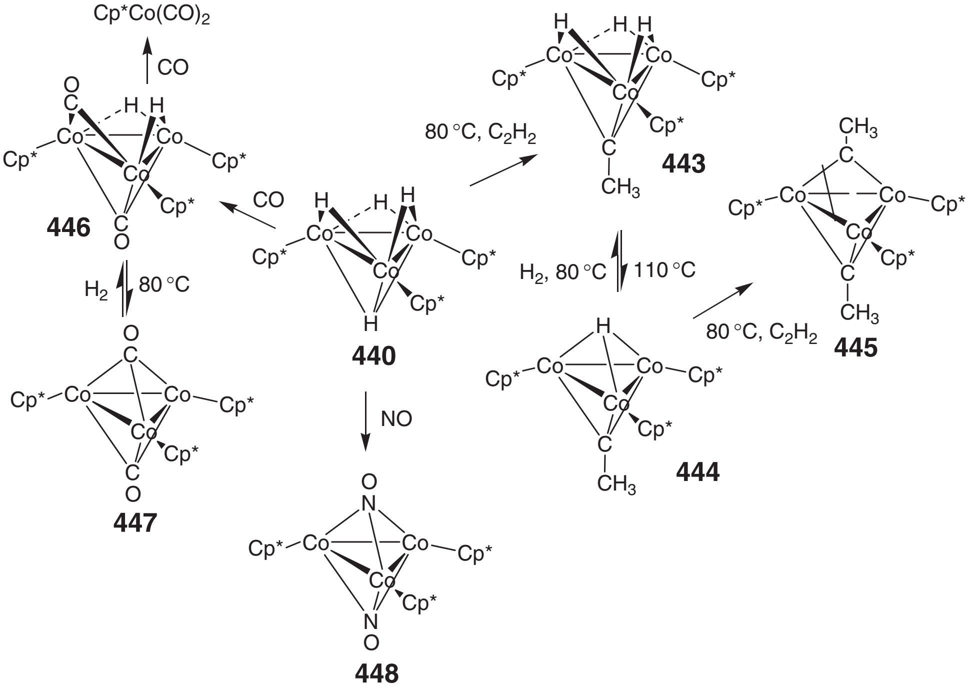
A reaction related to the latter ones was observed with isocyanide, as the triply bridging and one bridging hydrogens were substituted by two isocyanide ligands (Scheme 64). Interestingly, the migration of one hydrogen on the terminal carbon atom of the isocyanide was observed giving raise to a formimidoyl monohydride Co_3 cluster, **450**.[548] The reaction with CO_2 led to the reduction of carbon dioxide affording the dicobalt dicarbonyl dimer. With CS_2, a mixture of products was obtained, of which only the thiocarbonyl sulfide cluster $Cp^*{}_3Co_3(\mu_3\text{-CS})(\mu_3\text{-S})$, **452**, was fully characterized. The reaction with phenyl isocyanate afforded also a mixture of two carbonyl-bridged Co_2 and Co_3 compounds, respectively, together with an *N*,*N*′-diphenylureylene dicobalt complex.[549]

The paramagnetic mono(ethylidyne) monohydride cluster $Cp^*{}_3Co_3(\mu_3\text{-CCH}_3)(\mu_3\text{-H})$, **444**, also showed an interesting set of reactivity with CO, $CNBu^t$, and NO to afford the cluster compounds in which the bridging hydrogen atom was substituted by CO, $CNBu^t$, and NO, respectively.[550] The same cluster **444** reacted also in a somewhat similar fashion with ethyl diazoacetate and trimethylsilyldiazomethane, with the important difference however that the migration of the hydride ligand on the incoming reagent was observed (Scheme 65).[551]

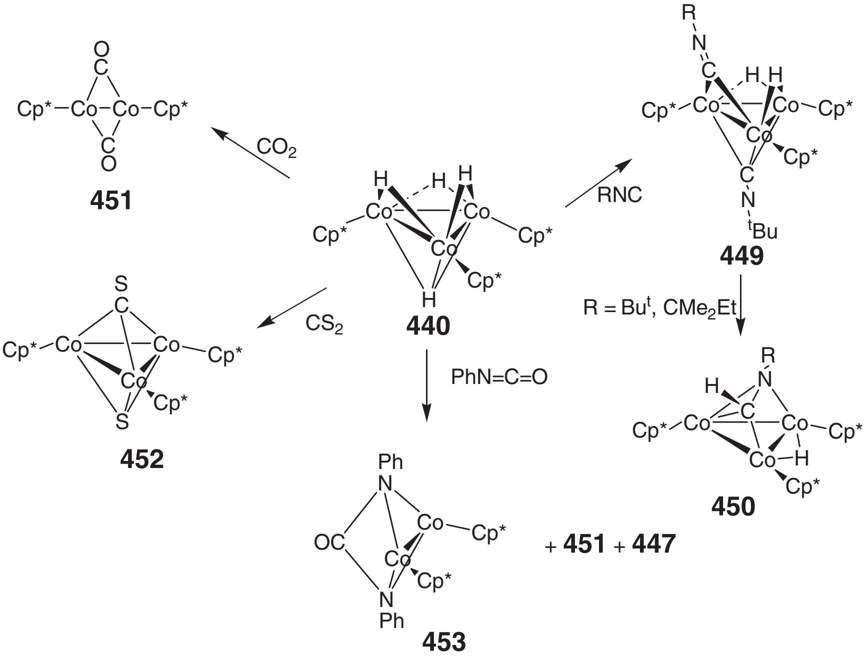


439

Figure 88

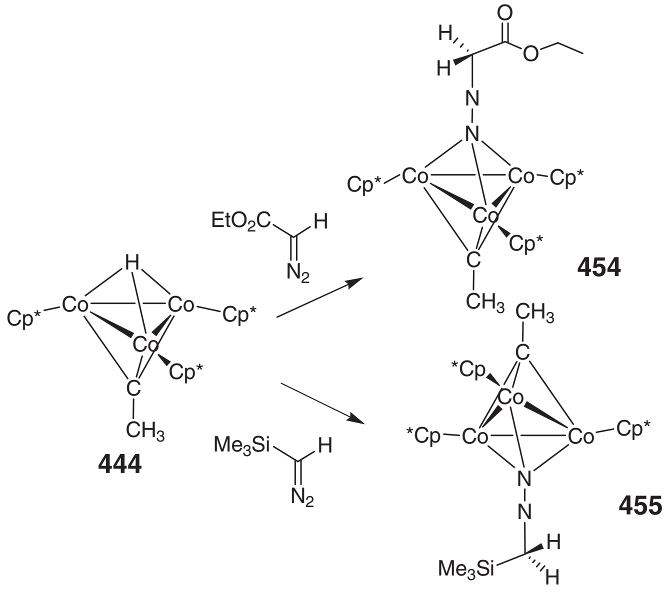


Scheme 63



Scheme 64

On the other hand, the reactivity of Cp$^*{}_3$Co$_3$(μ_2-H)$_3$(μ_3-H), 440, with oxidant reagents such as X$_2$ (X = Br, I), CCl$_4$, HCI$_3$, (CH$_2$)$_2$Br$_2$, Hacac, CH$_2$Br$_2$, PhCOOOBut, HBF$_4$, and BrCN, was such that it afforded mainly mononuclear organometallic cobalt clusters without a metal–metal bond. In all cases, formal oxidation of the metal center was observed.[552]

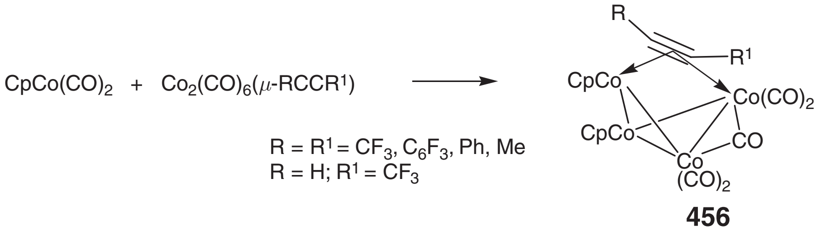


Scheme 65

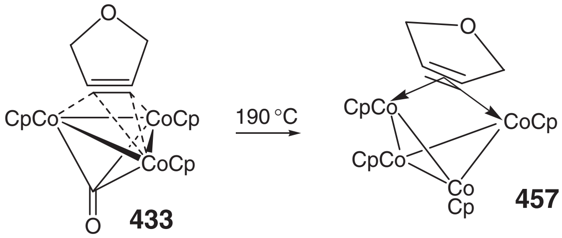
7.01.5.2 Cluster Complexes with Four and More Cobalt Atoms

There has been a relatively low number of new Co_4 clusters studied since COMC (1995) has appeared.

closo-“C_2Co_4” clusters are frequently encountered when alkynes or alkenes are coordinated to Co_4 units. A few representative examples of such synthesis are represented in Equations (73) and (74).[497,527,553–555]



(73)



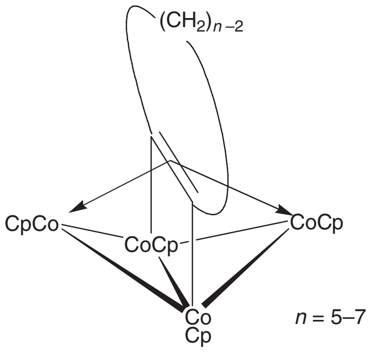
(74)

During the synthesis of the alkene-bridged Co_3 cluster **397** via the reaction of carbocyclic alkenes and $CoCp_2$/K, small amounts of tetranuclear Co clusters, **458**, were also formed (Figure 89).[480]

Reinvestigating the reaction between $Co_4(CO)_{12}$ and cycloheptatriene and cyclooctatetraene, Wadepohl *et al.* found several new Co_4 cluster compounds in which the cyclopolyene ligands were capping a triangular face of the clusters (**459** and **460**, Figure 90).[556]

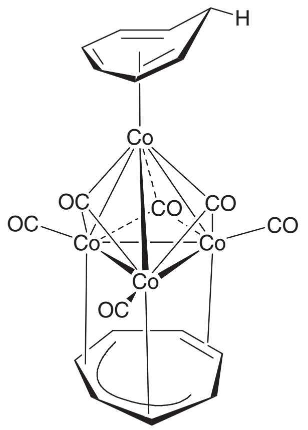
Treating the latter complex **460** respectively with $Fe(CO)_5$, cyclohexadiene, or 6,6-diphenylfulvene gave the derivatives **461–463** (Figure 91).

These latter complexes can be reversibly reduced via cyclic voltammetry, the reduced anionic forms leading to the trinuclear anion **438** under reductive conditions. $Co_4(CO)_{12}$ was also found to be interacting with the arene rings of



458

Figure 89



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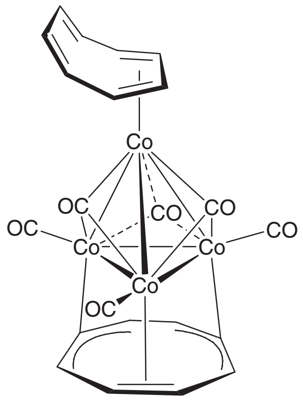
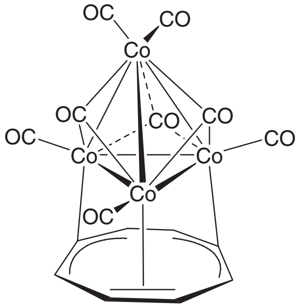


460

Figure 90



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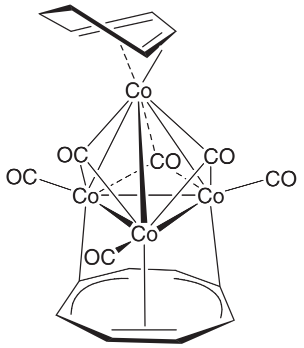

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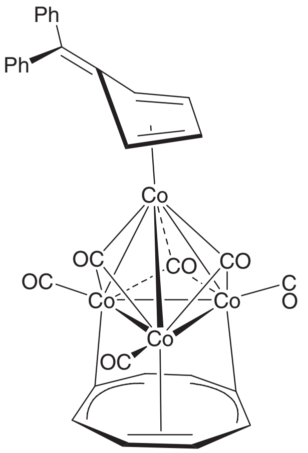
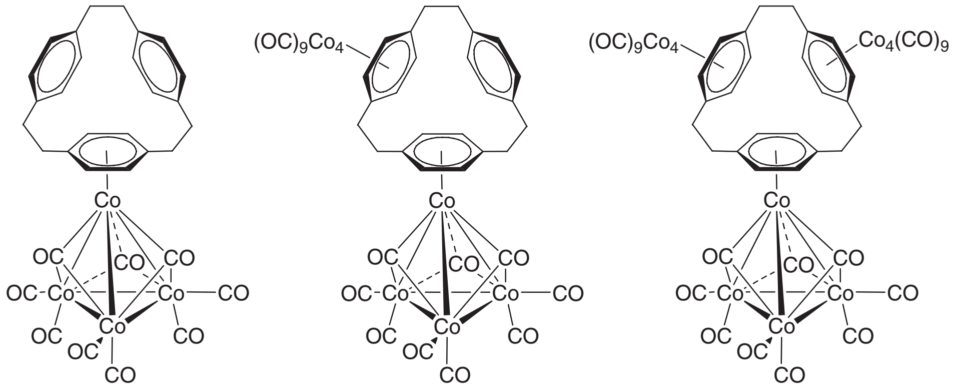


463

Figure 91



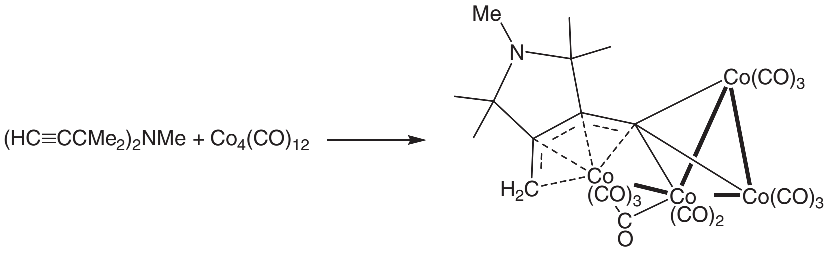
464 **465** **466**

Figure 92

[2.2.2]-paracyclophane, as up to three $Co_4(CO)_9$ units could be bound to the three *p*-phenyls **464–466**. The yield of the bis- and the tris-cluster species was however much lower than that of the monocluster derivative (Figure 92).[557]

A crystal structure analysis was obtained for the mono- and the bis-cluster adducts of the cyclophane. These compounds are believed to allow novel types of electronic communication.

The reaction of the dipropargylamine $(HC{\equiv}CCMe_2)_2NMe$ with $Co_4(CO)_{12}$ afforded a compound **467**, in which the dialkyne reagent was partly cyclized and coordinated to all four Co atoms (Equation (75)).[558]

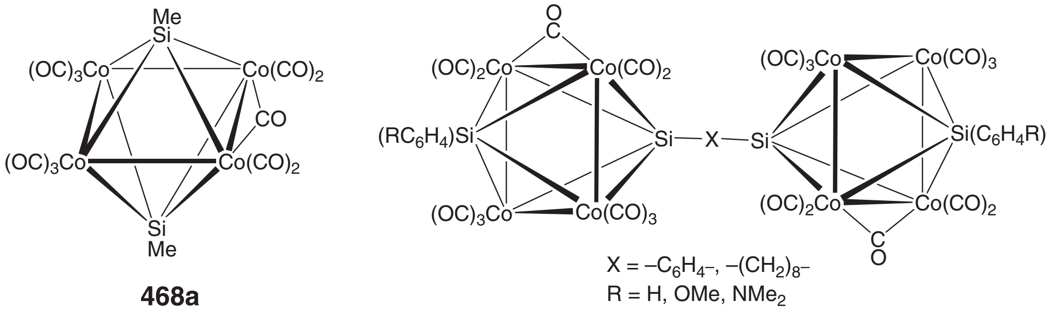


(75)

467

$Co_4(CO)_{12}$ also reacted with $SiMeH_3$ to afford a square-bipyramidal cluster **468a**.[559,560] This reaction proved to be general for a range of SiH_3R reagents.[561] The use of bifunctional silanes $H_3Si{-}X{-}SiH_3$ provided a systematic way of linking clusters together (Figure 93).[562]

The reaction between $Co_2(CO)_8$ and Na_2Te_2 in the presence of PPh_4Cl at the molar ratio 4 : 2 : 1 afforded the tetranuclear Co_4 cluster **469**, displaying a trapezoidal cobalt arrangement (Figure 94).[563]

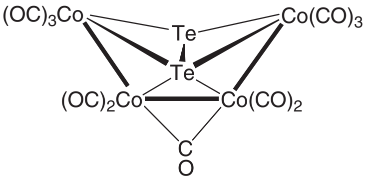


468a

X = $-C_6H_4-$, $-(CH_2)_8-$
R = H, OMe, NMe_2

468b

Figure 93



469

Figure 94

Two types of Ln(II)–Co_4 compounds (Ln = Yb and Eu) containing different isomers of $[Co(CO)_{11}]^{2-}$ have been synthesized. The cluster in $[(Et_2O)_{3-x}(THF)_xLn{-}Co_4(CO)_{11}]_\infty$ possesses pseudo-C_{3v}-symmetry and connects to Ln(II) centers through η^2,μ_4- and η^2,μ_3-carbonyls to generate a 2D puckered sheet. $[(THF)_5Eu{-}Co_4(CO)_{11}]_\infty$ incorporates a C_{2v}-symmetric cluster and isocarbonyl linkages (η^2,μ_4-carbonyls) to Eu(II) atoms creating a 1D zigzag chain.[564]

The neutron-diffraction study of the known compound $H_4Co_4(\eta^5\text{-}CMe_4Et)_4$ has been reported recently. The hydride ligands are located off the Co_3 plane by an average distance of 0.923(8) Å. The dimensions of the HCo_3 provided reasonable estimates for analogous distances and angles associated with chemisorbed H atoms on threefold hollows of a cobalt surface.[565]

7.01.5.3 Cluster Complexes with Five and More Cobalt Atoms

COMC (1995) provided many examples of clusters up to a Co_{14} carbonyl example. However, as some polynuclear cobalt clusters with more than four atoms have been described during the last decade, the area of large cobalt carbonyl clusters seemed to have been much less investigated during this period of time. Nevertheless, several interesting examples of homometallic cobalt clusters with 5–18 cobalt atoms have been reported.

7.01.5.3.1 Co_5 and Co_8

Carbon–sulfur bond cleavage was observed when $Co(PPh_3)_3Cl$ reacted with $K_2S_2C{=}C(CN)_2$ to afford two compounds: a pentanuclear cobalt cluster $[Co_5(\mu_3\text{-}S)_4(\mu\text{-}SC{=}C(CN)_2)_2(PPh_3)_4]$ **470** and an octanuclear cobalt cluster with mixed Co(I) and Co(II) atoms $(PPh_4)[Co_8(\mu_4\text{-}S)_6Br_2Cl_2(PPh_3)_4]$ **471** (Figure 95).[566]

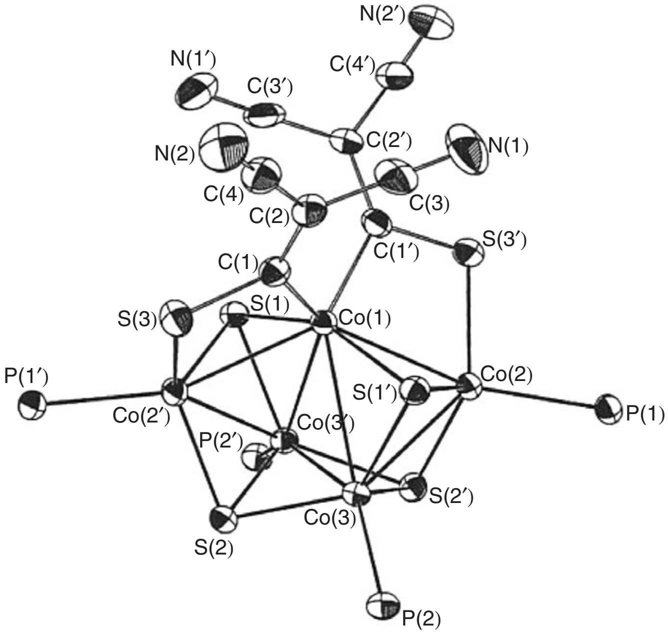
The five cobalt atoms in **470** form a highly distorted trigonal bipyramid, of which four Co_3 faces, among the six such faces present, are each triply bridged by a sulfur atom. Two types of cobalt coordination environments are present: Co(2, 2′, 3, 3′) are in the tetrahedrons formed by three sulfur and one phosphorous atom, while Co(1) is in a distorded tetrahedron formed by two sulfur and two carbon atoms. The eight cobalt atoms in **471** form a slightly distorted cube, of which six Co_4 faces are each quadruply bridged by a sulfur atom. The four cobalt atoms Co(1, 1a, 4, 4a) are in a tetrahedral environment formed by three sulfur and one phosphorous atom, while each of the four cobalt atoms Co(2, 2a, 3, 3a) are in a distorted environment formed by three sulfur atoms and one halogen atom (see (V) for Co_6).

7.01.5.3.2 Co_7

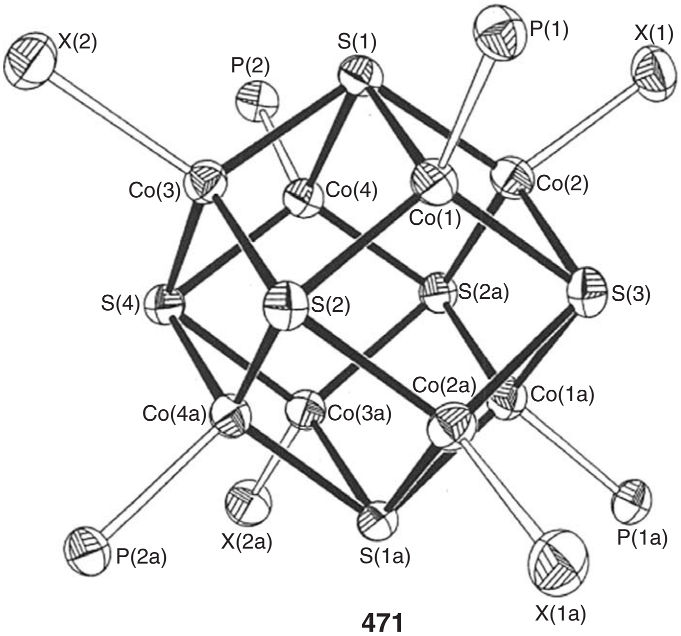
The reaction between $Co(PPh_3)_3Br$ and Na_2edt (edt = 1,2-ethanedithiol) afforded $[Co_7(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3(PPh_3)_6Br]$, **472** (Figure 96),[567] in which the cobalt atoms are at lower oxidation levels as compared to closely related complexes reported already in COMC (1995) (see (i) for Co_8).

7.01.5.3.3 Co_9 and Co_{11}

A mixture of two cobalt–tellurium clusters $[Cat_2][Co_9Te_6(CO)_8]$, **473**, and $[Cat_2][Co_{11}Te_7(CO)_{10}]$, **474** (Cat = $Cp^*{}_2Nb(CO)_2{}^+$), has been obtained while treating $Co_2(CO)_8$ and $Cp^*{}_2NbTe_2H$ at higher temperature as for the synthesis of the compounds **415** and **416** (see above).[503] The latter dianionic Co_{11} cluster, **474**, was readily transformed, upon treatment with HPF_6 into a monoanionic cluster, $[Cat][Co_{11}Te_7(CO)_{10}]$, **475**, with an anaologous structure as the dianion. The structure of the anionic part of **474** was very similar to that of the anionic cluster Co_{11} stabilized by two PPh_4 cations which was synthesized previously.[563]



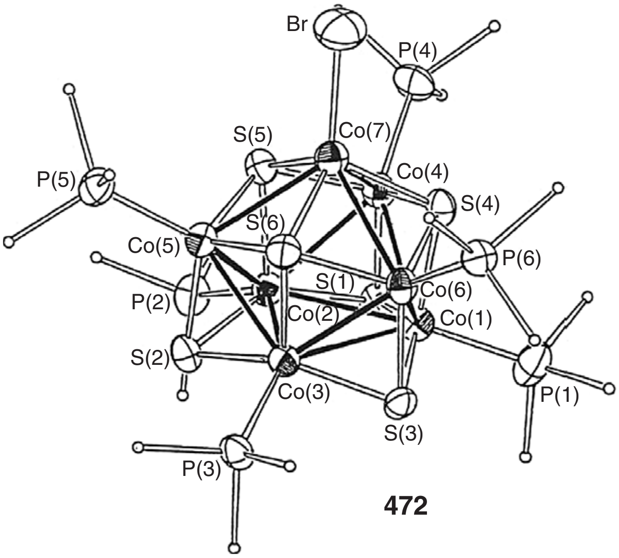
470



471

Figure 95 ORTEP drawing of 470 and 471. Reproduced from Hong, M.; Su, W.; Cao, R.; Jiang, F.; Liu, H.; Lu, J. *Inorg. Chim. Acta* **1998**, *274*, 229, with permission from Elsevier.

The geometry of the anionic part of 473 can be described as a hexacapped Co_8 cube which contains an interstitial Co atom. If each tellurium ion is considered to be Te^{2+}, there are eight Co(I) and one Co(II) centers, the remaining two negative charges being compensated by the cations. The cluster anion $[Co_{11}Te_7(CO)_{10}]^-$ forms a pentagonal prism consisting of 10 Co atoms in the center of which lies a further Co atom. The faces of the prism are capped by two μ_5- and five μ_4-Te^{2-} ligands.



472

Figure 96 Perspective view of **472**. Reproduced from Jiang, F.; Lei, X.; Hong, M.; Huang, Z.; Kang, B.; Liu, H. *J. Organomet. Chem.* **1993**, *443*, 229, with permission from Elsevier.

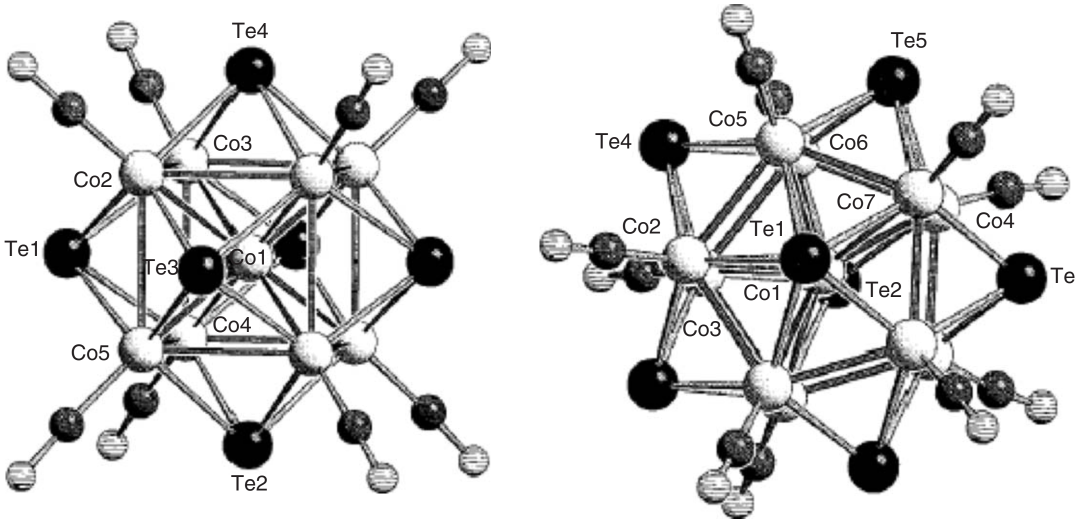


Figure 97 Molecular structure of the $Co_9Te_6(CO)_8$ and the $Co_{11}Te_7(CO)_{10}$ anions of 473 and 474, respectively. Reproduced from Brunner, H.; Lucas, D.; Monzon, T.; Mugnier, Y.; Nuber, B.; Stubenhofer, B.; Stückl, C. A.; Wachter, J.; Wanninger, R.; Zabel, M. *Chem. Eur. J.* **2000**, *6*, 493–503, with permission from Wiley-VCH.

When the synthesis of 473 was performed with a different source of tellurium such as Cp'_2NbTe_2H ($Cp' = t\text{-}BuC_4H_5$) instead of $Cp^*_2NbTe_2H$, the neutral $[(Cp'_2NbCO)_3Co_9(CO)_8Te_6]$ cluster **476** was obtained. This compound reacted further with $Cr(CO)_5THF$ to afford a tris-$Cr(CO)_5$ adduct of the Co_9 cluster, 477. Its X-ray structure analysis (Figure 98) revealed a Co_9Te_6 core of a similar geometry as that of 473 on which three Nb and three Cr atoms atom are bound to the tellurium ligands in a meridional fashion.[568,569]

When Cp'_2NbTe_2H ($Cp' = t\text{-}BuC_4H_5$) was first treated with MeLi and then with $Co_2(CO)_8$, it afforded another neutral Co_9 cluster $[Cp'_2Nb(CO)]_2[Co_9Te_6(CO)_8]$, **478**. The structure of this latter compound derived from that of 477, in that two Te atoms at the apical position of the Te_6 octahedron are capped by a $Cp'_2Nb(CO)]_2$, whereas the remaining four equatorial Te atoms are “free”.[570]

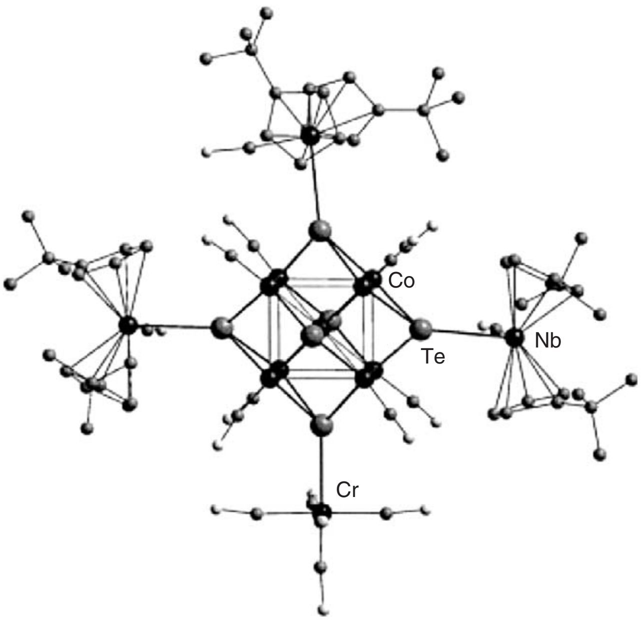


Figure 98 Molecular structure of $[(t\text{-}BuC_5H_4)_2Nb(CO)]_3Co_9Te_6(CO)_8[Cr(CO)_5]_3$ **477**; two of the $Cr(CO)_5$ fragments attached at the "free" μ_4-Te ligands have been omitted for clarity. Reproduced from Wachter, J. *Eur. J. Inorg. Chem*. **2004**, 1367, with permission from Wiley-VCH.

The substitution of four to five CO ligands could be achieved when reacting **474** with PMe_2Ph affording the paramagnetic neutral clusters $Co_{11}Te_7(CO)_6(PMe_2Ph)_4$, **479** and $Co_{11}Te_7(CO)_5(PMe_2Ph)_5$, **480**, respectively (Figure 99).[571]

The geometry of the $Co_{11}Te_7$ core of the structure of **480** is essentially the same as that of **474**, the PMe_2Ph ligands found in an eclipsed conformation with respect to the five-membered Co faces. Isomers of **480** might well exist; however, this could not be checked by NMR due to the paramagnetic nature of the compound.

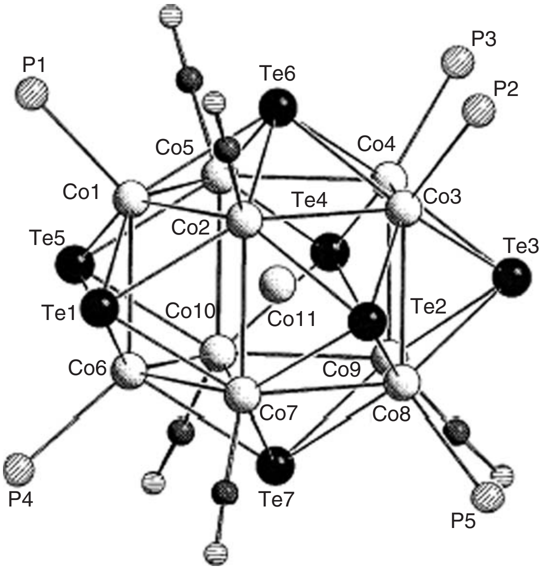
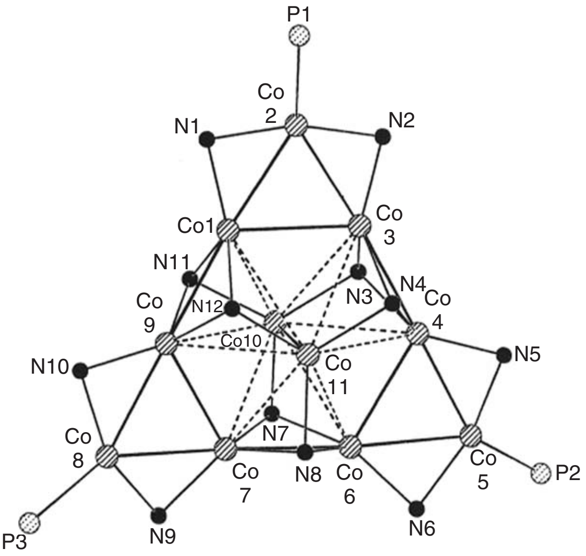


Figure 99 $Co_{11}Te_7(CO)_5P_5$ core of **480**. Reproduced from Brunner, H.; Cattey, H.; Meier, W.; Mugnier, Y.; Stückl, C. A.; Wachter, J.; Wanninger, R.; Zabel, M. *Chem. Eur. J.* **2003**, *9*, 3796, with permission from Wiley-VCH.



481

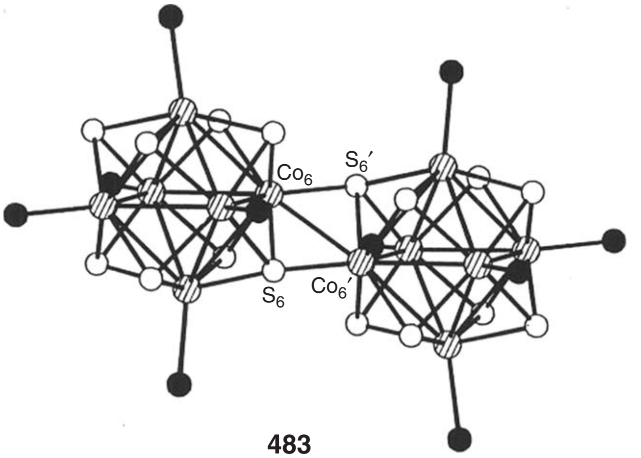
Figure 100 Molecular structure of **481**. Reproduced from Decker, A.; Fenske, D.; Maczek, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2863, with permission from Wiley-VCH.

The transmetallation reaction between PhN(SnMe$_3$) and a Co(II) compound [CoCl$_2$(PPh$_3$)$_2$] led to the formation of an unstable Co$_{11}$ cluster, **481** (Figure 100).[572]

The central metal framework in **481** consists of a planar Co$_6$ ring. Two cobalt atoms lie above and below this Co$_6$ plane, and three alternate edges of the ring are μ_2-bridged by Co atoms. The six N atoms N3, N7, N11, N4, N8, and N12 form an almost undistorted trigonal prism. The overall charge of the Co$_{11}$ cluster should be +24, which points to a mixed-valent cluster. A possible charge distribution would be nine Co^{2+} and two Co^{3+} ions; thus, this cluster is paramagnetic. From the structure of the compound, the two Co^{3+} ions might be assigned to the bridging cobalt atoms Co10 and Co11.

7.01.5.3.4 Co$_{12}$

The paramagnetic octahedral cluster [Co$_6$(μ_3-S)$_8$(PEt$_3$)$_6$]$^+$, **482**, was described earlier. It was obtained together with a diamagnetic dodecamer side-product [Co$_{12}$(μ_3-S)$_{14}$(μ_3-S)$_2$(PEt$_3$)$_{10}$]$^{2+}$, **483** (Figure 101).[573,574] This Co$_{12}$ cluster is



483

Figure 101 Perspective view of **483**. Reproduced from Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Inorg. Chim. Acta* **1994**, *214*, 13, with permission from Elsevier.

the result of the condensation of two classic face-capped octahedral units. Upon loss of one of the six terminal PEt_3 ligands from each $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]^+$ unit, the inter-octahedral connectivity is achieved via the formation of one Co–Co and two Co–S bonds.

7.01.5.3.5 Co_{18} and Co_6 and Co_8

Through the reaction of cobalt(II) chloride with lithiumamide, Li_2NPh, Link and Fenske obtained a Co_{18} cluster: $[Li(DME)_3]_2[Co_{18}(\mu_4\text{-}NPh)_3(\mu_3\text{-}NPh)_{12}Cl_3]$ 484 (Figure 102).[575]

Twelve of the 18 Co atoms of 484 form a hexagonal prism of which Co17 occupies the center. Two Co atoms Co16 and Co18 are located above and below Co17, thus capping the two hexagons respectively formed with Co1–Co6 and Co7–Co12. Three Co–Cl units, Co13–Cl1, Co14–Cl2, and Co15–Cl3 are capping Co_4 moieties. In a symmetrical way, three N–Ph units also cap Co4 squares, whereas all other NPh groups are capping Co3 triangle. Co17 occupies an

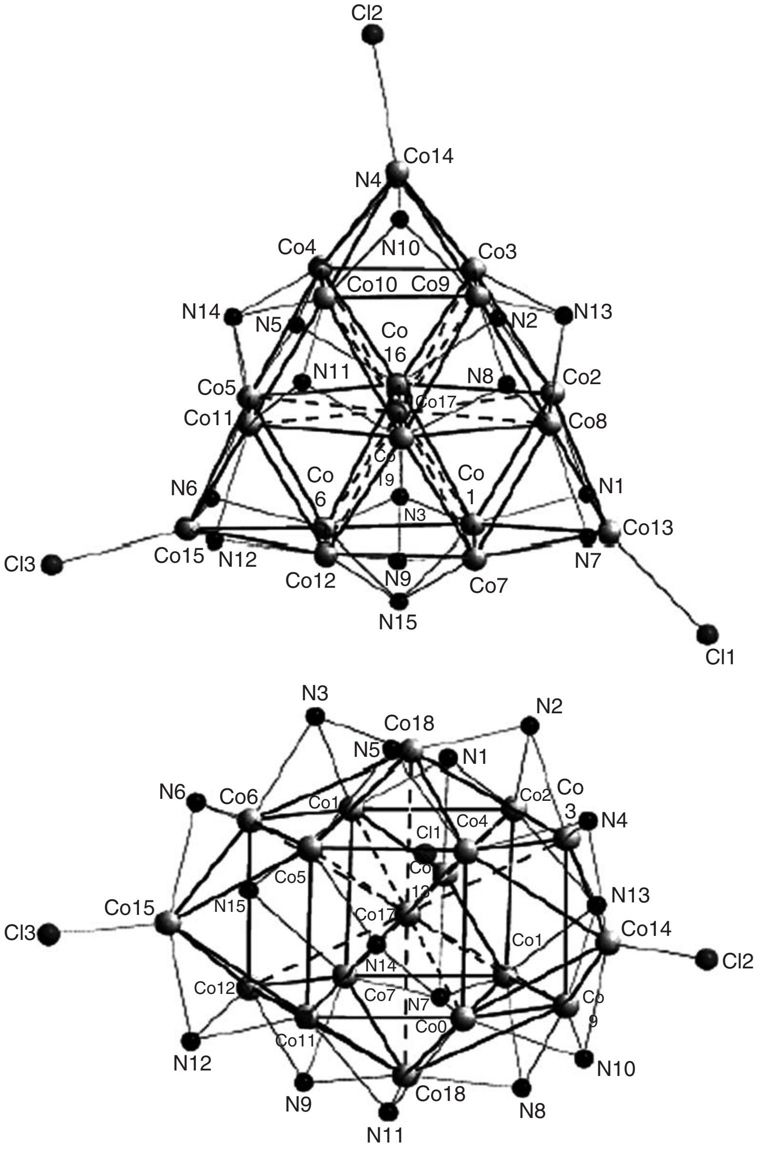


Figure 102 ORTEP drawings of two representations of 484; the phenyl groups were omitted for clarity. Reproduced from Link, H.; Fenske, D. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1878, with permission from Wiley-VCH.

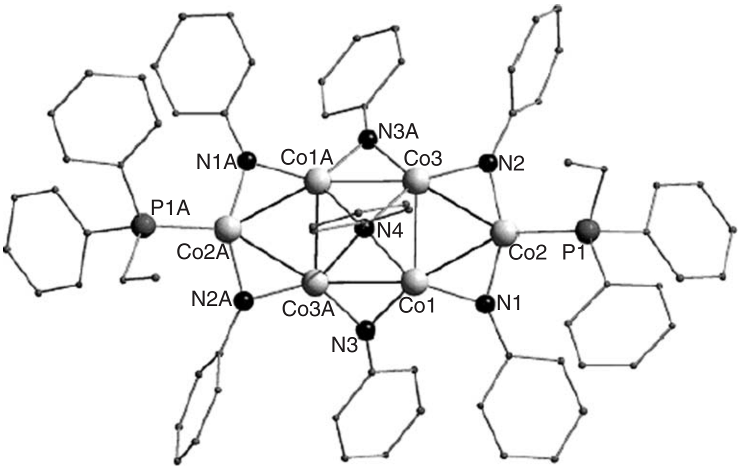


Figure 103 Molecular structure of **485**. Reproduced from Link, H.; Fenske, D. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1878, with permission from Wiley-VCH.

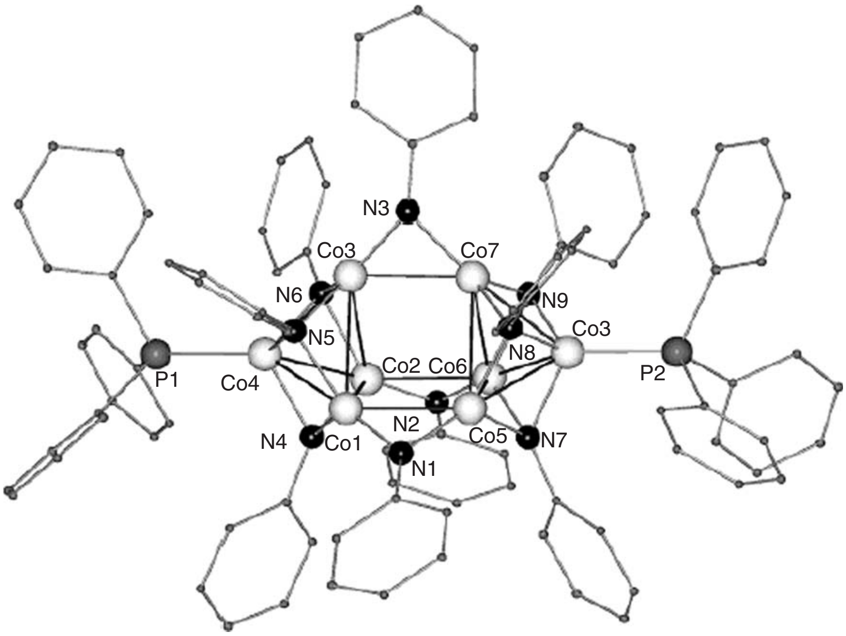


Figure 104 Molecular structure of **486**. Reproduced from Link, H.; Fenske, D. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1878, with permission from Wiley-VCH.

original situation as it is only surrounded by 14 cobalt atoms: the closest Co atoms (Co16 and Co18) are ca. 2.44 Å away, whereas the other Co17–Co bond distances with the other atoms of the prism are between 2.64 and 2.76 Å.

When the same reaction was performed in the presence of tertiary phosphines, PPh_2Et and PPh_3, respectively, two clusters with a core of respectively Co_6 and Co_8 units were produced: $[Li(DME)_3]_2[Co_6(\mu_4\text{-}NPh)(\mu_2\text{-}NPh)_6(PPh_2Et)_2]$ **485** (Figure 103) and $[Li(THF)_2]_3[Co_8(\mu_3\text{-}NPh)_6(\mu_2\text{-}NPh)_3(PPh_3)_2]$ **486** (Figure 104).

The six Co atoms of the anion **485** are almost coplanar, and they form a square geometry of which two opposite edges are μ_2-bridged by two Co atoms. These two bridging Co atoms are only 0.2 Å away from the best plane of the Co_4 square.

The cluster anion 486 is formed of a trigonal Co_6 prism, of which the two Co_3 triangles are capped by two Co–PPh_3 units. All Co atoms of the prism are in a planar-trigonal environment formed by three NPh atoms. On the other hand, the capping cobalt atoms are in a tetrahedral environment. This Co_8 cluster should have a formal charge of +17. This is possible if one considers that the cluster is a mixed-valent molecule built with seven Co^{2+} and one Co^{3+} ions.

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7.02
Rhodium Organometallics

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7.02.1 Introduction

7.02.1.1 Perspective and Scope

Research in the chemistry of organorhodium compounds has evolved dramatically since the mid-1990s. Most of the published work describes new chemistry aspects of long-known complexes. An extraordinarily large number of papers concerns catalytic aspects of new and previously described complexes of rhodium. The Web of Science database provides access to SCI Expanded, which is a very useful tool for selection and classification of the material described in this chapter. The introduction of the word "rhodium" on the "topic box" of the SCI expanded database, and with a time span of 1994–2004, results in more than 11 000 references, which gives a good idea of the interest that rhodium chemistry has generated in the last few years. Surprisingly, a high percentage (ca 40%) of the references found do not deal at all, or do only slightly, with rhodium chemistry. Using rhodium as a keyword certainly makes a work more rapidly accessible to general chemistry readers. This, in fact, also gives an idea of how rhodium is still one of the metals that is receiving significant interest. Nearly 3000 of the above-mentioned references were selected. Out of these, references describing the chemistry of long-known compounds, non-organometallic species, merely catalytic research studies, or continuations from aspects described in COMC (1982) and COMC (1995) were discarded. From the remaining references, the authors selected those considered more relevant by the number of citations obtained and, obviously, considering their personal points of view. Obviously, some papers may have been omitted. During the period 1994–2004, a large number of reviews appeared concerning the chemistry of rhodium complexes and related aspects. Among these reviews, highly useful material was obtained regarding ligand design and coordination capabilities,[1,1a,2,2a–2q,3–5] structural properties and new rhodium complexes,[6–8,8a–8h,9–11] catalysis,[9,12,12a–12q,13] spectroscopic properties,[14,14a–14e] biological properties,[15,15a] and electrochemical applications.[16]

7.02.1.2 Organization of Material

The material in this chapter is organized in much the same way as in COMC (1982) and COMC (1995), the main difference being that this chapter will contain only those aspects related to the chemistry of new rhodium organometallic compounds. A separate chapter contains the applications of rhodium species in catalytic processes with carbon monoxide (Chapter 7.03). In any case, this chapter may contain only simple references to catalytic properties of certain complexes when this activity is clearly related to aspects of synthetic chemistry, or implies the detection of new catalytic intermediates. The compounds are presented according to ligand types. In general, compounds with two different organometallic ligands are discussed at the end of the last subsection, except for those examples where the chemistry is clearly dominated by other ligands.

7.02.2 Compounds without Hydrocarbon Ligands

This section is divided into three parts. Section 7.02.2.1 deals with carbonyl species. Section 7.02.2.2 covers thiocarbonyl, carbon disulfide, and carbon dioxide complexes. Section 7.02.2.3 covers isocyanide and diazoalkane compounds.

7.02.2.1 Carbonyl Complexes

This section is further divided on the basis of ancillary ligand types. Section 7.02.2.1.1 covers binary halocarbonyl and hydridecarbonyl complexes. Section 7.02.2.1.2 deals with group 16 donor complexes, and section 7.02.2.1.3 with group 15 donor complexes.

7.02.2.1.1 Binary halocarbonyl and hydridecarbonyl complexes

There has been little new work in the area of binary halocarbonyl and hydridecarbonyl species. Most of these complexes have been used in the preparation of other carbonyl species which are reported in other sections of this chapter. The development of spectroscopic techniques has afforded the characterization of several new species, some of them too unstable to be isolated, which remained elusive during recent decades. The *cis–trans* isomerization of $[RhI_4(CO)_2]^-$ was studied by IR spectroscopy.[17] Dimeric rhodium(I) bis(carbonyl) chloride, $[Rh(\mu\text{-}Cl)(CO)_2]_2$, is the starting material for the syntheses of new cationic carbonyl complexes of both rhodium(I) and rhodium(III) such as $[Rh(CO)_4][M_2Cl_7]$ (M = Al, Ga), $[Rh(CO)_4][Sb_2F_{11}]$, $[Rh(CO)_5Cl][Sb_2F_{11}]_2$.[18] The compound $[Rh(CO)_4][1\text{-}Et\text{-}CB_{11}F_{11}]$ was also isolated and its molecular structure was determined by X-ray diffraction methods.[19]

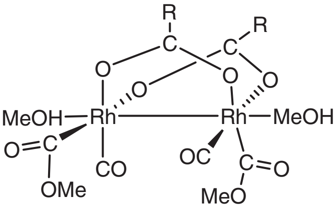
Rh^+, Rh, and electrons generated by laser ablation (a laser pulse focused on a rotating rhodium target) react with CO on condensation in excess of neon at 4 K to form $RhCO^+$, RhCO, $RhCO^-$, $Rh(CO)_2{}^+$, $Rh(CO)_2$, $Rh(CO)_2{}^-$, and higher carbonyls.[20] Carbon dioxide is activated on photochemically prepared $Rh^I(^{13}C^{18}O)$ sites to produce various isotopically labeled rhodium *gem*-dicarbonyl species. The two major products of CO_2 activation are $Rh^I(^{12}C^{16}O)(^{13}C^{18}O)$ and $Rh^I(^{13}C^{16}O)(^{13}C^{18}O)$.[21] Photolysis of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ led to facile and reversible ejection of the terminal CO yielding $Rh_2Cl_2(CO)_3$ in Ar, CH_4 and Nujol media and $Rh_2Cl_2(CO)_3(N_2)$ in N_2 matrices. Further reversible CO loss afforded $[Rh(\mu\text{-}Cl)(CO)]_2$ and $[RhCl(CO)(N_2)]_2$, respectively.[22]

The reaction of $[Rh_4(CO)_{12}]$ with a series of hydrosilanes such as Me_2PhSiH, Et_2MeSiH, or $^tBuMe_2SiH$ under CO yielded the monometallic species $Rh(SiR_2R^1)(CO)_4$ and $Rh(H)(SiR_2R^1)_2(CO)_3$.[23]

7.02.2.1.2 Carbonyl complexes containing group 16 donor ligands

7.02.2.1.2.(i) Oxygen-donor ligands

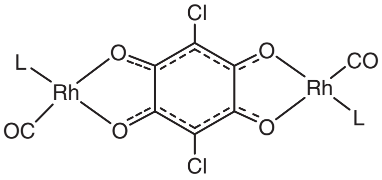
Oxidation of rhodium(I) carbonyl chloride, $[Rh(\mu\text{-}Cl)(CO)_2]_2$, with copper(II) acetate or isobutyrate in methanol yielded binuclear double carboxylato-bridged rhodium(II) complexes **1** with Rh–Rh bonds. The methoxycarbonyl ligand is shown to originate from CO group of the parent $[Rh(\mu\text{-}Cl)(CO)_2]_2$.[24]



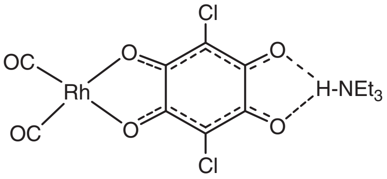
1

By reaction of $Rh_2(O_2CCF_3)_4$ and $Mo(CO)_6$ a compound in which one $Rh_2(O_2CCF_3)_4$ unit is sandwiched between two $Rh_2(O_2CCF_3)_2(CO)_4$ units was obtained, giving an essentially linear array of six rhodium atoms.[25]

A series of phosphine oxides was used in the preparation of complexes of the type RhCl(O,N)(CO) {(O,N) = $R_2N(CH_2)_nP(O)(R)^1{}_2$, R^1 = Ph, Cy; n = 0, 2, 3; R = Me, Et, ^{i}Pr, or NR_2 = 2-pyridyl} and used as efficient hydroformylation reagents.[26] A series of chloranilate complexes of general formula $Rh_2(\mu\text{-}C_6Cl_2O_4)(CO)_4$ **2** and $Rh_2(\mu\text{-}C_6Cl_2O_4)(CO)_2(PPh_3)_2$ **3** was obtained from $Rh_2(\mu\text{-}C_6Cl_2O_4)(cod)_2$.[27] The use of $NHEt_3{}^+$ as counter ion allowed the formation of monometallic units **4**, avoiding the formation of metallic stacks.[28]



2: L = CO
3: L = PPh_3



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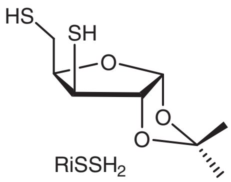
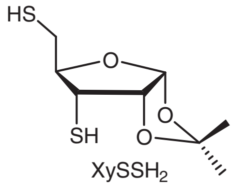
7.02.2.1.2.(ii) Sulfur- and selenium-donor ligands

This group has been fully dominated by the synthesis of dithiolate complexes, most of them prepared with the aim of obtaining efficient catalysts for hydroformylation. A large number of thioether ligands were prepared for the design of chiral rhodium catalysts.[4]

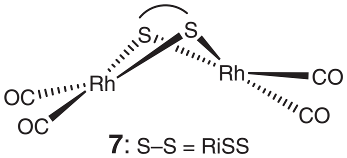
The reactivity of $[Rh(\mu\text{-}S\text{-}t\text{-}Bu)(CO)_2]_2$ with $[Ph_2PCH_2CH_2NMe_3]BPh_4$ has been reported.[29] Further studies on the reaction of $Rh_2(\mu\text{-dithiolate})(CO)_4$ {dithiolate═$S(CH_2)_4S$, 1,4-butanedithiol) and ((+)-*trans*-2,3-bis(mercaptomethyl)-bicyclo[2.2.2]octane)} with diphosphines allowed the preparation of the ionic species $[Rh(CO)(\text{diphosphine})_2]^+$ $[Rh(\text{dithiolate})(CO)_2]^-$ (diphosphine = diphenylphosphinopropane (dppp)) and $[Rh(\text{diphosphine})_2]^+$ $[Rh(\text{dithiolate})(CO)_2]^-$ [diphosphine = dppe diphenylphosphinoethane, dppp].[30] Other dithiolate carbonyl complexes were reported by the same research group.[31,31a] Chiral dithiol compounds $RiSSH_2$ **5** and $XySSH_2$ **6** provided the binuclear tetracarbonyls $Rh_2(\mu\text{-}RiSS)(CO)_4$ **7** and $Rh_2(\mu\text{-}XySS)(CO)_4$ **8**. These complexes reacted with 2 equiv. of PPh_3 to form the corresponding mixed carbonyl–phosphine complexes $Rh_2\text{-}(\mu\text{-}RiSS)(CO)_2(PPh_3)_2$ and $Rh_2(\mu\text{-}XySS)(CO)_2(PPh_3)_2$.[32]


RiSSH$_2$

5

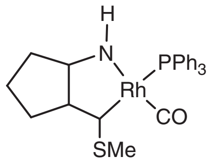

XySSH$_2$

6



7: S–S = RiSS
8: S–S = XySS

The new complex (methyl-2-(amino)-1-cyclopentene-1-dithiocarboxylato-κN,κS)-carbonyl(triphenylphosphine) rhodium(I), [Rh(hacsm)(CO)(PPh$_3$)] 9, was obtained.[33]



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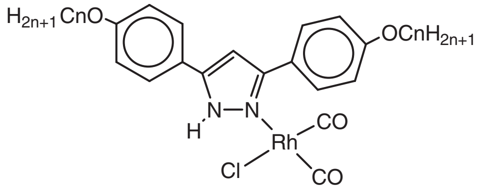
7.02.2.1.3 Carbonyl complexes containing group 15 donor ligands

7.02.2.1.3.(i) Monodentate nitrogen-donor ligands

Very little has been published regarding new carbonyl rhodium complexes containing nitrogen-donor ligands. $[Rh^I(CO)_2]^+$ supported on zeolites can be partly decarbonylated in an atmosphere of nitrogen yielding the dinitrogen–carbonyl complex $[Rh^I(CO)(N_2)]^+$.[34] $[Rh(CO)_2(MeCN)_2]BF_4$ converted to $[Rh(CO)(MeCN)_3]BF_4$ in solution, which was crystallized and found to contain a weakly interacting 1D chain of Rh^I cations.[35] New 3,5-disubstituted pyrazoles Hpz^{R2} containing long-chain 4-*n*-alkyloxyphenyl substituents [R=$C_6H_4OC_nH_{2n+1}$; $n = 4$, 6, 12, and 14] were prepared and used as ligands toward RhCl(CO)$_2$ and Rh(CO)$_2$ fragments. RhCl(CO)$_2$(Hpz^{R2}) 10 complexes evolved to [Rh(μ-pz^{R2})(CO)$_2$]$_2$ 11 in solution.[36,37] The structure of [Rh(μ-Pz)(CO)$_2$]$_2$ (pz = pyrazolate) was determined by X-ray diffraction.[38]



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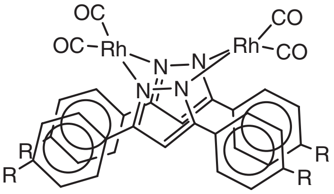

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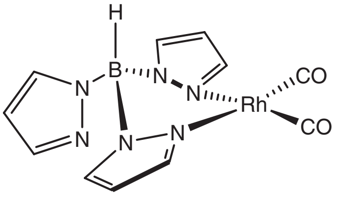
The products resulting from the progressive addition of pyridine (py) to a solution of [Rh(μ-Cl)(CO)$_2$]$_2$ were found to depend both upon the solvent and the atmosphere (CO or N$_2$). A detailed study of reactivity was performed.[39] Other examples of *cis*-RhClL(CO)$_2$ were obtained from the bridge-splitting reactions of [Rh(μ-Cl)(CO)$_2$]$_2$ with benzo[*c*]cinnoline (exhibiting intramolecular metal–nitrogen 1,2-fluxional shifts),[40] alkynylamines,[41] and substituted pyrazole ligands.[36]

The azavinylidene complexes [Rh(μ-N=CPh$_2$)(CO)$_2$]$_2$, Rh$_2$(μ-N=CPh$_2$)$_2$(CO)$_3$PCy$_3$, and [Rh(μ-N=CPh$_2$)(CO)(PCy$_3$)]$_2$ were obtained from [Rh(μ-N=CPh$_2$)(diolefin)]$_2$ by reaction with CO and PCy$_3$ (diolefin = COD, tetrafluorobenzobarrelene).[42]

The complex [Rh(CO)$_2${HC(pz′)$_3$}]PF$_6$, {HC(pz′)$_3$ = tris(3,5-dimethylpyrazolyl)methane}, was prepared by reacting [RhCl(CO)$_2$]$_2$ with HC(pz′)$_3$ in the presence of TlPF$_6$. The three isomers derived from the κ^2- 12, 13 and κ^3-14 hapticity of the ligands were studied by IR spectroscopy.[43]



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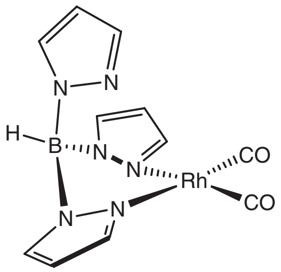

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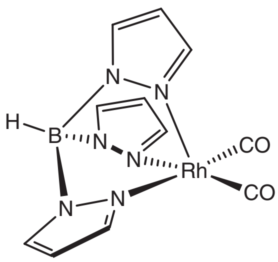
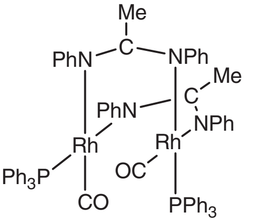


14

7.02.2.1.3.(ii) Bidentate nitrogen-donor ligands

The iodide-abstraction reaction of $[\{Rh(\mu\text{-}I)(\mu\text{-}RNNNR)_2(CO)(bipy)\}_2][PF_6]_2$ (bipy = 2,2′-bipyridyl, R = *p*-tolyl) with $AgPF_6$ in MeCN gave $[Rh_2(CO)(NCMe)_2(bipy)(\mu\text{-}RNNNR)_2][PF_6]_2$ which slowly decarbonylated at room temperature to $[Rh_2(NCMe)_3(bipy)(\mu\text{-}RNNNR)_2][PF_6]_2$.[44] The molecular structures of a series of dirhodium carbonyl complexes with local planar symmetry about each rhodium atom were extensively studied. Different bridging N–N **15** and N–O **16** ligands support the dimetallic structures.[45] Many such complexes are long known,[46,46a] but a complete molecular orbital analysis has been described.



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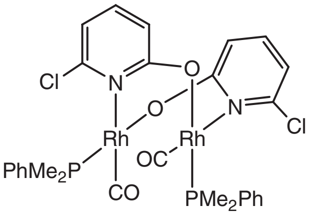
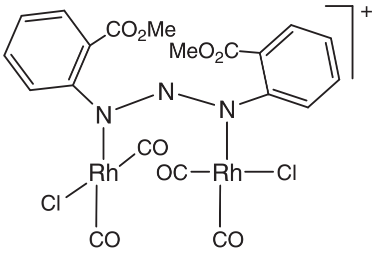


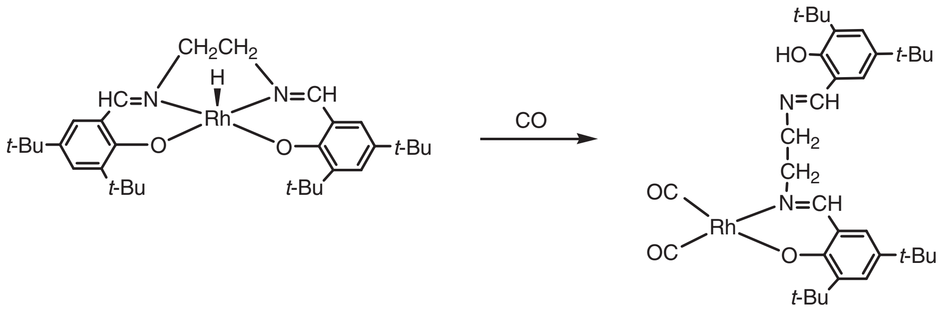
16

Starting from $[Rh(\mu\text{-}Cl)(CO)_2]_2$ and the triazene ArNNNHAr (Ar = *o*-$CO_2MeC_6H_4$) a series of mono- and bimetallic **17** complexes were obtained.[47]

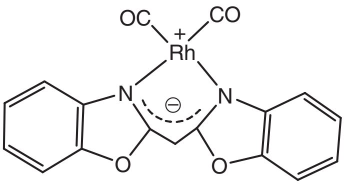


17

Some β-ketoiminoates provided new Rh carbonyl complexes of the type $Rh\{O\text{-}N\}(CO)_2$ ($\{O\text{-}N\} = CF_3C(O)CHC(NH)CF_3$). The carbonyl ligands can be substituted by several phosphines.[48] The use of novel chelating nitrogen ligands of the bis(azaheteroaryl)methane type afforded complexes such as $Rh(BBOM)(CO)_2$ **18** (HBBOM = bis(2-benzoxazolyl)methane).[49]



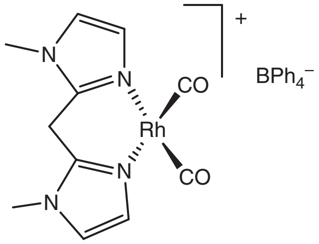
Scheme 1



18

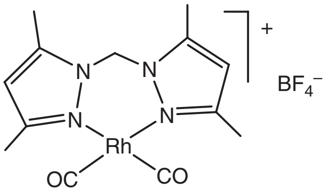
Mesomorphic Schiff base (O–N–salen type) ligands H_2L_a–H_2L_c[$H_2L_x = \{C_{10}H_{21}C_6H_3(O)CH{=}N\}_2R_x$; $R_a = CH_2CH_2$, $R_b = 1,4\text{-}C_6H_4$, $R_c = 1,4\text{-}C_6H_{10}$] yielded square-planar *cis*-Rh(CO)$_2$ complexes which showed smectic A behavior.[50] A rhodium(III) salen hydride, (ttbs)RhH, reacted with CO inducing migration of H^+ from rhodium to the salen ligand to form a rhodium(I) dicarbonyl complex, (Httbs)Rh(CO)$_2$ (Scheme 1).[51]

Imidazolium ligands afforded the preparation of dirhodium species such as $Rh_2(\mu\text{-Bzim-}N^3,C^2)_2(CO)_4$[52] and chelate cationic Rh(I) dicarbonyl complexes [Rh((mim)$_2$CH$_2$)(CO)$_2$]BPh$_4$ **19** [mim = *N*-methylimidazol-2-yl] were also obtained.[53,53a] The related methylbenzimidazol complexes were also prepared.[54]



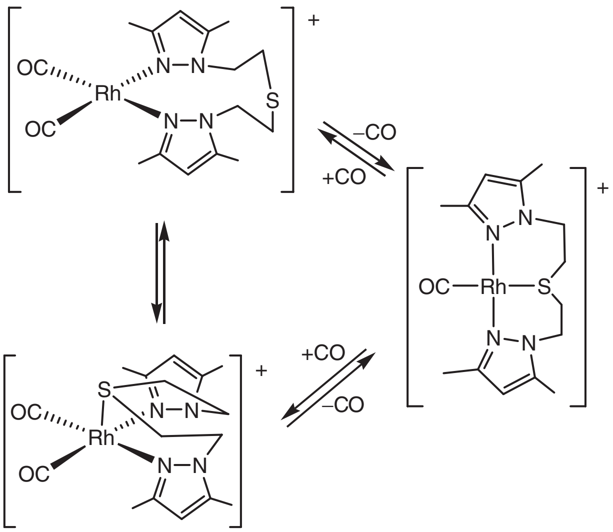
19

A structurally similar complex was obtained by addition of $H_2C(3,5\text{-}Me_2pz)_2$ (Bpm*) to [Rh(cod)(acetone)$_2$]BF$_4$, affording the complex [Rh(Bpm*)(cod)]BF$_4$, which was carbonylated under mild conditions into [Rh(Bpm*)(CO)$_2$]BF$_4$ **20**.[55]



20

The pyrazolato (pz) rhodium(I) complexes [Rh(μ-pz)(CO)(L)]$_2$ (L = CNBu^t, P(OMe)$_3$, PMe$_2$Ph, P(OPh)$_3$, P(*p*-tolyl)$_3$) result from the reaction of [Rh(μ-pz)(CO)$_2$]$_2$ with the appropriate L ligand in a *trans*:*cis* ratio ranging from

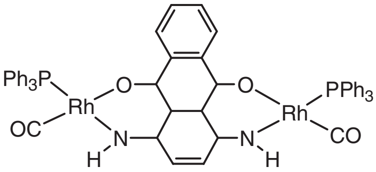


Scheme 2

60 : 40 (L = CNBu^t) to 95 : 5 (L = P(p-tolyl)$_3$).[56] Several chelate bis(benzotriazolyl)borato complexes of rhodium carbonyl were obtained.[57]

Rh(I) complexes of the N–S–N ligand 1,5-bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane (bdtp) were synthesized and characterized and showed hemilabile properties (Scheme 2).[58]

Mercaptopyrimidine and its methylated derivatives afforded N–S chelate monomeric Rh(I) carbonyl complexes, which were active in hydroformylation reactions.[59] The ligand 1,4-diaminoanthraquinone was used to obtain a series of binuclear compounds of Rh(I) **21** and Ir(I).[60]



21

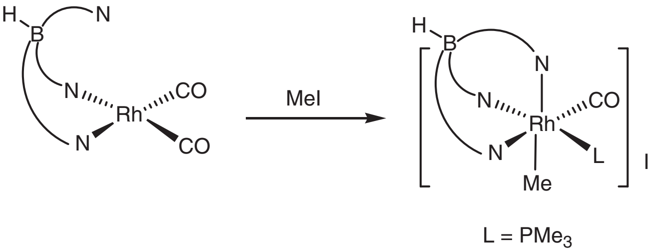
The reaction of N-acetyl-3-butanoyltetramic acid (Habta) with Rh(acac)(CO)$_2$ gave Rh(abta)(CO)$_2$.[61]

7.02.2.1.3.(iii) Tridentate nitrogen-donor ligands

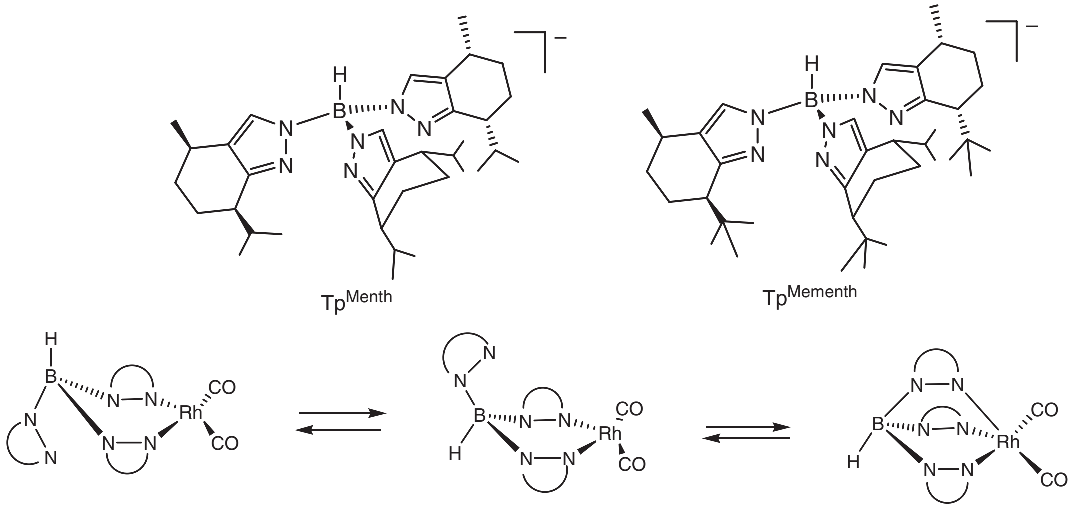
Rhodium complexes with tridentate nitrogen-donor ligands are fully dominated by the tris(pyrazolyl)borates. Trispyrazolylborate ligands (Tp) have afforded a series of new complexes.[62,63,63a–63c,64–68] A review appeared on the coordination chemistry of trispyrazolylborate complexes of rhodium and their catalytic properties.[7] Substitution reactions involving the carbonyl ligands were studied[43] and the stabilization of a square-pyramidal Rh(II) κ^3-Tp species was reported.[69] The coordination flexibility of Tp ligands is shown in the reaction of methyl iodide with square-planar Rh(κ^2-Tp*)(CO)(PMe$_3$) (Tp* = HB(3,5-Me$_2$pz)$_3$) at room temperature, affording [Rh(κ^3-Tp*)Me(CO)(PMe$_3$)]I (Scheme 3).[64] The kinetic results strengthen the evidence in favor of an S$_N$2 mechanism for oxidative addition of MeI to square-planar d^8 transition metal complexes.

The solution- and solid-state structural features and fluxional energetics of the optically pure RhTp$^{\text{Menth}}$(CO)$_2$ complex allowed to identify both η^2- and η^3-Tp$^{\text{Menth}}$ coordination modes (Scheme 4). The activation parameters for the interconversion of two η^2-boat geometries were determined.[62]

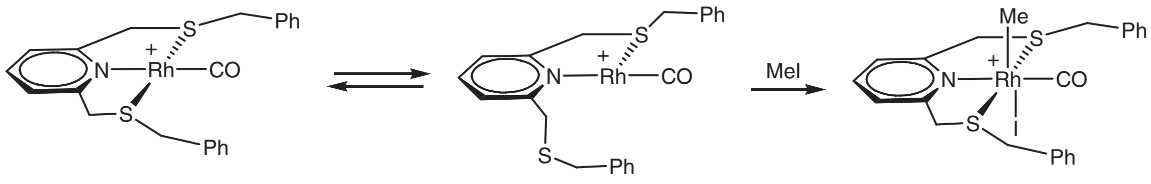
Complex [Rh(κ^3-N,N,N-pybox)(CO)]PF$_6$ was prepared by the reaction of the precursor [Rh(μ-Cl)(C$_2$H$_4$)$_2$]$_2$ with pybox (2,6-bis[4′(S)-isopropyloxazolin-2′-yl]pyridine), CO, and NaPF$_6$. This complex reacted with monodentate phosphines to give the complexes [Rh(κ^1-N-pybox)(CO)(PR$_3$)$_2$]PF$_6$ (R$_3$ = MePh$_2$, Me$_2$Ph, (C$_3$H$_5$)Ph$_2$), which showed an unprecedented monodentate coordination of pybox.[70] The first kinetic evidence of an arm-off mechanism



Scheme 3



Scheme 4



Scheme 5

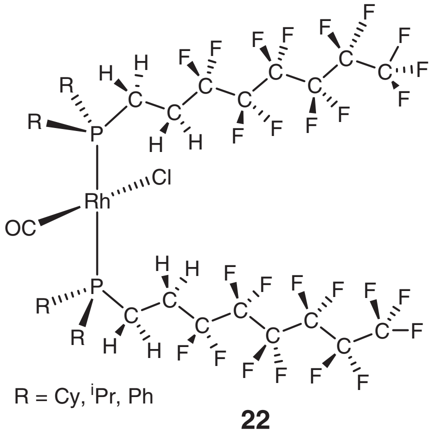
in tridentate S–N–S complexes of a hemilabile hybrid ligand was described. Oxidative addition of methyl iodide to the complex [Rh(2,6-bis(benzylthiomethyl)pyridine)(CO)]PF_6 afforded [RhI(2,6-bis(benzylthiomethyl)pyridine)(Me)(CO)]PF_6 (Scheme 5).[71]

7.02.2.1.3.(iv) Monodentate phosphorus-donor ligands

Many of the obtained carbonyl–phosphine complexes come from the preparation of new phosphines, most of them designed to enhance the catalytic activity.

A series of new Vaska's type complexes of the form *trans*-[RhCl(CO)$(PX_3)_2$] were prepared and their structural and solution properties related to their steric and electronic properties.[6,72,72a–72g,73,74]

Many new complexes were obtained starting from [Rh(μ-Cl)$(CO)_2]_2$. A series of mixed alkyl (or aryl) phosphinite compounds prepared from the alcohol $CF_3(CF_2)_5CH_2CH_2OH$ (R_fOH) and an appropriate $ClPR_2$ ($R = OR_f$, Ph, ^iPr, Cy) reacted with [Rh(μ-Cl)$(CO)_2]_2$ yielding the complexes RhCl(CO)$(PR_3)_2$.[75] A similar complex was obtained with the phosphine 2-(diphenylphosphino)methyl benzoate.[76] The fluorinated phosphine ligands [PR_2R_f (R = Cy, ^{i}Pr, Ph; $R_f = CH_2CH_2(CF_2)_5CF_3$)] reacted with [Rh($\mu$-Cl)$(CO)_2]_2$ to yield the corresponding $RhCl(CO)(PR_2R_f)_2$ complexes **22**.[73] Reaction of tris(*o*-trifluoromethylphenyl)phosphine with [Rh(μ-Cl)$(CO)_2]_2$ led to replacement of one carbonyl group to give dimeric units $Rh_2(\mu\text{-}Cl)_2(CO)_3\{P(o\text{-}CF_3\text{-}C_6H_4)_3\}$ **23**.[77] *o*-(Diphenylphosphino)benzaldehyde (PCHO) gave *trans*-[RhCl(CO)(PCHO)$_2$] **24**.[78]



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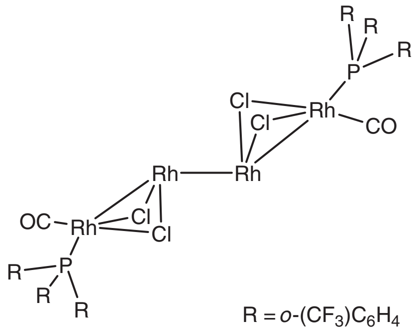

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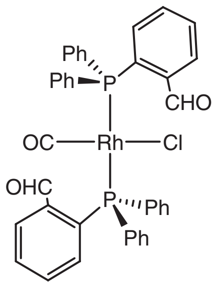


24

Systems of the form Rh(L-L′-BID)(CO)$(YR_3)_2$ that contained a five-membered monocharged bidentate ligand of the type L-L′-BID (L,L′-BID = monocharged bidentate ligand with donor atoms L,L′: variations of oxygen, nitrogen, and sulfur), such as cupferrate or tropolonate and derivatives, showed a tendency to accommodate an additional phosphine/arsine ligand (YR_3, Y = P, As).[6,33]

Particularly interesting is the unusually stable five-coordinate monomeric divalent rhodium complex, $[Rh^{II}(H)(CO)(PPh_3)_3]^+$, produced by bulk oxidative electrolysis or chemical oxidation of $Rh^I(H)(CO)(PPh_3)_3$ in dichloromethane.[79]

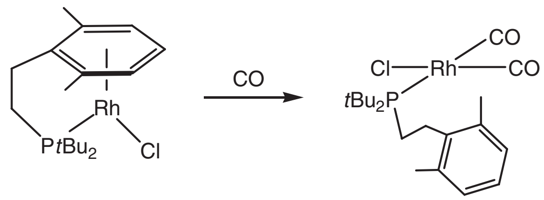
N-pyrrolylphosphines ($P\text{–}NC_4H_4$) readily form coordination compounds, as the Rh(I) complexes *trans*-RhCl(CO)$[PPh_x(pyrrolyl)_{3-x}]_2$ ($x = 0$–2). IR spectroscopy showed that these phosphines are poor sigma donors.[80] Starting from Rh(acac)$(CO)_2$ and the same N-pyrrolylphosphines, complexes of formula Rh(acac)(CO)$[PPh_x(pyrrolyl)_{3-x}]$ were obtained.[81] Irradiation of *trans*-[RhCl(CO)$(PMe_3)_2$] in benzene afforded three main products: RhCl(Ph)H$(PMe_3)_2$(CO) (two stereoisomers) and *trans*-Rh(Ph)$(PMe_3)_2$(CO).[82]

The bulky phosphine $^tBu_2P(CH_2)_2C_6H_3\text{-}2,6\text{-}Me_2$ is known to coordinate in a variety of forms. The ligand can be P-monodentate or chelate (P,C_{aryl} or P,η^6-arene) (Scheme 6). The arene moiety is weakly coordinated and can be replaced by CO without breaking the metal–phosphorus bond, leading to the first structurally characterised *cis*-configurated compound *cis*-[RhCl$(CO)_2(PR_3)$].[83]

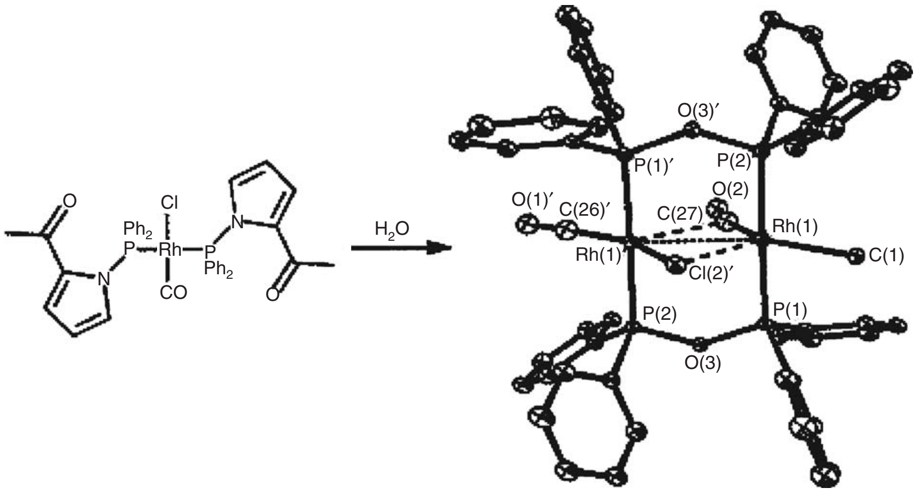
Complexes of the form RhX(CO)$(PR_3)_2$ [X = Cl, Br, or I; R = Me or Ph] were used in H_2 activation yielding a series of mono- and bimetallic hydride species.[84,84a] The complex *trans*-[Rh(CO)(py)$(PPh_3)_2$]ClO_4 was synthesized and characterized spectroscopically and did not react with H_2 at room temperature.[85]

7.02.2.1.3.(v) Bidentate P–P ligands

The reaction of $Rh_2(CO)_3(dppm)_2$ (dppm = diphenylphosphinemethane) with an excess of triflic acid, HSO_3CF_3, yielded the dicationic tricarbonyl complex $[Rh_2(CO)_3(dppm)_2]^{2+}$, which is fluxional and undergoes terminal and



Scheme 6

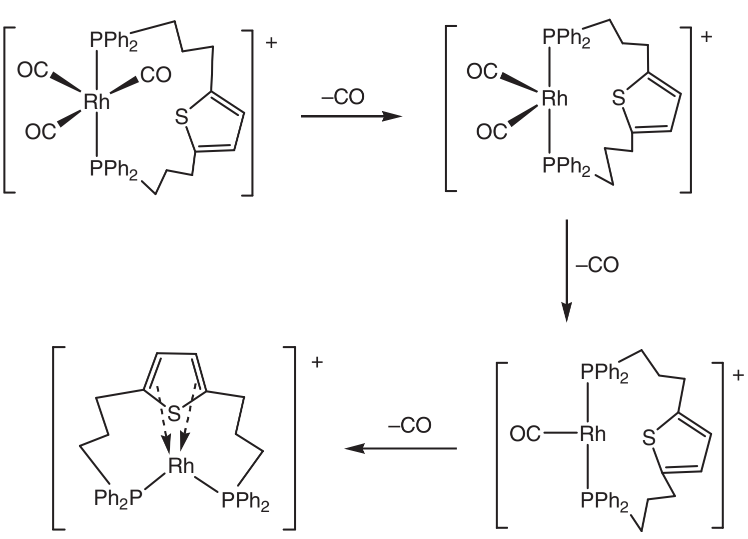


Scheme 7 Reprinted with permission from the American Chemical Society by Burrows *et al*. *Inorg*. *Chem*. **2002**, *41*, 1695.

bridging CO exchange.[86] The π-allyl(carbonyl)rhodium(I) complex Rh(η^3-C_3H_5)(CO)(κ^2-$^iPr_2PCH_2P^iPr_2$), which was obtained from Rh(η^3-C_3H_5)(κ^2-$^iPr_2PCH_2P^iPr_2$) and CO, reacted with H_2 at room temperature to give the dinuclear hydrido compound [Rh(CO)(μ-H)(μ-$^iPr_2PCH_2P^iPr_2$)]$_2$ in nearly quantitative yield.[87] Complex [Rh_2(μ-RNNNR)$_2$(CO)(solv)$_2$(bipy)]$^{2+}$ (solv = CH_2Cl_2, R = *p*-tolyl) reacted with dppm ($Ph_2PCH_2PPh_2$) affording [Rh_2(μ-CO)(dppm)(bipy)(μ-RNNNR)$_2$][PF_6]$_2$.[44] Rhodium(I) complexes *trans*-[RhCl(CO)(PR$_2${NC_4H_3C(O)Me})$_2$] (R = Ph, NC_4H_4) reacted with water to give the diphosphoxane-bridged dimers $Rh_2Cl_2(CO)_2$(μ-PR_2OPR_2)$_2$ following cleavage of the P–N bonds to the 2-acetyl-*N*-pyrrolyl groups (Scheme 7).[88]

The new phosphine 2,5-bis[3-(diphenylphosphino)propyl]thiophene (L) allowed the preparation of [Rh(CO)$_3$L]ClO_4. Progressive decarbonylation causes the formation of different electron-deficient complexes (Scheme 8).[89]

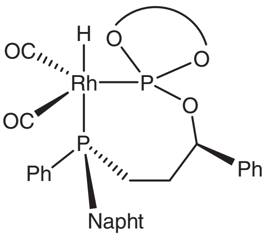
The reaction of $Rh_2(CO)_3(dppm)_2$ with an excess of triflic acid, HSO_3CF_3, yielded the dicationic tricarbonyl complex [$Rh_2(CO)_3(dppm)_2$]$^{2+}$ which, in solution, is in equilibrium with the triflate-coordinated cation [$Rh_2(SO_3CF_3)(CO)_3(dppm)_2$]$^+$.[86] In acetone [$Rh_2(CO)_3(dppm)_2$]$^{2+}$ underwent CO substitution by the solvent to produce an oxygen-bound acetone species [$Rh_2(SO_3CF_3)$(acetone)$(CO)_2(dppm)_2$]$^{2+}$ which was structurally characterized. [$Rh_2(CO)_3(dppm)_2$]$^{2+}$ reacted with CO to form the face-to-face square-planar dimer [$Rh_2(CO)_4(dppm)_2$]$^{2+}$.[86] Furanoside-based phosphines have also been used as chelate ligands for rhodium. In particular, two Rhodium(I) complexes were obtained



Scheme 8

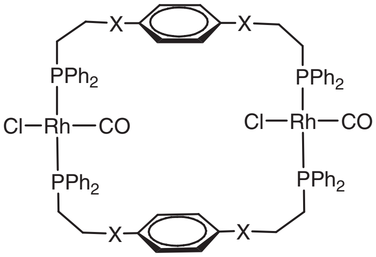
with two furanoside diphosphines, 3,5,6-trideoxy-3,5-bis-diphenylphosphine-1,2-*O*-isopropylidene-β-L-idofuranose and 3,5,6-trideoxy-3,5-bis-diphenylphosphine-1,2-*O*-isopropylidene-α-L-glucofuranose, which form six-membered chelate rings when they coordinate to rhodium. The configuration of the complexes and their fluxional behavior was studied on the basis of NMR spectroscopy and molecular mechanic calculations.[86a]

A series of chiral phosphine–phosphite ligands afforded complexes RhH(L–L)(CO)$_2$ like **25**, which showed catalytic activity toward asymmetric hydroformylation.[90] Chiral diphosphite ligands derived from D-(+)-glucose were also coordinated to Rh(I), affording complexes rhodium-hydrido-carbonyl-diphosphite species of the type RhH(PP)(CO)$_2$ (PP = diphosphite), which also proved to be effective asymmetric catalysts for the hydroformylation of vinyl arenes.[90a]



25

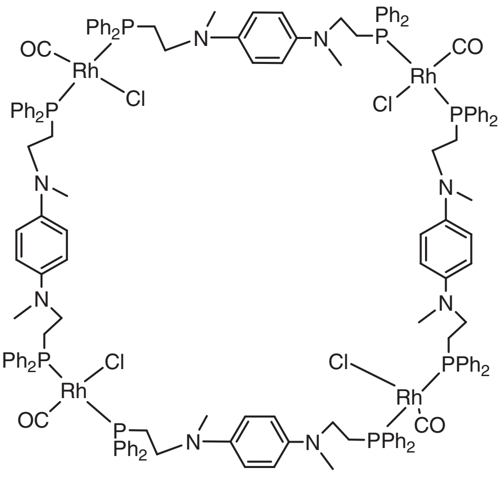
New chelate chiral phosphorus ligands provided a source for a large number of Rh and other metal-based catalysts.[5] The bis(phosphinoalkyl-ether)arene[91] and bis(phosphinoalkyl-thioether)arene ligands were synthesized allowing the preparation of symmetric bimetallic structures with Rh^{I} centers **26**.[92]



X = O, S, NMe

26

Other tetranuclear rhodium macrocycles **27** were synthesized by the reaction of *N*,*N*′-dimethyl-*N*,*N*′-bis[2-(diphenylphosphino)ethyl]-1,4-phenylenediamine with [Rh(μ-Cl)(coe)$_2$]$_2$ (coe = cyclooctene) and AgOTs (OTs = *p*-toluenesulfonate).[93]



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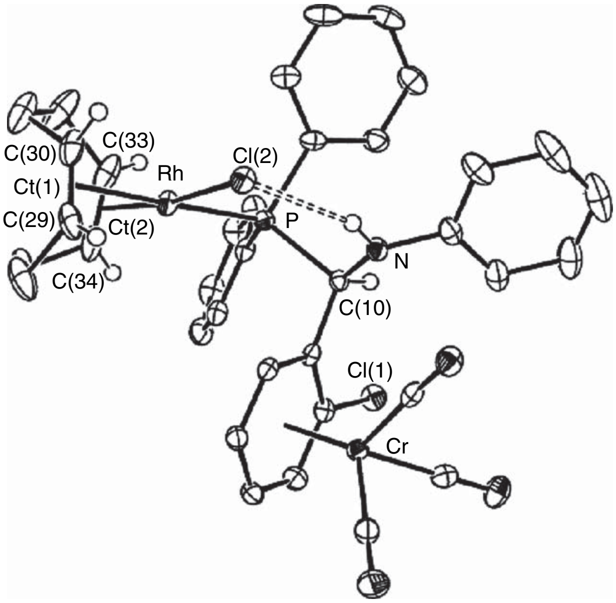
7.02.2.1.3.(vi) Bidentate P–O, P–S and P–N ligands

New Rh(I) complexes, $[RhCl(CO)(\mu\text{-}L)]_2$ and Rh(acac)(CO)L, were obtained with L = 1,3,2-dioxaphosphorinane containing an exocyclic codeine fragment. It was found that the chlorocarbonyl rhodium complex is a dimer with the bridge-type P–N-bidentate ligands coordinated in the "head-to-tail" mode.[11] The chiral aminophosphines (α-P–N) $Ph_2P\text{–}CH(Ar^1)\text{–}NHAr^2$ ($Ar^1 = o\text{-}C_6H_4Cl[Cr(CO)_3]$, $Ar^2 = Ph$) reacted with $[Rh(\mu\text{-}Cl)(cod)]_2$ to form the corresponding complexes RhCl(cod)(α-P,N), $[RhCl(cod)(Ph_2P\text{–}CH\{o\text{-}C_6H_4Cl[Cr(CO)_3]\}\text{–}NHPh)]$ **28**, and $RhCl(cod)(Ph_2P\text{–}CH(o\text{-}C_6H_4Cl)\text{–}NHPh)$.[94]



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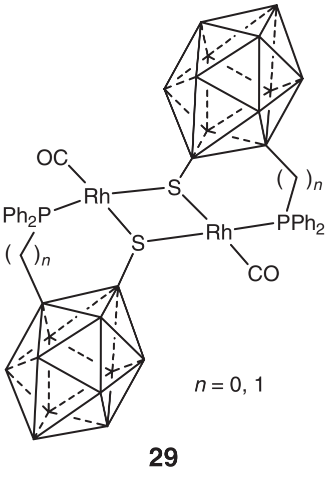
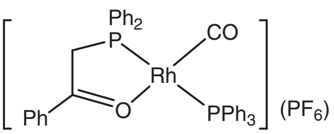
The synthesis of dirhodium complexes **29** containing the P–S-chelate ligands *P,S*-$[SC_2B_{10}H_{10}(CH_2)_nPPh_2]$ was described.[95] A mixed bidentate ferrocenyl ligand $Fe(\eta^5\text{-}C_5Me_4P(S)Ph_2)(\eta^5\text{-}C_5Me_4PPh_2)$ (abbreviated {P–P=S}) was synthesized and used for complexation with $[Rh(\mu\text{-}Cl)(CO)_2]_2$. The neutral [4]-ferrocenophane RhCl(CO){P–P=S} and the unusual dimeric cationic species $[\{P,P{=}S\}Rh(CO)(\mu\text{-}Cl)(CO)Rh\{P,P{=}S\}]^+$ were obtained.[96]



29

Several ketophosphines provided new rhodium carbonyl complexes,[76,97,97a,97b] such as **30**,[98] which oxidatively added MeI to give the corresponding octahedral Rh(III) species **31**.[99]



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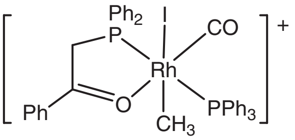
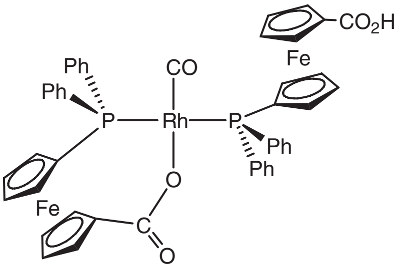


31

The reaction of the ferrocenylcarboxylic-functionalized phosphine 1′-(diphenylphosphino)ferrocenecarboxylic acid (Hdpf) with $[Rh(\mu\text{-}X)(CO)_2]_2$ (X = Cl or Br) afforded rhodium(I) complexes *trans*-$[RhX(CO)(Hdpf\text{-}P)_2]$ containing the ligand as the *P*-bonded phosphine. The compound $Rh(acac)(CO)_2$ reacted with 2 equiv. of Hdpf to give *trans*-[Rh(dpf-*O,P*)(Hdpf-*P*)(CO)] **32**, while $Rh(acac)(PCy_3)(CO)$ afforded *trans*-$[Rh(dpf\text{-}O,P)(PCy_3)(CO)]$ **33**, in which the phosphine is O–P-chelating.[100]



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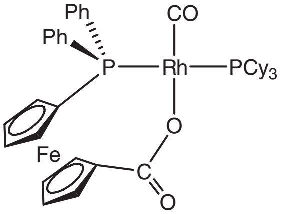
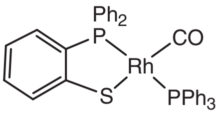


33

Reaction of $RhF(CO)(PPh_3)_2$ with bulky aromatic thiols ArSH (SAr = $SC_6H_2{}^iPr_3$-2,4,6 or $SC_6H_4SiPh_3$-2) gave the monometallic $Rh(SAr)(CO)(PPh_3)_2$ and the dimetallic $[Rh(\mu\text{-}SAr)(CO)(PPh_3)]_2$ species. Related phosphinothiol ligands PSH (PS = $SC_6H_4PPh_2$ or $SCH(CH_3)CH_2PPh_2$) gave a series of phosphinothiolate rhodium carbonyl complexes of formulas $Rh(PS)(CO)(PPh_3)$ **34**, $[Rh(PSMe)(CO)(PPh_3)]^+$ **35**, and the dimer $[Rh_2(H)_2(\mu\text{-}SC_6H_4PPh_2\text{-}2)_2(CO)_2(PPh_3)_2]^{2+}$ **36** among other PS-chelate Rh complexes.[101] Similar complexes containing phosphinothiolate and thioether ligands were active in catalyzing the carbonylation of methanol to ethanoic acid.[102]



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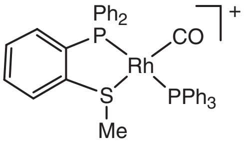

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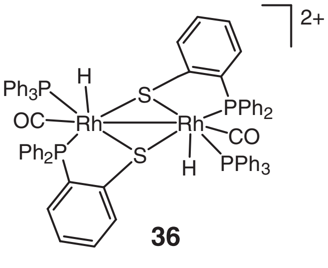
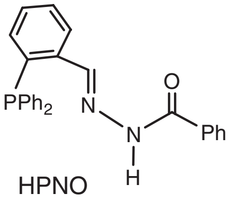


36

A large number of aminophosphine phosphinite ligands was used in the preparation of enantioselective catalysts.[1,103]

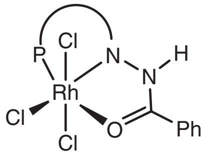
7.02.2.1.3.(vii) Tridentate and tetradentate phoshorus ligands

The tridentate hydrazonic ligand 2-(diphenylphosphino)benzaldehyde benzoylhydrazone **37** (HPNO) reacted with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ leading to the formation of the Rh(III) chloro complex $RhCl_3(HPNO)$ **38** and the Rh(I) carbonyl complex Rh(PNO)(CO) **39** or to the Rh(I) complex RhCl(PNO)(CO) **40** depending on the reaction conditions. On bubbling gaseous HCl into a solution of the latter complex, the Rh(III) hydride carbonyl complex $RhCl_2H(HPN)(CO)$ was tentatively suggested as intermediate, $RhCl_3(HPNO)$ being the final reaction product.[104] The pincer ligand 2,2′-bis(diphenylphosphino)diphenylamine gave a square-planar carbonyl complex.[105]



HPNO

37



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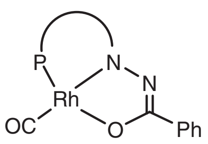

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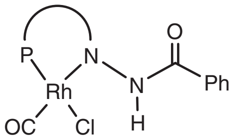
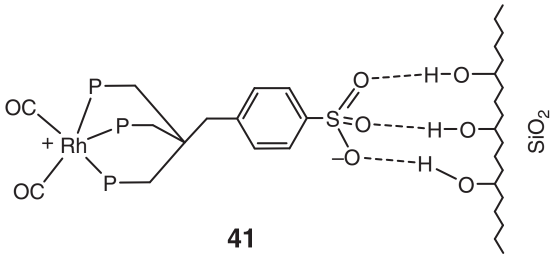


40

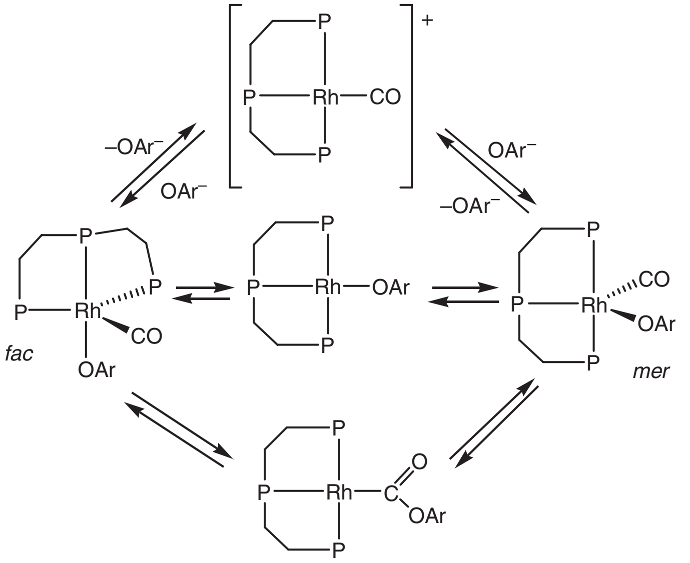
The zwitterionic Rh(I) catalyst Rh(sulfos)$(CO)_2$ **41** [sulfos═$O_3S(C_6H_4)CH_2C(CH_2PPh_2)_3$] was heterogenized on partially dehydroxylated high surface area silica and used in the catalyzed hydroformylation of alkenes.[106]



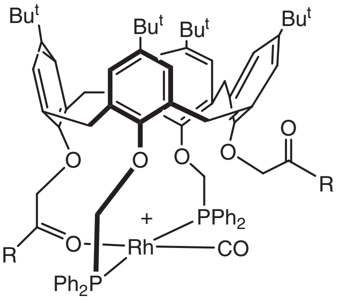
41

The reactivity of [Rh(triphos)CO]PF_6 {triphos═bis(2-diphenylphosphinoethyl)phenyl phosphine} with aryloxides ArO^- {Ar═C_6H_5, C_6H_4-*p*-CH_3, C_6H_4-*p*-OCH_3) allowed the formation of a series of aryloxycarbonyl complexes Rh(triphos)(CO)(OAr), which were observed by FTIR spectroscopy. These aryloxycarbonyl complexes decayed via different pathways involving the *fac*- and *mer*-isomers of Rh(triphos)(CO)(OAr) (Scheme 9).[107]

The tetracoordinated diphosphine complex $[Rh(CO)_2(dppoo)]ClO_4$ (P–P–O-coordinated, dppoo = $(Ph_2PCH_2CH_2OCH_2)_2$) was obtained.[108] Calix[4]arene ligands with phosphorus-containing groups provided new tetracoordinated P–P–O-tridentate Rh–CO complexes, like **42**.[109]



Scheme 9



42

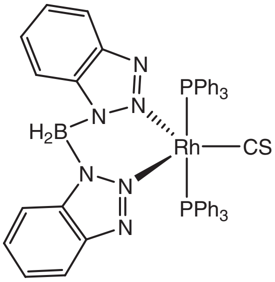
Phosphines derived from calix[4]arene (L_a) and *p-tert*-butylcalix[4]arene (L_b) reacted with Rh(acac*)(CO)$_2$ (acac* = ^{t}BuCOCHCO^{t}Bu) to give the mononuclear complexes Rh(acac*)(CO)(L_a) and Rh(acac*)(CO)(L_b), respectively. Treatment of [Rh(μ-Cl)(CO)$_2$]$_2$ with L_b gave a mixture of products which were assigned to the *cis*/*trans* isomers of [Rh(μ-Cl)(CO)(L_b)]$_2$.[110] Other diphosphines derived from calix[4]arene also yielded RhCl(CO)[(*P*,*P*)-diphen-calix[4]arene].[111]

7.02.2.1.3.(viii) Arsine and stilbane complexes

Few new arsine[6,112,112a,112b,113] and stilbane complexes were obtained.[114–116] The electronic and steric properties of the Vaska-type complex of general formula *trans*-[RhCl(CO)(YR$_3$)$_2$] (YR$_3$ = arsine or stilbane) were studied.[6,113,117,117a] The five-coordinate rhodium(I) stilbane complexes RhX(SbPh$_3$)$_3$(CO) (X = Cl, Br) reacted with organic propargyl compounds to afford the η^1-allenyl and η^1-propargyl products.[114]

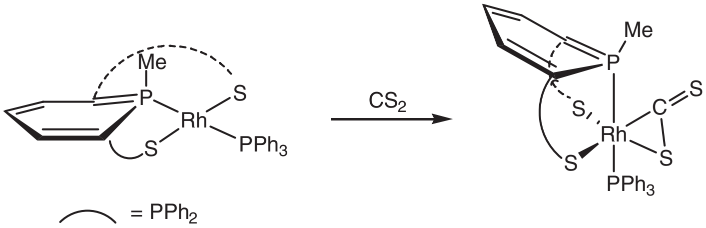
7.02.2.2 Thiocarbonyl, Carbon Disulfide, and Carbon Dioxide Complexes

Very little has been reported regarding the coordination of CS to rhodium complexes, probably due to the instability of free CS which makes this compound difficult to handle and use as a ligand. RhCl(CS)(PPh$_3$)$_2$ reacted with K[H$_2$B(bta)$_2$] (bta = benzotriazol-1-yl) providing Rh{κ^2-H$_2$B(bta)$_2$}(CS)(PPh$_3$)$_2$ **43**.[57]



43

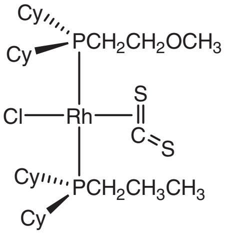
The photooxidation of RhCl(CS)(PPh$_3$)$_2$ to RhCl$_3$(PPh$_3$)$_2$(CS) was studied; the reaction proceeded via a metal-to-ligand charge-transfer (MLCT) excitation.[118] Pincer SPS-type Rh(I) complexes reacted with CO, CO$_2$, O$_2$, CS$_2$ (Scheme 10), and SO$_2$ affording the corresponding Rh(I) or Rh(III) adducts.[119]



Scheme 10

Other carbon disulfide complexes were obtained by the reaction of the cationic bis(chelate) complex $[Rh(P–O)_2]BPh_4$ $[(P–O){=}(C_6H_{11})_2PCH_2CH_2OCH_3]$ with CS_2, providing the compound $[Rh(CS_2)(P–O)_2]BPh_4$.[120] The phenylacetylide-bridged heterobinuclear complexes $[RhIr(CO)_2(\mu\text{-}\eta^1:\eta^2\text{-}C_2Ph)(dppm)_2]X$ ($X = BF_4$, SO_3CF_3; dppm $= Ph_2PCH_2PPh_2$) reacted with carbon disulfide to give several products such as $[RhIr(CO)(\eta^2\text{-}CS_2)(\mu\text{-}CO)(\mu\text{-}\eta^1:\eta^2\text{-}C_2Ph)(dppm)_2]X$ as the result of CS_2 coordination at Ir. Upon warming, two products $[RhIr(CO)(\mu\text{-}\eta^1:\eta^3\text{-}CC(Ph)SCSCS_2)(\mu\text{-}CO)(dppm)_2]X$ and $[RhIr(CO)(C_2S_4)(\mu\text{-}C_2Ph)(\mu\text{-}CO)(dppm)_2]X$ were formed by condensation of two CS_2 groups.[121]

The reaction of the pseudo-14-electron complex $RhCl(\eta^2\text{-}P,O)(\eta^1\text{-}P,O)$ ($P,O = Cy_2PCH_2CH_2OCH_3$) with carbon disulfide resulted in the formation of $RhCl(\eta^1\text{-}P–O)_2(CS_2)$ **44**, and $RhCl(\eta^1\text{-}P–O)_2(CS)$ **45**.[122]



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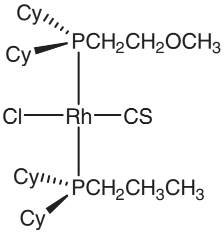
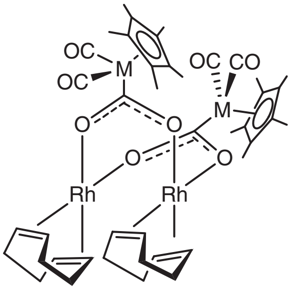


45

Carbon dioxide heterometallic complexes of formulas $[Cp^*(CO)(NO)Re(CO_2)Rh(cod)]_2$ and $[Cp^*(CO)_2MCO_2Rh(cod)]_2$ **46** (M = Fe, Ru) were obtained by the reaction of $[Rh(\mu\text{-}OH)(cod)]_2$ and cationic carbonyl complexes. The cyclooctadiene ligand was removed by the addition of CO, providing **47**.[123,123a]



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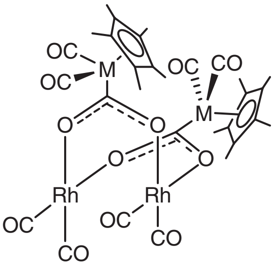
M = Fe, Ru

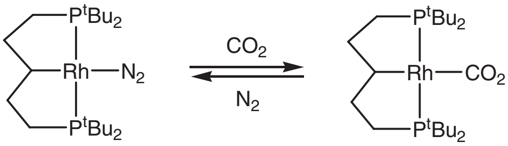


47

The mechanistic details of 1,2-cycloadditions of CO_2 and CS_2 to metalloaromatic complexes of Ir and Rh were studied.[124]

The complex $[Rh(P–O)_2](BPh_4)$ [P–O = (O,P)-chelated $Cy_2PCH_2CH_2OCH_3$] acted as an efficient catalyst for the hydrogenation of carbon dioxide to produce formic acid.[125] Other chelate phosphine complexes of rhodium also catalyze this reaction.[126,126a,127] Theoretical studies of this catalytic reaction were performed using Rh(III) and Rh(I) model complexes.[128,128a–128d] Carbon dioxide was also photochemically activated by $[Rh(CO_2)]^+/Al_2O_3$, for which an $Rh–CO_2$ intermediate adduct was proposed.[21]

The T-shaped complex $Rh(N_2)[HC(CH_2CH_2P(t\text{-}Bu)_2)_2]$, prepared by elimination of HCl with sodium hydride from the hydrido chloride $RhH(Cl)[HC(CH_2CH_2P(t\text{-}Bu)_2)_2]$, reacted with CO_2 yielding the first 16-electron rhodium–carbon dioxide complex that was spectroscopically characterized (Scheme 11).[129]

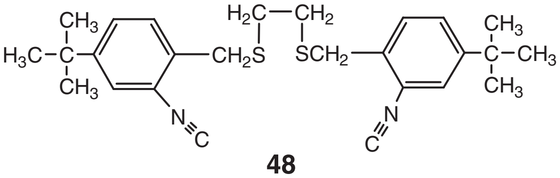


Scheme 11

7.02.2.3 Isocyanide (Isonitrile) and Diazoalkane Complexes

7.02.2.3.1 Binary complexes

New diisonitrile ligands like **48** were synthesized and coordinated to rhodium to give compounds of formulas $RhClL_2$ and $[RhL_2]BF_4$.[130,130a]

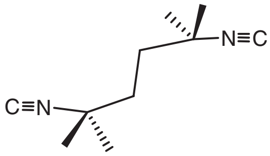


48

The photochemical properties of $[Rh_2(dimen)_4]^{2+}$ (dimen = 1,8-diisocyanomenthane) were studied, revealing Rh–Rh bond shortening in the lowest electronic excited states.[131] The ligand flexibility allowed a wide range of metal–metal distances, from 3.6 to 4.5 Å.[132]

An extensive review on the coordination of 1,8-diisocyano-*p*-menthane **49** and 2,5-dimethyl-2′,5′-diisocyanohexane **50** appeared.[3]

49



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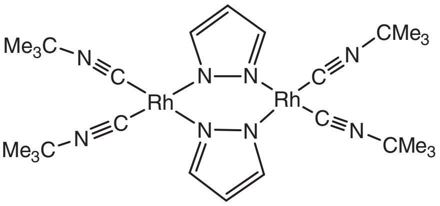
Several theoretical studies were carried out on the nature of $[Rh_2(CNR)_4]^{2+}$ species. For example, the nature of the ground state and the lowest triplet excited state of the $[Rh_2(1,3\text{-diisocyanopropane})_4]^{2+}$ ion was investigated by DFT methods. Two locally stable geometrical conformations were found on the potential energy surfaces of both the ground and excited states, corresponding to the eclipsed and twisted conformations.[133]

7.02.2.3.2 Isocyanide complexes containing O- and N-donor ligands

Rhodium isocyanide complexes $RhCl(CO)[CN(CH_2)_3Si(OC_2H_5)_3]_2$ and $RhCl[CN(CH_2)_3Si(OC_2H_5)_3]_3$ were tethered to the silica-supported metal heterogeneous catalysts $M–SiO_2$ (M = Pd, Pt, Ru) and were used to catalyze the hydrogenation of arenes under mild conditions.[134] Complexes of formulas *trans*-$[RhCl(CNR)(As^iPr_3)_2]$ and *trans*-$[RhCl(CNR)(Sb^iPr_3)_2]$ (R = Me, CH_2CMe_3, $C_6H_3Me_2$) were obtained by ethylene displacement from *trans*-$[RhCl(C_2H_4)(As^iPr_3)_2]$ and *trans*-$[RhCl(C_2H_4)(Sb^iPr_3)_2]$.[116] DFT calculations were carried out for *trans*-$[RhCl(CNR)(PMe_3)_2]$ (R = 2,6-$Me_2C_6H_3$) in order to study the *trans*-influence of the isocyanide ligand.[135] The enthalpy of the addition of CN^tBu to $[RhCl(P^iPr_3)_2]_2$ to give $RhCl(P^iPr_3)_2(CN^tBu)$ was reported.[136]

Replacement of the olefin in the complexes $[Rh(\mu\text{-pz}')(C_2H_4)_2]_2$ (pz′ = pyrazolate (pz), 3-methylpyrazolate (Mepz), 3,5-dimethylpyrazolate (Me_2pz)) by *tert*-butyl isocyanide gave $[Rh(\mu\text{-pz}')(CN^tBu)_2]_2$ **51**.[38] These complexes oxidatively added MeI, as a consequence of the metal basicity induced by the isocyanide ligands.[137] The mechanisms of the oxidative addition of other electrophiles of the type RCH_2Cl were also studied.[138]



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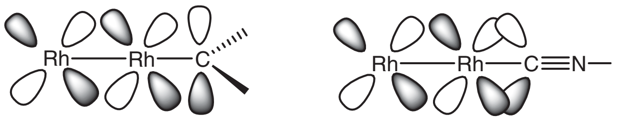
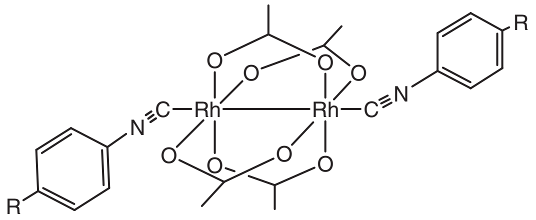


Rhodium carbene complex

Rhodium isonitrile complex

Scheme 12

New rhodium acetate bisisonitrile adduts of the type $Rh_2(O_2CCH_3)_4 \cdot 2CNC_6H_4R$ **52** ($R = (CH_3)_2N$-, -H, $-CF_3$) were obtained. The short Rh–C distances suggest the existence of π-bonding, by analogy with other rhodium carbenoid systems (Scheme 12).[139]

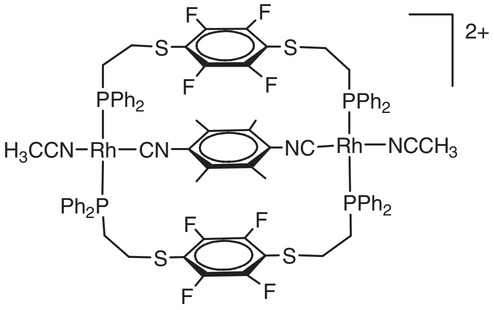


52

The synthesis, electrochemical and spectroscopic properties of the bisdirhodium complex containing dpf-bridging ligand, $(dpf)_4Rh_2(CNC_6H_4NC)Rh_2(dpf)_4$ (dpf = *N*,*N′*-diphenylformamidinate ion), were investigated. The “simple” dirhodium species, $Rh_2(dpf)_4(CNC_6H_5)$, with the same bridging ligand, was also synthesized and its properties compared with that of the related bisdirhodium complex.[140] The oxidative addition of electrophiles, such as MeI or I_2, to the chloranilate complex of formula $Rh_2(\mu\text{-}C_6Cl_2O_4)(CNR)_4$ (R = toluene-*p*-sulfonyl-methyl) was investigated.[27]

The reaction of $K[H_2B(bta)_2]$ (bta = benzotriazol-1-yl) with $RhCl(CO)(PPh_3)_2$ provided $Rh\{\kappa^2\text{-}H(bta)_2\}(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2$. The formation of the isonitrile derivative seemed to proceed via an associative mechanism involving a blue intermediate complex formulated as $Rh\{\kappa^1\text{-}H_2B(bta)_2\}(CNR)(CO)(PPh_3)_2$.[57] The compound $[RhTp]_2(\mu\text{-}CNCy)_3$ was obtained and characterized by X-ray crystallography.[68] The generation of the 16-electron fragment $[HB(3,5\text{-dimethylpyrazolyl})_3]Rh(CNCH_2CMe_3)$ (Tp′RhL) in the presence of cyclopropane resulted in C–H activation of the hydrocarbon.[141]

The bis(phosphinoalkyl-thioether)arene ligand with a fluorinated aryl group ($1,4\text{-}(Ph_2PCH_2CH_2S)_2C_6F_4$) was synthesized and allowed the preparation of symmetric bimetallic isocyanide structures with Rh^I, like **53**.[92]



53

Several diazoalkane complexes were reported.[142,143,143a,144,145] For example, the preparation of a series of complexes was achieved by the reaction of $RhCl(PR_3)_n$ (R = Me ($n = 4$), Et ($n = 3$)) and $RhCl(CO)(PEt_3)_2$ with (trimethylsilyl)diazomethyl lithium, yielding $Rh[C(N_2)SiMe_3](PEt_3)_3$, $Rh[C(N_2)SiMe_3](PMe_3)_4$, and $Rh[C(N_2)SiMe_3](CO)(PEt_3)_2$.[146]

7.02.3 Compounds with Hydrocarbon Ligands

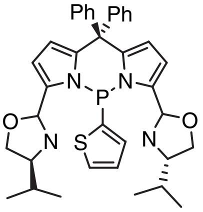
7.02.3.1 Cyclopentadienyl Complexes Containing no Other Hydrocarbon Ligands

Three divisions have been made in this section: (i) complexes with the unsubstituted Cp ligand, (ii) complexes with substituted cyclopentadienyl ligands (excluding Cp*), and (iii) complexes with the Cp* ligand.

7.02.3.1.1 Cp complexes

The number of works regarding the chemistry of Cp–Rh complexes without other hydrocarbon ligands reported in the 1994–2005 period has been scarce compared to the previous editions, COMC (1982) and COMC (1995). Most of the Rh–Cp complexes reported in the last decade contain other hydrocarbon ligands and hence are described in other sections of this chapter.

The bis(oxazoline)-thienylphosphine ligand ((*S*,*S*)-BOTPHOS) was synthesized in an enantiomerically pure *S*,*S* state. Treatment of the $CpRhRu_3(H)_2(CO)_{10}$ cluster with a slight excess of (*S*,*S*)-BOTPHOS **54** resulted in the substitution of two carbonyls at a ruthenium atom and chelate coordination of the ligand through the phosphorus and a nitrogen atom of an oxazoline ring to give $CpRhRu_3(H)_2(CO)_8(\kappa^2$-(*S*,*S*)-BOTPHOS) **55**.[147]



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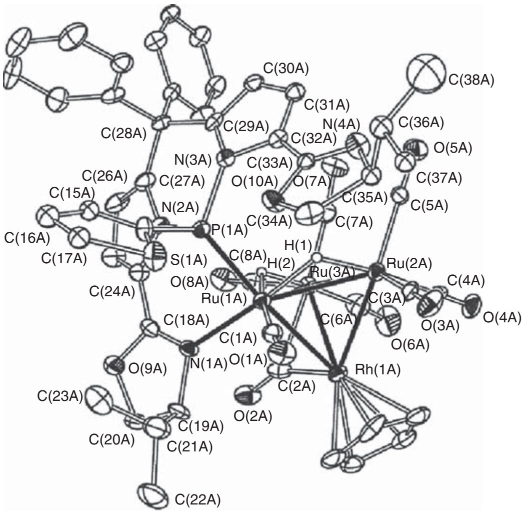
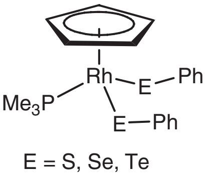


55

Scheme **55** is reprinted with permission from the American Chemical Society by Koshevoy *et al.* Organometallics, **2004**, *23*, 2641.

Diphenyl dichalcogenides reacted with $CpRh(PMe_3)(CO)$ to give several complexes of the type $CpRh(PMe_3)(EPh)_2$ **56** (E = S, Se, and Te). The complex $CpRh(PMe_3)(S_2C_6H_4)$ **57** was obtained in a similar way.[148]



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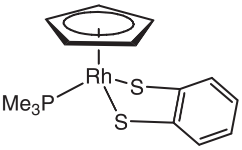
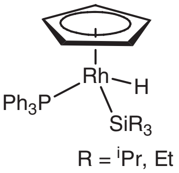


57

The photoreaction of $CpRh(PPh_3)(C_2H_4)$ with SiR_3H (R = Pr^i or Et) yielded $CpRh(PPh_3)(SiR_3)H$ **58** whose molecular structure was determined crystallographically.[149]



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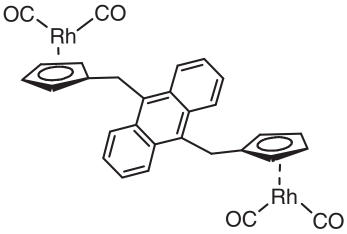
Photoelectron (PE) spectra with variable photon energy were recorded using He I, He II, and synchrotron radiation for the complex $CpRh(CO)_2$. The spectra were assigned using both ground-state Xα-SW calculations combined with a comparison of the experimental and theoretical branching ratios.[150]

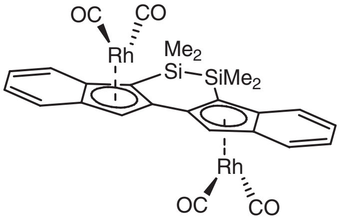
7.02.3.1.2 Substituted Cp complexes (excluding Cp*)

$[(C_5HPh_4)_2Rh]PF_6$ was prepared from the reaction of $Rh(acac)_3$ and $K(C_5HPh_4)$. Reduction of $[(C_5HPh_4)_2Rh]PF_6$ with sodium amalgam in THF yielded $(C_5HPh_4)_2Rh$ in high yield.[151] A comparison of the electronic properties and photochemical reactivity efficiencies for a series of rhodium dicarbonyl complexes with the general formula $[XRh(CO)_2]$, where $X = (\eta^5\text{-}C_5H_5)$, $(\eta^5\text{-}C_5H_4Me)$, $(\eta^5\text{-}C_5HMe_4)$, $(\eta^5\text{-}C_5Me_5)$, and $(\eta^5\text{-}C_9H_7)$, was achieved. The absolute reaction quantum efficiencies (ϕ_{cr}) are markedly different and strongly wavelength dependent for each of the molecules studied.[152] A study of the electrochemical behavior (CV) of 9-anthrylmethylcyclopentadienyl ($AnCH_2C_5H_4$) derivatives of rhodium(I) was reported.[153] 9,10-Bis(cyclopentadienylmethyl)anthracene was obtained by reacting 9,10-bis(bromomethyl)anthracene with cyclopentadienylsodium and transformed into its dithallium(I) derivative on reaction with thallium ethoxide. The reaction of this thallium compound with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ led to the bimetallic complex $(CO)_2Rh\{C_5H_4CH_2(9,10\text{-anthrylene})CH_2C_5H_4\}Rh(CO)_2$ **59**.[154]



59

A dinuclear rhodium complex with a ligand derived from 2,2′-bis(indenyl) system, $1,1'\text{-}(2,2'\text{-}C_9H_6)_2Si(Me)(^tBu)$ was prepared $1,1'\text{-}[(2,2'\text{-}\eta^5\text{-}C_9H_5)Rh(CO)_2]_2(SiMe_2)_2$ **60**.[155]



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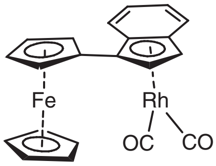
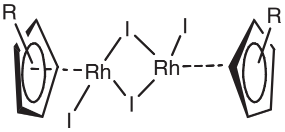
The binuclear $[\eta^5\text{-(1-ferrocenyl)indenyl}]Rh(CO)_2$ **61** complex was synthesized. The crystal structure determination showed that the iron and rhodium nuclei are disposed in a cisoid configuration. The results of the chemical and electrochemical oxidation of this compound suggested the existence of an effective interaction between the two metals.[156]



61

New cyclopentadienyl complexes prepared from $[Rh(\mu\text{-}Cl)(cod)]_2$ and $[Cp'' = C_5H_4COOCH_2CH{=}CH_2$, $C_5H_4CH_2CH_2CH{=}CH_2$, $C_5H(i\text{-}C_3H_7)_4$, $C_5H(i\text{-}C_3H_7)_4]$ were oxidized by iodine to give bridged dimers $[Cp''RhI_2]_2$ **62**. Addition of triphenyl phosphine, carbon monoxide or carbon disulfide promoted the cleavage of the iodine-bridged structure and produced monomer products $Cp''RhI_2L$ $[Cp'' = C_5H_4COOCH_2CH{=}CH_2$, $L = CS_2$ **63**, $L = PPh_3$ **64**; $Cp'' = C_5H(i\text{-}C_3H_7)_4$, $L = CO$ **65**]. The addition of CO to the complex $Cp''Rh(cod)$ afforded $Cp''Rh(CO)_2$ **66**.[157]



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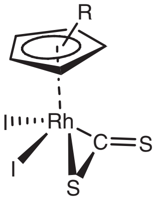

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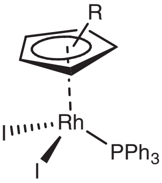

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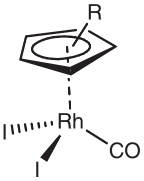

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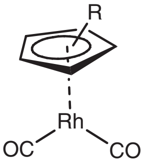

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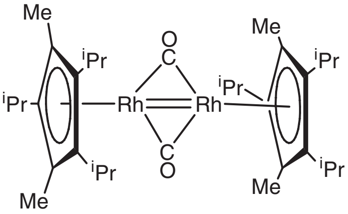
From the bulky (1,2,4-triisopropyl-3,5-dimethylcyclopentadienyl)rhodiumbis(ethylene) and (1,2,4-tri-*tert*-butylcyclopentadienyl)rhodiumbis(ethylene) the corresponding (cyclopentadienyl)rhodium carbonyl dimers **67** and **68** were obtained.[158]



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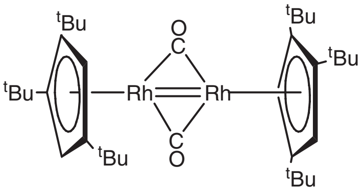
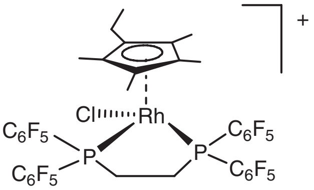


68

The reaction between $[(\eta^5\text{-}C_5Me_4Et)RhCl_2]_2$ and the diphosphine $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe) proceeded via the activation of two C–F and two C–H bonds and the formation of two C–C bonds to give a mixture of isomers of a salt with formulation "$[(\eta^5\text{-}C_5Me_4Et)RhCl\{(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2\}\text{-}2HF]^+\cdot Cl^-$". Treatment of $[(\eta^5\text{-}C_5Me_4Et)RhCl_2]_2$ with NH_4BF_4 followed by dfppe yielded $[(\eta^5\text{-}C_5Me_4Et)RhCl\{(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2\}]^+$ **69**.[159] The reaction between $[(\eta^5\text{-}C_5Me_4H)RhCl_2]_2$ and dfppe proceeded similarly in refluxing benzene to yield the cation $[\{\eta^5\text{-}C_5HMe_2\text{-}2,4\text{-}[(CH_2C_6F_4)P(C_6F_5)CH_2]_2\text{-}1,3\}RhCl]^+$ **70** with >90% selectivity.[160]



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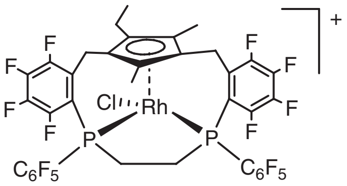
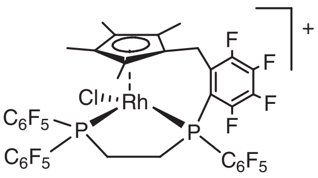


70

A similar process was observed in the reaction between $[Cp^*RhBr_2]_2$ and dfppe in benzene, which proceeded via the intermediate cation $[Cp^*RhBr(dfppe)]^+$, which underwent C–F and C–H bond activation and C–C bond formation to give sequentially $[\{\eta^5\text{-}C_5Me_4CH_2C_6F_4P(C_6F_5)CH_2CH_2P(C_6F_5)_2\}RhBr]^+$ and then $[\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}RhBr]^+$.[161] In refluxing ethanol $[Cp^*RhCl(dfppe)]BF_4$ underwent stepwise dehydrofluorinative carbon–carbon coupling to give $[\{\eta^5,\kappa P,\kappa P\text{-}C_5Me_4CH_2C_6F_4\text{-}2\text{-}P(C_6F_5)CH_2CH_2P(C_6F_5)_2\}\text{-}RhCl]BF_4$ **71**, then $[\{\eta^5,\kappa P,\kappa P\text{-}C_5Me_3[CH_2C_6F_4\text{-}2\text{-}P(C_6F_5)CH_2]_2\text{-}1,3\}RhCl]BF_4$ **72**.[162] The compound $[Cp^*RhCl\{(C_6F_5)_2PC_6H_4SMe\text{-}2\}]BF_4$ underwent rapid coupling on treatment with proton sponge affording $[\{\eta^5,\kappa P,\kappa S\text{-}C_5Me_4CH_2C_6F_4P(C_6F_5)C_6H_4SMe\}RhCl]BF_4$ **73**.[163]



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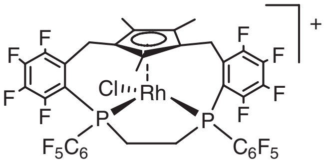

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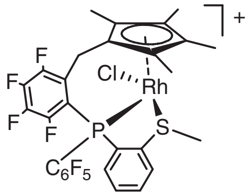
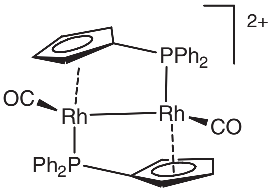


73

By the reaction of nitriles and pyridine with $[Rh^{II}(CO)(\mu\text{-}CpPPh_2)]_2{}^{2+}$ **74**, the monosubstituted $[Rh_2(CO)L(\mu\text{-}CpPPh_2)_2]^{2+}$ and disubstituted $[Rh(L)(\mu\text{-}CpPPh_2)]_2{}^{2+}$ compounds (L = MeCN, PhCN, pyridine) were obtained. With secondary and primary amines, $[Rh^{II}(CO)(\mu\text{-}CpPPh_2)]_2{}^{2+}$ was reduced to $[Rh^{I}(CO)(\mu\text{-}CpPPh_2)]_2$ **75**. From **74** compounds such as $[Rh^{II}(THF)(\mu\text{-}CpPh_2)]_2{}^{2+}$, $[Rh^{II}(\mu\text{-}H_2NC_5H_4N)(\mu\text{-}CpPh_2)_2]^{2+}$ **76**, and $[Rh^{II}(NO_2)(\mu\text{-}CpPh_2)]_2$ **77**, were synthesized, and their complexes were obtained by reaction of **74** with other pyridine, amine, nitrosyl and nitrite ligands.[164]



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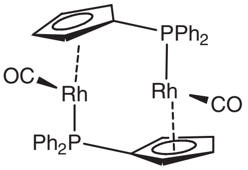

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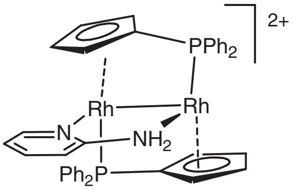

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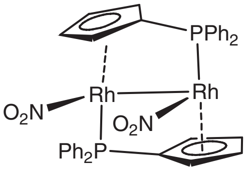
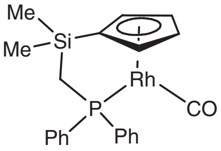


77

The linked Cp ligand $[C_5H_4SiMe_2CH_2PPh_2]^-$ was used to synthesize several rhodium derivatives. Reaction with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ gave $(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2CH_2PPh_2)Rh(CO)$ **78** complex, which was characterized by single crystal X-ray diffraction.[165] The synthesis of $(\eta^5{:}\eta^1\text{-}Me_2PCH_2SiMe_2C_5Me_4)RhX_2$ **79** (X = I, Br) was reported.[166]



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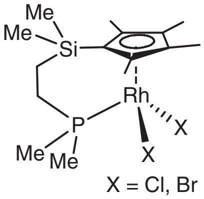
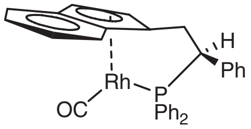


79

Addition of the lithium salts of the enantiopure bidentate indenyl-phosphine ligands (1*S*)-[2-(3*H*-inden-1-yl)-1-phenylethyl]diphenylphosphine and [(2*R*)-2-cyclohexyl-2-(3*H*-inden-1-yl)ethyl]diphenylphosphine to $[Rh(\mu\text{-}Cl)(CO)_2]_2$ gave $(\eta^5{:}\eta^1\text{-indenyl-}CH_2CH(Ph)PPh_2)RhCO$ **80** and $(\eta^5{:}\eta^1\text{-indenyl-}CH(Cy)CH_2PPh_2)RhCO$ **81** as 75 : 25 and 78 : 22 mixtures of diastereoisomers.[167]



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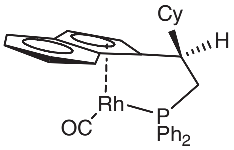
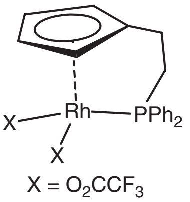


81

Iodide abstraction by silver salts from the complex $\{\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PPh_2\}RhI_2$ yielded products whose structures depend on the coordinating ability of the anion originally associated with silver. Silver trifluoroacetate gave fully characterized disubstituted derivatives of the type $\{\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PPh_2\}Rh(CF_3COO)_2$ **82**, in which the trifluoroacetate anions are bound in a monodentate fashion. Silver hexafluorophosphate gave a dinuclear dicationic compound $[\{\{\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PPh_2\}Rh(\mu\text{-}I)\}_2][PF_6]_2$ **83**.[168]



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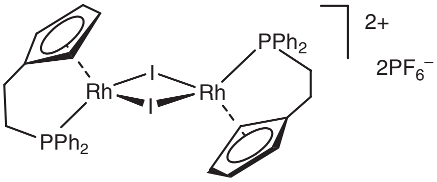
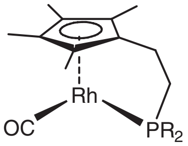
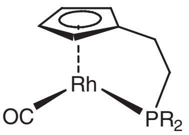


83

(Phosphanylalkyl/aryl)tetramethylcyclopentadienyl complexes of rhodium **84** were obtained from lithiated 1,2,3,4-tetramethyl-5-(2-P,P-dialkyl/arylphosphinoethyl)cyclopentadiene and $[Rh(\mu\text{-}Cl)(CO)_2]_2$. The electron-donating properties of these ligands were compared to the related (phosphanylalkyl/aryl)cyclopentadienyl complexes **85**. The P–Rh bond is shown to be stable under methanol carbonylation reaction conditions.[169]

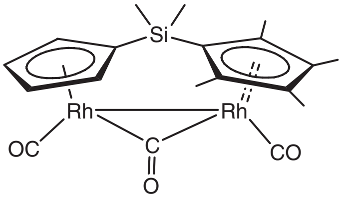




R = Et, Ph

84 **85**

The reaction of the dilithium salt $Li_2[Me_2Si(C_5H_4)(C_5Me_4)]$ with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ afforded the homodinuclear metal complex $\{Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5Me_4)\}Rh_2(CO)_2(\mu\text{-}CO)$ **86** and with $RhCl(CO)(PPh_3)_2$ afforded a mononuclear metal complex $\{Me_2Si(C_5HMe_4)(\eta^5\text{-}C_5H_4)\}Rh(CO)PPh_3$ **87** leaving the C_5HMe_4 moiety intact.[170]



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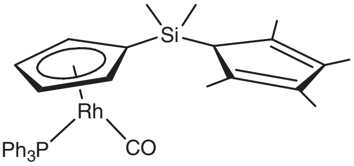
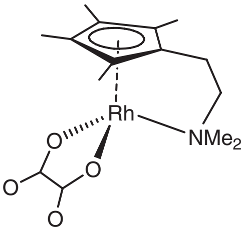


87

Some rhodium complexes such as **88, 89, and 90** with cyclopentadienyl ligands bearing a dimethylaminoethyl side-chain were prepared.[171]



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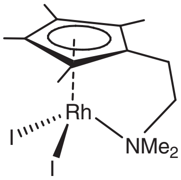

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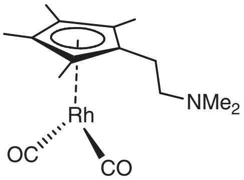
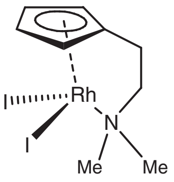


90

The syntheses and crystal structures of three water-soluble substituted cyclopentadienyl ligands were reported. The three ligands are 1,2,3-trichloro-4,5-bis(pyridinium)cyclo chloride, 1,2-dichloro-3,4,5-tris(pyridinium)cyclo dichloride, and 1,3-dichloro2,4,5-tris(pyridinium)cyclopentadienyl dichloride.[172] The synthesis of monometallic rhodium(III) **91** and rhodium(I) derivatives of dialkylamino-functionalized cyclopentadienyl ring using the corresponding cyclopentadiene as starting material is facilitated by the presence of the basic amino group. This procedure afforded the preparation of the substituted rhodicinium cation $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H)_2Rh^{III}]^{3+}$ **92** from the reaction of the [2-(dimethylamino)ethyl]cyclopentadiene with $Na_3Rh^{III}Cl_6\cdot 12H_2O$.[173]



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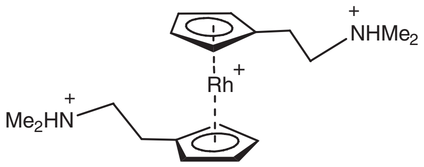
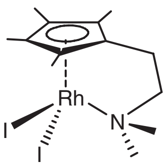


92

Some Rh(I) and Rh(III) complexes containing the 1-(2-(dimethylamino)-ethyl)-2,3,4,5-tetramethylcyclopentadienyl ligand were described. In some compounds, there is intramolecular coordination of the dimethylamino function (Cp-N)((Cp-N)RhI$_2$ **93** (Cp-N)Rh(C_2O_4) **94**), while in others the amino group remained uncoordinated ((Cp′)RhI$_2$(CO) **95**, (Cp′)Rh(CO)$_2$, (Cp′)Rh(C_2O_4)(PMe$_3$) **96**).[174]



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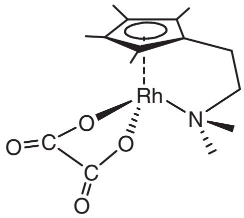

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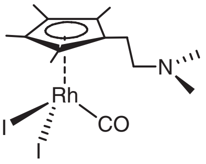

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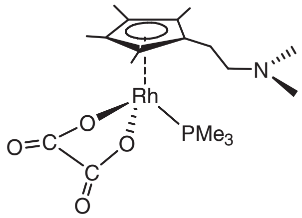
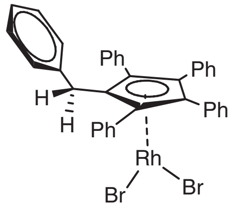


96

The compound (*S*)-1-(1-dimethylaminoethyl)-2-(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)benzene (HL) reacted with $RhCl_3\cdot 3H_2O$ to give a mixture of the chiral complexes $\{\eta^5\text{-}C_5Me_4C_6H_4CH(Me)NMe_2\}RhCl_2$ and $\{[\eta^5\text{-}C_5Me_4C_6H_4CH(Me)NMe_2\cdot HCl]Rh\ Cl_2\}_2$.[175] Phenethyltetraphenylcyclopentadiene was made from (*R*)-1-phenethyl bromide and lithium tetraphenylcyclopentadienide. This compound afforded the preparation of the chiral complexes $[\{C_5Ph_4CH(Me)Ph\}RhBr_2]_2$ **97** and $\{C_5Ph_4CH(Me)Ph\}Rh(cod)$.[176] The synthesis of several homochiral cyclopentadienes $C_5Ph_4R^*H$ (R^* = menthyl, neomenthyl) was reported, together with their coordination to rhodium complexes, such as $[(C_5Ph_4R^*)Rh(cod)]$ **98** and $[(C_5Ph_4R^*)RhBr_2]_2$ **99**.[177]



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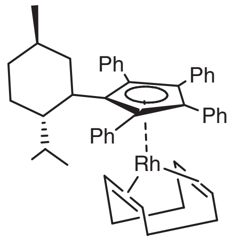

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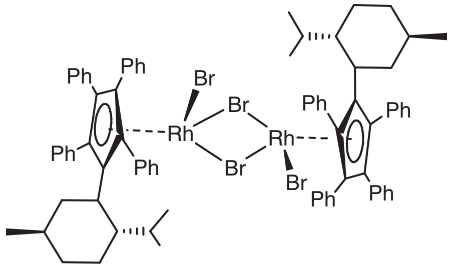
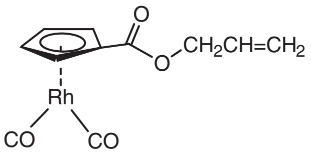


99

Reactions of $Na[C_5H_4CO_2CH_2CH{=}CH_2]$ or $Na[C_5H_4CO_2(CH_2)_2OH]$ with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ lead to the respective metal complexes $(C_5H_4CO_2CH_2CH{=}CH_2)Rh(CO)_2$ **100** and $\{C_5H_4CO_2(CH_2)_2OH\}Rh(CO)_2$ **101**. The diester-bridged dinuclear adduct $\{\mu\text{-}(C_5H_4CO_2CH_2)_2\}Rh_2(CO)_4$ **102** was also prepared.[178] Other ester-functionalized Cp ligands, and chiral hydroxyalkoxycarbonylcyclopentadienide complexes of Rh, [*rac*-$C_5H_4CO_2(CHMe)_2OH$]Rh(CO)$_2$ and [(1*S*,2*S*)-$C_5H_4CO_2(CHMe)_2OH$]Rh(CO)$_2$, were prepared by the same group.[179]



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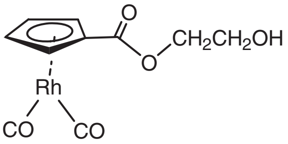

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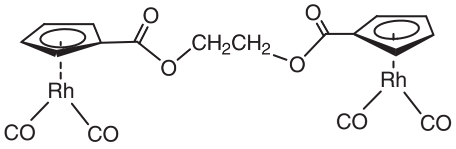
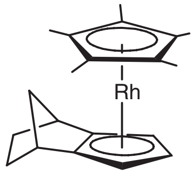


102

The complex *exo*-[Cp*Rh(Idcp)]PF$_6$ **103** was obtained from [Cp*Rh(OCMe$_2$)$_3$](BF$_4$)$_2$ and tricyclo[5,2,1,0^{2,6}]deca-2,5-diene (IdcpH) in acetone.[180]



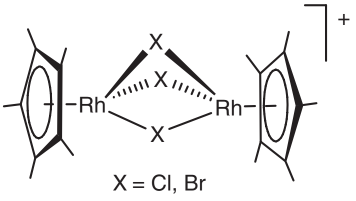
103

7.02.3.1.3 Cp* complexes

The chemistry of Cp* complexes of Rh follows the growth that was already pointed out in COMC (1995). In this section, only those complexes with Cp* ligand as the only organometallic ligand are described. In any case, most of the complexes described in this section are related to other complexes with more organometallic ligands, so some of the references cited here may also deserve some comments in other sections of this chapter. We have divided this section into: (i) compounds with group 16 and 17 donor ligands, (ii) group 15 and 14 donor ligands, and (iii) cluster compounds.

7.02.3.1.3.(i) Compounds with group 16 and 17 donor ligands

The substitution of water in [Cp*Rh(H$_2$O)$_3$]$^{2+}$ by Cl$^-$, Br$^-$, I$^-$, SCN$^-$, py-CN (4-cyanopyridine), py-nia (nicotinamide), py (pyridine), TU (thiourea), and DMS (dimethylsulfide) was studied. The equilibrium constants K_1 for the formation of the monosubstituted complexes [Cp*Rh(H$_2$O)$_2$L]$^{2+}$ lie in the range 10^2–10^5 M^{-1}.[181] The reaction of the complexes [Cp^{x}RhCl$_2$]$_2$ (Cp^x═C$_5$Me$_5$, C$_5$^{t}Bu$_2$H$_3$) with silver oxalate Ag$_2$C$_2$O$_4$ leads to polymeric species with the formula [Cp^{x}Rh(C$_2$O$_4$)]$_n$ in high yields. These compounds reacted with Lewis bases L [L = DMSO, P(OMe)$_3$, PPh$_3$, P(C$_8$H$_{17}$)$_3$] to yield products of the type Cp^{x}Rh(C$_2$O$_4$)L.[182] Cp*Rh(η^2-NO$_3$)(OTf) reacted with propargyl halides to give triply halide-bridged dinuclear compounds of formula [Cp*Rh(μ^2-X)$_3$RhCp*]OTf (X = Cl or Br) **104**.[183] Photolysis of the coordinatively unsaturated pentamethylcyclopentadienyl pinacolate complex of rhodium, Cp*Rh(pin) **105** (pin = pinacolate) generates [Cp*M] which can be detected in the presence of added traps. The oxidation of the resulting rhodium(II) product (Cp*Rh)$_2$(pin) **106** by air (or O$_2$) in the presence of pinacol regenerates the rhodium(III) pinacolate complex Cp*Rh(pin).[184]



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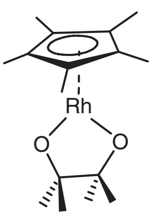

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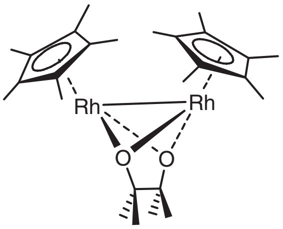
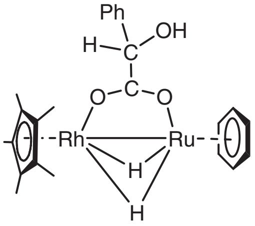


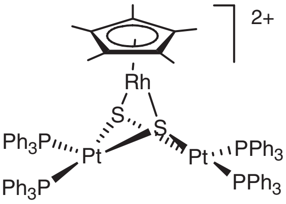
106

Heterobimetallic complexes in which a half-sandwich complex of rhodium(III) is connected by three bromo-bridges to Re(CO)$_3$ were prepared from metathesis reactions of [Cp*RhBr$_2$]$_2$ and [Re(μ-Br)(CO)$_3$(C$_4$H$_8$O)]$_2$. The crystal structure of Cp*Rh(μ-Br)$_3$Re(CO)$_3$ was determined by X-ray analysis.[185] The treatment of a mixture of [(η^6-C$_6$H$_6$)RuCl$_2$]$_2$ and [Cp*RhCl$_2$]$_2$ with silver carboxylates and subsequent hydrogenation afforded mixed metal monohydrido complexes $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\mu_2\text{-H})(\mu\text{-}\eta^2\text{-O}_2\text{CR})\text{RhCp}^*]^+$, containing two metal atoms in a chiral environment. The use of α-hydroxycarboxylates for this reaction caused the formation of the dihydrido complex $[(\eta^6\text{C}_6\text{H}_6)\text{Ru}(\mu\text{-H})_2\{\mu\text{-}\eta^2\text{-O}_2\text{CCH(OH)Ph}\}\text{RhCp}^*]^+$ **107**.[186]

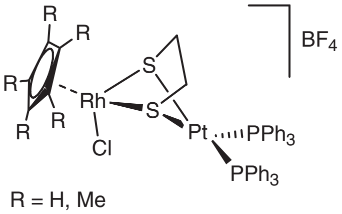


107

The complex $[\text{Cp}^*{}_2\text{Rh}_2\text{Cl}_2\{7,8\text{-}\mu\text{-S}(4'\text{C}_6\text{H}_3(\text{CH}_3)\text{S–C}_2\text{B}_9\text{H}_{10}\}]^+$, with a rigid non-deforming binucleating ligand was synthesized.[187] The reactivity of $\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4$ toward $[\text{Cp}^*\text{RhCl}_2]_2$ and other transition metal complexes was tested using electrospray ionization mass spectrometry. In all cases, dicationic products such as $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{RhCp}^*]^{2+}$ **108** were observed, and a number of complexes were prepared on the synthetic scale as their BPh_4^- or PF_6^- salts.[188] Cationic heterobimetallic complexes $[(\text{PPh}_3)_2\text{Pt}(\mu\text{-edt})\text{RhClCp}]\text{BF}_4$ ($\text{edt} = {}^-\text{S}(\text{CH}_2)_2\text{S}^-$; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ or $\eta^5\text{-C}_5\text{Me}_5$) **109** were prepared by the reaction of $\text{Pt(edt)(PPh}_3)_2$ with $\text{CpClRh}(\mu\text{-Cl})_2\text{RhClCp}$ in the presence of 2 equiv. of AgBF_4.[189]

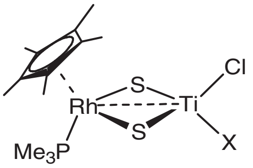


108

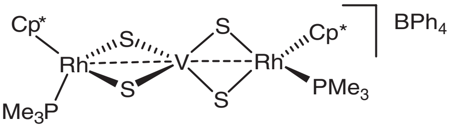


109

Reactions of the bis(hydrosulfido) complexes $\text{Cp}^*\text{Rh(SH)}_2(\text{PMe}_3)$ with Cp^*TiCl_3 and $[\text{TiCl}_4(\text{THF})_2]$ in the presence of triethylamine lead to the formation of the sulfido-bridged titanium–rhodium complexes $\text{Cp}^*\text{Rh}(\text{PMe}_3)(\mu\text{-S})_2\text{TiClCp}$ **110** and $\text{Cp}^*\text{Rh}(\text{PMe}_3)(\mu\text{-S})_2\text{TiCl}_2$ **111**, respectively. The last complex was further converted into the bis(acetylacetonato) complex $\text{Cp}^*\text{M}(\text{PMe}_3)(\mu\text{-S})_2\text{Ti(acac)}_2$ upon treatment with acetylacetone. $\text{Cp}^*\text{Rh(SH)}_2(\text{PMe}_3)$ also reacted with $\text{VCl}_3(\text{THF})_3$ and $\text{Mo(CO)}_4(\text{nbd})$ (nbd = 2,5-norbornadiene) to afford the cationic sulfido-bridged VRh_2 complex $[\{\text{Cp}^*\text{Rh}(\text{PMe}_3)(\mu\text{-S})_2\}_2\text{V}]^+$ **112** and the hydrosulfido-bridged MoRh complexes $\text{Cp}^*\text{Rh}(\text{PMe}_3)(\mu\text{-SH})_2\text{Mo(CO)}_4$.[190]

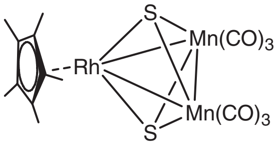


110: X = Cp
111: X = Cl



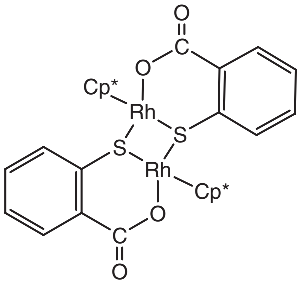
112

The reaction of $\text{Mn}_2(\text{CO})_7(\mu\text{-S}_2)$ with $\text{Cp}^*\text{Rh(CO)}_2$ yielded the heterometallic complex $\text{Cp}^*\text{RhMn}_2(\text{CO})_6(\mu_3\text{-S})_2$ **113** in moderate yield.[191]



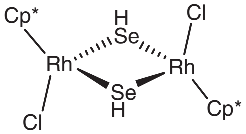
113

Reactions of the dimer $[Cp^*RhCl_2]_2$ with 2 equiv. of thiosalicylic acid ($HSC_6H_4CO_2H$, H_2tsal) and excess of base gave the dimeric rhodium(III) thiosalicylate complex $[Cp^*Rh(tsal)]_2$ **114**.[192]



114

Reactions of Cp^*RhCl_2 with H_2Se afforded the dirhodium complex containing bridging hydroselenido ligands $(Cp^*RhCl)_2(\mu\text{-SeH})_2$ **115**. Selenido-bridged trinuclear Rh(III) clusters $[(Cp^*Rh)_3(\mu_3\text{-Se})_2][PF_6]_2$ was prepared by the same procedure as the trinuclear Rh(III)$_2$Rh(I) clusters $[(Cp^*Rh)_2\{Rh(CO)_2\}(\mu_3\text{-Se})_2][RhCl_2(CO)_2]$ and $[(Cp^*Rh)_2\{Rh(PPh_3)_2\}(\mu_3\text{-Se})_2][PF_6]$ **116**. On the other hand, the reactions of $(Cp^*RhCl)_2(\mu\text{-SeH})_2$ with NEt_3 gave the tetranuclear selenido clusters with a cubane-type core $(Cp^*M)_4(\mu_3\text{-Se})_4$ [M = Rh **117**, Ir].[193]



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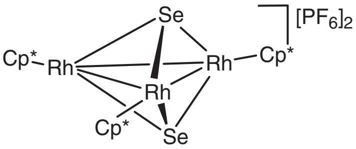

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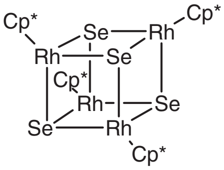
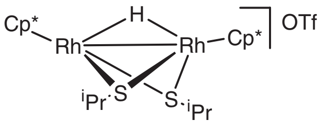
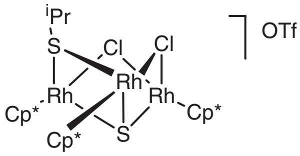


117

A cationic dinuclear complex with bridging thiolato and hydrido ligands $[Cp^*RhH(\mu\text{-S}^iPr)_2RhCp^*]OTf$ **118** was prepared by treatment of $[Cp^*Rh(\mu\text{-Cl})(\mu\text{-S}^iPr)_2RhCp^*]OTf$ and $HSiEt_3$. This complex reacted with nitrosobenzene to give the paramagnetic dinuclear nitrosobenzene complex $[Cp^*Rh(\mu\text{-PhNO})(\mu\text{-S}^iPr)_2RhCp^*]^+$. On the other hand, $[Cp^*Rh(\mu\text{-Cl})(\mu\text{-S}^iPr)_2RhCp^*]OTf$ reacted with nitrosobenzene to give the incomplete cubane-type trinuclear cluster $(Cp^*Rh)_3(\mu\text{-Cl})_2(\mu_3\text{-S})(\mu\text{-S}^iPr)$ **119**.[194]

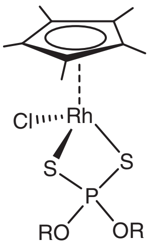


118



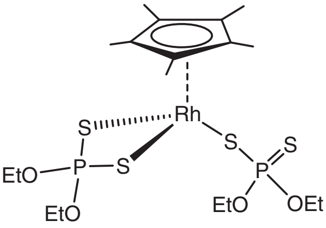
119

Reactions of $[Cp^*RhCl_2]_2$ with $NH_4S_2P(OR)_2$ in 1 : 1 and 1 : 2 stoichiometry gave complexes of the type $Cp^*RhCl[S_2P(OR)_2]$ **120** (R = Et, ^{n}Pr, ^{i}Pr) and $Cp^*Rh\{S_2P(OR)_2\}_2$ **121** (R = Et). The cationic complexes $[Cp^*Rh\{S_2P(OR)_2\}L]SO_3CF_3$ (R = Et; L = PPh_3; $P(C_6H_4Me\text{-}4)_3$, $AsPh_3$) were also obtained.[195]



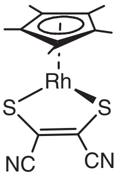
R = Et, ${}^nPr$, ${}^iPr$

120



121

The reaction between the pentamethylcyclopentadienyl complex $[Cp^*RhCl_2]_2$ and disodium maleonitriledithiolate (Na_2mnt) afforded the mnt-substituted compound $Cp^*Rh(mnt)$ **122** in moderate yield. Molecular weight measurements confirmed the monomeric nature of this complex. However, the solid-state structure was determined by X-ray diffraction analysis, revealing the presence of a dimeric structure for "$Cp^*Rh(mnt)$" **123** which possesses both bridging and chelating mnt ligands.[196]



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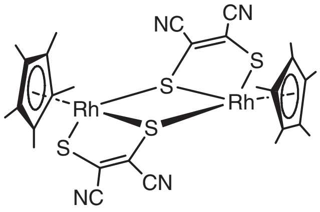
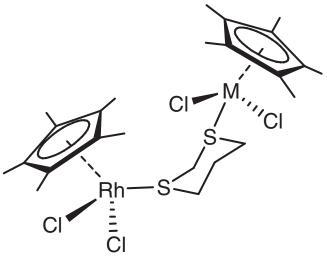


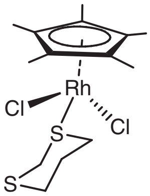
123

Reactions of $[Cp^*RhCl_2]_2$ with 1,3-dithiane (1,3-$S_2C_4H_8$) gave $[Cp^*RhCl_2]_2$(1,3-$S_2C_4H_8$) **124** and (Cp^*RhCl_2)(1,3-$S_2C_4H_8$) **125**. The reaction in the presence of KPF_6 afforded the corresponding ionic complex $[Cp^*RhCl$(1,3-$S_2C_4H_8)_2]PF_6$ **126**. Complex (Cp^*RhCl_2)(1,3-$S_2C_4H_8$) was treated with $[Cp^*IrCl_2]_2$, affording the heterobinuclear complex Cp^*RhCl_2(1,3-$S_2C_4H_8$)$IrCl_2Cp^*$. Reactions of $[Cp^*RhCl_2]_2$ with 1,4-dithiane (1,4-$S_2C_4H_8$) were carried out in a 1 : 1 molar ratio, generating the binuclear complex $[Cp^*RhCl_2]_2$(1,4-$S_2C_4H_8$) **127**. Reaction of $[Cp^*RhCl_2]_2$ with an excess of 1,4-dithiane afforded a neutral mononuclear complex (Cp^*RhCl_2)(1,4-$S_2C_4H_8$) **128**.[197]

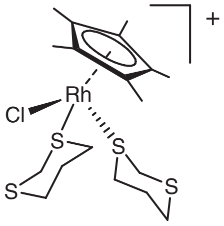


M = Rh, Ir

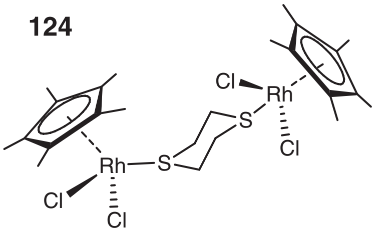
124



125



126



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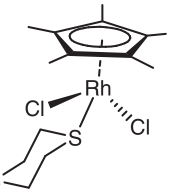
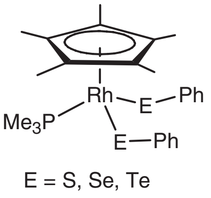
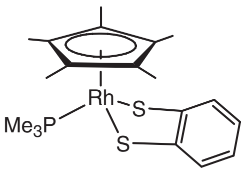


128

Diphenyl dichalcogenides reacted with $Cp^*Rh(PMe_3)(CO)$ to give several complexes of the type $Cp^*Rh(PMe_3)(EPh)_2$ **129** (E = S, Se, and Te). Similarly, $Cp^*Rh(PMe_3)(S_2C_6H_4)$ **130** was obtained.[148]

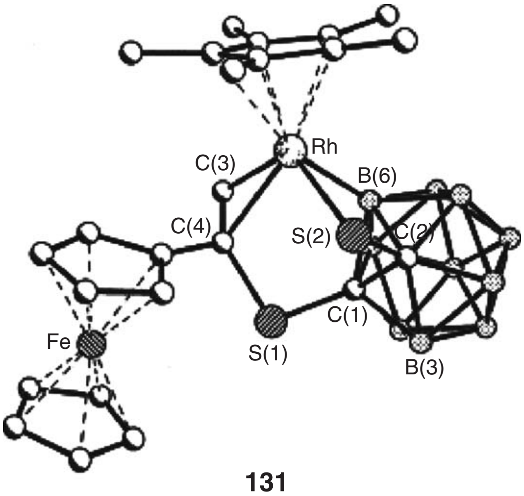


129



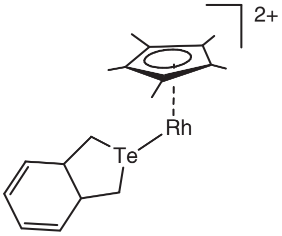
130

Cp*Rh[$S_2C_2(B_{10}H_{10})$] reacted with ethynylferrocene in a 1 : 1 ratio by inserting into one of the Rh–S bonds, followed by B–H activation, transfer of a hydrogen atom to carbon via rhodium, and formation of an Rh–B bond. The resulting compound **131** was characterized by X-ray structural analysis.[198]

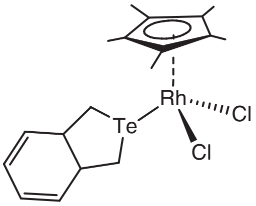


131

The electrochemical behavior of a series of heterodimetallic 2-metalla-1,3-dichalcogena-[3]ferrocenophanes of general formula Cp*(L)Rh[$(EC_5\text{-}H_4)_2Fe$] (E = S, Se, or Te; L = PMe$_3$) was investigated. These complexes underwent two successive oxidation steps. In spite of the fact that both metal centers are potentially able to lose electrons, EPR spectra and theoretical considerations suggested that the bridging chalcogen atoms also contribute to the electron-removal processes.[199] Rhodium complexes of 2-telluraindane were synthesized and the nature of metal–ligand interactions in solution was studied using NMR spectroscopy. [(Cp*Rh)(C_8H_8Te)][O_3SCF_3]$_2$ **132** was prepared by the reaction of [Cp*RhCl$_2$]$_2$ with 2-telluraindane in the presence of silver triflate, while (Cp*RhCl$_2$)(C_8H_8Te) **133** was synthesized by a direct reaction between the rhodium dimer and the ligand.[200]

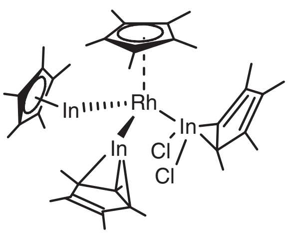


132

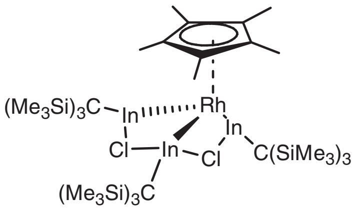


133

Insertion of the carbenoid group 13 metal species InCp* and InC(SiMe$_3$)$_3$ into the Rh–Cl bonds of [Cp*RhCl$_2$]$_2$ yielded the complexes Cp*Rh(InCp*)$_3$Cl$_2$ **134** and Cp*Rh(μ-Cl)$_2$[InC(SiMe$_3$)$_3$] **135**, respectively, exhibiting novel cage-like intermetallic complexes with In–Cl–In bridges.[201]



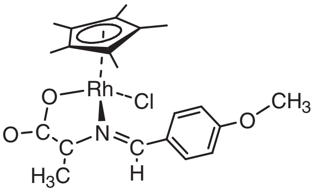
134



135

7.02.3.1.3.(ii) Complexes with group-15 and -14 containing ligands

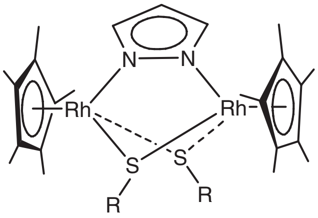
Reactions of the anions (L) of Schiff bases from *S*-α-amino acids and cinnamic aldehyde or 4-methoxy or 2,4-dimethoxy benzaldehyde with $[Cp^*RhCl_2]_2$ gave the (*N*,*O*) chelate complexes *cis*/*trans* $Cp^*RhCl(L)$. The complex $Cp^*RhCl[O_2CCH(CHMe_2)N{=}CH{-}CH{=}CHPh]$ **136** was formed with a high diastereoisomeric excess (9/1).[202]



136

The dinuclear complexes $[Cp^*ClRh(\mu\text{-}L)RhClCp^*](PF_6)_2$, L = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) or 2,5-bis(phenyliminoethyl)pyrazine (bpip), were reduced in several chemically reversible steps by up to six electrons to the species $[Cp^*Rh(\mu\text{-}L)RhCp^*]^{n-}$. The complexes clearly showed a reversible, ligand-centered one-electron reduction (E) preceding the first chloride-dissociative metal reduction step (EC).[203]

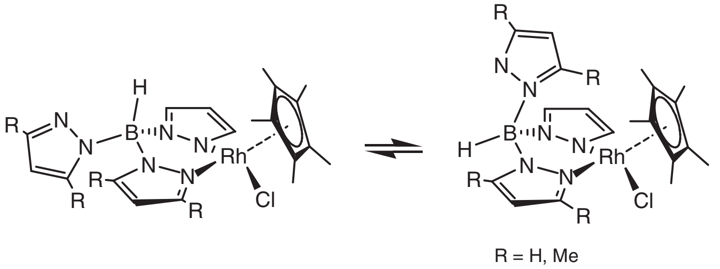
Binuclear thiolato-pyrazolate-bridged complexes of general formula $[Cp^*{}_2Rh_2(\mu\text{-pz})(\mu\text{-SR})_2]BF_4$ **137** (pz = pyrazolate; R = C_6F_5, *p*-C_6F_4H, *p*-C_6H_4F, or C_6H_5) were prepared by reacting the hydroxo–pyrazolato-bridged compound $[Cp^*{}_2Rh_2(\mu\text{-Pz})_2(\mu\text{-OH})]BF_4$ with the corresponding thiol. Each metal was found to be bound to a terminal Cp* group and to three bridging ligands: two monodentate thiolates and a bidentate pyrazolate group. The main structural dissimilarity affects the relative configuration of the thiolate phenyl substituents giving rise to *syn*- or *anti*-structures. The four complexes underwent fluxional processes observable by NMR.[204]



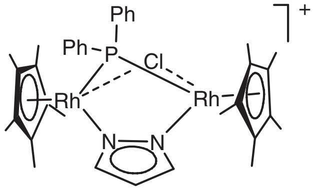
R = C_6F_5, *p*-C_6F_4H, *p*-C_6H_4F, C_6H_5

137

The reaction of $[(Cp^*Rh)_2(\mu\text{-}L)(\mu\text{-OMe})_2]BF_4$ (L = pyrazolate (pz), 3-methylpyrazolate, 3,5-dimethylpyrazolate, or 3(5)-bromo-5(3)-methylpyrazolate) with $HPPh_2$ was studied and afforded the preparation of complexes of general formulae $[(Cp^*Rh)_2(\mu\text{-}L)(\mu\text{-Cl})(\mu\text{-PPh}_2)]BF_4$ **138**, $[(Cp^*Rh)_2(\mu\text{-}L)(\mu\text{-PPh}_2)_2]BF_4$ **139**, and $[(Cp^*Rh)_2(\mu\text{-PPh}_2)_3]BF_4$ **140**.[205]



Scheme 13



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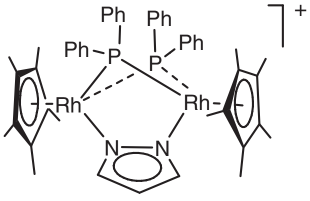
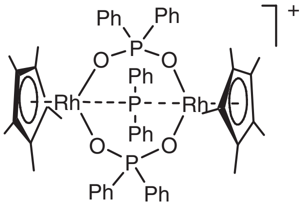
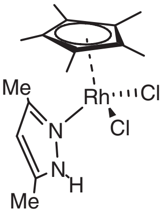


139



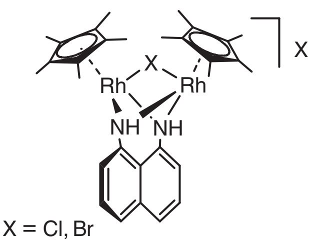
140

[RhCp*(Tp′)Cl] (Tp′ = hydrotris(pyrazolyl)borate (Tp) or hydrotris(3,5-dimethylpyrazolyl)borate (Tp*)) complexes were synthesized by the reaction of [Cp*RhCl$_2$]$_2$ with KTp$^-$, and their fluxional behavior was studied (Scheme 13). Reaction between Cp*RhCl(Tp) and AgNO$_3$ afforded ionic [Cp*RhTp]NO$_3$ species, whereas with Cp*RhCl(Tp*), B–N bond cleavage within the Tp* ligand occurred, affording **141**.[206]



141

Reaction of [Cp*RhX$_2$]$_2$ (X = Cl, Br) with (LiNH)$_2$C$_{10}$H$_6$-1,8 gave the amido-bridged dinuclear Rh(III) complex [Cp*Rh{(μ_2-NH)$_2$C$_{10}$H$_6$-1,8}(μ-X)RhCp*]X **142** which by Na/Hg reduction further converted to the Rh(II) complex Cp*Rh{(μ-NH)$_2$C$_{10}$H$_6$-1,8}RhCp* **143**. The latter afforded [Cp*Rh{(μ-NH)$_2$C$_{10}$H$_6$-1,8}(μ-H)RhCp*]O$_2$CCF$_3$ by protonation with CF$_3$CO$_2$H **144**.[207]



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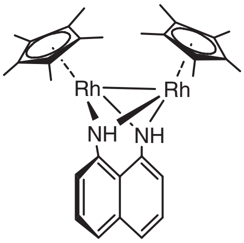

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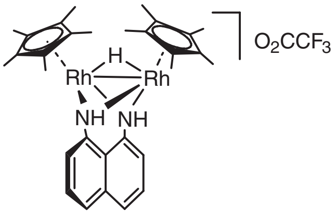
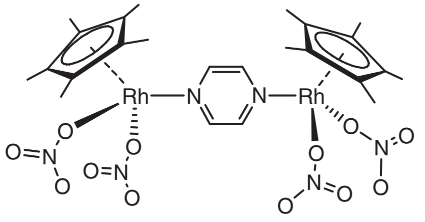


144

Cp*Rh(η^1-NO$_3$)(η^2-NO$_3$) reacted with pyrazine (pyz) to give a dinuclear complex [Cp*Rh(η^1-NO$_3$)$_2$(μ-pyz)$_{0.5}$]$_2$CH$_2$Cl$_2$ **145**. Tetranuclear rectangles of the type [Cp*Rh($\eta^1\mu$-X)(μ-L)$_{0.5}$]$_4$(OTf)$_4$ [X = N$_3$, L = bpy **146**; X = N$_3$, L = bpe **147**; X = NCO, L = bpy **148**] were prepared from [Cp*Rh(H$_2$O)$_3$](OTf)$_2$, a pseudohalide (Me$_3$SiN$_3$ or Me$_3$SiNCO), and a linear dipyridyl {4,4′-bipyridine (bpy) or *trans*-1,2-bis(4-pyridyl)ethylene (bpe)} by self-assembly through one-pot synthesis at room temperature. Other dinuclear rods and one-dimensional networks were also reported in the same work.[208]



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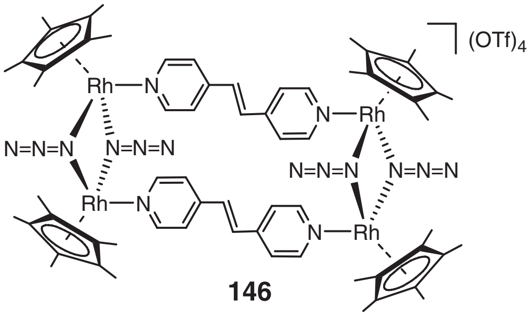

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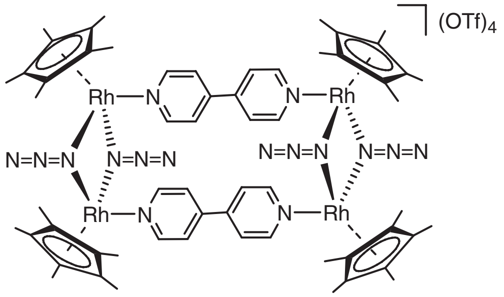

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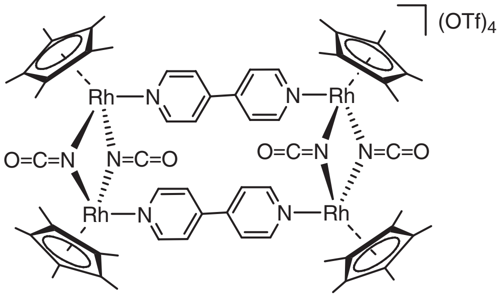
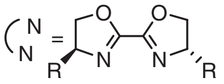


148

Reaction of the dimers $[Cp^*RhCl_2]_2$ with bisoxazolines [N–N = bis(2-oxazoline) (box) **149**, 2,2-bis(2-oxazolinyl)-propane (bop) **150**, 1,2-bis(2-oxazolinyl)benzene (benbox) **151**] in the presence of $NaSbF_6$ (or KPF_6) gave complexes $[RhCl(N–N)Cp^*]SbF_6$ **152** which were fully characterized by means of X-ray crystallography.[209]



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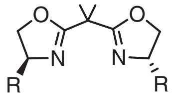

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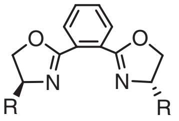

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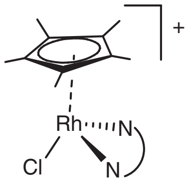
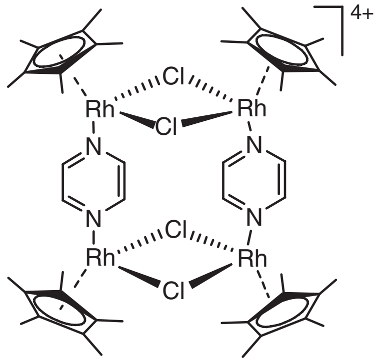


152

The pentamethylcyclopentadienyl complex of the general formula $[Cp^*Rh(acetone)_2(H_2O)][BF_4]_2$ was prepared. Reaction of this compound with pyridine afforded tris(pyridine) complexes $[Cp^*Rh(py)_3][BF_4]_2$.[210] Reactions of $[Cp^*RhCl_2]_2$ with bidentate ligands (L = pyrazine, L′ = diisocyanide) gave $[Cp^*RhCl_2(L \text{ or } L')]_2$, which were converted into tetranuclear complexes $[Cp^*{}_2Rh_2Cl_2L]_2(OTf)_4$ **153** and $[Cp^*{}_2Rh_2Cl_2(L)(L')]_2(OTf)_4$ **154** containing different number of ligands on treatment with Ag(OTf).[211]



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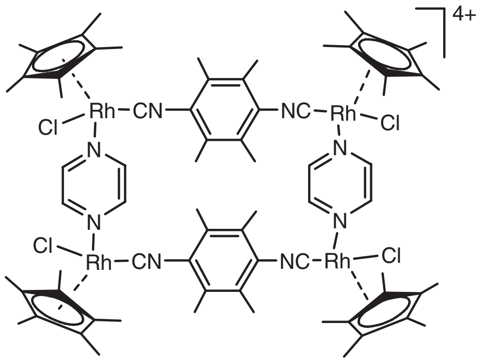
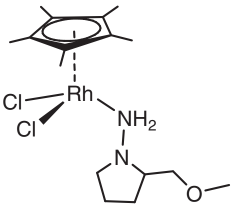


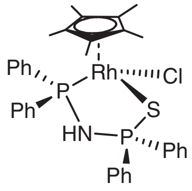
154

The chloro-bridged complexes $[Cp^*RhCl_2]_2$ reacted with (*S*)-1-amino-2-(methoxymethyl)pyrrolidin (SAMP) by cleavage of the chloro bridges to give the corresponding monomeric η^1-SAMP **155** complex.[212]



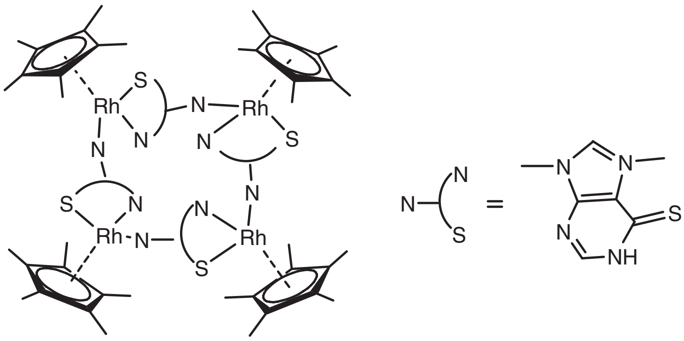
155

The reaction of *S*-$Ph_2P(S)N(CHMePh)PPh_2$ with $[Cp^*RhCl_2]_2$ in the presence of $AgBF_4$ leads to the cleavage of the C–N bond of the ligand yielding the cationic complex, $[Cp^*RhCl\{\eta^2\text{-P}, S\text{-}Ph_2PNHP(S)Ph_2\}]BF_4$ **156**.[213]



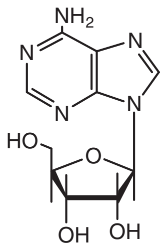
156

Cyclic tetranuclear complexes $[\{Cp^*Rh(L)\}_4]^{4+}$ **157** [HL = 6-purinethione (H_2put) and 2-amino-6-purinethione (H_2aput)] were prepared and fully characterized. The dimeric species were mainly formed in the reaction solutions but finally converted into the tetrameric species.[214]



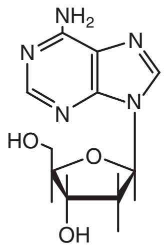
157

Cyclic C_3-trinuclear complexes $[(Cp^*RhL)_3]^{3+}$ [L = adenosine (Hado) **158**, 2′-deoxyadenosine (Hdeoado) **159**, and 5′-acetyl-2′,3′-isopropylideneadenosine (Haipado) **160**] were prepared and characterized by UV/Vis and circular dichroism spectra, NMR spectroscopy, electrospray ionization mass spectroscopy, and X-ray crystal structure analysis.[215]



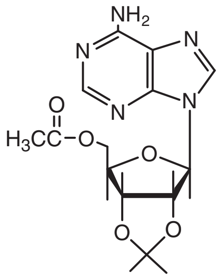
Hado

158



Hdeodado

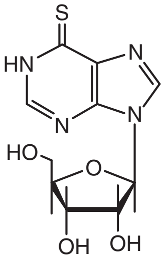
159



Haipado

160

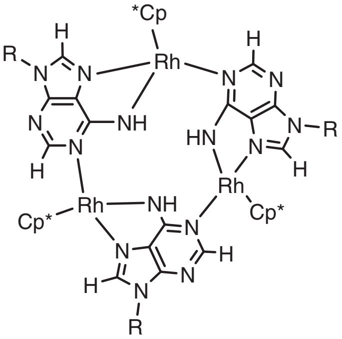
The reaction between $[Cp^*Rh(H_2O)_3]^{2+}$ and 6-purinethione riboside (Hputrb) **161** afforded the complex $[\{Cp^*Rh(putrb)\}_6](CF_3SO_3)_6$ which has a cyclic hexanuclear structure.[216]



HPutrb

161

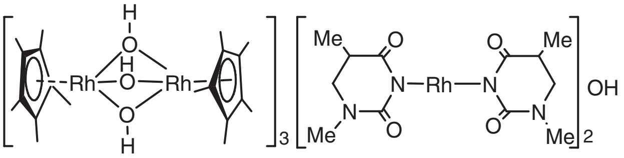
The reaction of [Cp*Rh(H$_2$O)$_3$](OTf)$_2$ with nicotine adenine dinucleotide (NAD$^+$) afforded the cyclic trimer structure, [Cp*Rh{μ-η^1(N1):η^2(N6,N7)-9-(5′-ribose pyrophosphate-5″-ribose-1″-nicotinamide)adeninato}]$_3$(OTf)$_3$ **162**, which was fully characterized.[217]



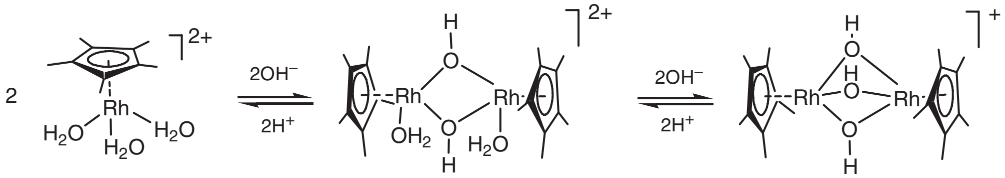
162

The structures of the (η^5-pentamethylcyclopentadienyl)rhodium aqua complexes, as a function of pH, were studied by ^{1}H, ^{13}C, ^{17}O, and 2D NOESY NMR spectroscopic techniques as well as by FAB mass spectrometry and potentiometric titration. [Cp*Rh(H$_2$O)$_3$](OTf)$_2$ was structurally characterized by single crystal X-ray crystallography. Both ^{1}H and ^{13}C NMR titration experiments of [Cp*Rh(H$_2$O)$_3$](OTf)$_2$ confirmed that as the pH of the solution was increased from 5 to 7, a dynamic and rapid equilibrium was observed to provide [Cp*Rh(μ-OH)(H$_2$O)]$_2$(OTf)$_2$ and [(Cp*Rh)$_2$(μ-OH)$_3$]OTf (Scheme 14).[218]

The reaction of [Cp*Rh(OH)$_3$](OTf)$_2$ with 1-methylthymine (1-MTH) in water, pH 10, afforded the complex [Rh(η^1,N3-1-MT)$_2$]$_2$[(Cp*Rh)$_2$(μ-OH)$_3$]$_3$(OH) **163**, containing a novel, linear, two-coordinate Rh(I) anionic amide complex and the triply OH-bridged cationic complex.[219]

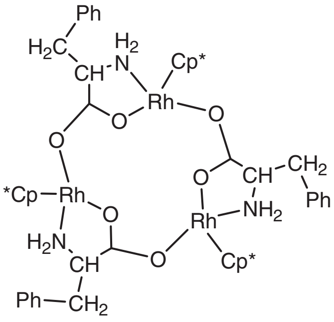


163



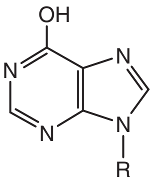
Scheme 14

The reaction of $[Cp^{*}Rh(H_2O)_3]^{2+}$ with L-phenylalanine, from pH 4 to 6, provided only one diastereomer of the known cyclic trimer $[(Cp^{*}Rh)(\mu\text{-}\eta^1\text{-}(OCO)\text{:}\eta^2\text{-}(N,OCO)\text{-L-phenylalanine})]_3{}^{3+}$ ($S_C,S_C,S_C,S_{Rh},S_{Rh},S_{Rh}$) **164**, an example of a one-step, highly diastereoselective reaction in H_2O.[220]



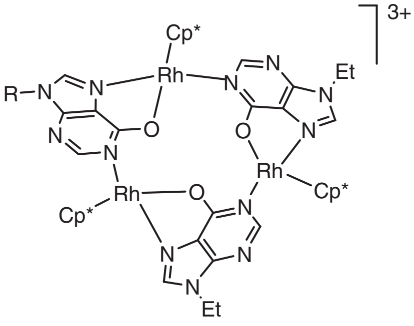
164

Molecular recognition, via non-covalent processes such as hydrogen bonding, π-π, and hydrophobic interactions, was studied using guests that encompassed aromatic and aliphatic amino acids with supramolecular, bioorganometallic hosts, ($Cp^{*}Rh$)-nucleobase, nucleoside, and nucleotide cyclic trimer complexes, $[Cp^{*}Rh(9\text{-methyladenine})]_3(OTf)_3$ (OTf = trifluoromethanesulfonate), $[Cp^{*}Rh(\text{adenosine})]_3(OTf)_3$, $[Cp^{*}Rh(2'\text{-deoxyadenosine})]_3(OTf)_3$, $[Cp^{*}Rh(2',3'\text{-dideoxyadenosine})]_3(OTf)_3$, and $[Cp^{*}Rh(\text{Me-}5'\text{-AMP})]_3$. The host–guest complexation occurred predominantly via non-covalent π-π, hydrophobic, and possible subtle H-bonding interactions, with steric, electronic, and molecular conformational parameters as important criteria.[221] New cyclic trimer and dimeric complexes were isolated from the reaction of $[Cp^{*}Rh(MeOH)_3](OTf)_2$ and 9-methylhypoxanthine (9-MH) or 9-ethylhypoxanthine (9-EH) **165** at different pH values. These two new complexes $[\{Cp^{*}Rh[\mu\text{-}\eta^1(N^1)\text{:}\eta^2(N^7,O^6)\text{-9-EH}]\}_3](OTf)_3$ **166** and $\{Cp^{*}Rh[\eta^1(N^1)\text{-9-MH}](\mu\text{-OH})\}_2$ **167** show several novel bonding modes of the nucleobase, 9-MH, and the ethyl analog 9-EH.[222]



R = Me(9-MH), Et(9-EH)

165



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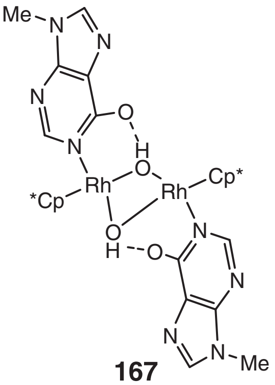
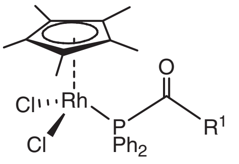


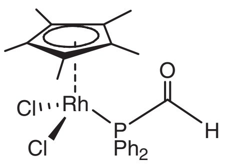
167

Several rhodium compounds with "phosphomide" ligands (P adjacent to carbonyl group) $Cp^{*}RhCl_2[Ph_2PC(O)R^1]$ were reported, including the crystal structure of $Cp^{*}RhCl_2[Ph_2PC(O)CH_3]$ **168**. The compound with $R^1 = (CF_2)_6CF_3$ is moisture sensitive to produce $Cp^{*}RhCl_2[Ph_2PC(O)H]$ **169**.[223]



R^1 = acetyl, $(CF_2)_6CF_3$, anisoyl

168



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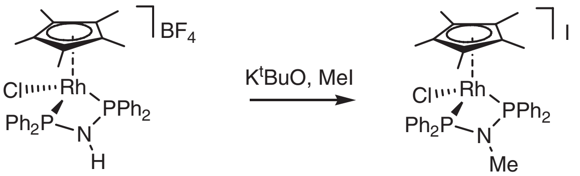
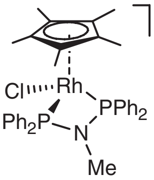


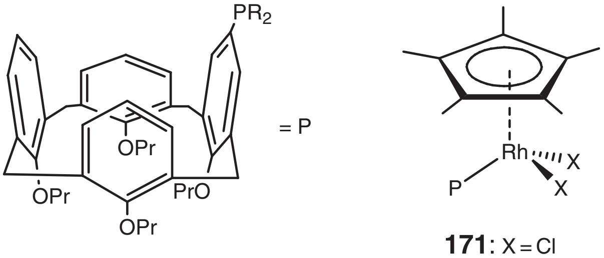
Scheme 15

Reaction of the dimer $[Cp^*RhCl_2]_2$ with the ligand $NMe(PPh_2)_2$ afforded the mononuclear cationic complex $\{Cp^*RhCl[\eta^2\text{-}P,P'\text{-}(Ph_2P)_2Nme]\}Cl$ **170**. A similar iodide complex, $\{Cp^*RhCl[\eta^2\text{-}P,P'\text{-}(Ph_2P)_2Nme]\}I$ was prepared by N-functionalization of coordinated dppa ligand in complex $\{Cp^*RhCl[\eta^2\text{-}P,P'\text{-}(Ph_2P)_2NH]\}BF_4$ obtained from the reaction of the dimer $[Cp^*RhCl_2]_2$ with the ligand $NH(PPh_2)_2$ and $AgBF_4$ (Scheme 15).[224]



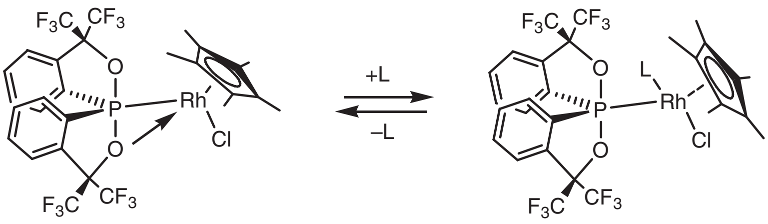
170

The complex $Cp^*Rh(Ph_2PPy)Cl_2$ in which 2-(diphenylphosphino)pyridine (Ph_2PPy) is *P*-monodentate was obtained. The cationic complex $[Cp^*Rh(Ph_2PPy)Cl]PF_6$, in which the Ph_2PPy is chelating, was also obtained.[225] A convenient synthesis of the upper-rim monobrominated calix[4]arene Br–calixPR$_2$ was reported. Reactions of these ligands with $[Cp^*RhCl_2]_2$ afforded the complexes $Cp^*RhCl_2(calixPR_2)$ **171** which were converted into their corresponding dihydrides $Cp^*RhH_2(calixPR_2)$ **172** using $NaBH_4$.[226,226a]



171: X = Cl
172: X = H

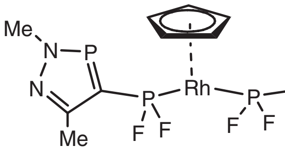
An Rh(III) complex bearing a hypervalent phosphorus(V) ligand, $Cp^*Rh(Cl)Rf_2P$ (Rf = Martin ligand = $o\text{-}C_6H_4C(CF_3)_2O$), was obtained by the reaction of $Rf_2P^-Li^+$ with $[Cp^*RhCl_2]_2$. This complex reversibly added L (solvent or PMe_3), as shown in Scheme 16.[227]



L = solvent or PMe_3

Scheme 16

The ligand 4-(difluorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (L) reacted with $CpRh(CO)_2$ to form $CpRh(L)_2$ **173** and with $[Cp^*RhCl_2]_2$ to form Cp^*RhCl_2L **174**, which was structurally characterized.[74]



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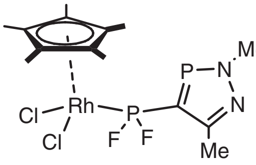
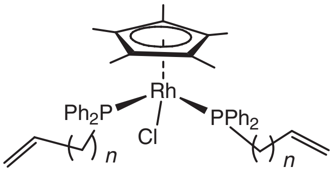


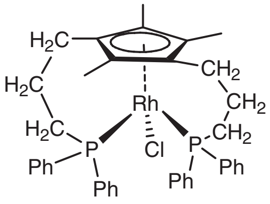
174

$[Cp^*RhCl_2]_2$ reacted with diphenylvinylphosphine or allyldiphenylphosphine ($PRPh_2$) to produce $Cp^*RhCl_2(PRPh_2)$ and $[Cp^*RhCl(PRPh_2)_2]X$ **175** ($X = Cl^-$, PF_6^-).[228] In acetonitrile, $[Cp^*RhCl_2]_2$ underwent a base-promoted hydroalkylation reaction with potassium *tert*-butoxide and diphenylvinylphosphine to produce $[\{\eta^5\text{-}C_5Me_3\text{-}1,3\text{-}[CH_2CH_2CH_2PPh_2]_2\}RhCl]X$ **176** ($X = Cl^-$, PF_6^-, BPh_4^-) and $[\{\eta^5\text{-}C_5Me_3\text{-}1,2\text{-}[CH_2CH_2CH_2PPh_2]_2\}RhCl]X$ **177** ($X = Cl^-$, PF_6^-, BPh_4^-).[229] $[(\eta^5\text{-}C_5Me_4CF_3)RhCl_2]_2$ reacted with diphenylvinylphosphine in the absence of potassium *tert*-butoxide producing $[\{\eta^5\text{-}C_5(CO_2Et)Me_3\text{-}2\text{-}[CH_2CH_2CH_2PPh_2]\}RhCl_2]$.[228]



n = 1, 2

175



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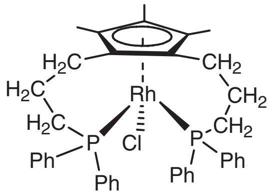
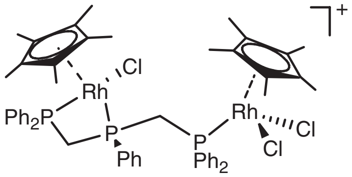


177

Diphenyl dichalcogenides reacted with $CpRh(PMe_3)(CO)$ to give several complexes $CpRh(PMe_3)(EPh)_2$ (E = S, Se, and Te). The analogous complexes $Cp^*Rh(PMe_3)(EPh)_2$ (E = S, Se, and Te) were prepared from $Cp^*RhCl_2(PMe_3)$ and the chalcogenolates, NaSPh or LiEPh (E = Se, Te). Similarly $CpRh(PMe_3)(S_2C_6H_4)$ and $Cp^*Rh(S_2C_6H_4)(PMe_3)$ were prepared and characterized.[148] The complex $[Cp^*Rh(dmpm)(H_2)][B(C_6F_5)_4]_2$ was prepared by the reaction of $[Cp^*RhCl(dmpm)]B(C_6F_5)_4$ (dmpm = bisdimethydiphosphinomethane) with $[Et_3Si][B(C_6F_5)_4]$ in methylene chloride under 1 atm of hydrogen.[230] Reaction of $[Cp^*RhCl_2]_2$ with bis(diphenylphosphinomethyl)phenylphosphine (dpmp) in the presence of KPF_6 generated mono- or dinuclear complexes $[Cp^*RhCl(dpmp)]PF_6$ or $[Cp^*RhCl_2(dpmp)\text{-}RhClCp^*]PF_6$ **178** and **179** depending on reaction conditions. A diastereomer $[Cp^*RhCl(dpmp)]PF_6$ was treated with $AuCl(C_4H_8S)$, generating a heterotetranuclear complex $[\{Cp^*RhCl_2(dpmp)Au\}_2](PF_6)_2$ **180**.[231]



RR/SS

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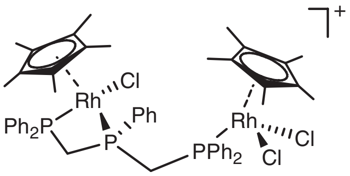

RS/SR

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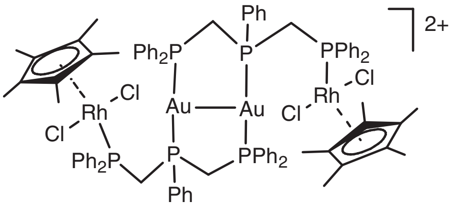
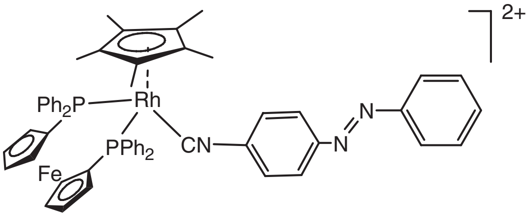


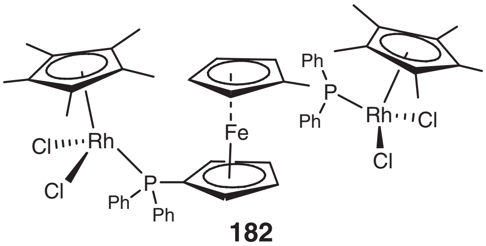
180

Reactions of $[Cp^*RhCl_2]_2$ with 4-isocyanoazobenzene (RNC) and 4,4′-diisocyanoazobenzene (CN–R–NC) gave the complexes $Cp^*Rh(CNC_6H_4N{=}NC_6H_5)Cl_2$ and $(Cp^*RhCl_2)_2(\mu\text{-}CNC_6H_4N{=}NC_6H_4NC)$. Reaction of $[Cp^*Rh(dppf)(MeCN)](PF_6)_2$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) with 4-isocyanoazobenzene gave $[Cp^*Rh(dppf)(CNC_6H_4N{=}NC_6H_5)](PF_6)_2$ **181**.[232]



181

Reactions of $[Cp^*RhCl_2]_2$ with 1,1′-bis(diphenylphosphinomethyl)ferrocene (dpmf) or dppf gave the bridged complex $[Cp^*RhCl_2]_2(\mu\text{-diphos})$ **182** (diphos = dpmf, dppf). Reaction with dppf in the presence of $NaPF_6$ gave the cationic chelated complex $[Cp^*RhCl(dppf\text{-}P,P')]PF_6$ **183**. Replacement of one chlorine atom by a neutral Lewis base afforded the corresponding cationic complexes $[Cp_2^*Rh_2Cl_2(CNR)_2(\mu\text{-diphos})](PF_6)_2$ **184** and $[Cp^*Rh(MeCN)(diphos)](PF_6)_2$ **185**.[233]



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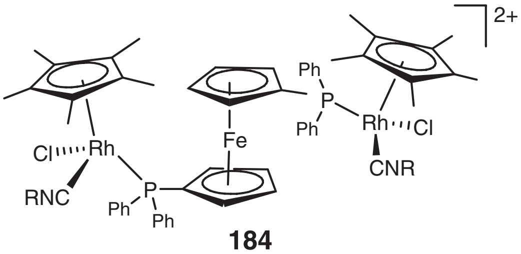

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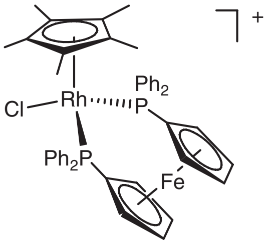

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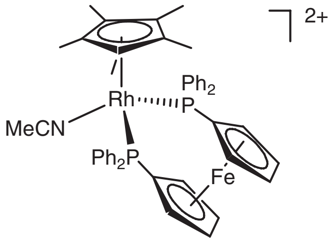
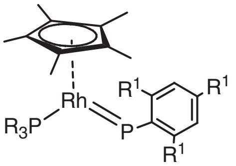


185

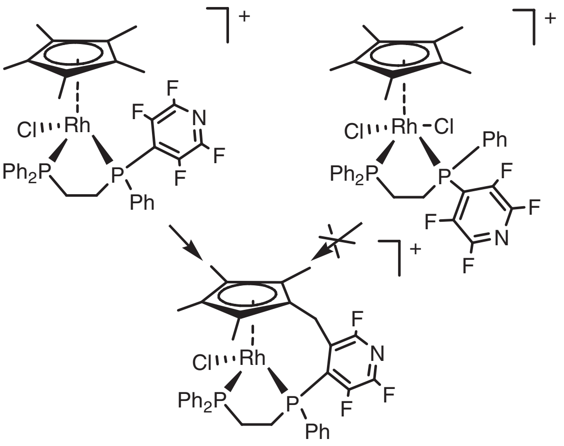
The reaction between $[Cp^*RhCl_2]_2$ and $Ph_2PCH_2CH_2PPh(C_5F_4N\text{-}4)$ in the presence of BF_4^- yielded racemic diastereoisomers of $[Cp^*RhCl\{Ph_2PCH_2CH_2PPh(C_5F_4N\text{-}4)\}]BF_4$. In the $S_{Rh}R_P$ and $R_{Rh}S_P$ pair of enantiomers, the Cp^* and tetrafluoropyridyl groups are close and underwent rapid dehydrofluorinative C–C coupling to give the respective enantiomers of $[\{\eta^5,\kappa P,\kappa P\text{-}C_5Me_4CH_2\text{-}2\text{-}C_5F_3N\text{-}4\text{-}PPhCH_2CH_2PPh_2\}RhCl]BF_4$ (Scheme 17).[234]

Terminal rhodium-complexed phosphinidenes, $Cp^*(PR_3)Rh{=}PAr$ **186**, were obtained by dehydrohalogenation of the primary phosphine complexes $Cp^*RhCl_2(PH_2Ar)$ in the presence of a phosphine.[235]



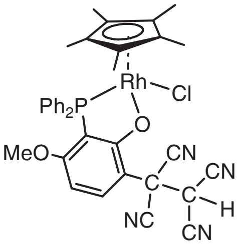
R = Ph, R^1 = *t*-Bu
R = Me, R^1 = *i*-Pr

186



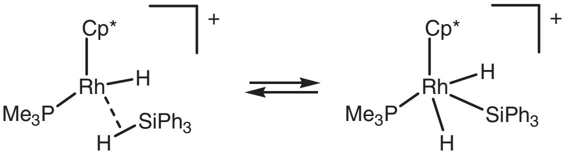
Scheme 17

Reaction of $[Cp^*RhCl_2]_2$ with (2,6-dimethoxyphenyl)diphenylphosphine (mdmpp) gave Cp^*RhCl_2(mdmpp-*P*) and Cp^*RhCl(mdmpp-*P*,*O*), depending on the reaction conditions. Treatment of the first compound with $NaPF_6$ formed the O-coordinated complex, $[Cp^*RhCl(mdmpp\text{-}P,OMe)](PF_6)$.[236] Complex Cp^*RhCl(mdmpp-*P*,*O*) readily reacted with tetracyanoethylene (tcne) or 7,7,8,8,-tetracyano-*p*-quinomethane (tcnq) to form the 1 : 1 adducts Cp^*RhCl(mdmpp-*P*,*O*)(tcne) 187 and Cp^*RhCl(mdmpp-*P*,*O*)(tcnq) derived from insertion of cyanoolefins into the C–H bond adjacent to the metal–O bond.[237]



187

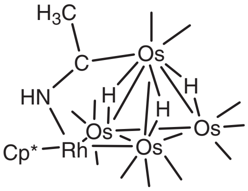
The solution photochemistry of C–H bond-activating complexes $CpRh(CO)_2$ and $Cp^*Rh(CO)_2$ was investigated at several excitation wavelengths. Quantitative photochemical measurements were obtained for ligand photosubstitution and intermolecular Si–H/C–H bond activation reactions through a determination of absolute quantum efficiencies. The experimental observations were related to the electronic absorption characteristics of the molecules and were interpreted on a photophysical scheme involving excited states with quite distinct photochemical reactivities.[238] Addition of trimethylsilane or triethylsilane to $[Cp^*Rh(Me)(PMe_3)(CH_2Cl_2)]BAr'_4$ resulted in Si–H bond activation and release of methane below −80 °C. Non-classical silane complexes $[Cp^*Rh(SiMe_3)(PMe_3)(\eta^2\text{-}HSiMe_3)]BAr'_4$ and $[Cp^*Rh(SiEt_3)(PMe_3)(\eta^2\text{-}HSiMe_3)]BAr'_4$ were generated and characterized by NMR spectroscopy. Addition of excess triphenylsilane to a CD_2Cl_2 solution of $[Cp^*Rh(Me)(PMe_3)(CH_2Cl_2)]BAr'_4$ gave a product that may be characterized as either a classical Rh(V) dihydridosilyl complex, $[Cp^*(PMe_3)Rh(H)_2(SiPh_3)]BAr'_4$, or a non-classical fluxional Rh(III) hydrido–silane complex, $[Cp^*Rh(H)(\eta^2\text{-}HSiPh_3)(PMe_3)]BAr'_4$ (Scheme 18).[239]



Scheme 18

7.02.3.1.3.(iii) Cluster compounds

The reaction of $[Os_4H_4(CO)_{11}]^{2-}$ with the cation $[Cp^*Rh(MeCN)_3]^{2+}$ afforded a number of penta- and hexanuclear mixed metal clusters depending on the reaction conditions. $Os_4Rh(\mu\text{-}H)_3(MeC{=}NH)(CO)_{11}(Cp^*)$ 188, $Os_4Rh_2(\mu\text{-}H)_2(CO)_{11}(Cp^*)_2$ 189, and $Os_4Rh(\mu\text{-}H)_2(CO)_{13}(Cp^*)$ 190 were obtained in low yield. The three complexes were characterized spectroscopically and crystallographically.[240]



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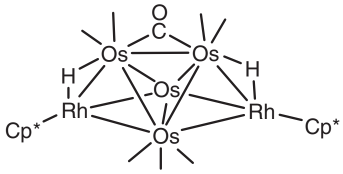

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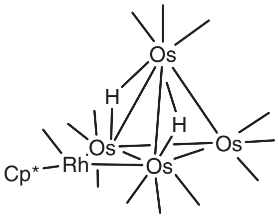
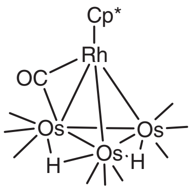


190

Treatment of the anionic triosmium cluster $[N(PPh_3)_2][Os_3(\mu\text{-}H)(CO)_{11}]$ with 1 equiv. of $[Cp^*Rh(MeCN)_3][\{PF_6\}_2]$ yielded three Cp^*-containing clusters including $Os_3Rh(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(Cp^*)$ 191, $Os_3Rh(\mu\text{-}CO)_2(CO)_9(Cp^*)$ 192, and $Os_3Rh_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_8(Cp^*)(\mu_2\text{-}\eta^5,\eta^1\text{-}CH_2C_5Me_4)$ 193.[241]



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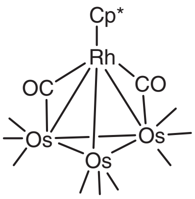

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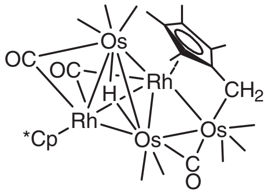
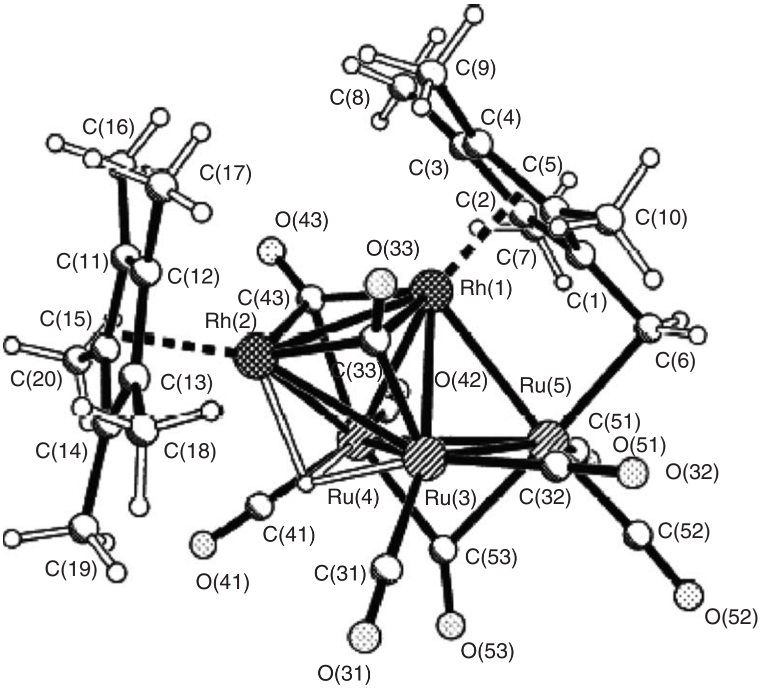


193

The reaction of the pentanuclear cluster $Ru_4RhC(CO)_{12}(Cp^*)$ with $[NEt_4]BH_4$ provided the complex $[Ru_4RhC(CO)_{11}H(Cp^*)]^-$. The reaction of the latter cluster with iodine gave $Ru_4RhC(CO)_{11}H(Cp^*)I$.[242] Thermolysis of $Ru_3RhH_2(CO)_{10}(Cp^*)$ in hydrocarbon solvents afforded the pentanuclear cluster $Ru_3Rh_2(\mu_3\text{-}H)(\mu_2\text{-}CO)(\mu_3\text{-}CO)_2(CO)_6(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)(Cp^*)$ 194, together with the complex $Ru_2Rh_2(CO)_8(Cp^*)_2$. The reaction of $Ru_3RhH_2(CO)_{10}(Cp^*)$ with Me_3NO followed by the addition of PPh_3 leads to the isolation of the mono- and diphosphine substituted complexes $Ru_3Rh(\mu\text{-}H)_2(\mu_4\text{-}\eta^2\text{-}CO)(\mu_2\text{-}CO)_2(CO)_6(PPh_3)(Cp^*)$ and $Ru_3Rh(\mu\text{-}H)_2(\mu_4\text{-}\eta^2\text{-}CO)(\mu_2\text{-}CO)_2(CO)_5(PPh_3)_2(Cp^*)$ 195, respectively.[243]



194

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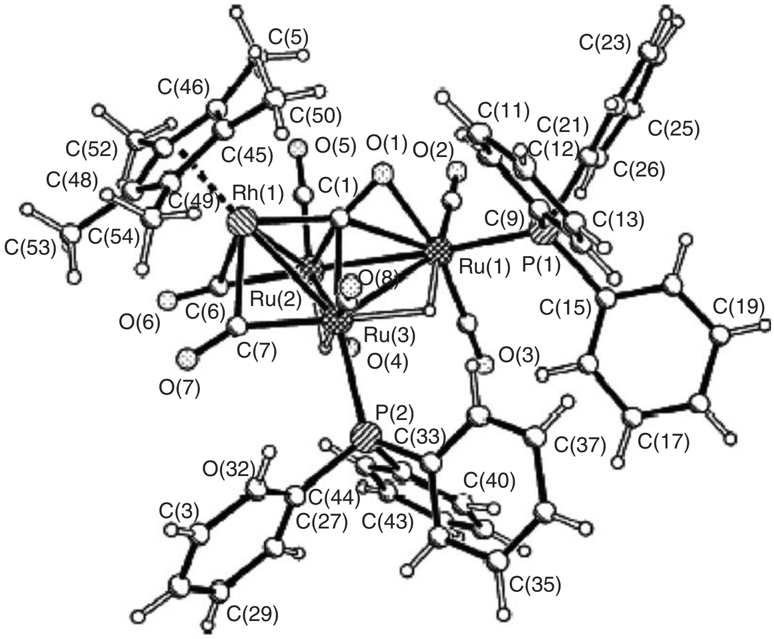

195

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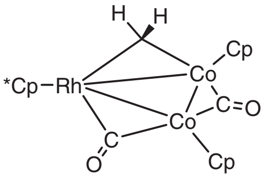
The reactions of diazoalkanes and trinuclear complexes of the form $Cp^*Rh(CpCo)_2(CO)_2$ were described. Two types of products 196 and 197 which preserve the trinuclear cluster skeleton were formed.[244]



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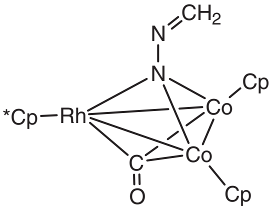


197

7.02.3.2 Monohapto Ligands

7.02.3.2.1 Alkyl, acyl, aryl, alkenyl, and alkynyl ligands

This part is divided into sections based on the type of reaction which gave the compounds. As usual, within these sections, rough grouping into ancillary ligand type is made.

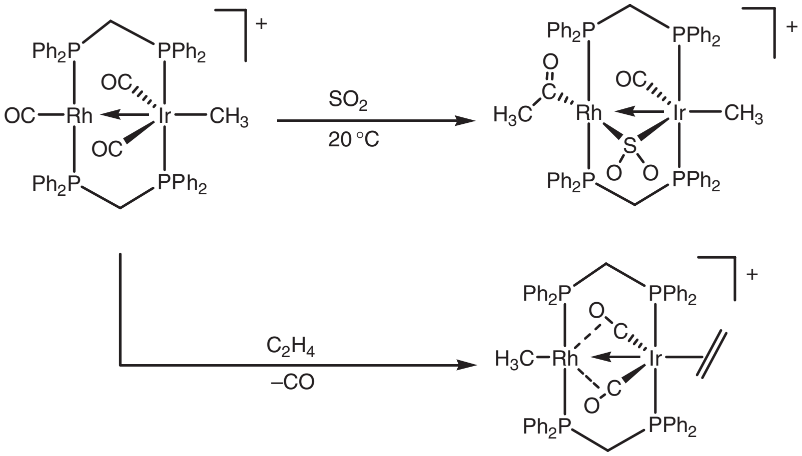
7.02.3.2.1.(i) Metathesis and transmetallation reactions

An unusual transmetallation of the methyl group from Ir to Rh was observed for the complex $[RhIr(CH_3)(CO)_3(dppm)_2]CF_3SO_3$. Addition of SO_2 did not yield the expected SO_2 insertion product, but $[RhIr(C(O)CH_3)(CO)_2(\mu\text{-}SO_2)(dppm)_2]^+$, the product of methyl migration to Rh and migratory insertion of the methyl to a carbonyl group. The reaction of $[RhIr(CH_3)(CO)_3(dppm)_2]CF_3SO_3$ with ethylene produced the substitution of one carbonyl and migration of the methyl group to Rh (Scheme 19).[245]

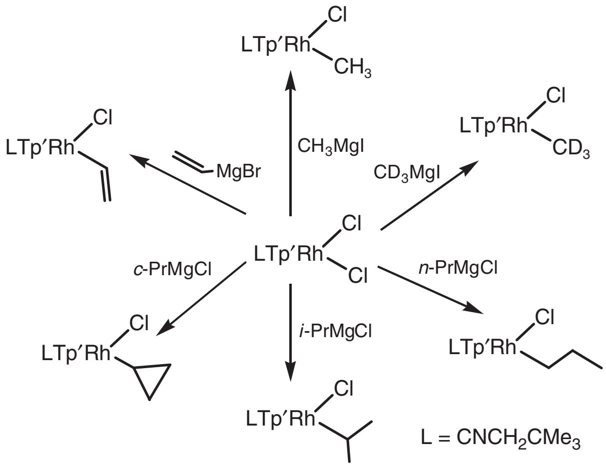
The reaction of $[RhCl(CO)(dppm)]_2$ with C_6H_5MgCl afforded the diphenyl–dirhodium complex $[Rh(C_6H_5)(CO)(dppm)]_2$.[246] A series of complexes of the type $RhTp'(R)Cl(CNCH_2CMe_3)$, where $R = CH_3$, CD_3, *n*-propyl, isopropyl, cyclopropyl, and vinyl and Tp′ = tris(3,5-dimethylpyrazolyl)borate, was obtained (Scheme 20). The complexes were prepared by the reaction of the corresponding Grignard reagent with $RhTp'Cl_2(CNCH_2CMe_3)$.[247] The reductive elimination of RH for the same complexes was also studied.[248]

The dialkynyl-di-μ-methylene-dirhodium complexes $[Cp^*Rh(\mu\text{-}CH_2)(C{\equiv}CR)]_2$ ($R = Ph$, $p\text{-}C_6H_4Me$) were prepared from $[Cp^*Rh(\mu\text{-}CH_2)Cl]_2$ and $RC{\equiv}CMgCl$.[249] The alkynylation of $Cp^*RhCl_2(PEt_3)$ with an excess of $LiC{\equiv}CR$ ($R = Ph$, ${}^tBu$, $SiMe_3$) in THF led to novel bis(alkynyl) $Cp^*Rh(C{\equiv}CR)_2(PEt_3)$ or mono(alkynyl) $Cp^*Rh(C{\equiv}CR)Cl(PEt_3)$ complexes.[250] By a similar method, bi- and trimetallic $PtRh_2$ bisalkynyl complexes were obtained and described.[251]

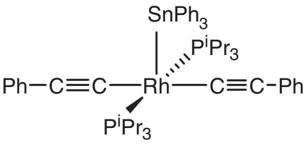
The reaction of $Rh(\eta^2\text{-}O_2CMe)(P\textit{i}Pr_3)_2$ with $Ph_3SnC{\equiv}CPh$ afforded, by elimination of Ph_3SnOAc, the five-coordinate complex $Rh(C{\equiv}CPh)_2(SnPh_3)(P\textit{i}Pr_3)_2$ 198. Treatment of the latter complex with excess PMe_3 gave the octahedral compound *mer,trans*-$Rh(C{\equiv}CPh)_2(SnPh_3)(PMe_3)_3$ 199, whose molecular structure was determined.[252]



Scheme 19



Scheme 20



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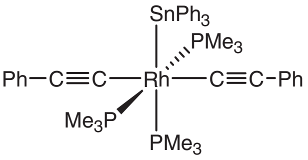
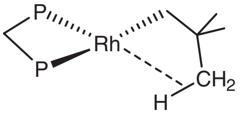


199

The reaction of $[(\kappa^2\text{-dtbpm})RhCl]_2$ (dtbpm = bis(di-*tert*-butylphosphanyl)methane) with an excess of NpLi (Np = neopentyl) led to the three coordinated alkylrhodium(I) complex RhNp(κ^2-dtbpm) **200**, a 14-electron species that is weakly stabilized by agostic interactions with the γ-CH bonds of the alkyl ligand. In the presence of a ligand L such as PMe_3, PPh_3, or CO, the complex evolved to the formation of RhNp(κ^2-dtbpm)(L) **201**.[253]



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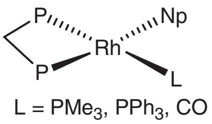
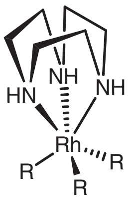
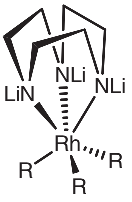


201

A series of complexes of the type (tacn)RhR_3 **202** (tacn = 1,4,7-triazacyclononane; R = Me, Et, Ph, vinyl) were obtained by the treatment of $RhCl_3$(tacn)·H_2O with an excess of RLi in THF, followed by protonation by methanol. The product before protonation was (Li_3tacn)RhR_3 **203** (Li_3tacn = 1,4,7-trilithio-1,4,7-triazacyclononane) which was also isolated.[254]





R = Me, Et, Ph

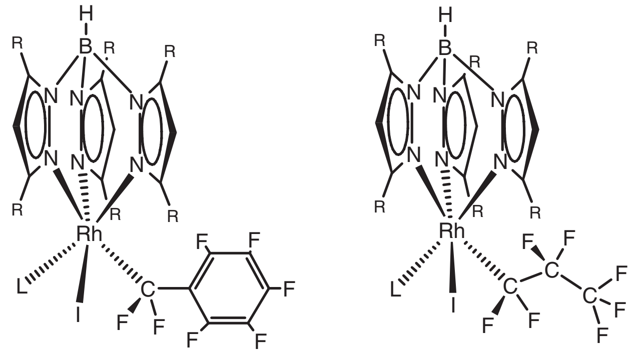
202 **203**

The paramagnetic rhodium(II) complex $[PBzPh_3]_2[Rh(C_6Cl_5)_4]$ was obtained from the arylation of $RhCl_3(tht)_3$ with LiC_6Cl_5. Reaction of $[PBzPh_3]_2[Rh(C_6Cl_5)_4]$ with CO afforded the rhodium(I) complex $[PBzPh_3][Rh(C_6Cl_5)_2(CO)_2]$. The oxidation of $[PBzPh_3]_2[Rh(C_6Cl_5)_4]$ with chlorine or iodine gave the rhodium(III) compound

$[PBzPh_3][Rh(C_6Cl_5)_4]$. The reaction of $[PBzPh_3][Rh(C_6Cl_5)_4]$ with methanolic solutions of HCl led to the breaking of only one of the Rh–C bonds, producing the monomeric complex $[PBzPh_3][Rh(C_6Cl_5)_3Cl]$. Treatment of $[PBzPh_3][Rh(C_6Cl_5)_4]$ with potassium thiocyanate or thallium(I) acetylacetonate gave rise to the substitution of the chlorine ligand with the formation of $[PBzPh_3][Rh(C_6Cl_5)_3X]$ (X = SCN, acac).[255] The compounds *fac*-$Rh(C_6Cl_5)_3(py)$ and *mer*-$Rh(C_6Cl_5)_3(^tBuNC)_3$ were also described.[256] A series of homo- and heterobridged mixed valence dimetallic complexes containing the fragment "$Rh(C_6F_5)_3$" were obtained and characterized.[257]

7.02.3.2.1.(ii) Metallation of C–X bonds

Electron-rich rhodium porphyrin alkyls Rh(omp)R (R = Me, ^iPr; omp = 2,3,7,8,12,13,17,18-octamethoxyporphyrin dianion) were photolyzed to give the non-bridged metal–metal bonded complex $Rh_2(omp)_2$. Reaction of Rh(omp)H with TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) also yielded $Rh_2(omp)_2$ quantitatively, which reacted with CH_3I to produce Rh(omp)Me and Rh(omp)I.[258] The oxidative addition of MeI to a series of Vaska-type rhodium(I) complexes of formula *trans*-$Rh(CO)X(PR_3)$ (X = halide, R = aryl or alkyl substituent) was extensively described in a review.[6] Oxidative addition of perfluorobenzyl iodide to $RhTp(C_2H_4)_2$ [Tp = tris(pyrazolyl)borate] afforded $RhTpI(CF_2C_6F_5)(C_2H_4)$, from which the ethylene ligand was displaced by CO or PMe_3 to afford $RhTpI(CF_2C_6F_5)(L)$ **204** (L = CO, PMe_3). Similar reaction of perfluorobenzyl iodide with $RhTp^*(CO)_2$ (Tp^* = tris(3,5-dimethylpyrazolyl)borate) afforded $RhTp^*I(CF_2C_6F_5)(L)$ **205**. Complexes of formulas $RhTp^*I(CF_2CF_2CF_3)(L)$ **206** and **207** were obtained by a similar method.[259] The mechanism of the oxidative addition of MeI to $Tp^*Rh(CO)L$ (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, and CO) was experimentally studied and related to the basicity of L.[64]



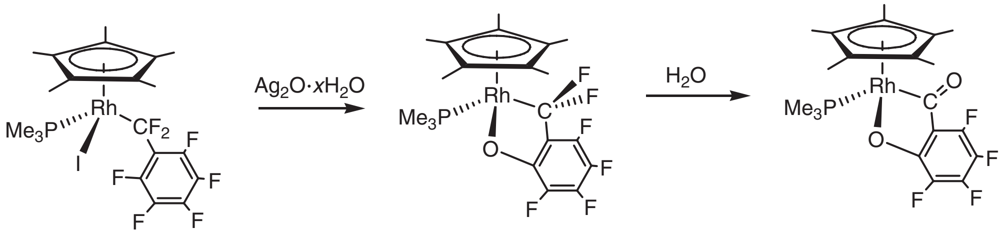
204: R = H
205: R = Me

L = CO, PMe_3
R = H, Me

206: R = H
207: R = Me

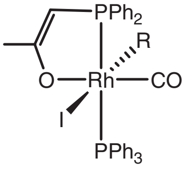
Oxidative addition of perfluorobenzyl iodide to $Cp^*Rh(CO)_2$ in benzene afforded the perfluorobenzyl complexes $Cp^*Rh(CF_2C_6F_5)I(CO)$. The CO ligand was replaced by PMe_3 affording $Cp^*Rh(CF_2C_6F_5)I(PMe_3)$.[260] The reaction of $Cp^*Rh(CF_2C_6F_5)I(PMe_3)$ with moist silver oxide afforded the oxametallacycle $Cp^*RhO(C_6F_4)CF_2(PMe_3)$, which underwent rapid hydrolysis of the α-CF_2 group by adventitious moisture to afford the complex analog $Cp^*Rh[O(C_6F_4)C{=}O](PMe_3)$ (Scheme 21).[261,261a]

The series of Rh(I) complexes RhI(CO)(diimine) was prepared (diimine = ArN=C(Me)C(Me)=NAr, Ar = 2-$^iPrC_6H_4$; diimine = ArN=C(Me)-2-py, Ar = C_6H_5, 2-$^iPrC_6H_4$). Oxidative addition of MeI gave the stable methyl complexes $RhI_2Me(CO)(diimine)$. For the diimines ArN=C(Me)C(Me)=NAr (Ar = 2,4,6-$Me_3C_6H_2$,



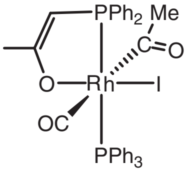
Scheme 21

2,6-$^{i}Pr_2C_6H_3$), the reaction with MeI gave the five-coordinate acetyl complexes $RhI_2(COMe)$ (diimine).[262] The reaction of the hydrazonic ligand 2-(diphenylphosphino)benzaldehyde benzoylhydrazone (HL) with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ in diethyl ether led to the isolation of RhCl(HL)(CO), where the neutral ligand was P–N bidentate. Addition of Et_3N or NaOMe caused the deprotonation of the ligand, with the consequent formation of the three-coordinated carbonyl Rh(I) complex Rh(L)(CO). Addition of MeI to the latter complexes allowed the preparation of RhClI(MeCO)(HL) and RhI(L)(COMe). Under different reaction conditions, the immediate precipitation of the hexacoordinated methylcarbonyl complex RhI(L)(CO)(Me)I was observed, which rapidly rearranged into RhI(L)(COMe) after dissolution in CH_2Cl_2 or $CHCl_3$.[263] Oxidative addition of MeI and PhI to the square-planar phosphino enolate complex $Rh\{Ph_2PCHC(O)Ph\}(CO)(PPh_3)$ afforded the hexacoordinate Rh(III) complexes $Rh\{Ph_2PCHC(O)Ph\}(R)(I)(CO)(PPh_3)$ **208** [R = Me, Ph]. The complex with R = Me underwent CO insertion into the Rh–Me bond affording the three isomers of the acyl species $Rh\{Ph_2PCHC(O)Ph\}\{COMe\}(I)(CO)(PPh_3)$, **209**, **210**, and **211**.[99]



R = Me, Ph

208



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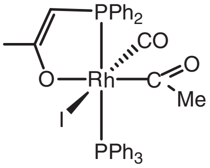

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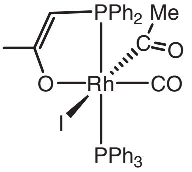
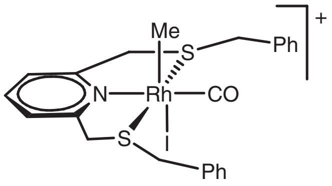


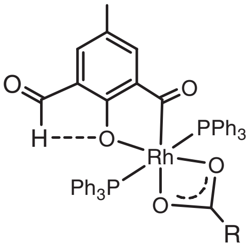
211

Addition of PPh_3 and MeI to the dimetallic rhodium complex $Rh_2(\mu\text{-}1,4\text{-}DA)(CO)_2$ (1,4-DA = 1,4-diaminoanthraquinonate) led to the preparation of the diacyl dirhodium(III) derivative $Rh_2(\mu\text{-}1,4\text{-}DA)(COMe)_2I_2(PPh_3)_2$.[60] The factors determining the course of the methyl iodide oxidative addition to diamidonaphtalene-bridged dirhodium complexes were studied.[264] Kinetic experiments of the oxidative addition of methyl iodide to the cationic rhodium(I) carbonyl complex $[Rh(L)(CO)]PF_6$ (L = 2,6-bis(benzylthiomethyl)pyridine) to yield $[RhI(Me)(L)(CO)]PF_6$ **212** were performed by FT-IR.[71]



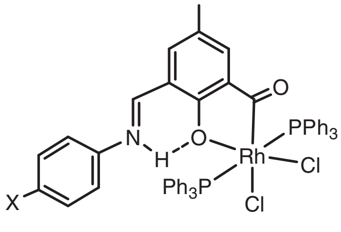
212

The oxidative addition of the Schiff mono bases of 2,6-diformyl-4-methylphenol with $RhCl(PPh_3)_3$ in the presence of dilute RCO_2H in ethanol afforded species of the type (carboxylato)[4-methyl-6-formylphenolato-*C*^{1},*O*]bis(triphenylphosphine)rhodium(III), $Rh(L_{al})(PPh_3)_2(RCO_2)$ **213** (R = H, Me, Et, Ph). Other similar complexes were also described [**214**, **215**, and **216**].[265]



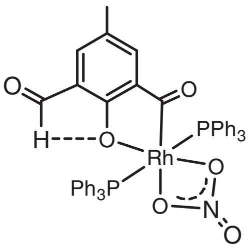
R = H, Me, Et, Ph

213



X = H, Me, OMe, Cl

214



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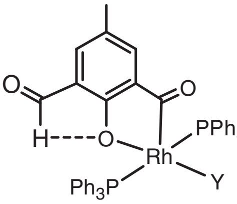
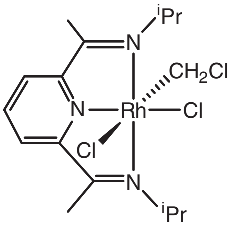


Y = Cl, NO_2

216

The complex $[Rh(\kappa^3\text{-}N,N,N\text{-}pybox)(CO)]PF_6$ underwent oxidative addition of CH_3I leading to the new compound $[RhI(CH_3)(\kappa^3\text{-}N,N,N\text{-}pybox)(CO)]PF_6$. The allenyl Rh(III)–pybox complex of formula $Rh(CH{=}C{=}CH_2)Cl_2(\kappa^3\text{-}N,N,N\text{-}pybox)$ was synthesized by a one-pot reaction from $[Rh(\mu\text{-}Cl)(\eta^2\text{-}C_2H_4)_2]_2$, pybox, and an equimolar amount of propargyl chloride.[70] The tridentate hemilabile ligands 2,6-bis(R^2-carbaldimino)pyridine and 2,6-bis(R^2-ethylidyneimino)pyridine (2,6-$(C(R^1){=}NR^2)_2C_5H_3N$; $R^1 = H$, $R^2 = i$-Pr, *t*-Bu, cyclohexyl, *p*-anisyl; $R^1 = Me$, $R^2 = p$-anisyl, *i*-Pr) were used to prepare the Rh(I) complexes $RhCl(2,6\text{-}(C(R^1){=}NR^2)_2C_5H_3N)$. These reacted with CH_2Cl_2, $CHCl_3$, benzyl chloride, and α,α-dichlorotoluene leading to Rh(III) complexes [**217**, **218**, **219**, and **220**, respectively] by C–Cl oxidative addition.[266]



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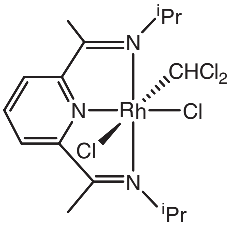

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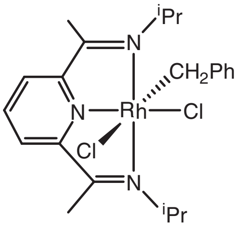

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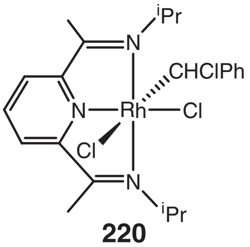
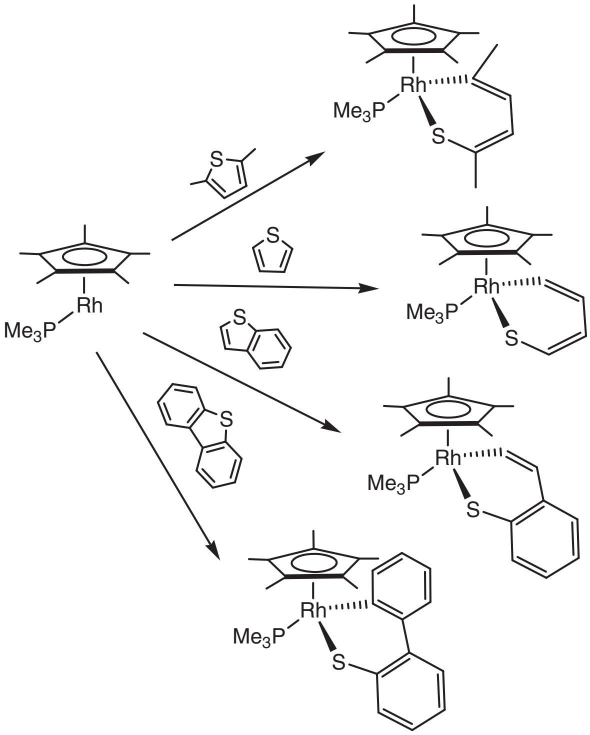


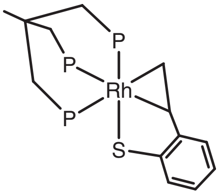
220

Diiodomethane was oxidatively added to $RhCl(CO)(PR_3)_2$ (R = Me, Et) to form $RhCl(I)(CH_2I)(CO)(PR_3)_2$. In polar solvents, $RhCl(I)(CH_2I)(CO)(PEt_3)_2$ underwent a halide-scrambling reaction to give several compounds containing CH_2I or CH_2Cl ligands.[267] Reaction of $RhH(PEt_3)_4$ with hexafluoropropene afforded the C–F activation product Rh{(*Z*)-CF=CF(CF_3)}$(PEt_3)_3$ and $Et_3P(F)$\{(*Z*)-CF=CF(CF_3)\}. In contrast, addition of (*E*)-1,2,3,3,3-pentafluoropropene to $RhH(PEt_3)_4$ yielded Rh{(*E*)-C(CF_3)=CHF}$(PEt_3)_3$ together with $RhF(PEt_3)_3$ and (*Z*)-1,3,3,3-tetrafluoropropene.[268] The unsaturated 16-electron fragment $Cp^*Rh(PMe_3)$ inserted into the sulfur–carbon bond in a variety of substituted dibenzothiophenes gave six-membered metallacycle products.[269] Molecular mechanics calculations were made on the products formed via insertion of the reactive 16-electron metal fragment $Cp^*Rh(PMe_3)$ into the C–S bonds of unsubstituted thiophene, benzothiophene, and dibenzothiophene (Scheme 22). The parent thiophene complex, unlike the previously reported ring-substituted analog (and as predicted by the molecular mechanics calculations), was found to adopt a planar six-membered ring structure. The benzothiophene insertion product showed a moderate degree of bending of the metallathiacycle, whereas the dibenzothiophene molecule was strongly bent.[270]



Scheme 22

A series of intermediates in the catalytic transformation of benzo[*b*]thiophene to 2-ethylthiophene were characterized. The 16-electron Rh(I) fragment (triphos)RhH [triphos = MeC(CH$_2$PH$_2$)$_3$] reacted with benzo[*b*]thiophene by C–S bond scission to yield the 2-vinylthiophenolate complex (triphos)Rh{η^3-S(C$_6$H$_4$)CH=CH$_2$} **221**. The complex (triphos)RhH{η^2-S(C$_6$H$_4$)CH(CH$_3$)} **222** was also obtained.[271] The complex (triphos)RhH$_3$ reacted with dinaphtho[2,1-*b*:1′,2′-*d*]thiophene (DNT) in a similar way as benzo[*b*]thiophene, although the heterometallacyclic species were not detected.[272]



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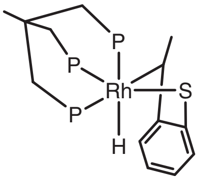
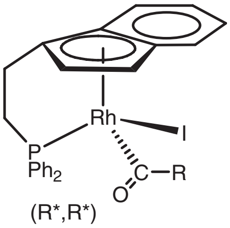


222

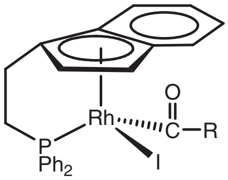
The complex [Rh(dmgH)$_2$(PPh$_3$)]$^-$ (dmgH = monoanion of dimethylglyoxime) reacted with (*E*)-1,2-dichloroethylene to give the (*E*)-vinylene-bridged dinuclear ethenyl-bridged rhodium complex [K(MeOH)$_2$]$_2$-{(PPh$_3$)(dmg)(dmgH)Rh(μ-CH=CH)Rh(dmg)(dmgH)(PPh$_3$)}.[273] [Rh(dmgH)$_2$(PPh$_3$)]$^-$, prepared by reduction of RhCl(dmgH)$_2$(PPh$_3$) with NaBH$_4$ in methanolic KOH reacted with *cis*/*trans*-XCH=CHCH$_2$X (X = Cl, Br) to give the σ-allyl complexes *cis*/*trans*-[Rh(–CH$_2$CH=CHX)(dmgH)$_2$(PPh$_3$)(–CH$_2$CH=CHX)] and *cis*/*trans*-[Rh(dmgH)$_2$(PPh$_3$)(–CH$_2$CH=CHOMe]. Propagyl halides reacted with [Rh(dmgH)$_2$(PPh$_3$)]$^-$ providing other alkenyl complexes.[274] Three series of alkylrhodoximes Rh(dmgH)$_2$RL (L = H$_2$O, R = Me, Et, ^{n}Pr, ^{n}Bu, ^{i}Bu, ^{neo}Pent; L = py, R = Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{i}Bu, ^{s}Bu, ^{t}Bu, ^{neo}Pent, adam, CH$_2$Cl, CH$_2$CH$_3$; L = PPh$_3$, R = Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{i}Bu, ^{t}Bu, ^{neo}Pent, adam) were prepared and characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectra.[275]

Highly diastereoselective oxidative addition of alkyl halides to {η^5:η^1-(Ind-P)$_n$}Rh(CO) [(Ind-P)$_n$ = C$_9$H$_6$(CH$_2$)$_n$PR$_2$; n = 2, 3, 4; R = Ph, Cy, Cy = cyclohexyl] was achieved and the stereoselectivity was governed by the kind of alkyl halide and the length of the spacer in the (Ind-P)$_n$ ligand. The reaction of {η^5:η^1-(Ind-P)$_2$}Rh(CO) with EtI in CH$_2$Cl$_2$ gave (R^*,R^*)-{η^5:η^1-(Ind-P)$_2$}RhI(COEt) **223**, whereas {η^5:η^1-(Ind-P)$_4$}Rh(CO) gave the other diastereomer, (R^*,S^*)-{η^5:η^1(Ind-P)$_4$}RhI(COEt) **224**.[276] The same complexes could be obtained by the reversible CO insertion into the Rh–Me bond in {η^5:η^1-(Ind-P)$_2$}Rh(CO)(Me) **225**, which in fact provided experimental evidence for methyl migration.[277]



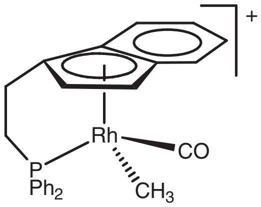
(R*,R*)

223



(R*,S*)

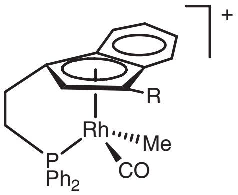
224



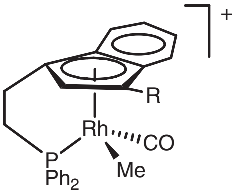
(R*,R*)

225

Reaction of the rhodium(I) carbonyl complexes [η^5:η^1-{3-(R)Ind-P}$_{n=2}$]Rh(CO) (R = H, Et, Cy, (1′*S*,2′*S*,5′*R*)-neomenthyl (NM), (1′*R*,2′*R*,5′*R*)-neoisomenthyl (NIM)) with Me$_3$OBF$_4$ afforded the cationic rhodium(III) complexes [[η^5:η^1-{3-(R)Ind-P}$_{n=2}$]RhMe(CO)]BF$_4$ **226 and 227** having metal-centered chirality in good to excellent yields.[278]



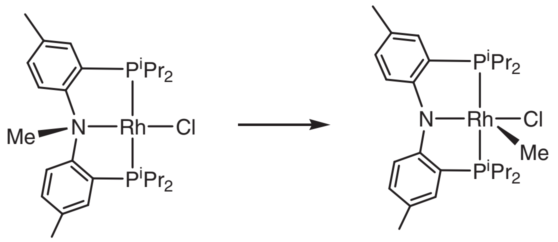
(R*$_{pl}$,S*$_{Rh}$)



(R*$_{pl}$,R*$_{Rh}$)

R = H, Et, Cy

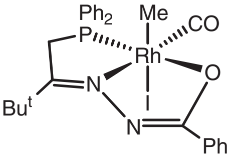
226 **227**



Scheme 23

The oxidative addition of the N–Me bond to Rh(I) in the pincer ligand types bis(*ortho*-phosphinoaryl)amine was studied (Scheme 23). The migration of Me from N of the coordinated amine moiety to Rh proceeded with near-zero entropy of activation in solution.[279]

The ligand phosphino-*N*-benzoylhydrazone ($\mathrm{PPh_2CH_2C(^tBu){=}NNHC({=}O)Ph}$ = PNNO) provided the preparation of the Rh(I) complex Rh(PNNO)(CO) **228**. This complex underwent oxidative addition with RI molecules (R = Me, $\mathrm{CH{=}CH{=}CH_2}$) providing the Rh(III) complexes Rh(PNNO)(R)(I)(CO) [R = $\mathrm{CH{=}CH{=}CH_2}$, **229**]. The reaction with $\mathrm{MeO_2CC{\equiv}CCO_2Me}$ gave a cyclometallated alkenylrhodium(III) complex **230**.[280]



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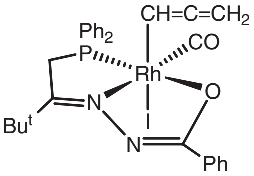

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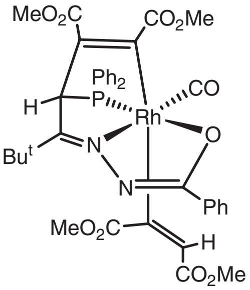
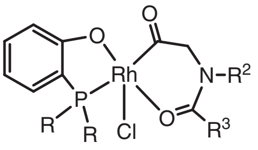


230

The synthesis and characterization of optically active amino acidate alkynyl complexes of formula CpRh(aa)(C≡CR) (aa = L-prolinate (Pro), R = CMe$_3$) were reported.[281] A series of dirhodium σ-alkynyl complexes were also studied.[282] The sterically demanding phosphine 2-(di-*o*-tolylphosphino)phenol was prepared and used to create a series of esters with *N*-acylated amino acids. The phosphine-containing esters reacted with [Rh(μ-Cl)(cyclooctene)$_2$]$_2$ to give products of oxidative addition of the ester carbonyl–oxygen bond to the Rh center, **231** and **232**. The ligand 2-{(diphenylphosphino)methyl}quinolin-8-acetate reacted with [Rh(μ-Cl)(cyclooctene)$_2$]$_2$ affording only one of the three possible diastereomers, **233**.[283]



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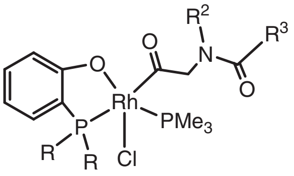

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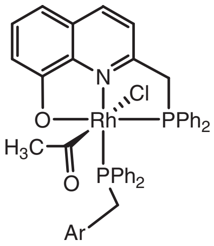
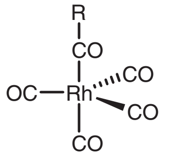


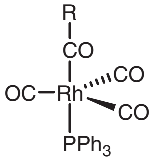
233

7.02.3.2.1.(iii) Insertion into Rh–X bonds (including migratory insertion of carbonyls)

In a continuation of the work developed in the 1990s, several theoretical calculations on catalytic carbonylation reactions were performed, some of them proposing rhodium–acyl intermediates. The olefin insertion in the Rh–H bond to generate alkylrhodium intermediates was theoretically studied in order to determine the factors affecting the regioselectivity of rhodium-catalyzed hydroformylation of vinyl substrates.[284] The potential energy profile of the full catalytic cycle of methanol carbonylation catalyzed by $[RhI_2(CO)_2]^-$ (see Section 7.02.2) was explored computationally using a gradient-corrected density functional method. The equilibrium structures of all isomers of the intermediates involved in the catalytic process were determined. The transition states of CH_3I oxidative addition, the CO migratory insertion, and the CH_3COI reductive elimination were also located.[285] The reaction product in the oxidative addition of MeI to $[RhI_2(CO)_2]^-$, $[RhI_3Me(CO)_2]^-$ was detected.[286] The oxidative addition of other alkyl halides to $[RhI_2(CO)_2]^-$, followed by migratory insertion of the carbonyl to yield the corresponding acyl species was also studied experimentally.[287] The oxidative addition of MeI to $RhCl(CO)(PEt_3)_2$ was shown to be 57 times faster than for $[RhI_2(CO)_2]^-$ in the course of other experimental studies.[288] The carbonylation of allylic halides catalyzed by $RhX(CO)(PEt_3)_2$ (X = Cl, Br, I) allowed to detect the oxidative addition products and the subsequent products of the CO insertion in the Rh–C bond.[289] Several intermediates in the rhodium-catalyzed reductive carbonylation of methanol were structurally characterized. The molecular structure of $[Rh(COCH_3)(I)_2(dppp)]_2$ was described.[290]

FTIR and polymer matrix techniques allowed the study of Rh-catalyzed hydroformylation of 1-octene, 1-butene, propene, and ethene, using either $Rh(acac)(CO)_2$ or $Rh(acac)(CO)(PPh_3)$ in a polyethylene matrix (see Section 7.02.2). Using Rh(acac)(CO). The acyl rhodium tetracarbonyl intermediates, $Rh(RCO)(CO)_4$ **234**, were detected by IR spectroscopy. For the PPh_3-modified reactions, the analogous acyl rhodium tricarbonyl triphenylphosphine intermediates, $RC(O)Rh(CO)_3(PPh_3)$ **235**, were also observed.[291]

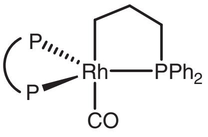




R = Et, *n*-Pr, *n*-Bu^t

234 **235**

The stoichiometric hydroformylation of allyldiphenylphosphine with $RhH(CO)_2(PR_3)$ (PR_3 is a bulky phosphine) allowed the preparation of several rhodacycles [236, 237, 238, and 239], which were characterized and gave some light on the reaction intermediates in rhodium-catalyzed hydroformylation.[292]



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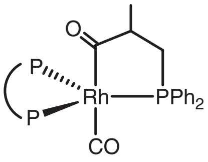

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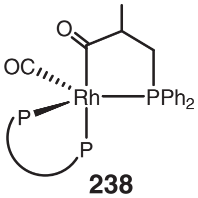

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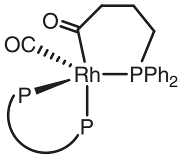
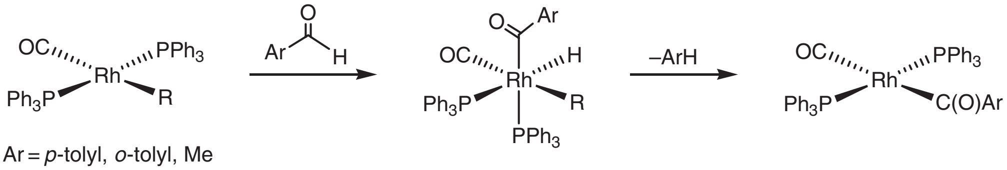


239

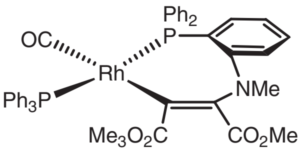
Several organorhodium(I) complexes of the general formula $RhR(PPh_3)_2(CO)$ (R = *p*-tolyl, *o*-tolyl, Me) were isolated and were shown to insert aryl aldehydes into the aryl-rhodium(I) bond (Scheme 24).[293]

The reaction of the dimetallic complex $[Rh(\mu\text{-}C_7H_4NS_2)(CO)(PPh_3)_2]_2$ ($C_7H_4NS_2$ = benzothiazole-2-thiolate) with iodomethane gave the diacyl complex $[Rh(\mu\text{-}C_7H_4NS_2)(COCH_3)(I)(PPh_3)_2]_2$, as the result of the addition of one MeI molecule to each metal atom followed by the insertion of the carbonyl groups into the Rh–Me bonds.[294] The reaction of $Rh(PNMe)(CO)(PPh_3)$ (PNMe = $2\text{-}Ph_2PC_6H_4NMe^-$) with dimethyl acetylenedicarboxylate yielded the product of the insertion of the activated alkyne into the Rh–N bond, forming a seven-membered metallaheterocycle **240**.[295]



Ar = *p*-tolyl, *o*-tolyl, Me

Scheme 24

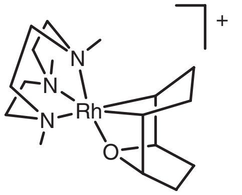


240

A series of vinyl, vinyl hydride, and vinyl alkyl heterobimetallic complexes of Rh and Os was obtained by the reaction of $RhOs(H)(CO)_3(dppm)_2$ with terminal alkynes and allenes.[296]

The formation of a stable 3-rhoda-1,2-dioxolane by dioxygenation of a rhodium–olefin complex supported the involvement of such complexes as intermediates in rhodium-catalyzed oxygenation of olefins to ketones.[297] This 3-rhoda-1,2-dioxolane complexes rearranged to rhodium formylmethyl hydroxycomplexes upon exposure to light or protons (Scheme 25).[298]

The complexes [Rh "N_3" (cod)] ("N_3" = 1,4,7-trimethyl-1,4,7-triazacyclononane, *n*-butylbis(pyridine-2-ylmethyl) amine) and [Rh(ethene)"N_4"] (N_4 = tris(pyridin-2-ylmethyl)amine) were oxidized to oxarhoda(III)tetracyclodecanes **241** and **242** and 2-rhodaoxetanes **243** by addition of H_2O_2.[299]



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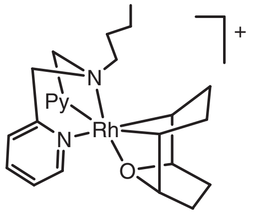

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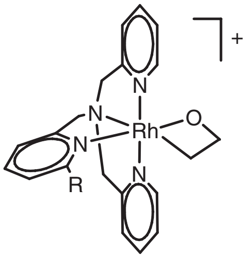
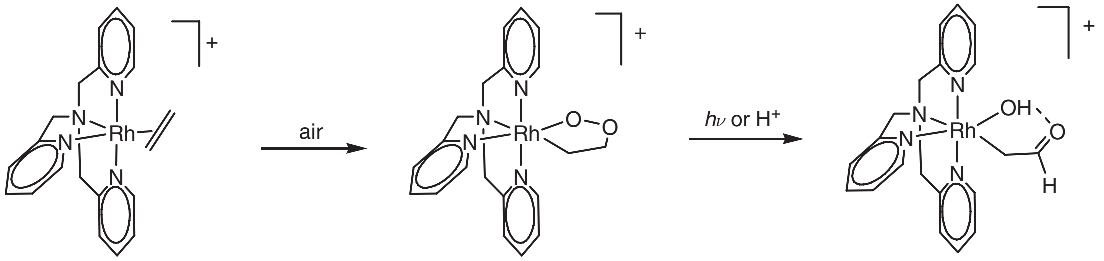
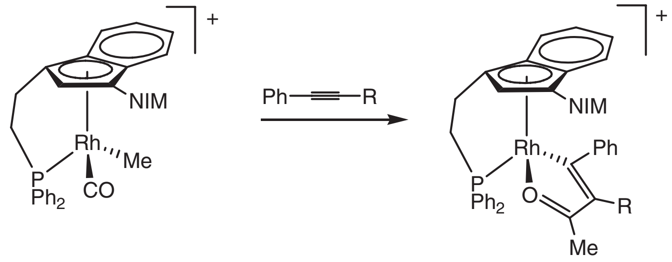


243

The rhodium cationic complex $[[\eta^5:\eta^1\text{-}\{3\text{-(NIM)Ind-P}\}_2]RhMe(CO)]BF_4$ reacted with 1-phenylpropyne regioselectively and stereospecifically to afford the alkenyl complex $[[\eta^5:\eta^1\text{-}\{3\text{-(NIM)Ind-P}\}_2]Rh\{\eta^2\text{-}O{=}C(CH_3)\text{–}C(CH_3){=}CPh\}]BF_4$, by insertion of the acetylene in the Rh–CH_3 bond (Scheme 26).[300]



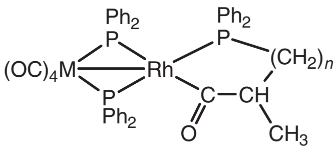
Scheme 25



Scheme 26

The complexes Cp*Rh(X)(Me)(CO) (X = I, Br, Cl, MeCO, CF_3CO_2) reacted with triphenylphosphine to yield the corresponding acyl species Cp*Rh(COMe)(X)(PPh_3). The rate of the process was shown to be dependent on the nature of the X ligand.[301] The reaction of RhMo(H)$(CO)_4(dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$) with a number of alkynes RC≡CR^1 (R = R^1 = C(O)OCH_3, CF_3; R = H, R^1 = C(O)CH_3, C(O)OCH_3) yielded the alkenyl complexes RhMo(C(R^1)═C(H)R)$(CO)_4(dppm)_2$ by insertion of the alkyne in the Rh–H bond. A series of analogous complexes RhMo(R)$(CO)_4(dppm)_2$ (R = $CHCH_2$, CH_3, CH_2CHCH_2, $CH_2C_6H_5$, C_6H_5) was prepared by the reaction of RhMoCl$(CO)_4(dppm)_2$ and the appropriate Grignard reagent.[302]

Several heterometallic acyl and μ-acyl-rhodium complexes were prepared from the reactions of the phosphido-bridged complexes $(CO)_4M(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$ (M = Cr, Mo, W; n = 1–3) with the phosphinoalkenes $Ph_2P(CH_2)_2CH{=}CH_2$ [compounds **244**, **245**, and **246**].[303]



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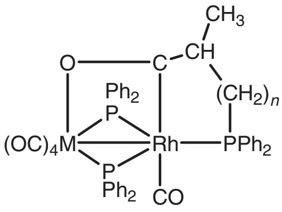

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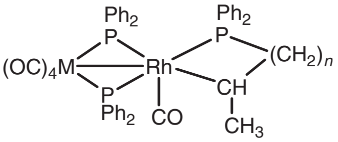
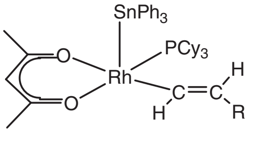


246

M = Cr, Mo, W
n = 1–3

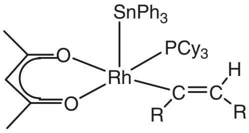
7.02.3.2.1.(iv) Metallation of C–H bonds

The olefinic unit of the complexes Rh(acac)(cod)(PR_3) (PR_3 = PCy_3, P^iPr_3) was displaced by 1,1-diphenyl-2-propyn-1-ol to afford Rh(acac){η^2-HC≡CC(OH)Ph_2}(PR_3). At 60 °C, and in the presence of 1 equiv. of phosphine, these complexes evolved into Rh(acac)H{C≡CC(OH)Ph_2}$(PR_3)_2$.[304] In the presence of methyl propiolate, phenylacetylene, and (trimethylsilyl)acetylene, the complex Rh(acac)H($SnPh_3$)(PCy_3) afforded the alkenyl compounds Rh(acac){(E)-CH═CHR}($SnPh_3$)(PCy_3) **247** (R = CO_2Me, Ph, $SiMe_3$). Similarly, the reactions of Rh(acac)H($SnPh_3$)(PCy_3) with diethyl acetylenedicarboxylate and diphenylacetylene yielded Rh(acac)(CR═CHR)($SnPh_3$)(PCy_3) **248** (R = CO_2Et, Ph). The addition of 1 equiv. of 1-ethynyl-1-cyclohexanol to a pentane suspension of Rh(acac)H($SnPh_3$)(PCy_3) led to the hydroxyalkenyl derivative Rh(acac)[(E)-CH═CHC(OH)$(CH_2)_4CH_2$]($SnPh_3$)(PCy_3) **249**. The reaction of Rh(acac)H($SnPh_3$)(PCy_3) with 2-methyl-1-buten-3-yne led to the α,β-unsaturated alkenyl complex Rh(acac)[(E)-CH═CHC(CH_3)═CH_2]($SnPh_3$)(PCy_3) **250**.[305]



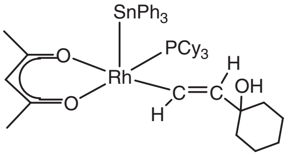
R = CO_2Me, Ph, $SiMe_2$

247



R = CO_2Me, Ph

248



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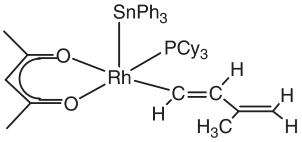
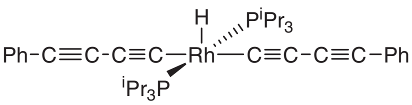


250

The complex Rh(acac)(cyclooctene)(PCy_3) reacted with HC≡CR/PCy_3 to give Rh(acac)H(C≡CR)$(PCy_3)_2$ (R = Ph, Cy, $SiMe_3$). On treatment of these complexes with $HBF_4{\cdot}OEt_2$, the cationic alkenylrhodium(III) complexes [Rh(acac){(E)-CH═CHCy}$(PCy_3)_2$]BF_4 and [Rh(acac)(CH═CH_2)$(PCy_3)_2$]BF_4 were obtained.[306] The rhodium complex Rh(η^2-$O_2CCF_3$$(P^iPr_3)_2$ reacted with 1-alkynes generating either four-coordinate alkynerhodium(I) or six-coordinate alkynyl(hydrido)rhodium(III) complexes.[307] The same complex reacted with 2 equiv. of phenylbutadiyne, in the presence of Na_2CO_3, to form the bis(diynyl)hydridorhodium(III) complex RhH(C≡CC≡CPh)$_2$$(P^iPr_3)_2$ **251**. This complex reacted with pyridine to give RhH(C≡CC≡CPh)$_2$(py)(P^iPr_3)$_2$ **252** and with CO to give Rh(C≡CC≡CPh)(CO)$(P^iPr_3)_2$ **253**. The binuclear complex Rh(CO)$(P^iPr_3)_2$(η^1,η^2-C≡CC≡CPh)RhCl$(P^iPr_3)_2$ **254** was also described.[308]



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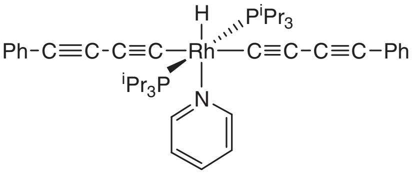

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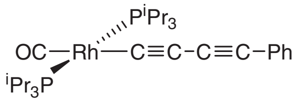

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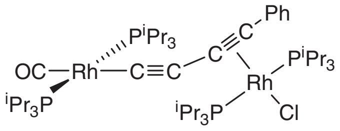
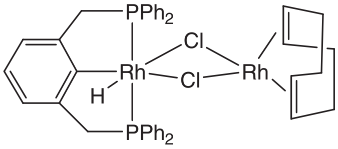


254

The chlororhodium(I) compound [Rh(μ-Cl)(P^{i}Pr$_3$)$_2$]$_2$ reacted with ethynylferrocene by oxidative addition to give the alkynyl(hydrido)rhodium(III) complex RhH(C≡CFc)Cl(P*i*Pr$_3$)$_2$ almost quantitatively (Fc = ferrocenyl). This complex slowly evolved to the vinylidene isomer *trans*-[RhCl(=C=CHFc)(P^{i}Pr$_3$)$_2$].[309] From the same Rh(I) precursor complexes *trans*-[Rh(C≡CR)(C$_2$H$_4$)(P^{i}Pr$_3$)$_2$] and *trans*-[Rh(C≡CR)[N$_2$CH(COPh)](P^{i}Pr$_3$)$_2$] were obtained.[310] Reaction of (PEt$_3$)$_3$Rh[C(N$_2$)SiMe$_3$] with 2 equiv. of HC≡CR (R = SiMe$_3$, Ph, or ^{t}Bu) afforded the Rh^{III} complex (PEt$_3$)$_3$RhH(C≡CR)$_2$ in high yield, showing that the trimethylsilyldiazomethyl group behaves like an alkyl group.[144] Reaction of 1,3-(PPh$_2$CH$_2$)$_2$C$_6$H$_4$ (PCHP) with [Rh(μ-Cl)(cod)]$_2$ in isopropanol afforded the orthometallated dinuclear complexes (PCP)HRh(μ-Cl)$_2$Rh(cod) 255 and [RhHCl(PCP)]$_2$(μ-PCHP) 256. Reaction of (PCP)HRh(μ-Cl)$_2$Rh(cod) with CCl$_4$ produced (PCP)ClRh(μ-Cl)$_2$Rh(cod) 257.[311]



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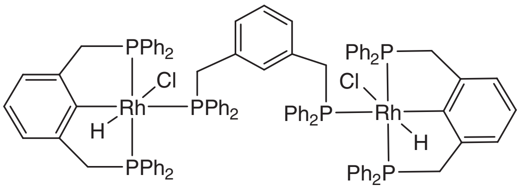

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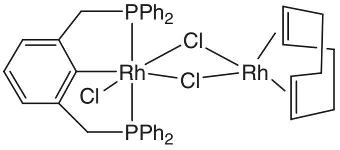
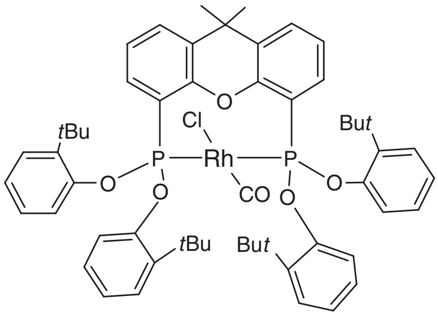


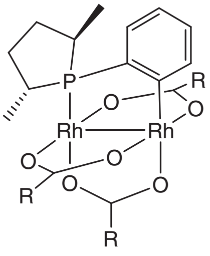
257

The coordination of sterically constrained diphosphinite ligands containing 2-*tert*-butylphenolate groups reacted with [Rh(μ-Cl)(CO)$_2$]$_2$ leading to an orthometallated complex of Rh 258.[312]



258

Several new phosphine-orthometallated complexes of dirhodium(II) were reported and structurally characterized.[145,313,314,314a–314c,315–321] Reactions of dirhodium(II)tetraacetate $Rh_2(OAc)_4$ with tris(*p*-methoxyphenyl)phosphine (PMP) yielded the orthometallated complexes $Rh_2(OAc)_3\{\mu\text{-}(p\text{-}CH_3OC_6H_3)P(p\text{-}CH_3OC_6H_4)_2\}(HOAc)_2$ and $Rh_2(OAc)_2\{\mu\text{-}(p\text{-}CH_3OC_6H_3)P(p\text{-}CH_3OC_6H_4)_2\}_2(HOAc)_2$.[315] Several kinetic studies on the reversible metallation–demetallation reaction of arylphosphines on carboxylate-bridged dinuclear rhodium(II) complexes were carried out,[317] including the exchange reaction of the carboxylate-bridging ligands.[318] Several new dirhodium(II) complexes with chelating and bridging orthometallated phosphines were described.[321] Dirhodium with bisorthometallated-bridging phosphines afforded chiral compounds that were used for the enantioselective C–H insertion of α-diazoketones.[320] Similar chiral dirhodium complexes with the phosphine (2*R*,5*R*)-2,5-dimethyl-1-phenylphospholane were also reported [compounds **259**, **260**, and **261**].[319]



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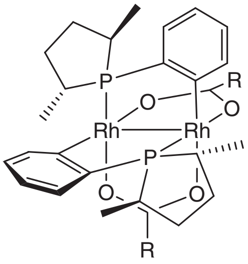

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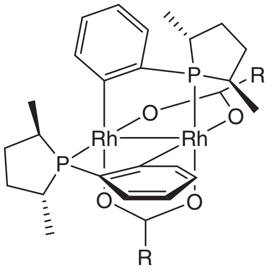
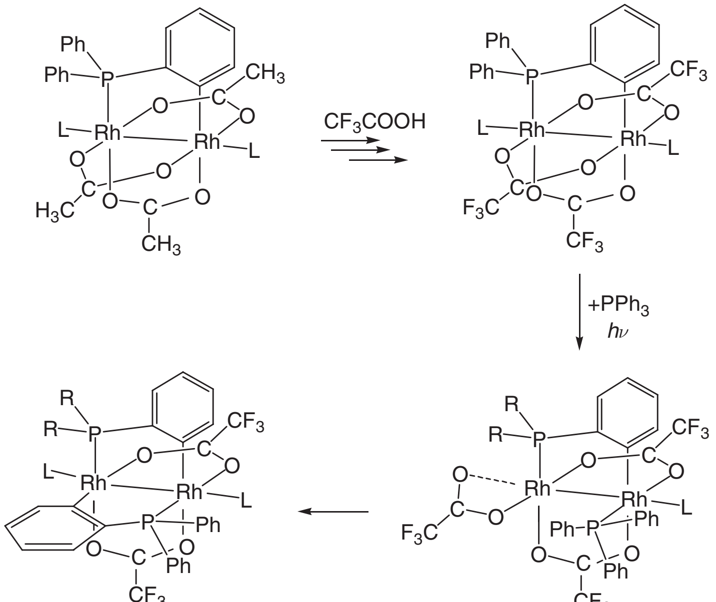


261

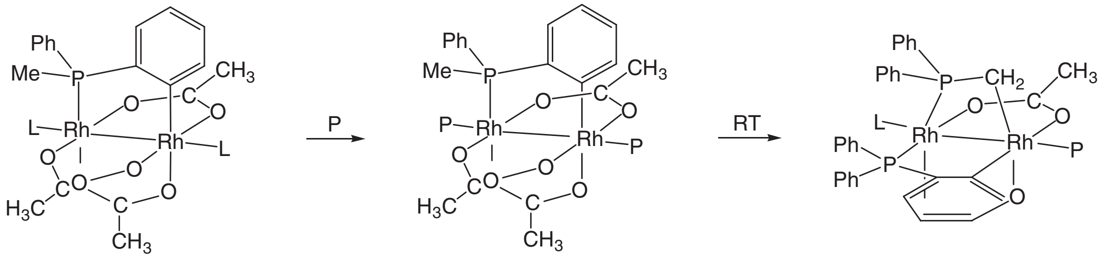
$Rh_2(O_2CCF_3)_3[(C_6H_4)PPh_2]\cdot(HO_2CCF_3)_2$ reacted with PPh_3 yielding the doubly metallated compound $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2\cdot(HO_2CCF_3)_2$. The reaction proceeded via a reactive intermediate with an equatorial phosphine, $Rh_2(\eta^2\text{-}O_2CCF_3)(\mu\text{-}O_2CCF_3)_2[\mu\text{-}(C_6H_4)PPh_2](PPh_3)\cdot(HO_2CCF_3)$, which could also be generated in moderate yield under photochemical conditions (Scheme 27).[322]

The reaction of $Rh_2(\mu\text{-}O_2CCH_3)_3[\mu\text{-}(C_6H_4)PMePh]$ with one mole of PPh_3 gave two phosphine monoadducts, which are in rapid equilibrium. Longer reaction times gave $Rh_2(\mu\text{-}O_2CCH_3)_2[\mu\text{-}(C_6H_4)PMePh][\mu\text{-}(C_6H_4)PPh_2](HO_2CCH_3)_2$, a doubly metallated compound with a head-to-head configuration. $Rh_2(\mu\text{-}O_2CCH_3)_3[\mu\text{-}(C_6H_4)PMePh]$ reacted with two moles of PPh_3, affording $Rh_2(\mu\text{-}O_2CCH_3)_2[\mu\text{-}(CH_2)PPh_2][\mu\text{-}(C_6H_4)PPh_2]^{\cdot}(PPh_3)$,



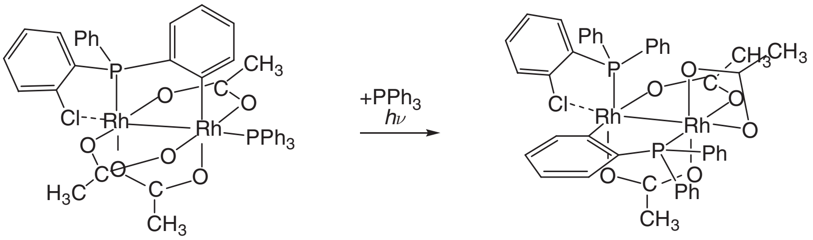
L = CF_3-COOH

Scheme 27



L = CH_3-COOH
P = PPh_3

Scheme 28



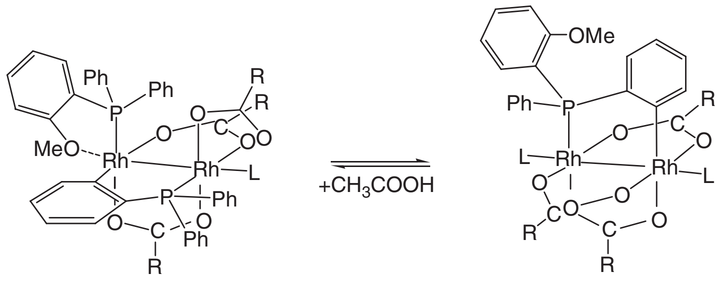
Scheme 29

which was crystallographically identified. This is the first example of selective activation of aliphatic versus aromatic C–H bonds (Scheme 28).[323]

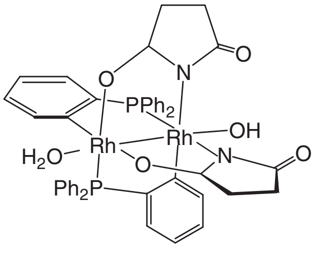
The photochemical reaction of the adducts $Rh_2(\mu\text{-}O_2CCH_3)_3[\mu\text{-}(C_6H_4)P(o\text{-}ClC_6H_4)Ph](P(p\text{-}XC_6H_4)_3)$ (X = H, Me, Cl) yielded the compounds $Rh_2(\mu\text{-}O_2CCH_3)_2](\eta^2\text{-}O_2CCH_3)[\mu\text{-}(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2](\eta^2\text{-}PCCl)$, ($PCCl{=}P(o\text{-}ClC_6H_4)Ph_2$). This process involved Rh–C bond cleavage at one metallated phosphine and C–H bond activation of one equatorial ligand (Scheme 29).[324]

$Rh_2(\mu\text{-}O_2CR)_2[\mu\text{-}PC]_2$ complexes (PC = different orthometallated substituted triarylphosphines and alquilaryl-phosphines, R = CH_3 or C_3F_7) were prepared and studied in competitive intramolecular cyclopropanation versus tertiary C–H insertion, cyclopropanation versus aromatic substitution, and C–H insertion versus aromatic substitution. The results obtained from these complexes were compared with those obtained for other rhodium(II) compounds, such as rhodium(II) caprolactamate, rhodium(II) perfluorobutyrate, and rhodium(II) acetate. To test the π-backbonding ability of these complexes, CO adducts were prepared in solution. The observed ν(CO) frequencies occurred at lower energy than that of the free CO, showing their π-backbonding ability. The highest values were for those catalysts with perfluorobutyrate and fluorinated phosphines as ligands.[313] Compounds of general formula $Rh_2(\mu\text{-}O_2CCH_3)_2(\eta^1\text{-}O_2CCH_3)[\mu\text{-}(C_6H_4)PPh_2]\cdot P(X\text{-}C_6H_4)_3\cdot H_2O$ (X = H, p-Me, p-Cl, m-Me, m-Cl) were prepared and the kinetics and mechanism of the cyclometallation reaction to give compounds $Rh_2(\mu\text{-}O_2CCH_3)_2(\eta^1\text{-}O_2CCH_3)[\mu\text{-}(C_6H_4)PPh_2][(X\text{-}C_6H_3)P(X\text{-}C_6H_4)_2]$ was studied.[325] The compound $Rh_2(\mu\text{-}O_2CCH_3)_3(\eta^1\text{-}O_2CCH_3)[\eta^2\text{-}P(2\text{-}MeO\text{-}C_6H_4)Ph_2]\cdot H_2O$ with one phosphine acting as chelating equatorial (*P*) axial (*O*) donor ligand underwent intramolecular C–H activation reaction at one of the phenyl rings in $CHCl_3$ and acetic acid medium (Scheme 30). The kinetics of this reaction was studied in different solvent conditions. Positive values found for $\Delta S^{\#}$ and $\Delta V^{\#}$ were attributed to the bond-breaking expansion of the axial Rh–O (phosphine) bond required in the initial product in order to reach the highly ordered transition state needed for the C–H bond activation.[326]

Two new dirhodium(II) catalysts of general formula $Rh_2(N\text{–}O)_2[(C_6H_4)P(C_6H_5)_2]_2$ ($N\text{–}O = C_4H_4NO_2$), **262** and **263**, were prepared, starting from $Rh_2(O_2CCH_3)_2(PC)_2L_2$ [PC = $(C_6H_4)P(C_6H_5)_2$ (head-to-tail arrangement), L = HO_2CCH_3]. Compound **262** is the thermodynamically stable product as shown by the slow isomerization of **263** to **262**.[327]



Scheme 30



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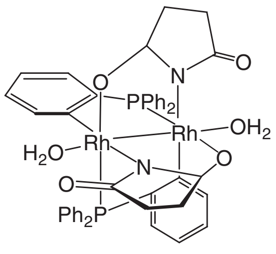
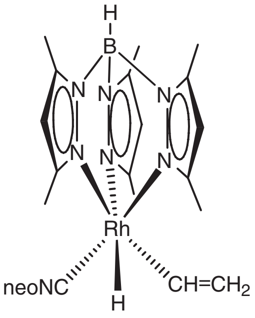


263

The reductive elimination of methane from Tp′Rh(L)(CH_3)H (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate, L = $CNCH_2CMe_3$) provided experimental evidences for the formation of methane σ-complexes.[328] Photolysis of Tp′Rh(CNneo)(PhN=C=Nneo) (neo = CH_2CMe_3) in the presence of ethylene led to the activation of a vinyl C–H bond to produce a vinyl hydride complex Tp′Rh(CNneo)(CH=CH_2)H **264**. This vinyl hydride complex was also produced quantitatively from the reaction of Tp′Rh(CNneo)(CH=CH_2)Cl and Cp_2ZrH_2 in C_6H_6. Photolysis of Tp′Rh (CNneo)(PhN=C=Nneo) in neat propylene yielded the allyl C–H bond-activated product Tp′Rh(CNneo)-(CH_2CH=CH_2)H **265**. Photolysis of Tp′Rh(CNneo)(PhN=C=Nneo) in the presence of isobutylene and *tert*-butylethylene yielded the first relatively stable allyl hydride **266** and vinyl hydride **267** complexes, respectively, for the present system. Both complexes reductively eliminated olefin in the presence of C_6H_6 to give Tp′Rh(CNneo)(C_6H_5)H **268**.[329]



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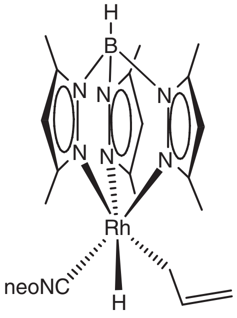

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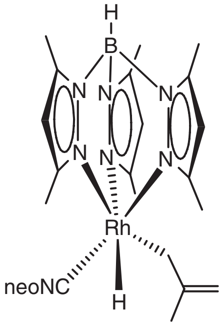

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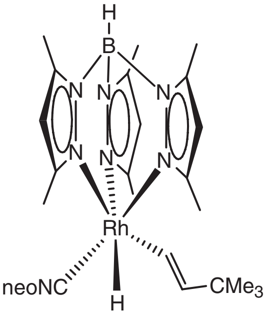

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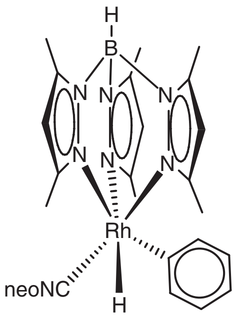
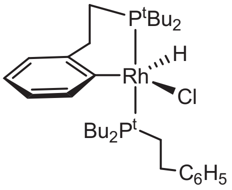


268

The mechanistic aspects of the oxidative addition of benzene to *trans*-$RhCl(CO)(PMe_3)_2$ to yield the Rh(III) species $Rh(Ph)(H)Cl(CO)(PMe_3)_2$ were studied by infrared and time-resolved optical spectroscopy. Two mechanisms were proposed: (i) direct oxidative addition and (ii) photodissociation of a CO ligand to yield the tricoordinate species $RhCl(PMe_3)_2$ followed by oxidative addition of benzene and then CO addition.[330] The complexes $Cp^*Rh(3,5\text{-}C_6H_3R_2)H(PMe_3)$ ($R = C(CH_3)_3$, $CH(CH_3)_2$, $Si(CH_3)_3$, CH_3, and CF_3) were prepared by irradiation of $Cp^*Rh(PMe_3)(C_2H_4)$ or by thermolysis of $Cp^*RhH(Ph)(PMe_3)$, both reactions in neat arene. The rates of the reductive elimination of the arene were also studied.[331] Aryl-functionalized phosphines of the general composition $R_2P(CH_2)_n$(aryl) with bulky substituents R at the phosphorus atom reacted with olefin–rhodium(I) compounds leading to an insertion of the metal into one of the C–H bonds of the aryl group to afford a six-membered chelate ring system. With the bulky phosphine *t*$Bu_2P(CH_2)_2C_6H_3$-2,6-Me_2, the isolation and structural characterization of a *cis*-configurated rhodium dicarbonyl *cis*-$[RhCl(PR_3)(CO)_2]$ **269** and of an unprecedented dinuclear alkylrhodium(III) compound **270** built up by two 14-electron $RhCl_2(alkyl)(PR_3)$ units was achieved.[83]



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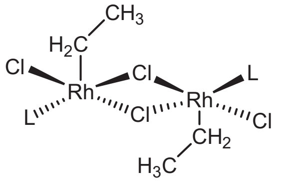
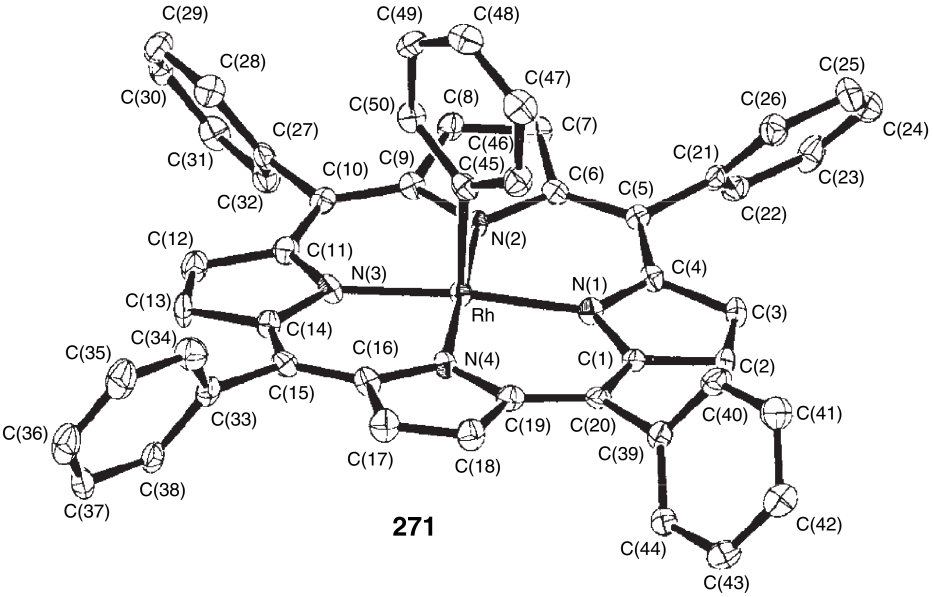


L = $^tBu_2P(CH_2)_2C_6H_3$-2,6-Me_2

270

The porphyrin–Rh complex $Rh_2(TPP)(CO)_4$ (TPP = tetraphenylprophyrin) reacted slowly with toluene at 80 °C yielding $Rh(TPP)(CH_2Ph)$. The metallation of benzene by the same starting complex yielded Rh(TPP)(Ph) **271**. The reaction was proposed to proceed via Rh^{II}(TPP) and Rh^{III}(TPP) derivatives resulting from oxidation of $Rh_2(CO)_4(TPP)$ by H_2O or O_2.[332] Other porphyrin complexes such as $[Rh(TPP)CH_3]_2(\mu$-4-cyanopyridine) and $Rh(TPP)(C_8H_{11})$ were also obtained and structurally characterized.[333]



271

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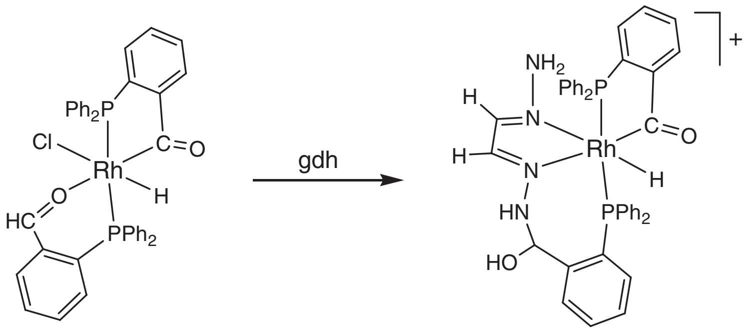
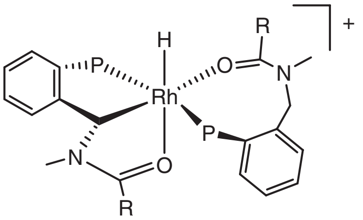
The complex $[RhCl(cod)]_2$ oxidatively added *o*-(diphenylphosphino)benzaldehyde (PHCO) giving a hydrido–acylphosphine compound, [RhH(PCO)Cl(PCHO)]. The reaction of this complex with glyoxaldihydrazone (gdh) gave selectively a complex with a tridentate P–N–N ligand containing a hemiaminal group (Scheme 31).[78] Similar hydroxyalkyl complexes were previously described by the same group.[334]



Scheme 31

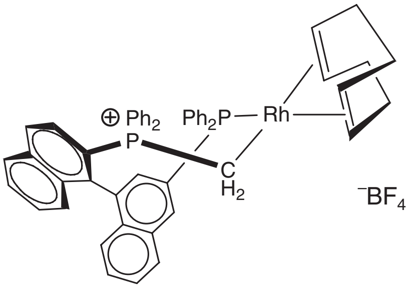
Addition of aldehyde (RCHO; R = *n*-octyl, Ph, *p*-tol, *p*-MeOC$_6$H$_4$, *p*-CF$_3$C$_6$H$_4$) to [Rh(μ-Cl)(P^{i}Pr$_3$)$_2$]$_2$ resulted in rapid addition of the aldehyde C–H bond to yield Rh(Cl)H(COR)(P^{i}Pr$_3$)$_2$. The reaction with acyl chlorides (RCOCl; R = octyl, Ph) rapidly gave Rh(Cl)H(COR)(P^{i}Pr$_3$)$_2$.[335] The reactivity of the dihydride (η^5:η^1-C$_5$H$_4$SiMe$_2$CH$_2$PPh$_2$)RhH$_2$ toward C–H bond activation was investigated. While benzene did not give a stable oxidative addition product, pentafluorobenzene yielded (η^5:η^1-C$_5$H$_4$SiMe$_2$CH$_2$PPh$_2$)Rh(C$_6$F$_5$)H, which was structurally characterized as its chloro derivative.[165] Oxidative addition of C–H bonds of partially fluorinated arenes, C$_6$F$_5$H and 1,3-C$_6$F$_2$H$_4$ to the Rh(I)-ethene complex CpRh(PPh$_3$)(C$_2$H$_4$), afforded the preparation of CpRh(R)(H)(PPh$_3$) (R = C$_6$F$_5$ and 1,3-C$_6$F$_2$H$_4$).[149] The phosphine *N*-methyl-*N*-propionyl-2-(diphenylphosphino)benzylamine (P–N) reacted with the precursor complex [Rh(nbd)(PN)]PF$_6$ and molecular hydrogen under ambient conditions, affording chelate-assisted C–H bond activation at the benzylic position, yielding the five-membered chelate complex *trans*-[RhH(P(C$_6$H$_4$-*o*-(CH$_2$N(CH$_3$)COCH$_2$CH$_3$))(C$_6$H$_5$)$_2$)(P(C$_6$H$_4$-*o*-(CHN(CH$_3$)COCH$_2$CH$_3$))(C$_6$H$_5$)$_2$)]PF$_6$ **272**.[336]



272

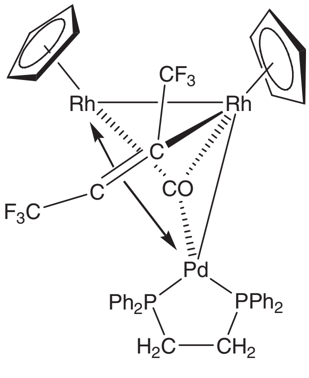
7.02.3.2.1.(v) Miscellaneous including insertions into C–C bonds

The phosphonium methylide of (*R*)-BINAP was used as a novel chiral disymmetric chelating ligand in the stable [Rh(cod)(BINAPCH$_2$)]$^+$ complex **273**. The complex was obtained by the reaction of [Rh(μ-Cl)(cod)]$_2$ and the methylbinapium ylide.[337]



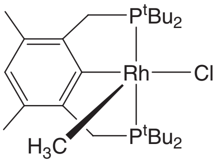
273

The reactions of some phosphines and diphosphines with the alkenyl-bridged dirhodium complex $[\mathrm{CpRh}]_2(\mu\text{-CO})(\mu\text{-}\eta^2\text{-CF}_3\mathrm{C{=}CCF}_3)$ were compared.[338] The heterotrimetallic complex of formula $\mathrm{Cp_2Rh_2Pd}(\mu_3\text{-CO})(\mu\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-CF}_3\mathrm{C_2CF_3})\{\eta^2\text{-Ph}_2\mathrm{P(CH_2)_2PPh_2}\}$ **274** was formed from the reaction between $\mathrm{Cp_2Rh_2(CO)}(\mu\text{-}\eta^1{:}\eta^1\text{-CF}_3\mathrm{C_2CF_3})\{\eta^1\text{-Ph}_2\mathrm{P(CH_2)_2PPh_2}\}$ and $\mathrm{CpPd}(\eta^3\text{-C}_3\mathrm{H}_5)$.[339]



274

The cationic Rh(III) complex $[\mathrm{Cp^*Rh(SiPh_3)(PMe_3)(CH_2Cl_2)}]\mathrm{BAr_4}$ activated the carbon–carbon bond of aryl and alkyl cyanides (R–CN, where R = Ph, $(4\text{-}(\mathrm{CF_3})\mathrm{C_6H_4})$, $(4\text{-}(\mathrm{OMe})\mathrm{C_6H_4})$, Me, ^{i}Pr, ^{t}Bu) to produce complexes of the general formula $[\mathrm{Cp^*Rh(R)(CNSiPh_3)(PMe_3)}]\mathrm{BAr_4}$.[340] The diphosphine 1,3-bis[(di-*tert*-butylphosphino)-methyl]-2,4,6-trimethylbenzene upon reacting with the rhodium olefin complexes $[\mathrm{Rh}(\mu\text{-Cl})(\mathrm{olefin})_2]_2$ underwent rapid and selective metal insertion into the strong unstrained aryl–methyl bond at room temperature, yielding $\mathrm{Rh(CH_3)\ Cl\{C_6H(CH_3)_2(CH_2P(\mathit{t}\text{-}Bu)_2)_2\}}$ **275**. The carbon–carbon bond activation was competitive with a parallel C–H activation process, which resulted in the formation of complexes $\mathrm{RhH(Cl)[CH_2C_6H(CH_3)_2(CH_2P(\mathit{t}\text{-}Bu)_2)_2]}$ **276**.[341]



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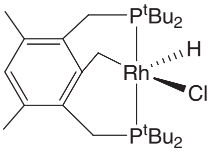
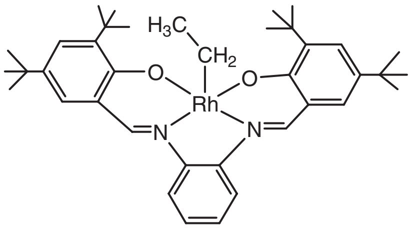


276

A rhodium(II) porphyrin bimetalloradical complex reacted with CO and ethene to form an ethanedionyl reductive coupling product, $\mathrm{Rh(CH_2)_6Rh}(\mu\text{-C(O)C(O)})$, and an ethylene-bridged complex, $\mathrm{Rh(CH_2)_6Rh}(\mu\text{-CH}_2\mathrm{CH}_2)$, respectively. Reaction with 1,3-butadiene yielded a four-carbon-bridged complex, $\mathrm{Rh(CH_2)_6Rh}(\mu\text{-CH}_2\mathrm{CH{=}CHCH_2})$. Solutions of the initial porphyrin bimetalloradical complex and CO reacted with H_2O, CH_3CH_2OH, and H_2 to produce multifunctionalized formyl complexes $\mathrm{H{-}Rh(CH_2)_6Rh{-}CHO}$, $\mathrm{H(O)C{-}Rh(CH_2)_6Rh{-}C(O)OCH_2CH}$, and $\mathrm{H(O)C{-}Rh(CH_2)_6Rh{-}CHO}$, respectively (Scheme 32).[342]

Several planar β-substituted ethyl porphyrinato rhodium(III) complexes were found to undergo reversible alkyl 1,2-rearrangements (Scheme 33). The molecular structures of the complexes $\mathrm{Rh(TTP)CH_2CH_2Ph}$ and $\mathrm{Rh(TTP)CH(CH_3Ph)}$ were described.[343]

The reaction of the free ligand $\mathrm{Bu_4salonphenH_2}$ with $[\mathrm{Rh}(\mu\text{-Cl})(\mathrm{H_2C{=}CH_2})_2]_2$ in the presence of $\mathrm{NR_4OH}$ in refluxing ethanol yielded the Schiff-base rhodium complexes $\mathrm{Rh(R)(Bu_4salophen)}$, with R = Et **277** and *n*-Bu^2 **278**, respectively. The reaction of $\mathrm{Rh(H)(Bu_4salophen)}$ with CO afforded the formyl complex $\mathrm{Rh(CHO)(Bu_4salophen)}$ **279**.[344]



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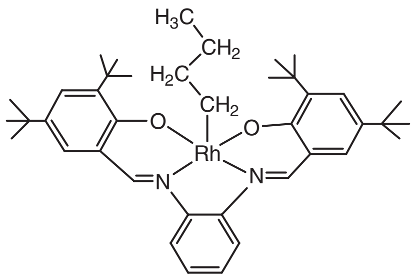

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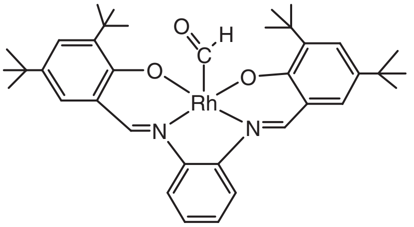

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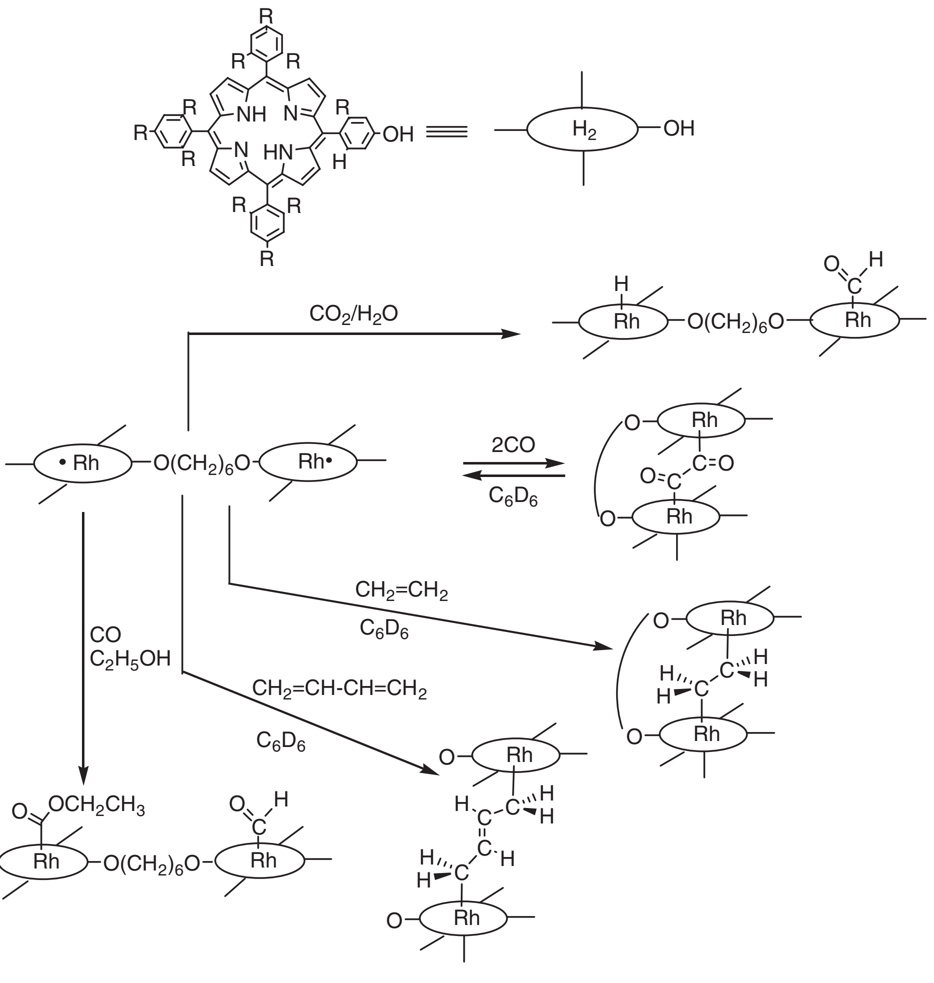
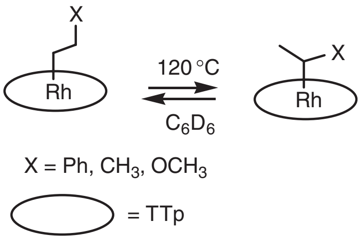
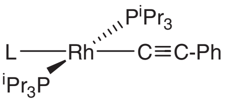


Scheme 32

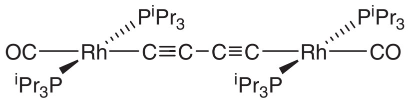


Scheme 33

The reaction of $[Rh(\mu\text{-}OH)(P^iPr_3)_2]_2$ with $PhC{\equiv}CSiMe_3$, in the presence of pyridine or CO, gave *trans*-$[Rh(C{\equiv}CPh)(py)(P^iPr_3)_2]$ 280 and *trans*-$[Rh(C{\equiv}CPh)(CO)(P^iPr_3)_2]$ 281, respectively. Treatment of *trans*-$[Rh(OH)(CO)(P^iPr_3)_2]$ with $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ yielded the binuclear diynyl complex $(P^iPr_3)_2(CO)Rh(C{\equiv}CC{\equiv}C)Rh(CO)(P^iPr_3)_2$ 282, while with $Me_3SiC{\equiv}CC{\equiv}CSnPh_3$ gave the mononuclear product *trans*-$[Rh(C{\equiv}CC{\equiv}CSiMe_3)(CO)(P^iPr_3)_2]$ 283.[345]



280: L = Py
281: L = CO



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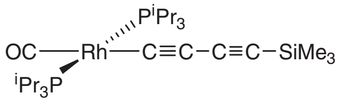


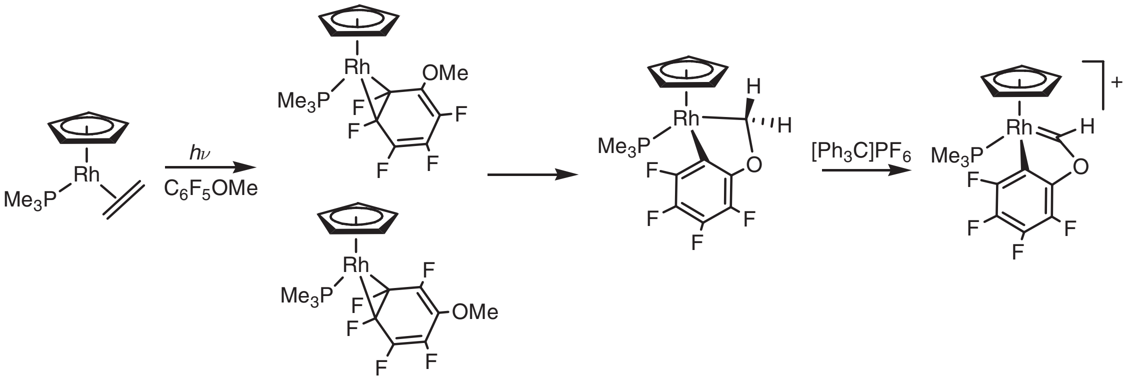
283

The reaction of Rh(β-diketonato)(alkene)$_2$ complexes with CF_3SO_3H in THF gave Rh(β-diketonato)(alkyl) species when the alkene is ethylene, *cis*-butene, or 5-methylene-cycloheptene whereas 1,5-cyclooctadiene complexes were unreactive.[346]

7.02.3.2.2 Metallacyclic complexes

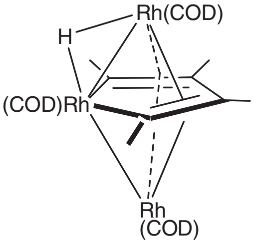
Metallacyclic complexes have been intensively studied as important intermediates for the cyclotrimerization of alkynes and/or diynes in terms of mechanistic view and discovery of new efficient catalysts. It has been proposed that a rhodium(I) catalyst triggers cycloaromatization of ω-trialkylsilylated acyclic enediynes to afford benzosilacycloalkane or vinylsilane products via a seven- and/or eight-membered rhodacycle intermediate.[347] In the case of the formation of benzene from butadiene and ethyne mediated by Rh^+ a mechanism was proposed in which the first step, dehydrogenation of butadiene by Rh^+, generates $RhC_4H_4{}^+$. This key intermediate reacts with ethyne to yield C_6H_6 and "bare" Rh^+. Structural investigations of the $RhC_4H_4{}^+$ intermediate by CID and ion–molecule reactions suggested a rhodium–cyclobutadiene complex as the most probable structure, although a metallacyclopentadiene structure cannot be ruled out.[348]

Irradiation of $CpRh(PMe_3)(C_2H_4)$ in pentafluoroanisole generated the metallacycle $CpRh(PMe_3)(\kappa^2\text{-}CH_2OC_6F_4)$. Reaction of this complex with 1 equiv. of $Ph_3C^+PF_6{}^-$ at 220 K generated $[Cp(PMe_3)Rh{=}CHOC_6F_4]PF_6$ (Scheme 34).[349]



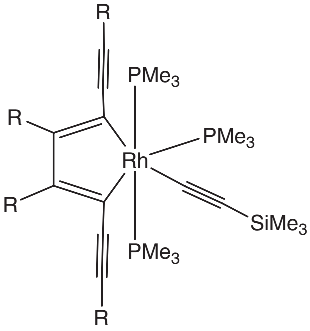
Scheme 34

Reaction of $[Rh(\mu\text{-}Cl)(cod)]_2$ with 2-butyne in the presence of *n*-PrLi afforded a trinuclear rhodacyclopentadienyl complex 284.[350]



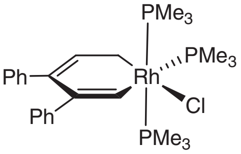
284

Reaction of 1,4-bis(*p*-tolylethynyl)buta-1,3-diyne with $Rh(C{\equiv}CSiMe_3)(PMe_3)_4$ gave the highly luminescent *mer*,-*cis*-[tris(trimethylphosphine)trimethylsilylethynyl-2,5-bis(*p*-tolylethynyl)-3,4-bis(*p*-tolyl)rhodacyclopenta-2,4-diene] 285 whose luminiscent properties were studied.[351]



285

Arylallenes reacted with $RhCl(PMe_3)_3$ in a 3 : 1 ratio to yield rhodacyclopentanes, *mer*-$Rh\{CH_2C({=}CHAr)C({=}CHAr)CH_2\}Cl(PMe_3)_3$ ($Ar = C_6H_5$ or C_6H_4F-*p*).[352] The reaction between 1,2-diphenyl-3-vinyl-1-cyclopropene with $RhCl(PMe_3)_3$ and addition of a third equivalent of trimethylphosphine yielded two meridional rhodacyclohexadienes 286 and 287, which exhibited facile solvent-dependent chloride dissociation.[353]



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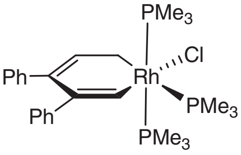
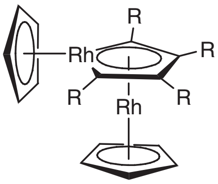


287

UV irradiation of $CpRh(C_2H_4)_2$ in pentane in the presence of alkynes C_2R_2 ($R = Me$, Et) gave the η^4-benzene complexes $CpRhC_6R_6$ and the rhodacyclopentadienyl species $Cp_2Rh_2C_4R_4$ 288 as main products.[354]



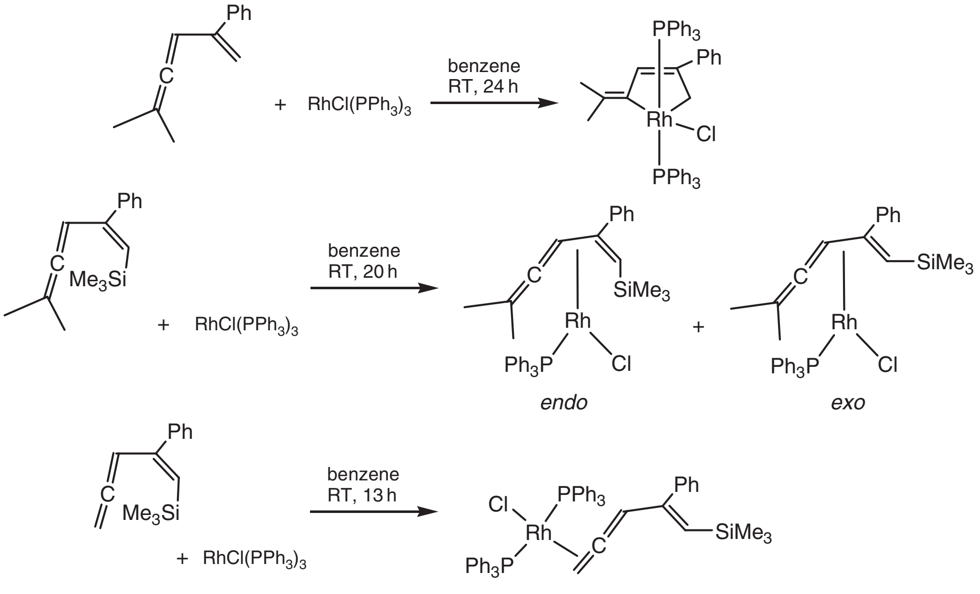
R = CH_3, C_2H_5

288

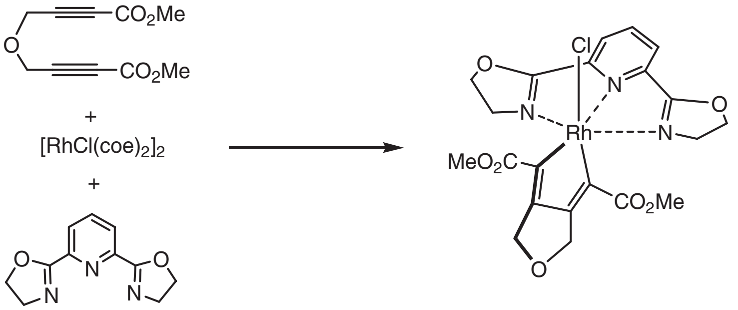
The complex $[Rh(CO)_2\{HC(pz')_3\}]PF_6$, $\{HC(pz')_3 =$ tris(3,5-dimethylpyrazolyl)methane$\}$, reacted with $HC{\equiv}CPh$ or $HC{\equiv}CH$ giving the octahedral, κ^3-rhodium(III) metallacyclopentadienes $[Rh(CO)(\eta^1{:}\eta^{1'}\text{-}CHCRCHCR)\{HC(pz')_3\}]PF_6$ (R = Ph, H) with the two alkynes linked head-to-tail when R = Ph.[43] Vinylallenerhodium complexes with three kinds of coordination modes, that is, η^2-coordination of the terminal π-bond of the allenyl group, η^4-coordination of the conjugated diene skeleton, and planar σ^2-coordination, were synthesized by ligand substitution of $RhCl(PPh_3)_3$ with vinylallenes of specific substitution patterns (Scheme 35). Coordination preferences were explained in terms of spatial interactions between the vinylallene substituents and the phosphine ligands as well as effective delocalization of the π-electrons of the endo- and exocyclic double bonds.[355]

The reaction of $[Rh(\mu\text{-}Cl)(coe)_2]_2$, bis(oxazolinyl)pyridine (pybox), and diynes $O(CH_2C{\equiv}CCO_2Me)_2$ and $PhC{\equiv}CCH_2OCH_2C{\equiv}CCO_2Me$ gave new types of metallacycle complexes, which showed catalytic activity for cycloaddition of diynes and several alkynes (Scheme 36).[356]

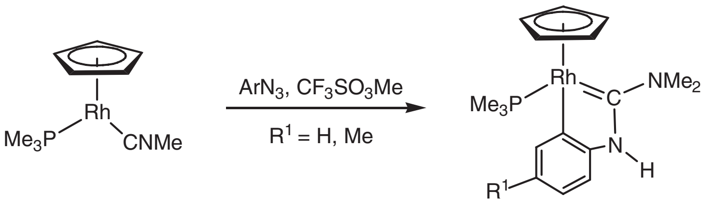
The oxidation of Rh^I(olefin) complexes with the ligand 1,4,7-trimethyl-1,4,7-triazacyclononane or *n*-butylbis(pyridine-2-ylmethyl)amine afforded the preparation of 2-rhoda(III)oxetanes 289 and 290.[357]



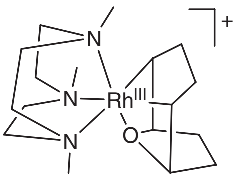
Scheme 35



Scheme 36



Scheme 37



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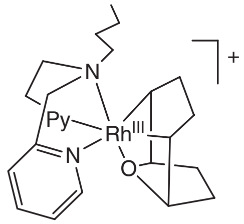
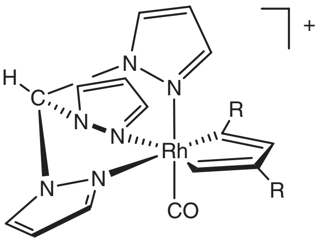


290

Treatment of CpRh(CNMe)(PMe$_3$) with ArN$_3$ afforded exclusively the metallacycle carbodiimide complexes CpPη(κ^2-*C,N*-MeN═C═NAr)(PMe$_3$) in good yields (Scheme 37).[358]

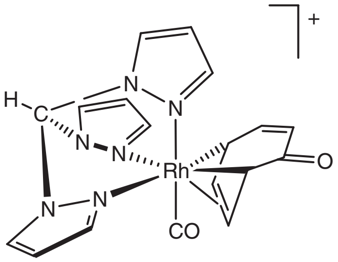
Generation of the 16-electron fragment Tp′Rh(CNCH$_2$CMe$_3$) (Tp′═[HB(3,5-dimethylpyrazolyl)$_3$]) in the presence of cyclopropane resulted in C–H activation of the hydrocarbon. The cyclopropyl hydride complex rearranged in benzene solvent to the metallacyclobutane complex Tp′Rh(CNCH$_2$CMe$_3$)(CH$_2$CH$_2$CH$_2$). Thermolysis of the rhodacyclobutane complex produced an η^2-propylene complex (Scheme 38).[141]

A similar rhodacyclobutane was proposed as an intermediate in the formation of Tp′Rh(η^3-allyl)H from Tp′Rh(η^3-allyl)Br and LiBHEt$_3$.[359] The complex [Rh(CO)$_2${HC(pz′)$_3$}][PF$_6$], {HC(pz′)$_3$ = tris(3,5-dimethylpyrazolyl)methane} reacted with HC≡CPh or HC≡CH to give the octahedral, κ^3-rhodium(III) metallacyclopentadienes {Rh(CO)(η^1:η^1-CHCRCHCR)[HC(pz′)$_3$]}PF$_6$ **291** (R = Ph, H). The reaction of {Rh(CO)$_2$[HC(pz′)$_3$]}PF$_6$ with HC≡CH also gave the cycloheptatrienone (tropone) derivative {Rh[η^4-C$_6$H$_6$C(O)][HC(pz′)$_3$]}PF$_6$ **292**, with a κ^3-ligand and the cycloheptatrienone ligand bound to the metal via two Rh–C σ-bonds and one Rh–monoalkene interaction.[43]



R = Ph, H

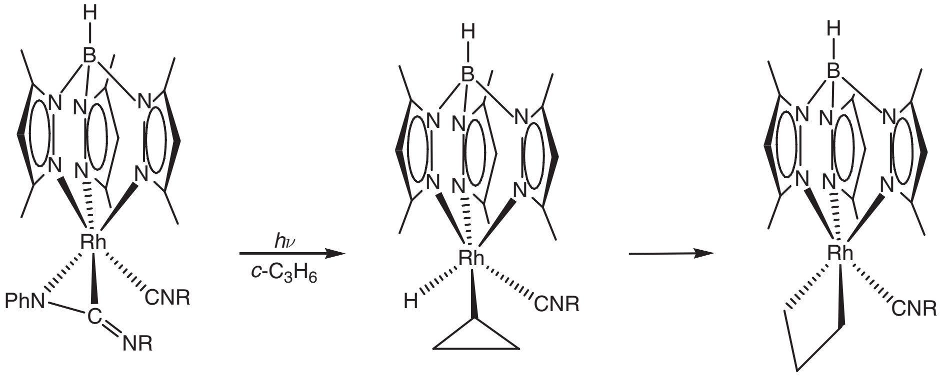
291



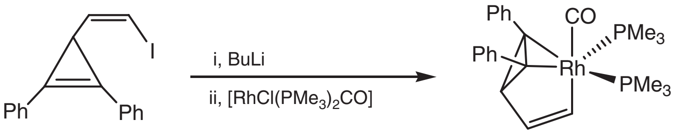
292

Treatment of *cis*-1,2-diphenyl-3-(2-lithioethenyl)cyclopropene with RhCl(CO)(PMe$_3$)$_2$ gave the corresponding rhodabenzvalene, which contains rare η^2-cyclopropene and σ-vinylic linkages to Rh (Scheme 39).[360]

Heterocyclic organotellurium complexes were used as precursors for new organometallic derivatives of rhodium, including the rhodacycle Cp*Rh{η^5-C$_5$H$_4$Rh(Cp*)} and Cp*Rh(C$_{12}$H$_8$)(η^1-dbt) (dbt = dibenzotellurophene).[361]



Scheme 38



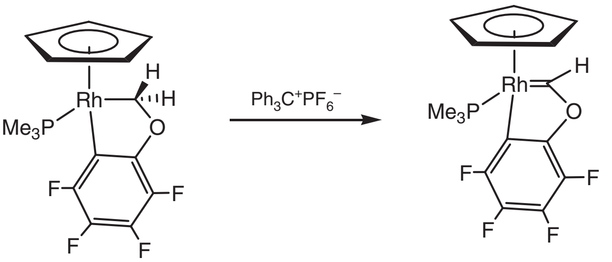
Scheme 39

7.02.3.2.3 Carbene and carbyne complexes

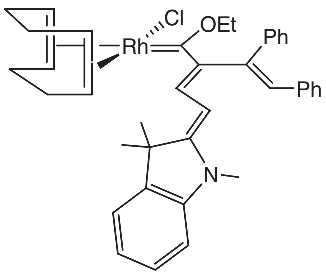
Most of the rhodium–carbene complexes reported during the period 1984–1994 were half-sandwich-based complexes, as described in COMC (1995). The number of carbene complexes was somewhat scarce in the last decade, but it has increased enormously, widening the variety of carbenes that we can now find in the literature. Some new half-sandwich carbene complexes have been prepared. Irradiation of $CpRh(PMe_3)(C_2H_4)$ in pentafluoroanisole generated a metallacycle that evolved to a cyclic carbene in the presence of an electrophile (Scheme 40).[349]

Reaction of $Cp^*Rh(H)_2(SiMe_3)_2$ with 2 equiv. of butyllithium, followed by addition of *N*-methyl-2-chloropyridinium tetrafluoroborate, gave the bis(carbene) complex $Cp^*Rh[{=}C(NMe)CH{=}CH]_2$.[362] Other dimetallic alkoxycarbene Cp^* complexes of Rh and Ir were also reported.[363] The chemistry of the di-μ-methylene-bis(pentamethylcyclopentadienyl-rhodium) complexes was reviewed.[364]

(η^5-Indenyl)rhodium(I) complexes of the general composition $(\eta^5\text{-}C_9H_7)Rh({=}CPh_2)(L)$ ($L = Sb^iPr_3$, P^iPr_3, PPh_3, P^iPrPh_2, and P^iPr_2Ph) were prepared from *trans*-$RhCl({=}CPh_2)(L)_2$ and C_9H_7K in THF. Treatment with carbon monoxide resulted in an unusual migratory insertion of the carbene ligand into one of the C–H bonds of the five-membered ring of the indenyl unit to give the compounds $\{\eta^5\text{-}C_9H_6(CHPh_2)\}Rh(CO)(L)$.[365] Other half-sandwich carbene complexes of Rh were obtained and their reactivity studied.[366,367] Transmetallation from a tungstaoctatetraene to $[Rh(\mu\text{-}Cl)(cod)]_2$ afforded the preparation of a carbene–rhodaoctatetraene **293**.[368]

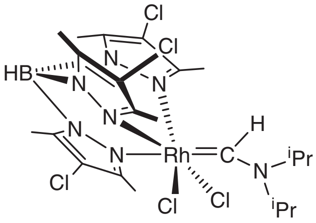


Scheme 40



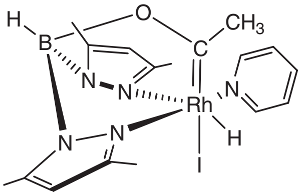
293

Dirhodium(II) complexes provided a good series of complexes for carbene-transfer reactions.[10,10a,13,316,320,321,369,369a–369e] The reaction of $(Tp^{Me_2,Cl})Rh(CO)_2$ with chloroform gave the rhodium(III) complex $(Tp^{Me_2,Cl})RhCl(CHCl_2)(CO)$ resulting from the oxidative addition of a C–Cl bond. Further reaction with diisopropylamine yielded the aminocarbene complex $(Tp^{Me_2,Cl})RhCl_2(CHN^iPr_2)$ **294**.[370]



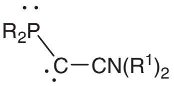
294

The bispyrazolyl-methane complex $(Bp^{Me_2})Rh(CO)(pyridine)$ was prepared and reacted with CH_3I yielding the Rh carbene hydride complex $HB(Me_2pz)_2Rh(H)(I)(C_5H_5N)(C(O)Me)$ **295**, resulting from formal addition of CH_3I across the Rh–C bond concomitant with hydride transfer from B to Rh.[371]



295

Direct complexation of an (amino)(phosphino)carbene **296** and an (amino)(oxy)carbene **297** featuring a phosphino group in position-6 to the carbene with $[RhCl(CO)_2]_2$ provided two new Rh(I) carbene complexes, **298 and 299**.[372]



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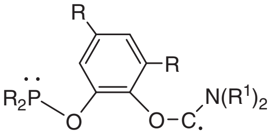

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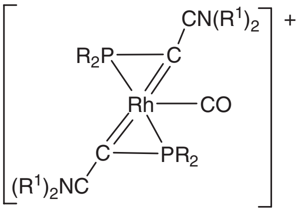

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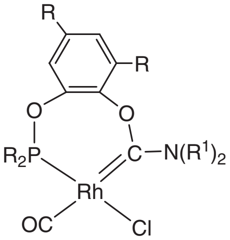
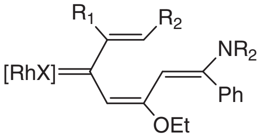


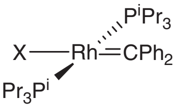
299

Transmetallation from chromium carbene complexes provided a new way of obtaining carbene Rh(I) complexes[368,373,374] of the rhodaoctatetraene type **300**.[374]



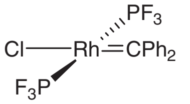
300

Metathetical reactions of $Rh_2Cl_2(\mu\text{-}CPh_2)_2(\mu\text{-}Sb^iPr_3)$ with NaBr and NaI afforded the dimetallic complexes $Rh_2X_2(\mu\text{-}CPh_2)_2(\mu\text{-}Sb^iPr_3)(X = Br,\ I)$. Analogous displacement reactions with sodium salts of acetylacetone (acacH), trifluoroacetyacetone (acacf$_3$H), and dipivaloylmethane (dpmH) led to the formation of the unsymmetrical rhodim(I) compounds $Rh_2(X)Cl(\mu\text{-}CPh_2)_2(\mu\text{-}Sb^iPr_3)$ (X = acac, acacf$_3$, dpm). The symmetrical compounds $Rh_2(X)_2(\mu\text{-}CPh_2)_2(\mu\text{-}Sb^iPr_3)$ (X = acac and dpm) were also obtained.[375] The complex $[RhCl(P^iPr_3)_2]_n$ reacted with $RR^1C{=}CHCl$ at room temperature providing a series of complexes of formula *trans*-$[RhCl({=}C{=}CRR^1)(P^iPr_3)_2]$.[376] The same precursor afforded the preparation of neutral diphenylcarbenerhodium(I) complexes of the general composition *trans*-$[RhX({=}CPh_2)(P^iPr_3)_2]$ **301** (X = F, OCN, CF_3CO_2, $PhCO_2$, CF_3SO_3).[377] Similar complexes can be obtained from the direct reaction of $RhCl(CO)(PR_3)_2$ with photochemically generated free diarylcarbenes.[378] The trifluorophosphine complex *trans*-$[RhCl({=}CPh_2)(PF_3)_2]$ **302** was also obtained and characterized.[366]



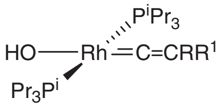
X = F, OCN, CF_3CO_2, $PhCO_2$, CF_3SO_3

301



302

The reaction of *trans*-$[RhCl({=}C{=}CHPh)(P^iPr_3)_2]$ and *trans*-$[RhCl({=}C{=}CMe_2)(P^iPr_3)_2]$ with 50% aqueous NaOH, in the presence of $[PhCH_2NEt_3]Cl$, afforded the hydroxorhodium complexes *trans*-$[Rh(OH)({=}C{=}CRR^1)(P^iPr_3)_2]$ **303**. Treatment of **303** with $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$ also led to the displacement of the hydroxo ligand and to the formation of the dinuclear complexes *trans, trans*-$\{[Rh({=}C{=}CRR^1)(P^iPr_3)_2]_2(\mu\text{-}C_4)\}$ **304**.[379] Rhodium vinylidenes *trans*-$[RhCl({=}C{=}CRR^1)(P^iPr_3)_2]$ and their homologous *trans*-$[RhCl({=}C({=}C)_nRR^1)(P^iPr_3)_2]$ ($n = 2$, 4) are long known[380,380a,380b] but several related compounds were recently reported. For example, the bis(stibine) derivatives *trans*-$[RhCl({=}CRR^1)(Sb^iPr_3)_2]$ were prepared and the two stibines could be easily replaced by two phosphine ligands.[115,381] Other similar vinylidene complexes derived from arsines were also described.[382] Both the bis(stibine) and the bis(phosphine) complexes were converted to the η^5-cyclopentadienyl compounds $CpRh({=}CRR^1)(EiPr_3)$ **305** (E = P, Sb).[145,383] A similar chelating bisphosphine carbenerhodium derivative was also described, showing that four-coordinate complexes with the *cis*-disposed $RhCl({=}CRR^1)$ unit are accessible, since the chelate phosphine is forcing the *cis*-coordination.[384]



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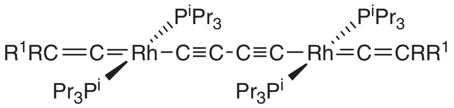

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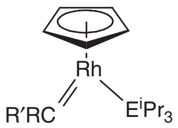
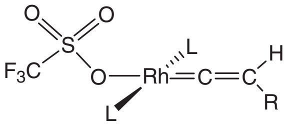


E = P, Sb

305

The reaction of $Rh\{\eta^2\text{-}O_2S(O)CF_3\}(P^iPr_3)_2$ with terminal alkynes $RC{\equiv}CH$ (R = Ph or ^tBu) led to the formation of *trans*-$[Rh\{\eta^1\text{-}OS(O)_2CF_3\}({=}C{=}CHR)(P^iPr_3)_2]$ **306**, which on treatment of tetrabutylammonium fluoride gave the fluororhodium(I) complexes *trans*-$[RhF({=}C{=}CHR)(P^iPr_3)_2]$ **307**.[385] The latter complex reacted with $Ph_3SnC{\equiv}C\text{–}C{\equiv}SnPh_3$ to give the dimetallic C$_4$-bridged rhodium(I) complexes *trans,trans*-$[Rh({=}C{=}CHR)(P^iPr_3)_2]_2(\mu\text{-}C{\equiv}C\text{–}C{\equiv}C)$ **308**. Other complexes such as *trans*-$[Rh(C{\equiv}C\text{–}C{\equiv}CH)(CNC_6H_3Me_2\text{-}2,6)(P^iPr_3)_2]$, *trans,trans*-$[Rh({=}C{=}CHPh)(PiPr_3)_2]\{Rh(CNC_6H_3Me_2\text{-}2,6)(P^iPr_3)_2](\mu\text{-}C{\equiv}C\text{–}C{\equiv}C)$ **309**, and *trans,trans*-$[Rh(CX)(P^iPr_3)_2\}_2\{\mu\text{-}C({=}CHR)C{\equiv}C\text{–}C{\equiv}C\text{–}C({=}CHR)]$ **310** were obtained by a similar route.[386] Other vinylidene Rh(I) complexes were studied by Werner and co-workers.[307,308,381,387,387a,387b] The rhodium complexes *trans*-[RhCl{=C=C=C(Ph)R}(P^{i}Pr$_3$)$_2$] provided efficient C–C and C–P coupling reactions affording a series of η^3-allylic, alkenyl intermediates that were characterized.[388]



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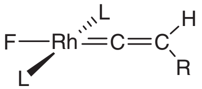

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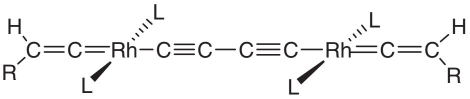

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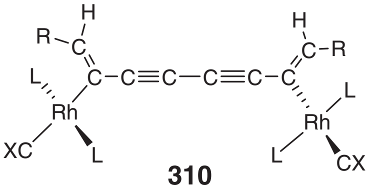

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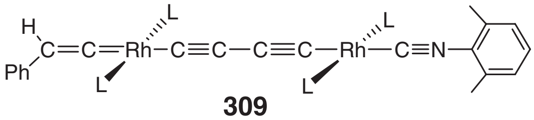
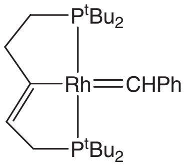


309

L = P^{i}Pr$_3$

R = Ph, ^{t}Bu, CX = CO, CN-C$_6$H$_3$Me2-2,6

Diphosphine pincer-type PCP–rhodium complexes were found to be robust precursors for the synthesis of carbene complexes such as **311 and 312** by reaction with phenyldiazomethane.[389]



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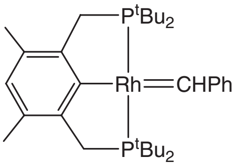
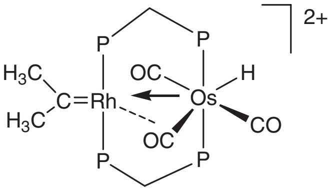


312

The reaction between the binuclear complex [Rh(μ-OOCCH$_3$)(CO)(PCy$_3$)]$_2$ with 1,1-diphenyl-2-propyn-1-ol gave Rh$_2$(μ-OOCCH$_3$)(μ-η^{1}:^{2}-C$_2$C(OH)R$_2$)(CO)$_2$(PCy$_3$)$_2$, which afforded [Rh$_2$(μ-OOCCH$_3$)(μ-σ,σ-C=C=CPh$_2$)-(CO)$_2$(PCy$_3$)$_2$]BF$_4$ by protonation with HBF$_4$·OEt$_2$ (Scheme 41).[390]

Rhodium/osmium heterobimetallic carbene complexes were obtained. Protonation of [RhOs(C(CH$_3$)=CH$_2$)(CH$_3$)(CO)$_3$(dppm)$_2$]CF$_3$SO$_3$ or [RhOs(C(CH$_3$)=CH$_2$)(H)(CO)$_3$ (dppm)$_2$]BF$_4$ at low temperature resulted in the formation of the carbene complexes [RhOs(=C(CH$_3$)$_2$)(R)(CO)$_3$(dppm)$_2$]$^{2+}$ [R = H **313**, CH$_3$ **314**] in which the carbene is terminally bound to Rh. Protonation of [RhOs(C(O)C(CH$_3$)=CH$_2$)(μ-H)(CO)$_3$(dppm)$_2$]BF$_4$ yielded the carbene complex [RhOs(=C(OH)C(CH$_3$)=CH$_2$)(μ-H)(CO)$_3$(dppm)$_2$][BF$_4$]$_2$ **315**.[296]



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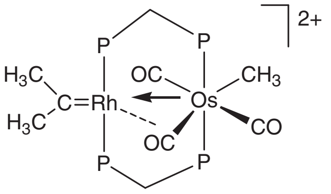

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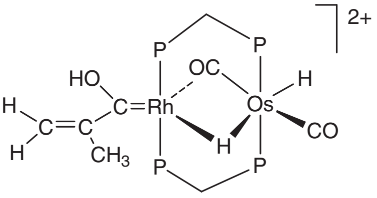
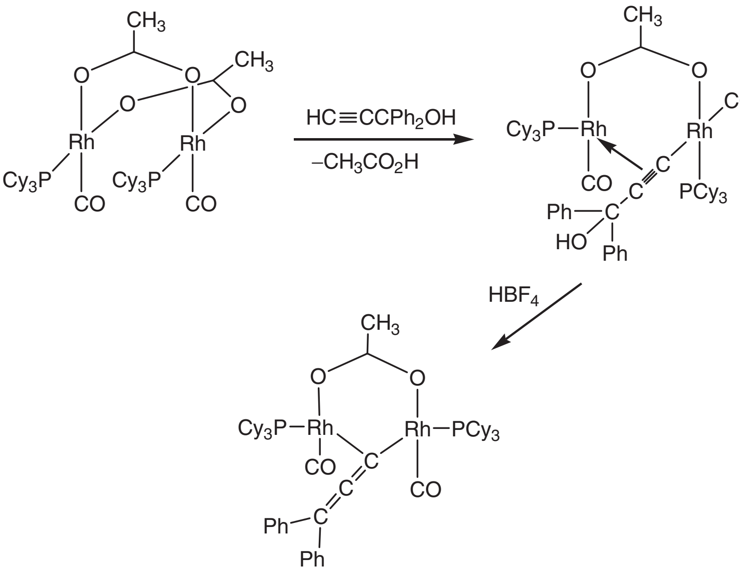
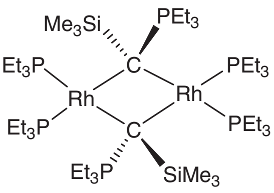


315

Photolysis of Rh{C(N$_2$)SiMe$_3$}(PEt$_3$)$_3$ led to the dimer [Rh{μ-C(SiMe$_3$)(PEt$_3$)}(PEt$_3$)$_2$]$_2$ **316** with two ylide bridges. Reaction with ^{n}BuNC or ^{t}BuNC led to stereo- and regioselective formation of a triazole complex Rh{CC(SiMe$_3$)N$_2$N^{t}Bu}(^{t}BuNC)$_2$(PEt$_3$) **317**.[146]



Scheme 41



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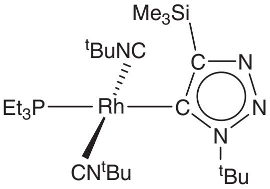
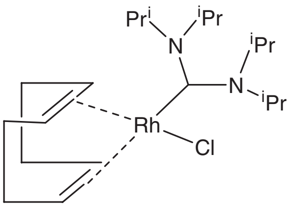


317

Enetetramine-derived carbene rhodium(I) complexes of general formula RhCl(cod)L and $RhClL_3$ (L = o-$C_6H_4\{N(Me)\}_2C$) were prepared and characterized.[391,391a] The synthesis of rhodium(I) complexes of the bis(diisopropylamino)carbene was described. The formamidinium chloride and the free bis(diisopropylamino)carbene (L) were used as consecutive precursor compounds to form these metal complexes. The complexes RhCl(cod)L **318** and $RhCl(CO)_2L$ **319** (L = bis(diisopropylamino)carbene) were characterized.[392]



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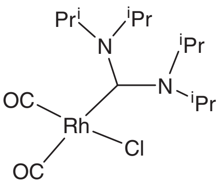
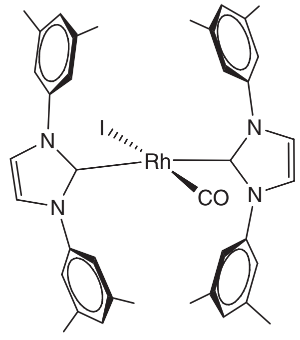


319

N-heterocyclic carbenes (NHCs) have appeared as a new type of ligands that provide remarkable stable complexes, mainly due to the high M–C bond stength. [393] Although the first examples of NHCs were described for Pd complexes, soon their coordination was extended to other metals, such as Rh. During the last decade, a large number of publications has appeared describing the coordination and properties of NHC complexes of Rh and a wide variety of complexes with different topologies were described. NHC-based complexes are relatively less accessible than the analogous phosphine compounds because the ligand has to be activated prior to coordination. Several activation strategies have been used in order to prepare NHC–metal complexes: (i) insertion of a metal into the C=C bond of bis(imidazolidin-2-ylidene) olefins (Lappert method), (ii) generation of a free carbene by deprotonation of the corresponding imidazolium precursor with a strong base (i.e., NaH, *t*-BuOK, *n*-Bu*t*Li) and addition to the metal fragment; (iii) transmetallation from a silver–NHC complex prepared from direct reaction of an imidazolium precursor and Ag_2O; (iv) *in situ* deprotonation of an imidazolium salt with a weak base (i.e., NEt_3, NaOAc, Cs_2CO_3), and (v) oxidative addition via activation of the C2–X (X = Me, I, H) of an imidazolium cation.

Several mono-NHC complexes were obtained. For example, transmetallation from a silver–NHC complex afforded the preparation of an Rh–NHC complex, in which the NHC ligand was obtained from caffeine.[394] Deprotonation of chiral ferrocenyl imidazolium salts allowed the preparation of chiral Rh(i)–NHC complexes[395] that could also be P,C and S,C chelate.[396] Dicyclophane imidazolium carbene ligands also provided an efficient way of obtaining chiral Rh–NHC catalysts.[397]

The oxidative addition of MeI to complexes of general formula $Rh(CO)(NHC)_2I$ [NHC = 3,5-dimethylimidazoline-2-ylidene **320**, 3,5-dimesitylimidazoline-2-ylidene **321**] was studied.[398] The carbene analog of Wilkinson's catalyst, $RhCl(IMes)(PPh_3)_2$ **322** (IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene), and the related carbonyl complex $RhCl(Imes)(PPh_3)(CO)$ were both prepared.[399,399a]



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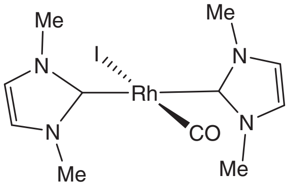

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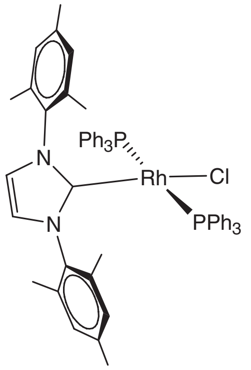
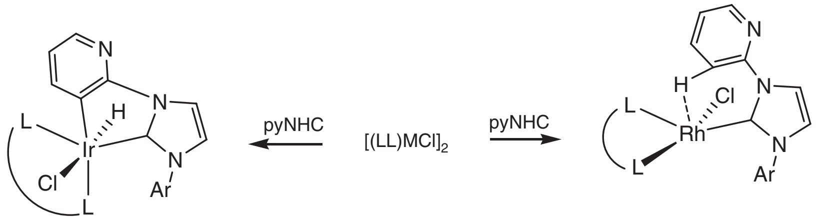


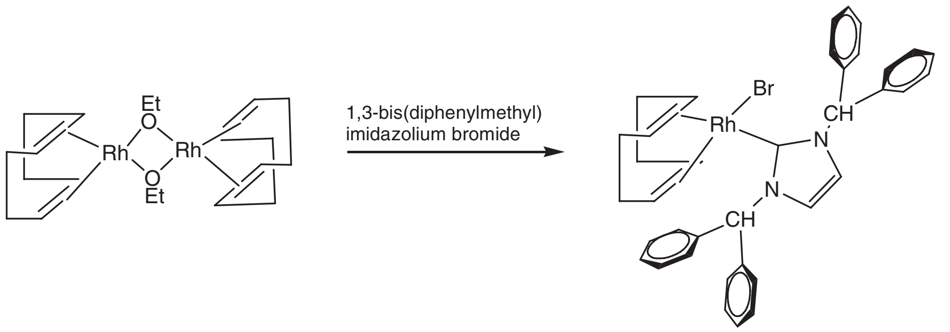
322

The oxidative addition of imidazolium salts to $RhCl(PPh_3)_3$ to give the Rh(iii) complex $Rh(H)Cl(NHC)(PPh_3)$ was theoretically studied,[400] providing a new synthetic route for the preparation of NHC–Rh complexes. The nucleophilic carbene IMes reacted with $[RhCl(coe)_2]_2$ affording an orthometallated rhodium–carbene complex Rh(H)Cl(IMes)(IMes′) (IMes′ = cycloorthometallated NHC carbene). The reaction proceeds by an intramolecular C–H activation of one aryl *ortho*-methyl group.[401] A pyridine-functionalized NHC provided a good example of and C–H···Rh H-bond interaction that turned into an intramolecular C–H activation for the analogous complex of Ir (Scheme 42).[402]

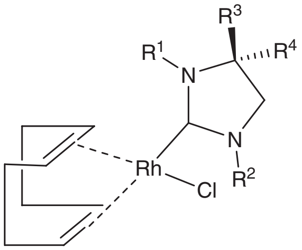
A series of rhodium NHC complexes of the type RhCl(NHC)(cod) were obtained by the direct reaction of $[Rh(\mu\text{-}Cl)(cod)_2]_2$ with the NHC[403,404] by insertion of the rhodium atom into the C═C bond of bis(imidazolidin-2-ylidene) olefins,[405] or by transmetallation from the corresponding silver(i) complexes.[406] The restricted rotation about the Rh–C bond was studied and the steric size of the N-alkyl wingtips of the carbene and the size of the auxiliary ligands were shown to be influenced significantly. The ν(CO) of the carbonyl derivatives obtained by bubbling CO over solutions of the cod precursors provided an efficient tool to estimate the electron-donor power of the carbene ligands.[406] The preparation of unsymmetrically saturated NHCs by the direct reaction of the carbene with $[Rh(\mu\text{-}Cl)(cod)_2]_2$ **323** also provided examples of coordination to Rh.[404]



Scheme 42



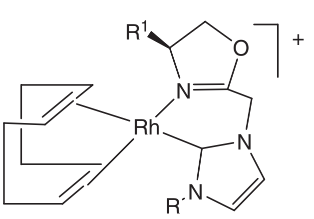
Scheme 43

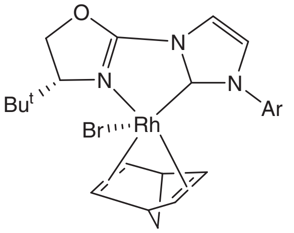


323

The compound $[Rh(\mu\text{-}OEt)(cod)]_2$ was also used as an efficient precursor for the preparation of NHC–Rh complexes, due to the facility of the EtO group to behave as an internal base, deprotonating the imidazolium salts (Scheme 43).[407]

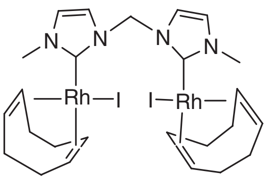
Complexes of the type *cis*-$[Rh(NHC)_2(cod)]^+$ reacted with CO yielding *trans*-$RhCl(NHC)_2CO$.[408] The combination of the imidazolium carbene ring with an imine provided a chelate NHC–imine ligand which can coordinate to rhodium by transmetallation from the corresponding silver(I) complex.[409] The combination of an imidazolylidene and an oxazoline ring provided new versions of chelate chiral ligands, which coordinated to Rh(I) as in complexes **324** and **325**.[410,410a,410b]

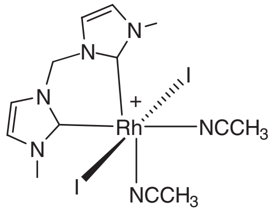


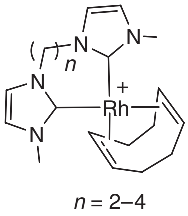


324 **325**

A series of bis-NHC ligands afforded the preparation of several dirhodium(I) complexes in which the biscarbene ligand is bridging the two metallic fragments **326**,[411,412] and other complexes in which the ligand is chelating the pseudo-square-planar Rh(I) **327**[411,412] or pseudooctahedral Rh(III) units **328**.[411,413] A study on the reactivity dependence on the length of the linker of the bisimidazolylidene carbenes was reported.[412]

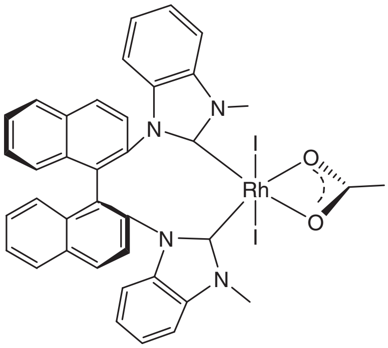






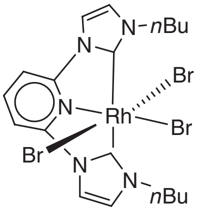
326 **327** **328**

Some chiral complexes were prepared from chelate bis-NHC complexes. For example, axially chiral Rh NHC complexes were prepared from axially dissymmetric 1,1′-binaphthalenyl-2,2′-diamine, providing a new Rh(III)–NHC chiral complex **329**.[414]



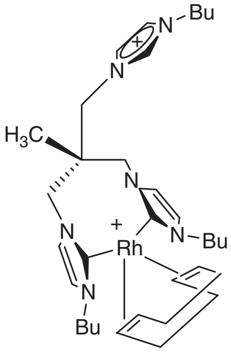
329

Pyridine-bridged bisimidazolium salts also afforded the preparation of dimetallic Rh(I) species by transmetallation from a silver(I)–NHC complex[415] and deprotonation with a weak base.[416] A pincer pyridine-bis-NHC Rh(III) complex **330** was obtained from the reaction of the corresponding bisimidazolium salt and $[Rh(\mu\text{-}Cl)(cod)]_2$ in the presence of NEt_3.[416]



330

A series of NHC-tripodal ligands were prepared and coordinated to Rh. Attempts to coordinate the precursor [1,1,1-Tris(3-butylimidazolium-1-yl)methyl]ethane trichloride ($TIMEH_3^{bu}$) resulted in the formation of the mono- **331** and bimetallic **332** species.[417]



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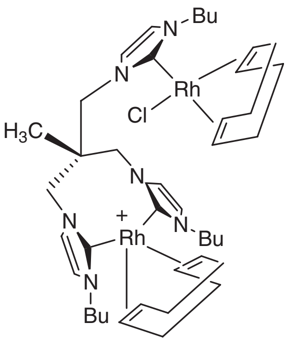
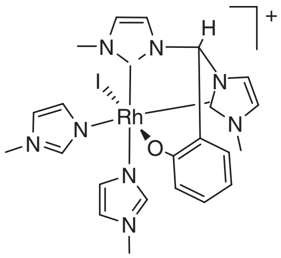


332

The bisimidazolium salt (2-hydroxyphenyl)bis(3-methylimidazolium-1-yl)methane reacted with $[Rh(\mu\text{-}Cl)(cod)]_2$ in the presence of NEt_3 affording a tripodal coordination of the NHC ligand in compound **333**.[418]



333

Triazolium-based carbenes also afforded mono-[419,419a,419b]and bis-NHC Rh complexes.[420]

7.02.3.3 Dihapto Ligands

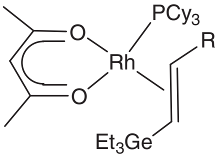
This section is divided into three different parts: Section 7.02.3.3.1 deals with complexes with alkene ligands; Section 7.02.3.3.2 describes complexes with η^2-cumulene ligands; and Section 7.02.3.3.3 describes alkyne complexes. In order to facilitate the classification of the numerous alkene complexes found, section 7.02.3.3.1 is further divided into three parts, based on the type of the ancillary ligands: group 16 and 17 donor ligands, group 15 donor ligands, and Cp and η^5-indenyl ligands.

7.02.3.3.1 Alkene complexes

7.02.3.3.1.(i) Groups 16 and 17 donor ligands

The compound Rh(acac)(coe)$_2$ is long known, but a new synthetic protocol from [Rh(μ-Cl)(coe)$_2$]$_2$ with Na(acac) (without the use of a thallium salt) was reported and the crystal structure of the compound was determined by X-ray diffraction studies.[421] The thermal reaction of Rh(acac)(CO)$_2$ with alkenes was studied and a series of rhodium alkene complexes, Rh(acac)(CO)(alkene) (alkene = ethylene, 1-propene, 1-octene), were characterized. The catalytic hydrogenation of these alkenes was monitored in the presence of high pressure hydrogen.[422] Some Rh(acac)(olefin)$_2$ (olefin = ethylene, *cis*-butene, *trans*-butene) complexes were prepared and characterized. The study of the ^{103}Rh NMR spectra allowed the establishment of a correlation between the chemical shift and the stability constant for the dissociation of one olefin from Rh(acac)(olefin)$_2$.[423] On the other hand, similar studies regarding X-ray crystallography and DFT calculations on rhodium–olefin complexes, together with ^{103}Rh NMR analysis, afforded parameters to establish stability correlations of complexes of the type Rh(2,4-pentanedionato) (olefin)$_2$[424]. Theoretical calculations on the stability of rhodium η^2-ethene hydrovinyl complexes were performed.[425]

The monoolefin complex Rh(acac)(cyclooctene)(PCy$_3$) reacted with HGeEt$_3$ giving Rh(acac)H(GeEt$_3$)(PCy$_3$). The reaction of the latter complex with methyl propiolate and phenylacetylene provided the complexes Rh(acac)[η^2-CH(GeEt$_3$)═CHR(PCy$_3$)] 334 (R = CO$_2$Me, Ph).[305] The same starting material, Rh(acac)(cyclooctene)(PCy$_3$), reacted with alkynes and CO displacing the olefin. Reactions with acetylenes afforded the corresponging alkenyl complexes.[306] Other acetylacetonate complexes of Rh-containing olefins were reported.[142]

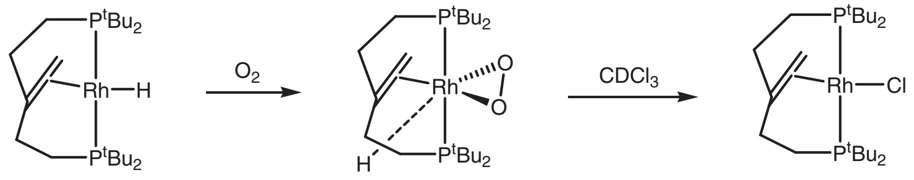


R = CO$_2$Me, Ph

334

An unexpectedly stable rhodium complex containing hydride, alkene, and dioxygen ligands in *cis*-positions relative to each other was described. The complex was obtained from oxidation in benzene of the hydrido alkene complex RhH[CH$_2$C(CH$_2$CH$_2$P^{t}Bu$_2$)$_2$]. The dioxygen–alkene complex decomposed in CDCl$_3$ yielding an alkene chloride (Scheme 44).[426]

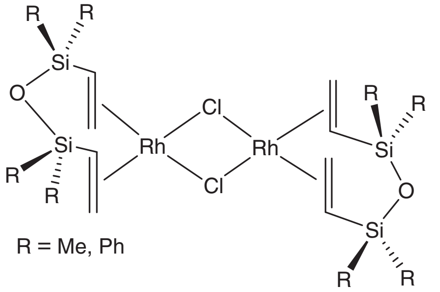
The oxidation of olefins catalyzed by Rh and Ir complexes was studied and 2-metallaoxetane intermediates were proposed.[427]



Scheme 44

The sulfonate complexes [Rh{μ-O$_2$S(O)R}(coe)$_2$]$_2$, *trans*-[Rh{η^1-OS(O)$_2$R}(C$_2$H$_4$)(P^{i}Pr$_3$)$_2$], *trans*-[Rh{η^1-OS(O)$_2$CF$_3$}(C$_2$H$_4$)(Sb^{i}Pr$_3$)$_2$], and [Rh{η^2-O$_2$S(O)CF$_3$}(olefin)(P^{i}Pr$_3$)] (olefin = coe, C$_2$H$_4$) were obtained using [Rh(μ-Cl)(coe)$_2$]$_2$ or [Rh(μ-OH)(coe)$_2$]$_2$ as starting materials.[428]

Reaction of [Rh(μ-Cl)(coe)$_2$]$_2$ with the appropriate divinyl disiloxane molecules (ViSiR$_2$)$_2$O (R = Me or Ph) gave the complexes [Rh(μ-Cl)(ViSiR$_2$)]$_2$ **335** (R = Me or Ph).[429] Di(silaalkenyl) chalcogenoether gave similar complexes as, for example the compound RhCl[S(CH$_2$SiMe$_2$CH=CH$_2$)$_2$] **336**.[430]



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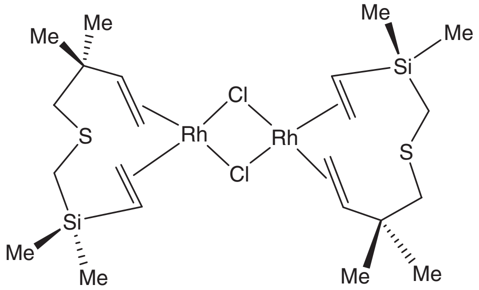
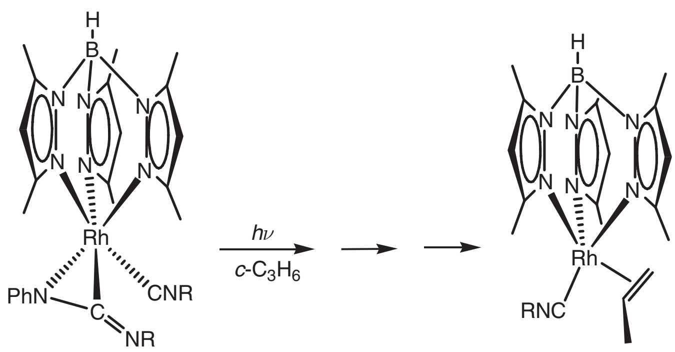


336

7.02.3.3.1.(ii) Group 15 donor ligands

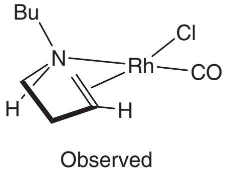
Solutions of TpRh(C$_2$H$_4$)$_2$ reacted with 1 equiv. of PPh$_3$ to yield TpRh(PPh$_3$)(C$_2$H$_4$). The complex adopts a trigonal-bipyramidal structure in solution with triphenylphosphine coordinated in the axial site and ethylene positioned in the equatorial plane. The axial and equatorial pyrazolyl arms of the Tp ligand exchange positions on the NMR time-scale.[431] The hapticity of trispyrazolate-type ligands (Tp) was studied by ^{11}B NMR spectroscopy for a series of Tp–Rh–olefin complexes.[432] Generation of the 16-electron fragment Tp′Rh(CNCH$_2$CMe$_3$) (Tp′=[HB(3,5-dimethylpyrazolyl)$_3$]) in the presence of cyclopropane resulted in C–H activation of the hydrocarbon. The cyclopropyl hydride complex rearranged in benzene solvent to the metallacyclobutane complex Tp′Rh(CNCH$_2$CMe$_3$)(CH$_2$CH$_2$CH$_2$). Thermolysis of the rhodacyclobutane complex produced an η^2-propylene complex (Scheme 45).[141]



Scheme 45

A series of olefin complexes with formula $[Rh(\mu\text{-}Rpz)(C_2H_4)_2]_2$ (Rpz = pyrazolate (pz), 3-methylpyrazolate (Mepz), 3,5-dimethylpyrazolate (Me_2pz)) was studied. The compound with Me_2Pz showed the shortest olefinic C=C distance found in ethylene rhodium complexes reported until 1996.[38]

Homo- and bishomoallylic secondary and tertiary amines reacted with the Rh(I) complexes $[Rh(\mu\text{-}Cl)(CO)_2]_2$, $[Rh(\mu\text{-}Cl)(CO)(CH_2{=}CH_2)]_2$, $[Rh(\mu\text{-}Cl)(CH_2{=}CH_2)_2]_2$ to yield bidentate mono- or dimeric complexes. The facial selectivity of binding is influenced by the presence of stereogenic centers on the tether between the alkene and amine, as seen for complexes 337 and 338.[433]



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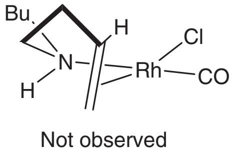
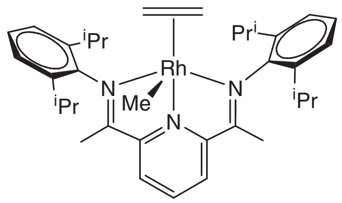


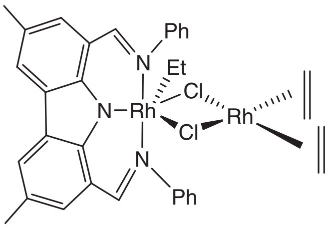
338

The synthesis of a dicationic alkyl-olefin complex of Rh(III) 339 allowed to study the effects of ligand geometry upon olefin insertion/alkyl migration, within a catalytic olefin polymerization reaction.[434]



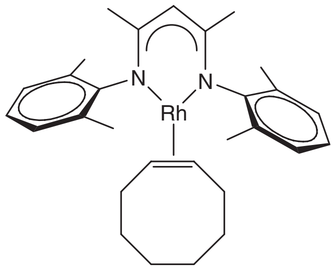
339

A dimetallic rhodium(I)–rhodium(III) complex 340 bearing a bis(imino)carbazolide ligand L and an olefin $LRh(C_2H_4)$ was prepared via a salt metathesis reaction between NaL and the dimeric rhodium precursors $[Rh(\mu\text{-}Cl)(C_2H_4)_2]_2$.[435]



340

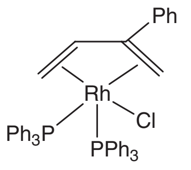
Reaction of LLi (L = ArNC(Me)CHC(Me)NAr, Ar = 2,6-$Me_2C_6H_3$) with $[Rh(\mu\text{-}Cl)(coe)_2]_2$ produced stable, three-coordinate complexes LRh(coe) 341.[436]



341

Theoretical calculations based on hybrid QM/MM studies were performed in order to elucidate the propene insertion into the Rh–H bond of $HRh(PPh_3)_2(CO)(\eta^2\text{-}CH_2{=}CHCH_3)$.[437] The steric influence of the phosphine was also studied.[438] Treatment of the arene-bridged dimer $[(PPh_3)_2Rh]_2[\textit{closo}\text{-}CB_{11}H_6Br_6]_2$ with 8 equiv. of cyclohexene afforded $[(\eta^4\text{-}C_6H_8)Rh(PPh_3)_2][\textit{closo}\text{-}CB_{11}H_6Br_6]$ with the concomitant formation of 1 equiv. of cyclohexane, while 1-methylcyclohexane and 4-methylcyclohexane both gave 2-methylcyclohexa-1,3-diene complexes.[439]

The reactions of 2-phenyl-1-methylenecyclopropane with $RhCl(PPh_3)_3$ gave $RhCl(\eta^4\text{-}CH_2{=}CPhCH{=}CH_2)(PPh_3)_2$ **342** and $RhCl(\eta^2\text{-}CH_2{=}CCH_2CHPh)(PPh_3)_2$ **343**, with a molar ratio depending on the temperature of the process. The latter complex can be converted into the first one in a solution of benzene at 50 °C, as a consequence of a ring-opening isomerization of the bisalkene ligand.[440] The molecular structures of the complexes were determined by X-ray diffraction methods.[441]



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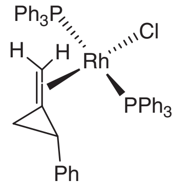
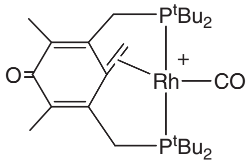


343

Significant structural changes were observed for the phosphine loss from bis(phosphine) complexes *trans*-$RhCl(\eta^2\text{-}(C,O)\text{-}Ph_2C{=}C{=}O)(PR_3)_2$ [$PR_3 = PMe(^tBu)_2$, $P(^iPr)_3$, or PCy_3], giving $RhCl(\eta^4\text{-}(C_4)\text{-}Ph_2C{=}C{=}O)(PR_3)$, where the diphenylketene is acting as a bis-η^4-olefin ligand (Scheme 46).[442]

The electron-deficient complex $[Rh(CO)L]CF_3SO_3$ **344** (L = 3,5-bis(di-*tert*-butylphosphinomethyl)-2,6-dimethyl-4-methylene-3,5-cyclohexadien-1-one) was prepared.[443] Protonation of the rhodium complex $RhCl(CH_3)[C_6H(CH_3)_2(CH_2P(t\text{-}Bu)_2)_2]$ with a strong acid (HOTf, trifluoromethanesulfonic acid) resulted in clean formation of the methylene arenium complex $[RhCl\{CH_2{=}C_6H(CH_3)_2(CH_2P(t\text{-}Bu)_2)_2\}]OTf$ which was fully characterized (Scheme 47).[444]



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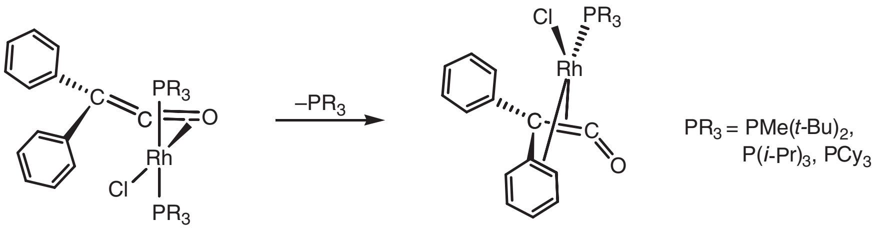
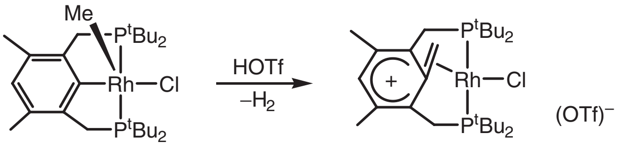
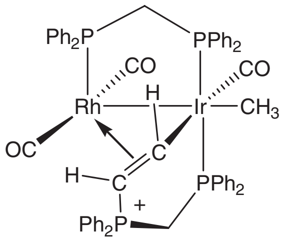


Scheme 46

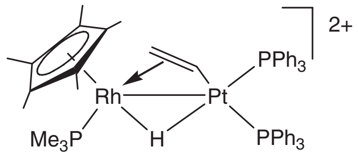


Scheme 47

The reaction of the mixed metal species $[RhIr(CH_3)(CO)_3(dppm)_2]CF_3SO_3$ with acetylene at room temperature resulted in the dissociation of the rhodium end of one of the diphosphines, which underwent nucleophilic attack at the Rh end of the alkyne to yield $[RhIr(CH_3)(\mu\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}HC{=}C(H)PPh_2CH_2PPh_2)(dppm)]CF_3SO_3$ **345**.[445] A similar heterometallic Rh–Pt complex **346** in which the the Pt–ethenyl ligand is η^2-coordinated to Rh was also reported.[446]

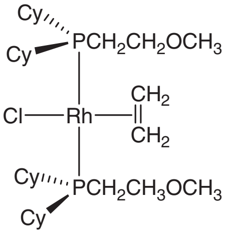


345



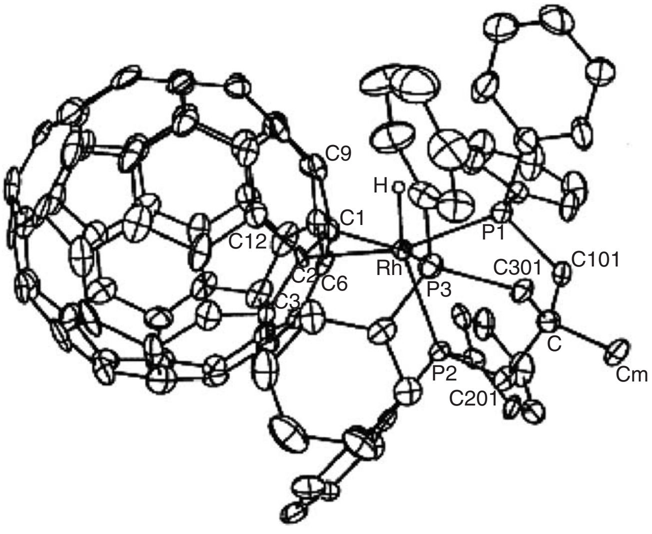
346

The reaction of the Wilkinson analogous complex $RhCl(\eta^2\text{-}P,O)(\eta^1\text{-}P,O)$ ($P\text{–}O = Cy_2PCH_2CH_2OCH_3$) with ethene resulted in the formation of $RhCl(\eta^1\text{-}P\text{-}O)_2$(ethene) **347**.[122]



347

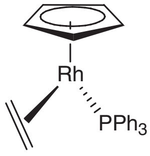
C_{60} and C_{70} fullerenes reacted with the rhodium hydride complex $RhH(CO)(PPh_3)_3$ displacing one phosphine ligand and leading to the formation of η^2-derivatives of the type $(\eta^2\text{-}C_n)RhH(CO)(PPh_3)_2$ ($n = 60$, 70).[447] Another fullerene complex, $(\eta^2\text{-}C_{60})RhH(triphos)$ **348** ($triphos = CH_3C(CH_2PPh_2)_3$), was prepared by the reaction of C_{60} with $RhH_3(triphos)$ in high yield and its molecular structure was determined by single crystal X-ray diffraction studies.[448]



348

7.02.3.3.1.(iii) Cp and η^5-indenyl ligands

The rhodium (triphenylphosphine)(ethene) complex $CpRh(PPh_3)(C_2H_4)$ **349**, was synthesized by the reaction of $[RhCl(C_2H_4)_2]_2$ with triphenylphosphine and thallium cyclopentadienide. As in $CpRh(PMe_3)(C_2H_4)$, the coordinated ethene ligand may be displaced photochemically, affording a series of oxidative addition reactions.[149] Complexes of the type $Cp^*Rh(olefin)_2$ are found to be excellent catalysts for the isomerization of aldehydes or transfer formylation reactions.[449] Divinyl disiloxane or divinyl disilazane afforded the preparation of several complexes of Rh–Cp, such as **350**, **351**, and **352**.[450]



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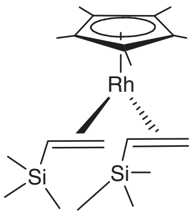
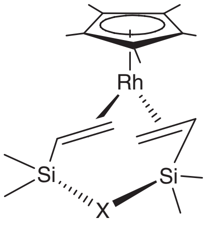


350

X = O, NH



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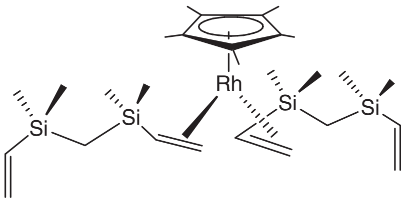
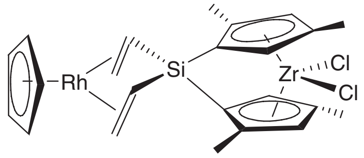


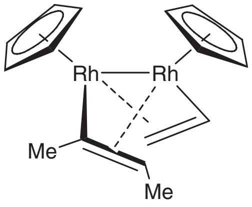
352

Similar complexes of the type *ansa*-zirconocene/rhodium–cyclopentadienyl, such as **353**, were also obtained and fully characterized.[451]



353

The bis(μ-vinyl) compound $Cp_2Rh_2(C_2H_3)(C_2HMe_2)$ **354** and the η^4-butadiene species $CpRh\{C_4HR_4\text{-}C_5H_4Rh(C_2H_4)_2\}$ **355** were obtained from $CpRh(C_2H_4)_2$.[354]



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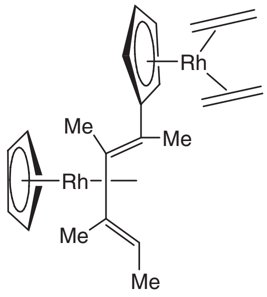
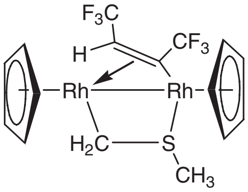


355

A series of dirhodium chalcogenide-bridged complexes with ethenyl **356**, **357**, and **358**,[452] and enone **359**[453] ligands was described and coordinated to CpRh dimetallic fragments.



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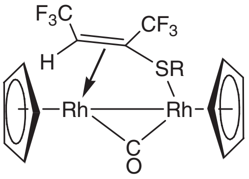

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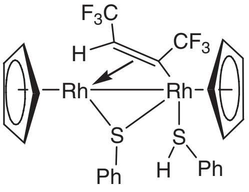
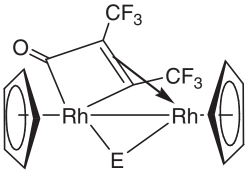


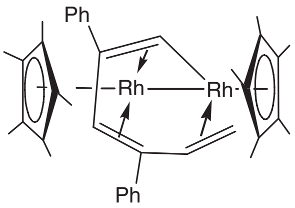
358



E = S, Se

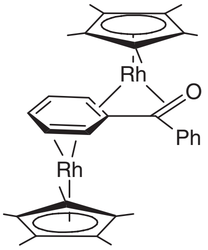
359

The compound $[(Cp^{*}Rh)_2\{\eta^1:\eta^4:\eta^2\text{-}\mu\text{-CHC(Ph)CHC(Ph)CHCH}_2\}]^{+}$ **360** was obtained by carbon–carbon bond formation between the μ-CH_2 group and alkynes in $[(Cp^{*}Rh)_2(\mu\text{-}CH_2)_2(CH_3CN)_2]^{2+}$.[454]



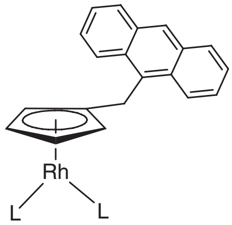
360

The rhodium bisolefin complex $Cp^{*}Rh(\eta^2\text{-}C_2H_3SiMe_3)_2$ was found to be a catalyst for the selective addition of olefins to the *ortho*-position of aromatic ketones. In the presence of excess ketone, the formation of a benzophenone complex, $(Cp^{*}Rh)_2\text{-}\eta^4\text{-}\eta^4\text{-}C_6H_5C(O)Ph$ **361**, was observed. In this complex, the arene is η^4-coordinated to one Rh atom and η^2-coordinated to the other one.[455]



361

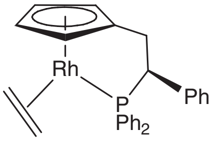
The ligand 9-anthrylmethylcyclopentadiene afforded the preparation of a series of complexes of formula $(\eta^5\text{-}AnCH_2C_5H_4)Rh(olefin)_2$ **362** (olefin = coe, C_2H_4).[456] The redox properties of these complexes were extensively studied, and the corresponding cation radicals were studied by EPR methods.[153,154]



L = COE, C_2H_4

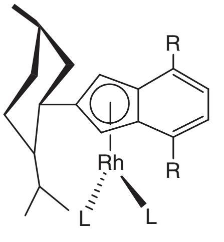
362

The phenylspiro ligand (*S*)-$[Li(C_5H_4CH_2CHPhPPh_2)]$ afforded the preparation of the optically active complex (*S*)-$[(\eta^5\text{-}C_5H_4CH_2CHPhPPh_2\text{-}\kappa P)Rh(\eta^2\text{-}C_2H_4)]$ **363**.[457]



363

Optically active complexes of Rh containing the chiral menthyl-substituted indenyl ligands (−)-2-menthylindene and (−)-2-menthyl-4,7-dimethylindene were described. Metathetic reaction of the chiral lithium salts of these indenyl systems with the appropriate starting materials of Rh yielded the complexes (−)-(2-menthylindenyl)Rh(C_2H_4)$_2$ and (−)-(2-menthyl-4,7-dimethylindenyl)Rh(C_2H_4)$_2$ **364**. Similar complexes with cod and coe were also obtained.[458]

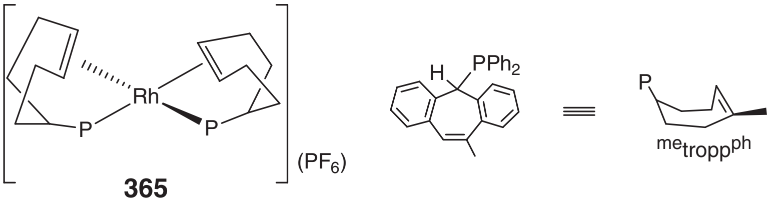


L–L = COD, COE, C_2H_4
R = H, Me

364

In situ UV irradiation of toluene solutions containing bis(alkene)rhodium complexes enabled the characterization of unstable η^2-solvent complexes and dihydrogen activation products (Scheme 48).[459]

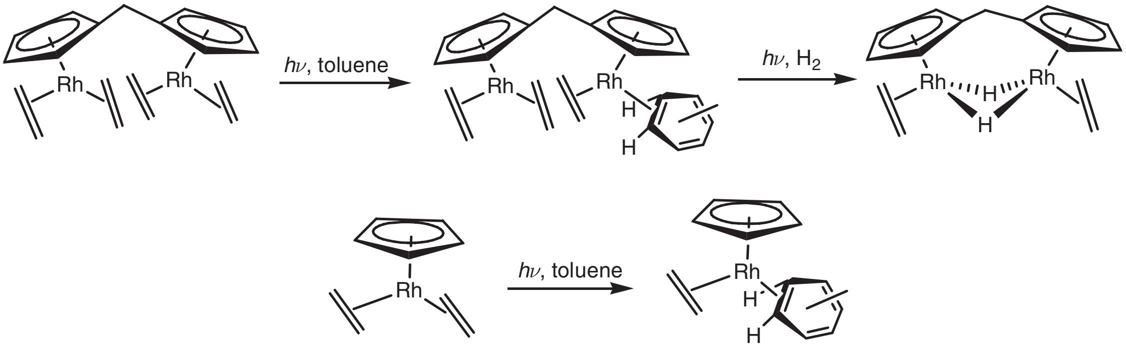
The synthesis of the ligand 5-diphenylphosphanyl-10-methyl-5H-dibenzo[*a*,*d*]cycloheptene (^{me}tropp^{ph}) was developed in order to prepare highly distorted tetracoordinated rhodium(I) complexes. Four equivalents of the ligand ^{me}tropp^{ph} reacted with [RhCl(cod)]$_2$ in the presence of KPF_6 to yield almost quantitatively [Rh(^{me}tropp^{ph})$_2$]PF_6 **365**.[460]



365

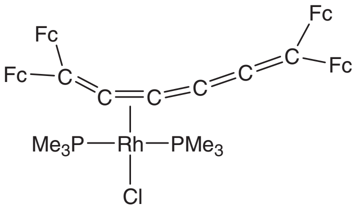
7.02.3.3.2 Cumulene complexes

Addition of methyl iodide to *trans*-[RhCl(=C=CHR)(P^{i}Pr$_3$)$_2$] gave an η^2-butatriene complex, thus implying that CH_3I can behave as an effective source of CH_2.[461] The addition of CH_3I and CH_2N_2 to metallabutatrienes to yield the corresponding η^2-butatriene complexes, as well as the related isomerization reactions, was extensively studied



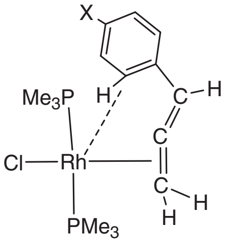
Scheme 48

and summarized in a review by Werner.[462] Tetraferrocenyl[5]cumulene, $(Fc)_2C{=}C{=}C{=}C{=}C{=}C(Fc)_2$ (Fc = ferrocenyl), formed an η^2-coordinated complex with Rh(I) when reacted with $RhCl(PMe_3)_3$.[463,463a] Reactions of $[RhCl(PMe_3)_2]_2$ with phenylallene or (4-phenyl)allene gave complexes with π-coordinated arylallenes, $RhCl(\eta^2\text{-}CH_2{=}C{=}CHAr)(PMe_3)_2$ **366** ($Ar = C_6H_5$, C_6H_4F-*p*). The position of an *ortho*-hydrogen of the phenyl group in the ligand suggested an agostic interaction between the C–H group and the Rh center. The arylallenes also reacted with $RhCl(PMe_3)_3$ in a 1.2 : 1 molar ratio to yield pentacoordinated Rh(I)–arylallene complexes, $RhCl(\eta^2\text{-}CH_2{=}C{=}CHAr)(PMe_3)_3$ **367**.[352]



Fc = Ferrocenyl

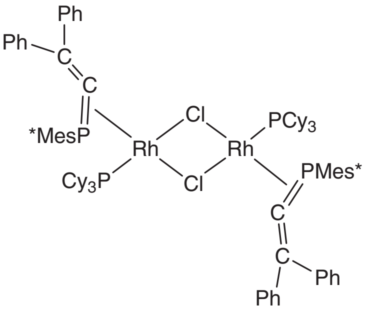
366



X = H, F

367

The compound $RhCl(PCy_3)_2$ catalyzes the isomerization of the phosphacumulene $Mes^*P{=}C{=}CPh_2$ ($Mes^* = 2,4,6\text{-}(t\text{-}Bu)_3C_6H_2$) to $2,4\text{-}(t\text{-}Bu)_2C_6H_2(6\text{-}CMe_2CH_2PCH{=}CPh_2)$. The intermediate $[Rh(PCy_3)[\eta^2(P,C)\text{-}Mes^*P{=}C{=}CPh_2]Cl]_2$ **368** was detected.[464] The reaction of $RhCl({=}C{=}C{=}C{=}C{=}CPh_2)(P^iPr_3)_2$ with CH_2N_2 afforded a compound **369** in which the hexapentaene $H_2C{=}C{=}C{=}C{=}C{=}CPh_2$ is π-coordinated to the $RhCl(P^iPr_3)_2$ fragment.[465]



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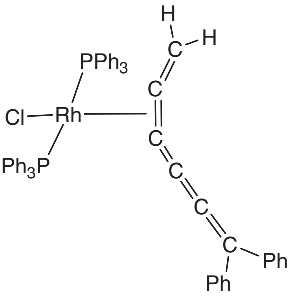
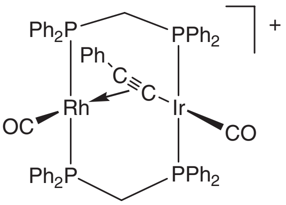


369

7.02.3.3.3 Alkyne complexes

Disubstituted alkynes reacted with $Rh_4(CO)_{12}$ to yield a series of complexes that were characterized according to FTIR analyses. The formation of $[Rh(CO)_2]_2(\mu\text{-}\eta^2\text{-}RC_2R^1)$, a complex analog to the well-known dicobalt carbonyl alkyne, was tentatively proposed.[466] The reactivity of the alkynyl-bridged complex $[RhIr(CO)_2(\mu_2\text{-}\eta^1{:}\eta^2\text{-}C_2Ph)(dppm)_2]X$ ($X = BF_4$, SO_3CF_3; dppm = $Ph_2PCH_2PPh_2$) provided a new series of alkynyl-bridged species, **370**, **371**, **372**, **373**, and **374**.[467] The same bimetallic precursor reacted with carbon disulfide to give several products. For example, $[RhIr(CO)(\eta^2\text{-}CS_2)(\mu\text{-}CO)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2Ph)(dppm)_2]X$ was the result of CS_2 coordination at Ir. Upon warming, two products were formed after condensation of two CS_2 groups, $[RhIr(CO)(\mu\text{-}\eta^1{:}\eta^3\text{-}CC(Ph)SCSCS_2)(\mu\text{-}CO)(dppm)_2]X$ and $[RhIr(CO)(C_2S_4)(\mu\text{-}C_2Ph)(\mu\text{-}CO)(dppm)_2]X$.[121] Other heterobimetallic phenylacetylide complexes were also described by the same group.[468]



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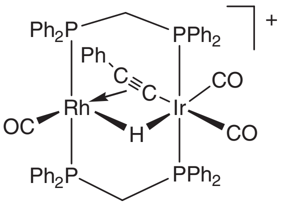

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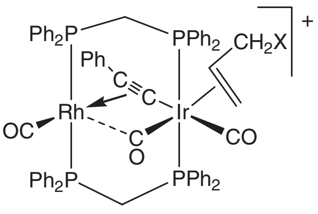

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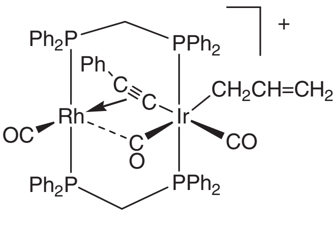

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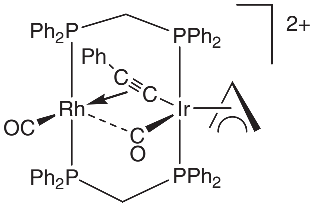
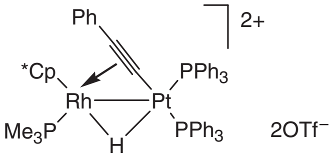


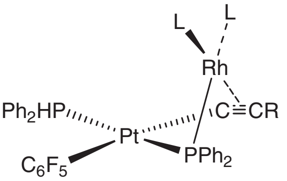
374

The reaction of Cp*Rh(OSO$_2$CF$_3$)$_2$ with Pt(HC≡CH)(PPh$_3$)$_2$ afforded the complex [Cp*Rh(μ-H)(PMe$_3$)(μ-η^2:η^1-HC≡CH)Pt(PPh$_3$)$_2$][SO$_3$CF$_3$]$_2$ **375**.[446]



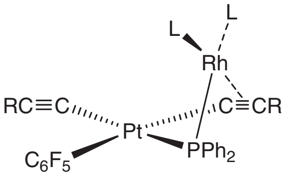
375

Treatment of *trans*-[Pt(C$_6$F$_5$)(C≡CR)(PPh$_2$H)$_2$] [R = *t*-Bu, Ph] with Rh(acac)L$_2$ (L$_2$ = cod, 2CO) produced the corresponding alkynyl/diphenylphosphido-bridged complexes *trans,cis*-[(C$_6$F$_5$)(PPh$_2$H)Pt(μ-κC^{α}:η^2-C≡CR)(μ-PPh$_2$)RhL$_2$] **376** and *cis,cis*-[(C≡CR)(PPh$_2$H)Pt(μ-κC^{α}:η^2-C≡CR)(μ-PPh$_2$)RhL$_2$] **377**. The related mixed alkynyl/phosphinite complexes {(PPh$_2$O)$_2$H}Pt(μ-κC^{α}:η^2-C≡CR)(μ-κP,κO-PPh$_2$O)RhL$_2$ **378** were prepared by reacting Pt(C≡CR){(PPh$_2$O)$_2$H}(PPh$_2$OH) with Rh(acac)L$_2$.[469]



R = *t*Bu, Ph
L$_2$ = COD, 2CO

376



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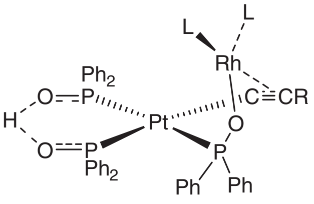
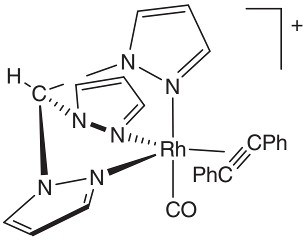


378

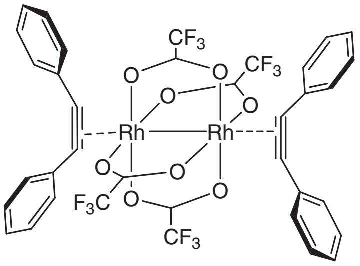
The rhodium complex Rh(η^2-O$_2$CCF$_3$)(P^{i}Pr$_3$)$_2$ reacted with 1-alkynes to give either four-coordinate alkynerhodium(I), *trans*-[Rh(η^1-O$_2$CCF$_3$)(HC≡CR)(P^{i}Pr$_3$)$_2$], or six-coordinate alkynyl(hydrido)rhodium(III), RhH(C≡CR)(η^2-O$_2$CCF$_3$)(P^{i}Pr$_3$)$_2$, derivatives.[307] Heating both types of compounds yielded the corresponding vinylidene–rhodium(I) complexes.[470] The pseudo-14-electron rhodium complex [RhCl(P–O)(P,O)] (P–O = η^2-chelated Cy$_2$PCH$_2$CH$_2$OCH$_3$; P,O = η^1-(P)-coordinated) reacted with diphenylacetylene to yield the complex RhCl(PhC≡CPh)(P,O)$_2$.[122] The olefin complex Rh(acac)(cyclooctene)(PCy$_3$) reacted with alkynes RC≡CR by ligand displacement to give Rh(acac)(η^2-RC≡CR)(PCy$_3$) [R = CO$_2$Me, Ph].[306] The complex

$[Rh(CO)_2\{HC(pz')_3\}]PF_6$, $\{HC(pz')_3 = $tris(3,5-dimethylpyrazolyl)methane$\}$, reacted with $PhC{\equiv}CPh$ to give $[Rh(CO)(\eta^2\text{-}PhC{\equiv}CPh)\{HC(pz')_3\}]^+$ **379**, in which the two-electron donor alkyne occupies an equatorial position in a trigonal κ^3-structure.[43]



379

In the presence of a strong base (KO^{t}Bu), the π-alkyne complex $[(triphos)Rh(\eta^2\text{-}MeO_2CC{\equiv}CCO_2Me)]PF_6$ behaved as a catalyst precursor for the homogeneous hydrogenolysis of dinaphtho[2,1-*b*:1′,2′-*d*]thiophene to 1,1′-binaphthalene-2-thiol.[272] The solid-state reactions of $Rh_2(O_2CCF_3)_4$ with diphenylacetylene (Ph_2C_2) produced the first two dirhodium(II, II) carboxylate complexes with coordinated alkynes having overall compositions of 1 : 2 **380** and 1 : 1 **381**.[471]



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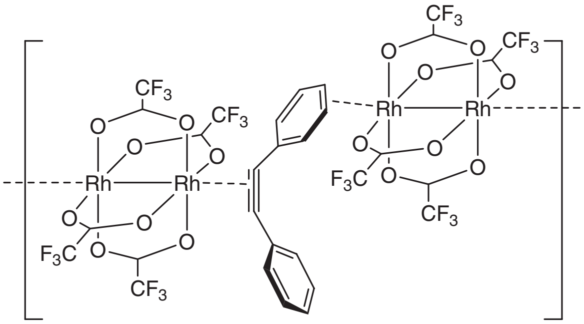
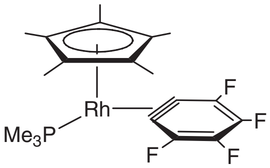


381

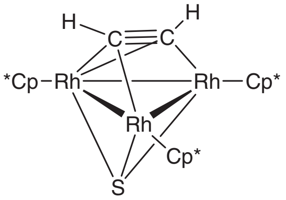
The transformation of a rhodium(I) η^2-alkyne model complex $RhCl(PH_3)_2(HC{\equiv}CH)$ into the vinylidene form $RhCl(PH_3)_2({=}C{=}CH_2)$ was examined by *ab initio* theoretical calculations using MP2 level geometry optimizations and localized molecular orbital (LMO) analysis.[472]

UV irradiation of $CpRh(C_2H_4)_2$ in pentane in the presence of alkynes C_2R_2 [R = Me, Et] gave a variety of products, and several compounds were isolated.[354] Treatment of $Cp^*Rh(C_6F_5)H(PMe_3)$ with *n*-BuLi gave the rhodium tetrafluorobenzyne complex $Cp^*Rh(\eta^2\text{-}C_6F_4)(PMe_3)$ **382**.[473]



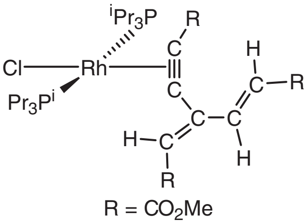
382

Deprotonation of the double-bridging μ-CH_2 complex $[Cp^*{}_2Rh_2(\mu\text{-}CH_2)_2(\mu_2\text{-}SH)]BPh_4$ with $[Cp^*{}_2Rh_2(\mu\text{-}OH)_3]BPh_4$ led to the isolation of the trirhodium μ_3-S complex $[Cp^*{}_3Rh_3(\mu_3\text{-}\eta^2\text{-}\|\text{-}C_2H_2)(\mu_3\text{-}S)](BPh_4)_2$ **383**, including an acetylene ligand generated by a unique C–C bond coupling and deprotonation of two μ_2-CH_2 groups.[474]



383

The rhodium(I) diyne complex *trans*-[RhI(η^2-Ph*C*≡*C*C≡CPh)(P^{i}Pr$_3$)$_2$] was obtained from [RhCl(P^{i}Pr$_3$)$_2$]$_2$, 1,4-diphenylbutadiyne, and NaI.[252] The rhodium-mediated trimerization of an alkyne to hexadienyne allowed the isolation of the corresponding rhodium-π-hexadienyne intermediate **384**.[475]



384

7.02.3.4 Tetrahapto Ligands

This section has been divided in two parts, one of them describes a major group regarding cod, nbd, and tfb complexes, and the other describes complexes containing conjugated diene ligands.

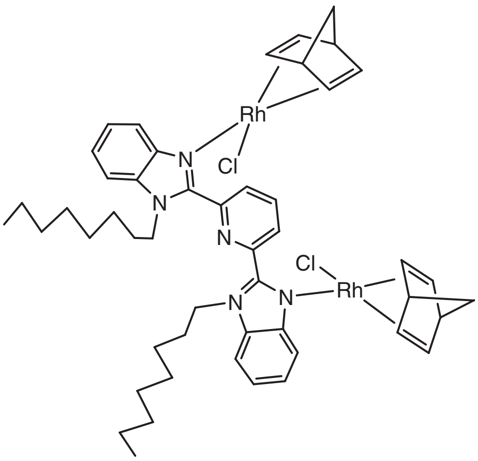
7.02.3.4.1 Cod, nbd, and tfb complexes

Complexes containing cod, nbd, and tfb dienes have been widely used due to their availability and use as starting materials. The compounds have been classified in three groups regarding compounds with group 15 ligands, compounds with group 16 and 17 ligands, and other complexes.

7.02.3.4.1.(i) Compounds with group 15 ligands

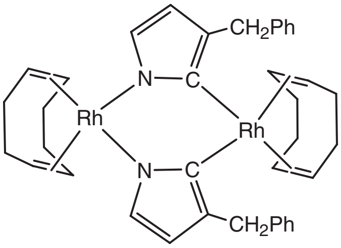
The steric and electronic effects of a series of [Rh(cod)(phosphine)]$^+$ complexes were studied by ^{103}Rh NMR studies.[476]

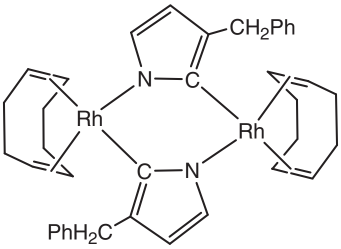
Some bidentate and tridentate 1-alkylaminopyrazoles or bdtp[58] provided mononuclear complexes of the type [Rh(L)(cod)]$^+$ (L = NN′ and NN′N-coordinated alkylpryrazolate ligands in the η^2-form),[477] while 3,5-dimethyl-4-(ethylamino)methylpyrazole, 3,5-dimethyl-4-(isopropylamino)methylpyrazole,[478] 3,5-bis(trifluoromethyl)pyrazol,[479] 3-ferrocenylpyrazole,[65] 3-[4-phenoxyphenyl]pyrazole, and 3-[4-butoxyphenyl]pyrazole[480] allowed the preparation of dimetallic species of the type [Rh(μ-pz)(cod)]$_2$. Several pyrazolate-bridged Rh–nbd complexes with general formula [Rh(μ-pz)(nbd)]$_2$ (pz = pyrazolate, 3,5-dimethylpyrazolate, 3(5)*tert*-butylpyrazolate, 3-methyl-5-*tert*-butylpyrazolate, 3-methyl-5-phenylpyrazolate, and 3(5)-*p*-methoxyphenylpyrazolate) were also prepared.[481] Other dimetallic species were obtained with the ligands 1,2-bis[3-(3,5-dimethyl-1-pyrazolyl)-2-thiapropyl]benzene (bddf) and 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo) that gave the dinuclear complexes [Rh$_2$(bddf)(cod)$_2$][BF$_4$]$_2$ and [Rh$_2$(bddo)(cod)$_2$][BF$_4$]$_2$, respectively.[58] A topologically similar ligand, bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether, (L$_1$), reacted with [Rh(cod)(THF)$_2$]BF$_4$ giving [Rh(L$_1$-κ^2*N*,*N*)(cod)]BF$_4$.[482] Heterobridged dinuclear complexes Rh$_2$(μ-pz)(μ-PPh$_2$)(cod)$_2$ (pz = pyrazolate or 3,5-dimethylpyrazolate) were prepared by the reaction of M$_2$(μ-Cl)(μ-pz)(cod)$_2$ with LiPPh$_2$.[483] Heterobimetallic Rh,Ir pyrazolate-bridged complexes containing cod were also reported.[484] The ligand 2,6-bis(1-methylbenzimidazol-2-yl)pyridine (L1) or its lipophilic analog 2,6-bis(1-octylbenzimidazol-2-yl)pyridine (L2) reacted with [Rh(μ-Cl)(nbd)]$_2$ producing poorly soluble dimetallic complexes [RhCl(nbd)]$_2$L [L = L1 or L2 **385**]. The ligand is connecting two RhCl(nbd) units through the nitrogen atoms of the benzimidazole side arms.[485]



385

Complexes $[\mathrm{Rh}(\mu\text{-Cl})(\mathrm{diene})]_2$ (diene = cod, nbd) reacted with lithium *N*-benzyl-2-imidazolate (LiBzim) to yield dinuclear $\mathrm{Rh}_2(\mu\text{-Bzim-}N^3,C^2)_2(\mathrm{diene})_2$, in which the bridging ligands can be coordinated in a head-to-head 386 or head-to-tail 387 form.[52]

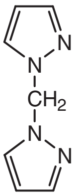




386 **387**

The cationic compounds $[(\eta^6\text{-}p\text{-cymene})\mathrm{OsCl(Hpz)_2}]\mathrm{BF_4}$ were prepared by treating the dimeric $[(\eta^6\text{-}p\text{-cymene})\mathrm{OsCl}]_2(\mu\text{-Cl})_2$ with pyrazole (*p*-cymene = *p*-isopropylmethylbenzene, Hpz = pyrazole). These compounds are precursors to new heterobinuclear complexes of stoichiometry $(\eta^6\text{-}p\text{-cymene})\mathrm{OsCl}(\mu\text{-pz})_2\mathrm{Rh(cod)}$.[486]

The coordination of tris(pyrazolyl)amine and bis(pyrazolyl)amine ligands toward $[\mathrm{Rh}(\mu\text{-Cl})(\mathrm{cod})]_2$ was studied and the crystal structure of the trimetallic compound $\mathrm{Rh_3Cl_3(cod)_3(tdma)}$ was reported.[487] Trispyrazolylborate ligands also provided a series of complexes of the type TpRh(LL) (LL = nbd or cod), whose NMR spectroscopic properties and structural features were studied.[67,488,488a,488b] The fluxional behavior of complexes of formula $\mathrm{Tp^RRh(LL)}$ (LL = nbd, 2CO, cod; R = H, Me, Ph, Br) was studied by means of NMR spectroscopy. Two κ^2-square-planar isomers and one κ^3-pentacoordinated complex were observed. The structure of the complex $\kappa^3\text{-}\mathrm{Tp^{Me}Rh(nbd)}$ was confirmed by X-ray diffraction.[66] The hapticity of the Tp ligand was also studied on the basis of the ν(B–H) obtained by IR spectroscopy.[489] Reactions of $[\mathrm{Rh}(\mu\text{-Cl})(\mathrm{nbd})]_2$ with a series of bis- and tris(azolyl) methanes 388, 389, 390, 391, and 392 were also reported.[490]



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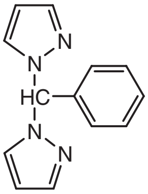

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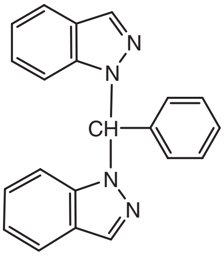

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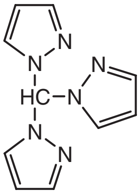

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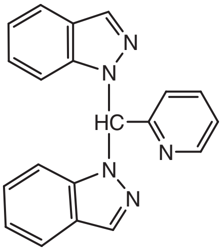
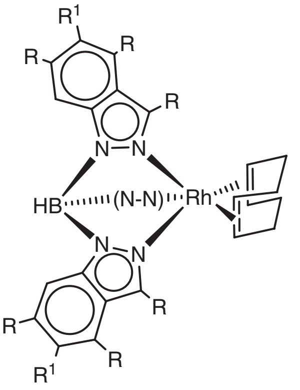


392

Hydrotris(indazolyl)borates showed similar topological features as tris(pyrazolyl)borates, and their regiochemistry can be modulated by the introduction of several substituents. A series of complexes [**393**, **394** and **395**] with the Rh–cod fragment was described.[491]



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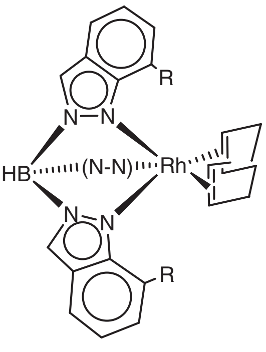

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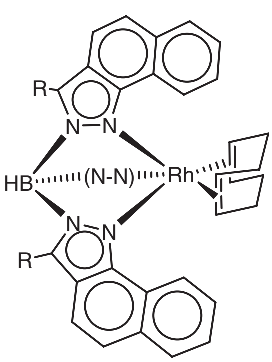
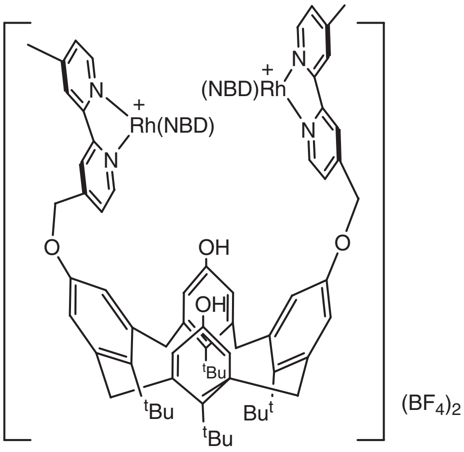


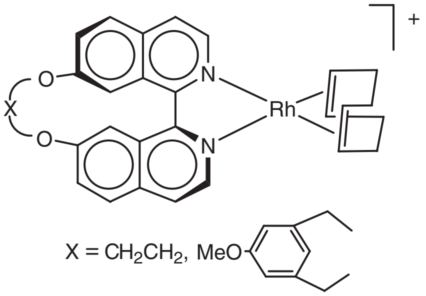
395

The preparation of ferrocenyl substituted pyridines, such as 4-ferrocenylpyridine and 1,1′-di(2-pyridyl)ferrocene (L), allowed the preparation of complexes with formula $[Rh(cod)L_2]ClO_4$.[492] The multitopic ligands, *N*,*N*′-bis[(*S*)-prolyl)phenylenediamine, *N*,*N*′-bis{[(*S*)-pyrrolidin-2-yl]methyl}phenylenediamine, *N*,*N*′-bis[(*S*)-*N*-benzylprolyl]phenylenediamine, and *N*,*N*′-bis{[(*S*)-*N*-benzyl-pyrrolidin-2-yl]methyl}phenylenediamine, were synthesized and their coordination properties with Rh(I) studied. [493] The ligand bis(bipyridine)-calix[4]arene (BBPC) reacted with 2 equiv. of $[Rh(nbd)_2]BF_4$ or $[Rh(nbd)(CH_3CN)_2]BF_4$ yielding the bimetallic compound $[Rh(nbd)(BBPC)]_2[BF_4]_2$ **396**.[494]



396

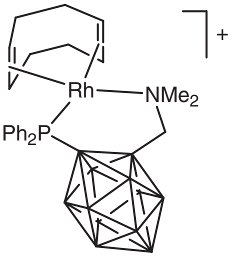
Reaction of $[Rh(\mu\text{-}Cl)(diene)]_2$ (diene = cod or nbd) with the *N-N-N* nitrogen ligands $2,6\text{-}(C(R^1){=}N\text{–}R^2)_2C_5H_3N$ yielded the five-coordinate complexes $RhCl(2,6\text{-}(C(H){=}N\text{–}R^2)_2C_5H_3N)(diene)$ (R^2 = *i*-Pr, *t*-Bu, and *p*-anisyl).[495] One-electron oxidation of $[Rh^I(dpa)(cod)]^+$ yielded $[Rh^{II}(dpa)(cod)]^{2+}$, which reversibly bound dioxygen. In solution, $[Rh^{II}(dpa)(cod)]^{2+}$ disproportionated to $[Rh^I(Hdpa)(cod)]^{2+}$ and two isomers of $[Rh^{III}(dpa)(cyclooctadienyl)]^{2+}$ (dpa = dipicolylamine).[496] A similar process is observed for the nbd complex.[497] Chiral C_2-diamines such as 2,2′-diamino-1,1′-binaphthyl (BNDA) and N,N′-dimethyl-2,2′-diamino-1,1′-binaphthyl (DMBNDA) afforded the preparation of chiral Rh catalysts by the reaction of $[Rh(\mu\text{-}Cl)(diene)]_2$ with $AgBF_4$ and the corresponding amount of the diamine.[498] Dinuclear rhodium(I) complexes, $[Rh_2(2\text{-}bpbd)_2(cod)_2]X_2$ (X = BF_4, PF_6 or ClO_4) and 1D rhodium(I) coordination polymers with the linkage of square-planar rhodium(I) centers, $\{[Rh(4\text{-}bpbd)(cod)]X\}_n$ and $\{[Rh(4\text{-}bpe)(cod)]X\}_n$, were systematically synthesized using 1,4-bis(2-pyridyl)butadiyne (2-bpbd), 1,4-bis(4-pyridyl)butadiyne (4-bpbd) and *trans*-1,2-bis(4-pyridyl)ethylene (4-bpe).[499] Complexes of formula $[Rh(\mu\text{-}Cl)(diene)]_2$ (diene = cod, nbd) reacted with α-diimines (LL) derived from glyoxal, to give $Rh_2Cl_2(cod)(LL)$ or $RhCl(nbd)(LL)$. Solutions of these compounds contained dinuclear $\{RhCl(cod)\}_2(\mu\text{-}LL)$ species with bridging LL groups and ionic $[Rh(cod)(LL)]^+[RhCl_2(cod)]^-$ species, in temperature-dependent ratios.[500] Similar studies were made with the Rh–nbd related complexes.[501,501a] Optically pure 7,7′-ethylenedioxy-1,1′-biisoquinoline and the 7,7′-(5-methoxy-*m*-xylylenedioxy) analog were coordinated to rhodium(I) affording $[Rh\{NN\}(cod)]^+$ **397**, (NN = biisoquinoline). Only the first biisoquinoline gave an enantiomerically pure complex, while the second afforded the racemic mixture.[502]



397

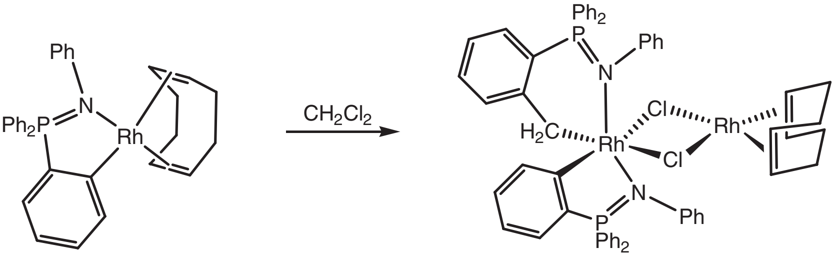
The conformational flexibility of cationic Rh(diolefin) complexes with (P,N)-iminophosphine ligands was studied.[503] Lithiated phosphinimines of the type $[Li(o\text{-}C_6H_4PPh_2NR)_2]\cdot Et_2O$ (R = Ph, 2,6-$Me_2C_6H_3$, 3,5-$Me_2C_6H_3$, and 2,6-$^iPr_2C_6H_3$) were used to obtain complexes of the general formula $Rh(o\text{-}C_6H_4PPh_2NR)(cod)$, which in the case of R = Ph oxidatively added CH_2Cl_2 yielding $(o\text{-}C_6H_4PPh_2NPh)(CH_2\text{-}o\text{-}C_6H_4PPh_2NPh)Rh(\mu\text{-}Cl)_2Rh(cod)$ (Scheme 49).[504]

A series of chiral thioether–phosphite ligands derived from 1,2-*O*-isopropylidenexylofuranose were synthesized. Reaction of these chiral ligands with $[M(cod)_2]BF_4$ (M = Ir, Rh) yielded the complexes $[M(cod)(P\text{–}S)]BF_4$.[505] The synthesis of rhodium complexes of the type $M(Cab^{P,S})(cod)$ ($Cab^{P,S}$ is the P,S-chelate ligand *P*,*S*-$[SC_2B_{10}H_{10}PPh_2]$) was described.[95] Similarly, the *N*,*P*-chelating *o*-carboranylaminophosphine ligand $Cab^{N,P}$ [$Cab^{N,P}$=*o*-$C_2B_{10}H_{10}(CH_2NMe_2)(PPh_2)$-*N*,*P*] was prepared from *o*-carboranylamine $LiCab^N$ [Cab^N=*o*-$C_2B_{10}H_{10}(CH_2NMe_2)$-*N*] and chlorodiphenylphosphine. The reaction of $[M(cod)(solv)_2]BF_4$ (M = Rh, Ir) with $Cab^{N,P}$ afforded complexes of the type $[Rh(Cab^{N,P})(cod)]BF_4$ **398**.[506]

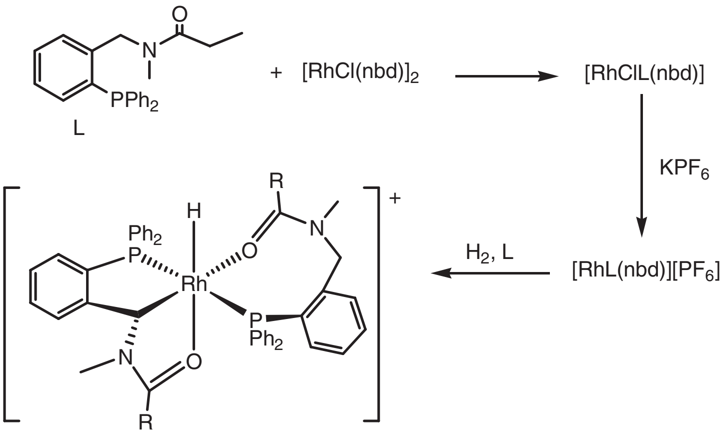


398

The phosphine *N*-methyl-*N*-propionyl-2-(diphenylphosphino)benzylamine, L, reacting with the precursor complex $[Rh(nbd)L]PF_6$ and molecular hydrogen underwent chelate-assisted C–H bond activation at the benzylic



Scheme 49

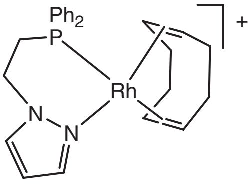


Scheme 50

position, quantitatively yielding the five-membered chelate complex *trans*-[RhH(P(C_6H_4-*o*-($CH_2N(CH_3)COCH_2CH_3$))(C_6H_5)$_2$)(P(C_6H_4-*o*-(CHN(CH_3)$COCH_2CH_3$))(C_6H_5)$_2$)]PF_6 (Scheme 50).[336]

The trifunctional ligand 1-(diphenylphosphino)-2-ethoxy-1-(2-pyridyl)ethane (pepye) allowed the preparation of the complex [Rh(cod)(pepye)]ClO_4, in which the ligand is *P*,*N* bonded.[507] A series of chiral non-racemic bis(phosphinites) derived from (*R*,*R*)-*trans*-2,5-tetrahydrothiophenedimethanol was prepared. This allowed the preparation of complexes of the type $[Rh(P,S)(cod)]^+$ in which the ligand is P,S coordinated with a phosphine arm unbound.[508] P,S and P,O-chelating phosphines like $Ph_2P(CH_2)_nP(O)Ph_2$ ($n=1$ (dppmO), $n=2$ (dppeO)) and $Ph_2P(CH_2P(S)Ph_2$ (dppmS) allowed the preparation of $[Rh(P,S)(cod)]^+$ and $[Rh(P,O)(cod)]^+$ complexes.[509] Other chiral P,S-coordinated ligands were also described and coordinated to Rh–cod and Rh–nbd fragments.[510]

The chiral complexes [Rh(C_5H_4N(2-CH_2)PPhMe)(cod)]BF_4 and [Rh{C_5H_3N(2-Me)(6-CH_2PPh_2}(cod)]BF_4, in which the phosphine is P,N–coordinate, were described.[511] Chiral phosphines were also obtained by the introduction of an oxazoline unit, as in the case of the coordination of several oxazolinylferrocenylphosphines, yielding [Rh(P,N)(cod)]BF_4 (P,N = oxazolinylferrocenylphosphine ligand).[512] Other chiral bidentate *N*-*N′*- and *N*-*P*- donor ligands gave rhodium–cod complexes of the type [Rh(L_2)(ligand)]PF_6 (L_2 = cod or PPh_3), which were fully characterized and were anchored on modified zeolites in order to study their catalytic properties.[513] Chiral diphosphinite ligands derived from (2*S*,4*R*), (2*S*,4*S*)-1-benzyl-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)pyrrolidinylmethanol and (2*S*,4*R*), (2*S*,4*S*)-1-(3-triethoxysilyl)propylaminocarbonyl-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)pyrrolidinylmethanol were prepared in high yields and reacted with [Rh(μ-Cl)(cod)]$_2$ to yield cationic $[Rh(diphosphinite)(cod)]^+$ complexes which were also heterogenized on zeolites.[514] The cationic Rh(I) complex with the mixed P,N-donor bidentate ligand 1-(2-diphenylphosphino)ethylpyrazole (PyP) $[Rh(PyP)(cod)]^+$ **399**, was synthesized and characterized by NMR.[515]

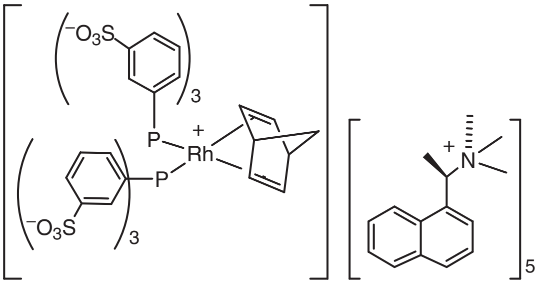


399

A series of rhodium(I) complexes [RhClL* (nbd)] (L* = chiral cyclic phosphonite with a fused 1,4-dioxane or cyclobutane ring in the backbone) was synthesized via the corresponding borane–phosphonite adducts.[516]

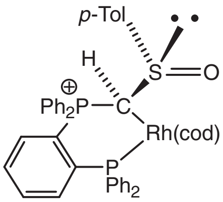
The ligand P(CH_2CH_2Py)$_nPh_{3-n}$ (PePy$_n$; Py = 2-pyridyl; $n=1$, 2) allowed a series of complexes of the type $[Rh(diene)(PePy)]^+$ and $[Rh(diene)(PePy_2)]^+$ (diene = tetrafluorobenzobarrelene (tfb), cod, and nbd). The coordination of PePy afforded square-planar species while $PePy_2$ formed pentacoordinated compounds.[517] The ligand 2,5-bis[3-(diphenylphosphino)propyl]thiophene (PSP) was obtained and reacted with Rh(acac)(cod) in the presence of perchloric acid, giving the complex [Rh(PSP)(cod)]ClO_4. Its low solubility suggests a polymeric structure.[89] Highly charged phosphine ligands allowed the preparation of achiral complexes with chiral counter ions.

Tristriphenylphosphinosulfonate (TPPS) allowed the formation of the zwitterionic complexes [Rh(nbd)(TPPS)$_2$][(*R*)-*N*,*N*-dimethyl-1-(naphtyl)ethylammonium]$_5$ **400** and [Rh(nbd)(TPPS)$_2$]BF$_4$ [(*R*)-*N*,*N*-dimethyl-phenethylammonium]$_6$.[518]

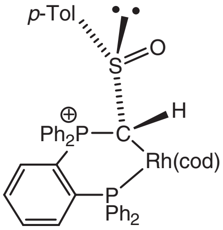


400

A phosphine–phosphonium ylide ligand bearing a chiral sulfinyl moiety was prepared by the reaction of (*o*-diphenylphosphinophenyl)diphenylphosphonium methylide with (*S*)-menthyl *p*-tolylsulfinate. Reaction of this ylide with [Rh(cod)$_2$]PF$_6$ gave stable cationic disymmetrically P,C-chelated rhodium complexes **401** and **402** with an asymmetric ylidic carbon atom anchored to the metal center.[519]

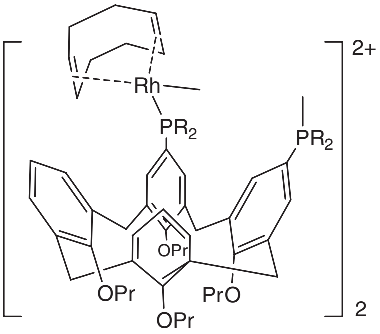


401



402

Ligands of the type 1,2- and 1,3-diphosphinated calyx[4]arenes were coordinated to Rh–cod complexes affording efficient catalysts [**403** and **404**] for hydroformylation of terminal olefins.[520] The chiral versions of these phosphines were used in the preparation of Rh–cod complexes used in asymmetric hydrogenation of olefins.[521]



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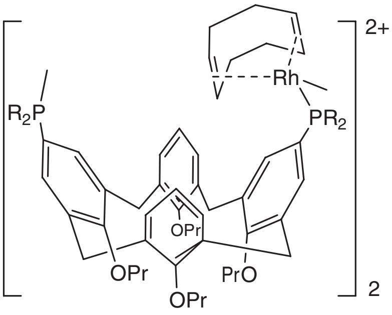
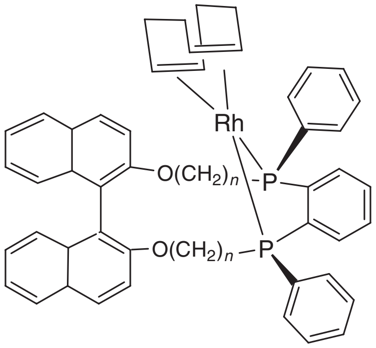


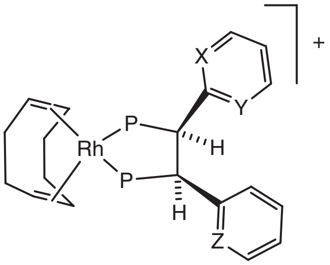
404

The diphosphine ligand 1,3-bis(diphenylphosphino)propane (dppp) allowed the preparation of the complex [Rh(SnCl$_3$)(1,5-cyclooctadiene)(dppp)], which has a distorted trigonal-bipyramidal geometry. [522] Another diphosphine ligand derived from β-cyclodextrin was prepared by the reaction of LiPPh$_2$ and 6A,6B-bis(trifluoromethanesulfonyl)-permethylated-β-cyclodextrin. This ligand allowed the preparation of a compound of formula [Rh(PP)(cod)]BF$_4$ (PP = 6A,6B-bis(diphenylphosphino)-6A,6B-dideoxy-permethylated-β-cyclodextrin).[523] The rhodium complex of (*S*,*S*)-1,2-bis(*tert*-butylmethylphosphino)ethane (BisP*), [Rh(BisP*)(nbd)]BF$_4$, was studied by multinuclear NMR.[524] The phosphonium methylide of (*R*)-BINAP acts as a novel chiral dissymmetric chelating ligand in the stable [Rh(cod)(BINAPCH$_2$)]$^+$ complex.[337] Other macrocyclic 1,1′-binaphthyl-based diphosphines (OC$_n$P) afforded mononuclear complexes [Rh(OC$_n$P)(cod)]BF$_4$ **405** by adding macrocyclic ligands (OC$_n$P, $n = 4$–6) to a dichloromethane solution of [Rh(cod)$_2$]BF$_4$.[525]



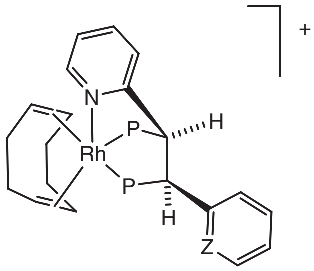
405

The P,P,P tridentate phosphines (*R*)- and (*S*)-1,3-bis(diphenylphosphino)-2-((diphenylphosphino)methyl)-1-phenylpropane ((*R*)- and (*S*)-heliphos) were obtained and reacted with [Rh(nbd)$_2$]ClO$_4$, yielding [Rh((*R*)-heliphos)(nbd)]ClO$_4$.[526] *meso*-[Ph$_2$PCH(Ph)CH(Ph)PPh$_2$], *meso*-[Ph$_2$PCH(pyr)CH(pyr)PPh$_2$], *erythro*-[Ph$_2$PCH(Ph)CH(pyr)PPh$_2$], *rac*-[Ph$_2$PCH(pyr)CH(pyr)PPh$_2$], *threo*-[Ph$_2$PCH(Ph)CH(pyr)PPh$_2$], and *threo*-[Ph$_2$PCH(Ph)CH(pym)PPh$_2$], [pyr = 2-pyridyl, pym = 2-pyrimidyl] reacted with [Rh(μ-Cl)(cod)]$_2$ to give cationic rhodium(I) complexes [Rh(cod){L}]$^+$ [**406**, **407** and **408**, L = diphosphine ligand]. The ligands can adopt both P-P′- and P-P′-N-coordination.[527]



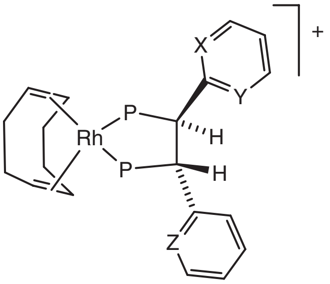
X	Y	Z	*Stereochemistry*
CH	CH	CH	*meso*

406



Z	*Stereochemistry*
N	*meso*
CH	*erythro*

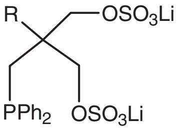
407



X	Y	Z	*Stereochemistry*
N	CH	N	*rac*
N	CH	CH	*threo*
N	N	N	*threo*

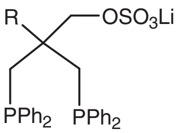
408

Cyclic sulfates reacted with LiPPh$_2$ to form a series of new amphiphilic or water-soluble ligands: monotertiary phosphines with one or two alkylene sulfate chains **409** and ditertiary phosphines with one or two hydrophilic tails attached to bridgehead carbon atom **410**. The coordination to Rh^{I} complexes afforded water-soluble Rh(sulfatephos)$_2$(cod) and Rh(sulfatediphos)(cod).[528]



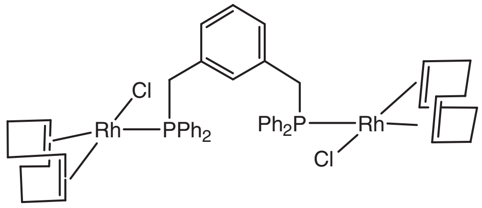
409

R = Me, Et

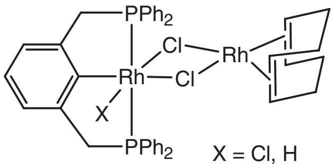


410

The [Rh(dppoo)(cod)]$^+$ cation (dppoo = (Ph$_2$PCH$_2$CH$_2$OCH$_2$)$_2$) reacted with chloroform at room temperature giving [RhCl$_2$(dppoo)]$^+$, in which the ligand is P,P,O,O-coordinated.[108] Reaction of 1,3-(PPh$_2$CH$_2$)$_2$C$_6$H$_4$ (PCHP) with [Rh(μ-Cl)(cod)]$_2$ in isopropanol produced a mixture of dinuclear complexes [RhCl(cod)]$_2$(μ_2-PCHP) **411**, RhH(PCP)(μ-Cl)$_2$Rh(cod) **412**, and [RhHCl(PCP)]$_2$(μ_2-PCHP).[311]



411



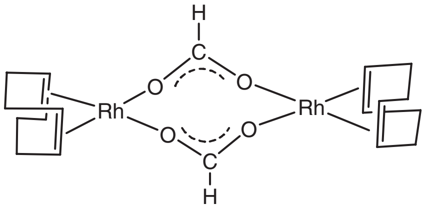
412

The coordination of a series of mixed donor tripod ligands of the type $RCH_2C(CH_2X)(CH_2Y)(CH_2Z)$ (X, Y, Z = PPh_2, NR_2, pyrazol-1-yl; R = H, OH) on Rh(cod) complexes was studied by NMR spectroscopy and X-ray diffraction. In contrast to the parent $MeC(CH_2PPh_2)_3$, these potential tripod ligands were found to coordinate in a bidentate mode.[529] Other chiral tripod ligands $X_2POCH(CH_2P(Ph)_2)(CH_2PR_2)$ (X_2 = 2,2′-biphenoxy-; PR_2 = P(4-Me-$C_6H_4)_2$, dibenzophospholyl) and $MeC(CH_2P(Ph)_2)(CH_2PR'_2)(CH_2PR''_2)$ (PR'_2 = P(3,5-Me_2-$C_6H_3)_2$) reacted with $[Rh(\mu\text{-}Cl)(cod)]_2$ yielding tripod rhodium cod complexes with tripod ligand coordinated by all three donor groups.[530] Other similar tripodal groups were also investigated on Rh complexes with the cod ligand.[531,531a,531b]

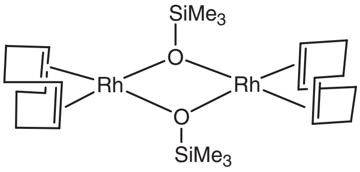
The peralkylated arsino(phosphino)methanes $R_2AsCH_2PR_2$ (R = *i*Pr, Cy) reacted with $[Rh(\mu\text{-}Cl)(cod)]_2$ by cleavage of the chloro bridges to give the mononuclear compounds RhCl(cod)(κ-*P*-$R_2PCH_2AsR_2$).[532]

7.02.3.4.1.(ii) Compounds with groups 16 and 17 ligands

Formate-bridged complexes of the type $[Rh(\mu\text{-}\kappa^2O,O'\text{-}HCO_2)(cod)]_2$ **413** were obtained. Reaction with diphosphines such as $R_2P(CH_2)_2PR_2$ (R = Ph, ^{i}Pr, Cy) induced hydrogen transfer to give η^3-cyclooctadienyl complexes.[533] The rhodium(I) complexes of general formula $[Rh(\mu\text{-}OSiMe_3)(diene)]_2$, [diene = cod **414** or nbd] were synthesized in the reaction of $[Rh(\mu\text{-}Cl)(diene)]_2$ with sodium trimethylsilanolate.[534]

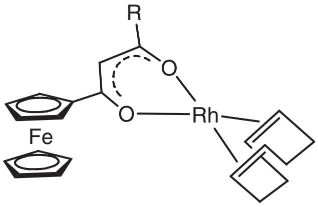


413



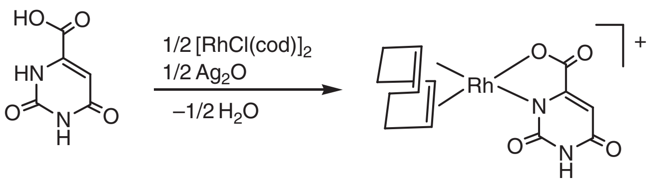
414

The synthesis and complete characterization of the chloranilato anionic rhodium complexes $(NHEt_3)[Rh(C_6Cl_2O_4)(cod)]$ and $(NHEt_3)[Rh(C_6Cl_2O_4)(CO)_2]$ were reported.[28] The chloroanilate dianion chelates the metal through the 1,2-oxygen atoms. Dimetallic and tetrametallic Rh(cod) species were also reported with the same ligand.[535] A series of ferrocenyl-based β-diketones like 1-ferrocenyl-4,4,4-trifluorobutane-1,3-dione, 4,4,4-trichloro-1-ferrocenylbutane-1,3-dione, 1-ferrocenylbutane-1,3-dione, 1-ferrocenyl-3-phenylpropane-1,3-dione, and 1,3-diferrocenylpropane-1,3-dione were obtained and provided Rh(β-diketonate)(cod) **415** by reaction with $[Rh(\mu\text{-}Cl)(cod)]_2$.[536,536a,536b]



R = CH_3, CH_3CH_2, CCl_3, CF_3, Ph

415



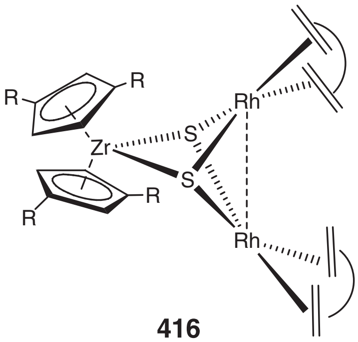
Scheme 51

The complexes [NEt$_3$H][Rh(HL)(cod)] (H$_3$L = 2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylic acid, orotic acid) were prepared by the reaction between [Rh(μ-Cl)(cod)]$_2$ and orotic acid in dichloromethane in the presence of Ag$_2$O and NEt$_3$ (Scheme 51).[537]

In order to elucidate the nature and the structure of the elusive (CO)$_2$Rh(Ph$_3$SiO)$_2$Rh(cod) complex, the compound (CO)$_2$RhCl$_2$Rh(cod) was synthesized and structurally characterized by *ab initio* X-ray powder diffraction.[538]

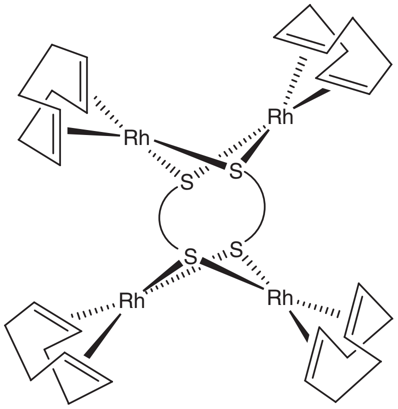
The complexes of rhodium(I) Rh(Q″)(diene) (where HQ″ = 1-phenyl-3-methyl-4-acetylpyrazol-5-one and diene = cod, nbd, or 1,5-hexadiene) were synthesized and characterized. Rh(Q″)(cod) reacted with 4,5-dimethyl-1,10-phenanthroline (Me$_2$Phen) and 2,2′-bipyridyl (Bipy) yielding the cationic derivatives [Rh(Me$_2$Phen)(cod)](Q″)(H$_2$O), [Rh(Q″)(Bipy)(cod)](H$_2$O) upon displacement of the (Q″)$^-$ donor from the coordination sphere of the metal center.[539] Starting from [Rh(μ-OH)(cod)]$_2$ several new complexes were obtained, for example, with HF (Et$_3$N·3HF) or 50% HF (in THF), [Rh$_3$(μ-OH)$_2$(cod)$_2$]HF$_2$ was produced.[540] Cp*TaMe$_4$ reacted with 4 equiv. of [Rh(μ-OH)(cod)]$_2$ yielding complexes Cp*Ta(μ-O)$_4$[Rh(cod)]$_4$.[541] The reactions of [Rh(μ-OMe)(cod)]$_2$ with *p*-tolylamine, α-naphthylamine, and *p*-nitroaniline gave complexes with mixed bridging ligands, [Rh(cod)]$_2$(μ-NHAr)(μ-OMe).[542] Similarly, the related complexes [Rh(cod)]$_2$(μ-NHAr)(μ-OH) were prepared from the reactions of [Rh(μ-OH)(cod)]$_2$ with *p*-tolylamine, α-naphthylamine, and *p*-nitroaniline. The reactions of [Rh(μ-OR)(cod)]$_2$ (R = H, Me) with *o*-nitroaniline gave the mononuclear complex Rh(*o*-NO$_2$C$_6$H$_4$NH)(cod).[542] Benzylthiourea (Hbztu) acts as a monodentate ligand and afforded the complex of formula RhCl(Hbztu)(cod) which was immobilized onto silica xerogels producing recyclable hydroformylation catalysts.[543] Thiophene, 2-methylthiophene, and 2,5-dimethylthiophene were used for the preparation of S-coordinated monometallic Rh–cod complexes, while benzothiophene and dibenzothiophene preferred an η^6-arene coordination of the S-containing ligand.[544]

Homo- and heterodinuclear complexes of general formulas Rh$_2$(μ-SPPh$_2$)(μ-Cl)(diene)$_2$ (diene = cod, tetrafluorobenzobarrelene) and RhPd(μ-SPPh$_2$)(μ-Cl)(diene)(η^3-C$_3$H$_5$) (diene = cod, nbd), containing one chloride anion and one thiophosphinito group as bridging ligands, were synthesized by redistribution reactions starting from the corresponding homo bridged compounds Rh$_2$(μ-SPPh$_2$)$_2$(diene)$_2$, Rh$_2$(μ-Cl)$_2$(diene)$_2$, or Pd$_2$(μ-Cl)$_2$(η^3-C$_3$H$_5$)$_2$.[545] Reactions of the zirconium–sulfide metallocene anion [Cp$^{tt}{}_2$ZrS$_2$]$^{2-}$ (Cp^{tt} = η^5-1,3-di-*tert*-butylcyclopentadienyl) with [Rh(μ-Cl)(diene)]$_2$ gave the d^0–d^8 complexes Cp$^{tt}{}_2$Zr(μ_3-S)$_2${Rh(diolefin)}$_2$ **416** (diene = nbd, cod) with a triangular ZrM$_2$ core capped by two symmetrical μ_3-sulfido ligands.[546]



416

Addition of the atropisomeric racemic sulfur compound 4,4′-biphenantrene-3,3′-dithiol(H$_2$biphes) to [Rh(μ-OMe)(cod)]$_2$ afforded dithiolate-bridged complexes of the type [Rh$_2$(μ-biphes)(cod)$_2$]$_n$ (n = 1, 2).[547] Other monometallic[548] and bimetallic[549,549a] dithiolate compounds were also obtained. Dithiocarbamate-[550] and diaminoanthraquinonate-bridging ligands[60] also resulted as good building blocks for the preparation of dimetallic Rh–cod complexes. Other thiolate-bridged complexes are, for example, $Rh_4\{\mu\text{-}S(CH_2)_2S\}_2(cod)_4$ **417** and $Rh_2\{\mu\text{-}S(CH_2)_2S\}(cod)_2$ **418**.[551]



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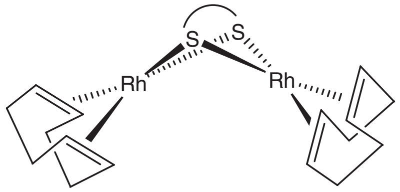
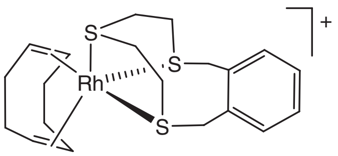


S–S = μ-biphes

418

Complexes with 2,5,8-trithia[9]-*o*-cyclophane (TT[9]OC) and 5-oxa-2,8-dithia[91-*o*-cyclophane (ODT[9]OC) were obtained in the form of $[Rh(TT[9]OC)(cod)]BF_4$ **419** and $[Rh(ODT[9]OC)(cod)]BF_4$ **420** in which the ligand is κ^3-S,S,S- and κ^2-S,S-coordinated.[552]



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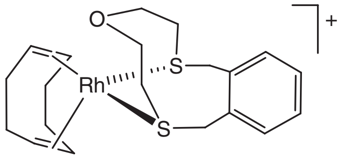
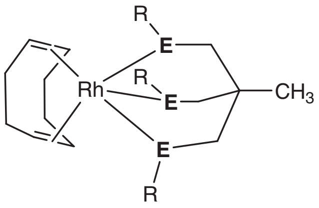


420

The preparation of a new ferrocenyl phosphodithioate ligand allowed the preparation of the κ^2-S,S complex $Rh(cod)[(C_5H_5)Fe(C_5H_4PS_2OCH_2C_6H_4N_3)]$.[553] The rhodium amide complex $Rh(NHC_6H_4\text{-}o\text{-}SMe)(cod)$ was synthesized by reacting $[Rh(\mu\text{-}Cl(cod)]_2$ with $LiNHC_6H_4\text{-}o\text{-}SMe$. Thermolysis of this complex, at 100 °C, produced a new rhodium thiolate complex $[Rh(\mu\text{-}SC_6H_4\text{-}o\text{-}NHMe)(cod)]_2$.[554] Chiral ligands containing both nitrogen and sulfur such as *N,N′*-bis(sulfinyl)amidine were also prepared in order to obtain the complex Rh(N,S)(cod) (N,S = *N,N′*-bis(sulfinyl)-amidine).[555] Reaction of the dinuclear complex $Rh_2(\mu\text{-}HBzimt)_2(cod)_2$ (HBzimt = benzimidazole-2-thiolate) with $[Rh(\mu\text{-}Cl)(cod)]_2$ gave the neutral tetranuclear complex $Rh_4(\mu\text{-}HBzimt)_2Cl_2(cod)_4$ in dichloromethane and the trinuclear cationic complex $[Rh_3(\mu\text{-}HBzimt)_2(cod)_3]Cl$ in methanol, respectively. The S-atom of the ligand bridges two Rh atoms, while the nitrogen atom binds a third Rh fragment in both trimetallic and tetrametallic structures. The complexes $Rh_4(\mu\text{-}HBzimt)_2Cl_2(diene)_4$ (diene = tetrafluorobenzobarrelene (tfbb)) were also obtained.[556] The same ligand can afford mono- and dimetallic species of the type $RhCl(H_2Bzimt)(cod)$ and $[Rh(\mu\text{-}Bzimt)(cod)]_2$.[557] Starting from the chiral "ligand" $Pt_2(\mu\text{-}S)_2\{(-)\text{-}diop\}$ and $[Rh(\mu\text{-}Cl)(cod)]_2$, the trinuclear complex $[Pt_2Rh(\mu_3\text{-}S)_2\{(-)\text{-}diop\}_2(cod)]Cl$ was synthesized.[558] The reaction of $[Rh(\mu\text{-}Cl)(cod)]_2$ with two molar equivalents of L^3 ($L^3 = MeC(CH_2ER)_3$, E = Se, R = Me; E = Te, R = Me or Ph) at room temperature in CH_2Cl_2 afforded the species $[Rh(cod)(L^3)]^+$ **421**. These complexes are the first described seleno- or telluro-ether complexes of Rh^I.[559]



E = Se, Te; R = Me, Ph

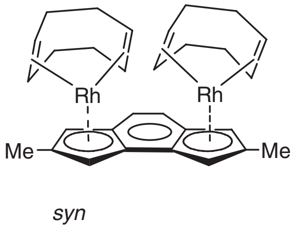
421

Fluoro complexes of Rh(I)-containing cyclooctadiene were reported and the reactivity of the Rh–F bond studied, showing significant differences from other Rh–halogen bonds.[560]

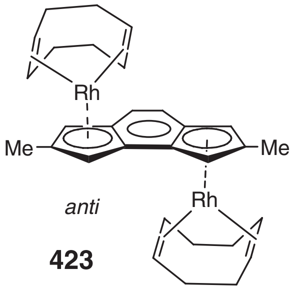
7.02.3.4.1.(iii) Other cod, nbd, and tfb complexes

Rhodium η^5-complexes bearing an indenyl-type fullerene ligand, Rh{$C_{60}(PhCH_2)_2Ph$}(cod), Rh{$C_{60}(PhCH_2)_2Ph$}(nbd), and Rh($C_{70}Ph_3$)(cod), were synthesized from the corresponding fullerene tri-adducts (Scheme 52).[520]

Heterobimetallic ferrocenyl(indenyl) rhodium–nbd complexes were also described.[156] The optically active complexes Rh{(−)-(2-menthylindenyl)}(cod) and Rh(−)-(2-menthyl-4,7-dimethylindenyl)(cod) were obtained and described.[458] The monometallic complexes with Rh(cod) of 5-hydro and 7-hydro-*s*-indacenide, where the indacenide is η^5-coordinated, were synthesized and structurally characterized.[561] The ligands 1,5- and 1,7-dihydro-*s*-indacene, 2,6-dimethyl-1,5-dihydro-*s*-indacene, and 2,7-dimethyl-1,6-dihydro-*as*-indacene provided similar complexes.[562] Indenyl heterometallic complexes containing the $Cr(CO)_3$ and Rh–nbd fragments were also described.[563] The Rh(cod) homobimetallic complexes of *s*-indacene-diide, 2,6-dimethyl-*s*-indacene-diide, *as*-indacene-diide, and 2,7-dimethyl-*as*-indacene-diide were synthesized from the dilithium salts of the dianions and metal dimers [Rh(μ-Cl)(diene)]$_2$ (diene = cod, nbd) as mixtures of *syn*- [422 with 2,6-dimethyl-*s*-indacene-diide] and *anti*-[423 with 2,6-dimethyl-*s*-indacene-diide] isomers.[564]

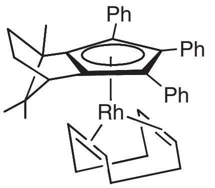


422



423

The synthesis of phenethyltetraphenylcyclopentadiene allowed the preparation of the chiral complex Rh{$C_5Ph_4CH(Me)Ph$}(cod).[176] Chiral-annulated cyclopentadienyl ligands afforded the preparation of complexes such as (η^4-cycloocta-1,5-diene)[η^5-1,2,3-triphenyl-4-methyl-7-isopropyl-1H-indenyl]rhodium, as a mixture of the *exo*- 424 and *endo*-425 isomers, together with a chiral indenyl complex 426, which did not show any optical activity.[565]



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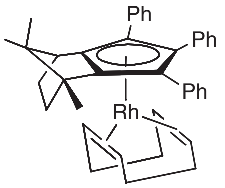

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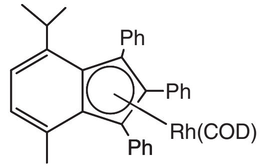

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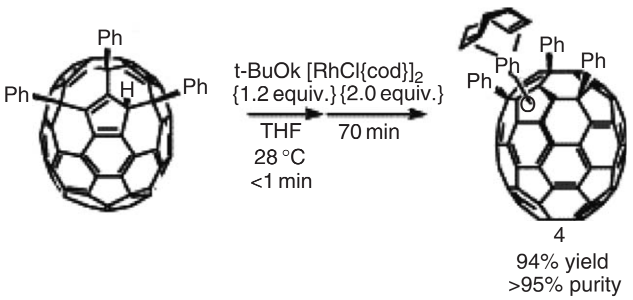
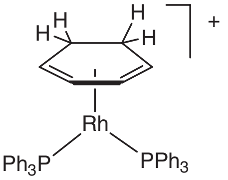


Scheme 52

Optically active complexes of Rh containing the chiral menthyl-substituted indenyl ligands (−)-2-menthylindene and (−)-2-menthyl-4,7-dimethylindene were described. Metathetic reaction of the chiral lithium salts of these indenyl systems with the appropriate starting materials of Rh yielded the complexes (−)-(2-menthylindenyl)Rh(cod)] and [(−)-(2-menthyl-4,7-dimethylindenyl)Rh(cod).[458]

7.02.3.4.2 Conjugated bis-alkenes

Treatment of the arene-bridged dimer [Rh{(η^6-C_6H_5)PPh_2}(PPh_3)]$_2$[*closo*-$CB_{11}H_6Br_6$]$_2$ with 8 equiv. of cyclohexene afforded [Rh(η^4-C_6H_8)(PPh_3)$_2$][*closo*-$CB_{11}H_6Br_6$] **427** with the concomitant formation of 1 equiv. of cyclohexane, while 1-methylcyclohexene and 4-methylcyclohexene both gave 2-methylcyclohexa-1,3-diene complexes **428**.[439]



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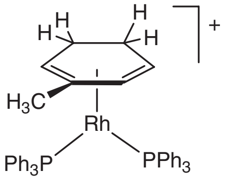
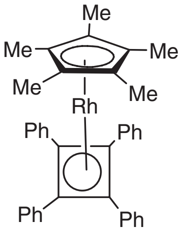


428

The Cp*Rh(η^2-NO_3)(OTf)-mediated cyclodimerization of alkynes afforded the preparation of (η^4-cyclobutadiene)–rhodium(I) intermediates **429 and 430**, which were isolated and characterized.[183]



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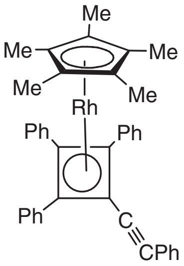
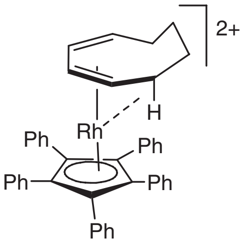


430

The redox properties of (η^5-C_5Ph_5)Rh(1,5-cod) and (η^5-C_5Ph_5)Rh(1,3-cod) were investigated by cyclic voltammetry and bulk coulometry. Both compounds displayed a four-membered electron-transfer series involving complexes of overall 2+, 1+, 0, and 1− charges. The 19-electron complexes [(η^5-C_5Ph_5)Rh(cod)]$^-$ are short-lived, rapidly releasing [C_5Ph_5]$^-$. The 1,3-cod ligand imparts an unexpected thermodynamic stabilization of the higher Rh oxidation states. The increasing stabilization of the Rh(II) and Rh(III) **431** complexes was ascribed to the progressive formation of an agostic interaction between the metal atom and the hydrogen on carbon 5 of the 1,3-cyclooctadiene ring.[566] The parent *o*-quinone methide (*o*-QM) and its dimethyl derivative were stabilized by complexation to Cp*Rh. Precursor oxodienyl rhodium complexes [Cp*Rh(η^5-2-alkyl-oxodienyl)]BF_4 were isolated and fully characterized. Selective alkyl deprotonation by *t*-BuOK in CH_2Cl_2 provided the first series of rhodium-*o*-QM complexes Cp*Rh(η^4-(R)$_2C_7H_4O$) **432** (R = H, Me).[567]



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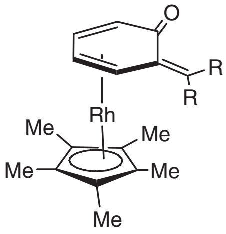
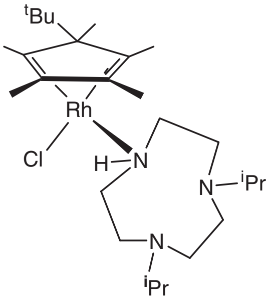


R = H, Me

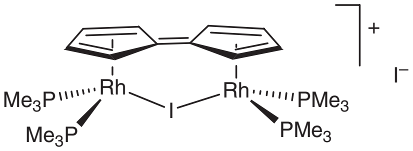
432

Addition of ^{t}BuLi to the η^1-triazacyclononane–rhodium(I) complex Cp*RhCl$_2$(η^1-^{i}Pr$_2$tacnH) afforded a change of binding on the Cp*, which converted into an η^4-C$_5$Me$_5{}^{t}$Bu ligand in RhCl(η^1-^{i}Pr$_2$tacnH)(η^4-C$_5$Me$_5{}^{t}$Bu) **433**.[568]



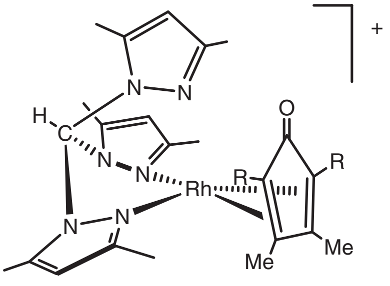
433

Reaction of perfluoroisopropyl iodide with CpRh(PMe$_3$)$_2$ generated a perfluorocarbanion intermediate along with [CpRh(PMe$_3$)$_2$I]$^+$, which reacted to give fluoroalkylation of the cyclopentadienyl ring. When the intermediate fluorocarbanion was trapped by CH$_3$OD to give (CF$_3$)$_2$CFD, the resultant methoxide anion reacted with [CpRh(PMe$_3$)$_2$I]$^+$ to give a dinuclear fulvalene complex **434**.[569]



434

The complex [Rh(CO)$_2${HC(pz′)$_3$}]PF$_6$, {HC(pz′)$_3$ = tris(3,5-dimethylpyrazolyl)methane}, reacted with MeC≡CR (R = Me or Et), to form the κ^2-square-planar complexes [Rh{η^4-C$_4$Me$_2$R$_2$C(O)}{HC(pz′)$_3$}]PF$_6$ **435** (R = Me, Et) in which the cyclopentadienone ligands are coordinated via two Rh–monoalkene bonds.[43]

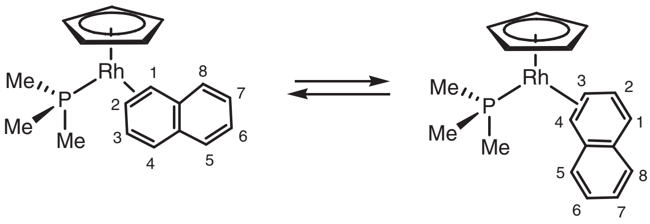


R = Me, Et

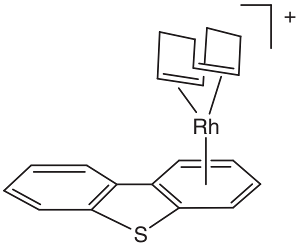
435

7.02.3.5 η-Arene Complexes

Benzothiophene and dibenzothiophene afforded an η^6-arene coordination of the S-containing ligand providing the preparation of cationic monometallic Rh–cod complexes **436** and **437**.[544]



Scheme 53



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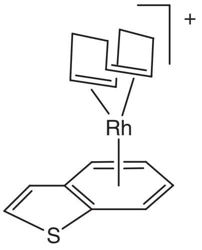
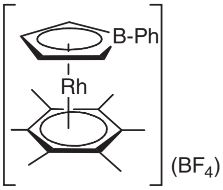


437

Ultraviolet irradiation of $CpRh(C_2H_4)_2$ in hexane in the presence of naphthalene or anthracene yielded the $CpRh(\eta^4$-arene) complexes.[354,570] The structure and the dynamic exchange in rhodium η^2-naphtalene and η^2-phenantrene complexes $CpRh(PMe_3)(\eta^2$-arene) (arene = naphtalene, phenantrene) were studied (Scheme 53).[571]

Reaction of $(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2CH_2PPh_2)RhH_2$ with C_6F_6 gave the η^2-complex $[(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2CH_2PPh_2)Rh(\eta^2\text{-}C_6F_6)]$ which was structurally characterized.[165] The crystal structure of $Cp^*Rh(PMe_3)(\eta^2\text{-}C_6F_6)$ was determined and compared to other $(\eta^2\text{-}C_6F_6)$ complexes of Re.[572] Reaction of $CpRh(PPh_3)(C_2H_4)$ with hexafluorobenzene yielded $CpRh(PPh_3)(\eta^2\text{-}C_6F_6)$.[149] The oxidative addition of benzene in the η^2-arene complex $Cp^*Rh(PMe_3)(\eta^2\text{-}C_6H_6)$ and the activation parameters for this reaction were determined.[331] The compound $[Rh(\eta^6$-naphtalene)(cod)]SbF_6 was obtained and its crystal structure determined by X-ray diffraction methods. The compound was found to be highly efficient in [5 + 2] cycloaddition reactions.[573]

The heterocubane $[Rh(\mu_3\text{-}I)(C_4H_4BPh)]_4$ reacted with Ag^+ salts in acetonitrile to give the labile salt $[Rh(NCMe)_3(C_4H_4BPh)]BF_4$. This salt reacted with hexamethylbenzene and mesitylene giving the arene complexes $[Rh(C_4H_4BPh)(C_6Me_6)]BF_4$ **438** and $[Rh(1,3,5\text{-}C_6H_3Me_3)(C_4H_4BPh)]BF_4$ **439**, respectively. $[Rh(NCMe)_3(C_4H_4BPh)]BF_4$ loses acetonitrile under vacuum producing the polymeric salt *catena*-$[\{Rh(\mu,\eta^5{:}\eta^6\text{-}C_4H_4BPh)\}BF_4]_x$ **440**.[574]



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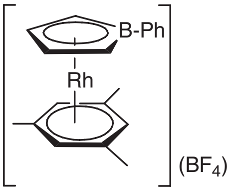

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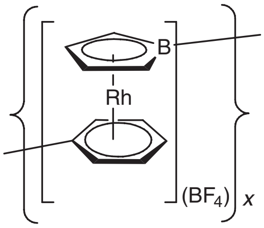
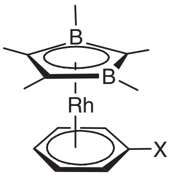


440

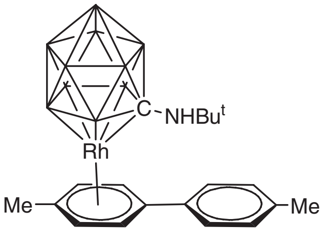
The reactions between $[Rh(\mu\text{-}Cl)(C_2H_4)_2]_2$ and 2,3-dihydro-1,3-diborole derivatives in toluene and benzene yielded sandwich η^6-arene-η^5-dihydro-diborolyl-rhodium complexes **441**, which were fully characterized.[575]



X = H, Me

441

The rhodium sandwich monocarbollide complexes Rh(η^6-arene)(η^5-7-NHBu^t-7-CB$_{10}$H$_{10}$) **442** and **443** (arene = C_6H_5Me, $C_6H_3Me_3$-1,3,5, $MeC_6H_4C_6H_4Me$-4,4,[2$_2$](1,4)-$C_{16}H_{16}$) were prepared from reactions between 1 : 1 molar mixtures of the arenes and RhCl(PPh_3)(η^5-7-NH$_2$Bu^t-7-CB$_{10}$H$_{10}$)[576] in CH_2Cl_2 in the presence of $AgBF_4$, and their crystal structures were determined.[577]



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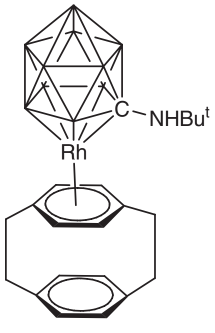
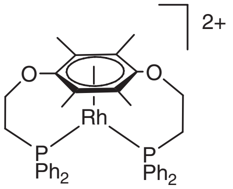


443

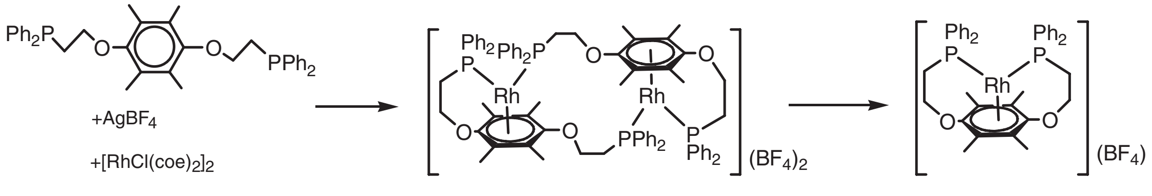
A series of new bis-1,4-phosphinoethoxyaryl hemilabile ligands of the form (1,4-($Ph_2PCH_2CH_2O$)$_2$-arene), where the nature and substituent pattern of the central arene ring is systematically varied, was reported. The reaction of these ligands with Rh(I) starting materials afforded a series of η^6-arene Rh(I) complexes.[578] For example, the phosphine 1,4-($PPh_2CH_2CH_2O$)$_2$-2,3,5,6-((CH_3)$_4C_6$) reacted with [Rh(μ-Cl)(coe)$_2$]$_2$ to give two different types of condensed arene-type macrocycles (Scheme 54).[91]

A series of similar Rh(I) bis(phosphine), η^6-arene, piano-stool complexes was reported, and the electrochemical investigations allowed a study of the electronic parameters that kinetically and thermodynamically stabilize the corresponding Rh(II) species. [579]Symmetrical and unsymmetrical bis(phosphino)methanes $R_2PCH_2P(R^1)_2$, and the arsino(phosphino) analogs, afforded the half-sandwich-type complexes [Rh(η^6-C_6H_6)(κ^2P,P'-$R_2PCH_2P(R^1)_2$)]PF_6.[580] The ligand 1,4-bis[4-(diphenylphosphino)butyl]-2,3,5,6-tetramethylbenzene was used to synthesize a mononuclear Rh(II) complex [(η^1:η^6:η^1-1,4-bis[4-(diphenylphosphino)butyl]-2,3,5,6-tetramethylbenzene)Rh](PF_6)$_2$ **444** in a two-legged piano-stool geometry.[581]

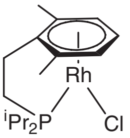


444

Aryl-functionalized phosphines of the general composition $R_2P(CH_2)_n$(aryl), with bulky substituents R at the phosphorus atom, reacted with olefin–rhodium(I) compounds to give complexes in which the phosphine behaves either as 2-electron or (2 + 6)-electron donor ligand (P-donor, η^6-arene). The aryl moiety is weakly coordinated and can be replaced by CO, acetonitrile, or H_2 without breaking the metal–phosphorus bond.[83] Similarly, the bulky functionalized phosphine 2,6-$Me_2C_6H_3CH_2CH_2P$*t*Bu$_2$ allowed the preparation of the half-sandwich complex RhCl(η^6-2,6-$Me_2C_6H_3CH_2CH_2P$*t*Bu$_2$-κP) **445**. Removal of the Cl ligand from the complex provided a good method to obtain the corresponding CO **446**, alkene **447**, and alkyne **448** cationic complexes.[582]



Scheme 54



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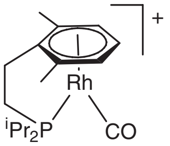

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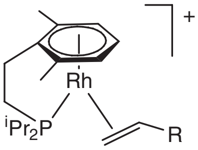

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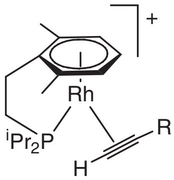
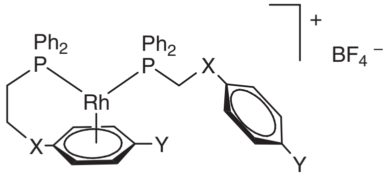


448

Other hemilabile (phosphinoalkyl)arene ligands of the type $ArX(CH_2)_2PPh_2$ ($Ar = C_6H_5$, FC_6H_4; $X = CH_2$, O) complexed Rh(I) to form similar bis(phosphine) η^6-arene piano-stool complexes such as **449**.[583]

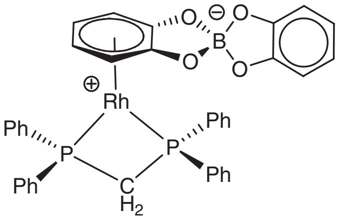


$X = CH_2$, O
Y = H, F

449

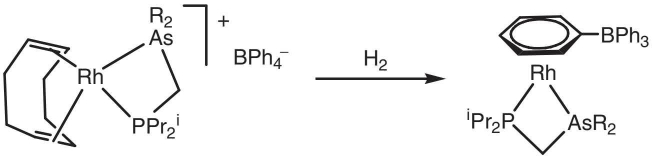
Zwitterionic sandwich complexes $Rh(\eta^6\text{-}C_6H_5BPh_3)(L\text{–}L)$ were reported during the decade of 1983–1993. New complexes of this type have been described and their catalytic properties studied. Using peralkylated arsino(phosphino)methanes $R_2AsCH_2PR_2$ (R = *i*Pr, Cy), the zwitterionic half-sandwich-type complexes $(\eta^6\text{-}C_6H_5BPh_3)Rh(\kappa^2\text{-}As,P\text{-}R_2AsCH_2P(R^1)_2)$ were obtained (Scheme 55).[532] Other zwitterionic piano-stool complexes of the type $(\eta^6\text{-}C_6H_5BPh_3)Rh(L\text{–}L)$ (L–L = cod, nbd, dppb) were reported and their catalytic properties studied.[584,584a–584c] The factors governing the phenyl-transfer reaction from coordinated BPh_4^- anion in $Rh(\eta^6\text{-}C_6H_5BPh_3)(L\text{–}L)$ to monoenes and dienes were studied.[585]

The reactions of $Rh(acac)L_2$ (L = alkene or phosphine) with B_2cat_3 yielded the zwitterionic complex $Rh(\eta^6\text{-}catBcat)L_2$. The crystal structure of $Rh(\eta^6\text{-}catBcat)(dppm)$ **450** was described.[586]

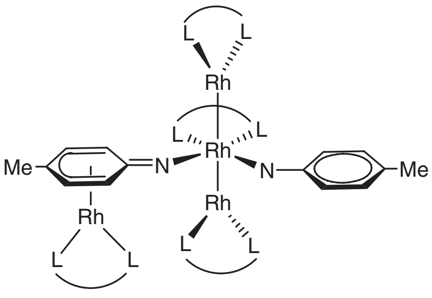


450

Reactions of $[Rh(\mu\text{-}Cl)(diene)]_2$ with a solution of *para*-toluidine and butyllithium afforded complexes of the type $Rh_4(\mu\text{-}N\text{-}tolyl)_2(diene)_4$ **451** (diene = cod, tfb). Two *para*-tolyl-imido ligands cap either side of a trihodium triangle through their nitrogen atoms, while the ring of the phenyl group of one of these ligands coordinates an isolated Rh(diene) fragment.[587]

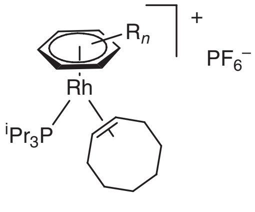


Scheme 55



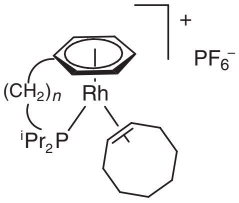
451

Reaction of the sulfonate compounds Rh{η^2-$O_2S(O)CF_3$}(olefin)(P^iPr_3) (olefin = C_8H_{14} or C_2H_4) with benzene led to the displacement of the sulfonate ligand and to the formation of the half-sandwich-type complexes [Rh{η^6-C_6H_6}(olefin)(P^iPr_3)]SO_3CF_3, containing a rather labile benzene–rhodium bond.[428] A series of similar arenerhodium(I) complexes [Rh(η^6-arene)(coe)(P^iPr_3)]PF_6 **452** (coe = cyclooctene) was prepared from the highly reactive starting material *cis*-[Rh(coe)(P^iPr_3)(acetone)$_2$]PF_6 and the corresponding arenes. Alkyldiisopropylphosphines $^iPr_2P(CH_2)_nC_6H_5$ provided complexes of formula [Rh{η^6-$C_6H_5(CH_2)_nPi Pr_2$-κ-P}{$C_6H_5(CH_2)_nPiPr_2$-k-P}]PF_6 **453**.[588]



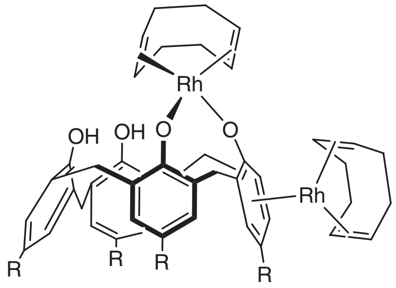
Arene = C_6H_6, C_6H_5F, 1,3,5-$C_6H_3(CH_3)_3$, $C_6H_5OCH_3$, 1,3,5-$C_6H_3(OCH_3)_3$

452



453

Calix[4]-derived ligands also provided η^6-arene complexation. The reaction of [Rh(μ-OMe)(cod)]$_2$ with calix[4]-arenes gave the complex [Rh(cod)]$_2$(η^6:η^2-LH_2) **454** in which one of the Rh(cod)$^+$ fragments is coordinated by an η^6-aryl group and the other by two phenolic oxygen atoms.[589]



R = H, Me

454

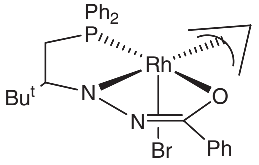
Similar complexes with cyclotriveratrylene (CTV) also provided macrocyclic species in which Rh(nbd)$^+$ fragments are coordinated by an η^6-aryl group. Monometallic [Rh(η^6-CTV)(nbd)]BF_4 and dimetallic [{Rh(nbd)}$_2$(η^6;η^6-CTV)]BF_4 compounds were described.[590] The reaction of [Rh(μ-Cl)(CO)$_2$]$_2$ with Ag(C_6H_6)(1-Et-$CB_{11}F_{11}$) resulted in the precipitation of AgCl and the formation of [Rh(η^6-C_6H_6)(CO)$_2$][1-Et-$CB_{11}F_{11}$] whose crystal structure was described.[19]

7.02.3.6 Allyl Complexes

Several rhodium–allyl complexes were immobilized on to solid supports. For example, the reaction of $Rh(\eta^3\text{-}C_3H_5)_3$ with the surface hydroxyl groups of partially dehydroxylated silica led to the formation of the surface organometallic complex $(\equiv SiO)(\equiv SiOX)Rh(\eta^3\text{-}C_3H_5)_2$ (where X is H or $Si\equiv$), with the evolution of propene.[591]

The structure and dynamics of $Rh(\eta^3\text{-}C_3H_5)_3$ were studied by DFT analysis.[592] The chemistry of $Ir(\eta^3\text{-allyl})_3$ and $Rh(\eta^3\text{-allyl})_3$ was compared. While addition of phosphorus ligands such as $P(OPh)_3$ to $Rh(\eta^3\text{-allyl})_3$ gave monovalent $Rh(\eta^3\text{-allyl})L$, the iridium analog provided stable mixed sigma/pi-tris(allyl) complexes, as evidenced by the structural characterization of mono-, bi-, and tridentate ligand complexes.[593] The addition of CO also provided substantial differences, as shown in Scheme 56.[594]

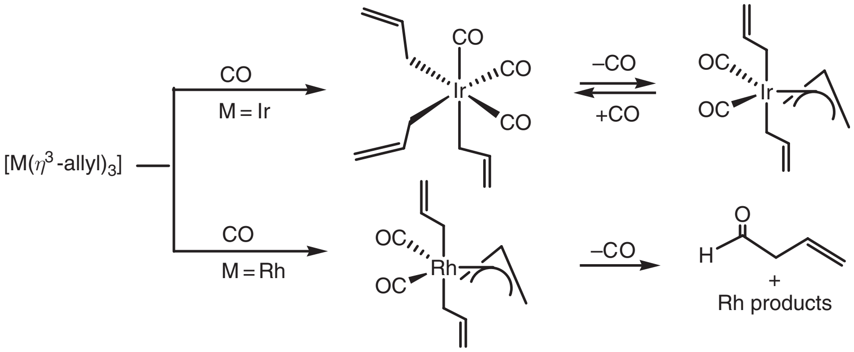
The rhodium(I) complex $Rh(CO)[PPh_2CH_2C(Bu^t){=}N\text{–}N{=}C(Ph)O]$, containing two fused five-membered chelate rings, reacted with allyl bromide causing loss of the carbon monoxide ligand to give the η^3-allylrhodium(III) complex $RhBr(\eta^3\text{-}C_3H_5)[PPh_2CH_2C(Bu^t){=}N\text{–}N{=}C(Ph)O]$ **455**.[280]



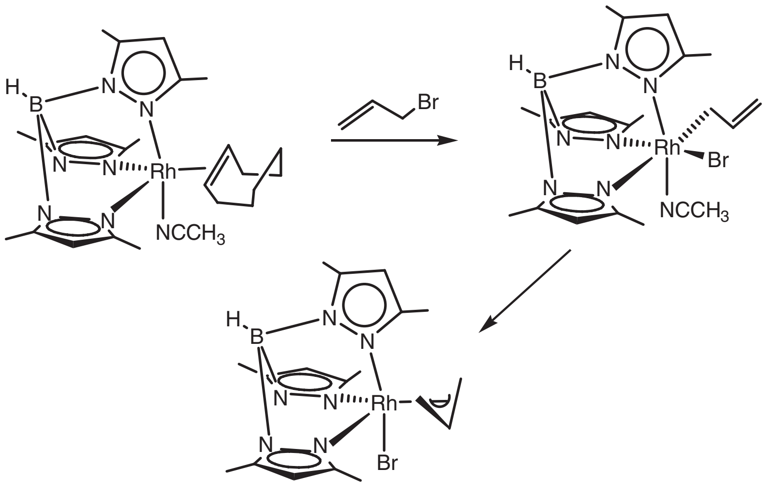
455

The butadiene species $Tp^{Me2}Rh(\eta^4\text{-}C_4H_6)$ (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borato) evolved in the solid state yielding the allyl compound $Tp^{Me2}RhH(\textit{syn}\text{-}\eta^3\text{-}C_3H_4Me)$, as a mixture of *exo-* and *endo*-isomers.[68] The complex $Tp^{Me2}Rh(coe)(MeCN)$ underwent oxidative addition of allyl bromide at room temperature to give $Tp^{Me2}Rh(\sigma\text{-allyl})Br(MeCN)$. On prolonged reaction time or heating, this complex converted to the π-allyl complex $Tp^{Me2}Rh(\eta^3\text{-allyl})Br$ with the liberation of MeCN (Scheme 57).[359]

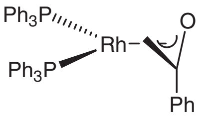
The π-allyl complexes $Rh(\eta^3\text{-}2\text{-}RC_3H_4)(\kappa^2\text{-}(R^1)_2PCH_2P\textit{i}Pr_2)$ (R = H, Me; R^1 = *i*Pr, Cy, Ph) were prepared from $[Rh(\mu\text{-}Cl)(cod)]_2$, 2-$RC_3H_4MgX$, and $(R^1)_2PCH_2P\textit{i}Pr_2$ via $Rh(\eta^3\text{-}2\text{-}RC_3H_4)(cod)$. Reaction of these complexes with CO gave the 1:1 adducts $Rh(\eta^3\text{-}C_3H_5)(CO)(\kappa^2\text{-}(R^1)_2PCH_2P\textit{i}Pr_2)$.[595] The π-allyl(carbonyl)rhodium(I) complex $Rh(\eta^3\text{-}C_3H_5)(CO)(\kappa^2\text{-}{}^iPr_2PCH_2P^iPr_2)$ was obtained from $Rh(\eta^3\text{-}C_3H_5)(\kappa^2\text{-}{}^iPr_2PCH_2P^iPr_2)$ and CO.[87] The *syn*-1-methylallyl complex $Cp^*RhBr(\eta^3\text{-}CH_2CHCHMe)$ was prepared by the reaction of $Cp^*RhBr_2(Me_2SO)$ with vinylmagnesium bromide.[596] The compounds $Rh(\eta^3\text{-}C_3H_5)(PPr^i{}_3)_2$ or $Rh(\eta^3\text{-}CH_2Ph)(PPr^i{}_3)_2$ are convenient starting materials for the preparation of the monomeric sulfonatorhodium(I) complexes $Rh\{\eta^2\text{-}O_2S(O)R\}(PPr^i{}_3)_2$ in high yield.[428] Monomeric (η^3-oxaallyl)rhodium complexes of formula $Rh(\eta^3\text{-}CH_2C(O)R)(PPh_3)_2$ [R = Ph **456**, *t*-Bu **457**] were obtained by the reaction of $K[RC(O)CH_2]$ and $[Rh(\mu\text{-}Cl)(Ph_3P)_2]_2$.[597] The same compounds were found to be efficient catalysts for the disproportionation of aldehydes,[598] and hydrosilylation of cyclopropylketones.[599]



Scheme 56



Scheme 57



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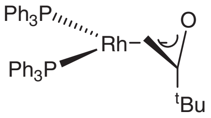
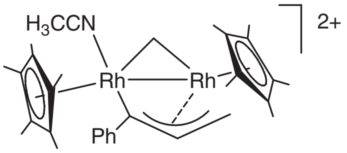


457

The reaction of $[(Cp^{*}Rh)_2(\mu\text{-}CH_2)(CH_3CN)_2](BF_4)_2$ with phenylacetylene provided the dimetallic complex $[(Cp^{*}Rh)_2(\mu\text{-}CH_2)(\eta^1{:}\eta^3\text{-}\mu\text{-}C(Ph)CHCH_2)(CH_3CN)]^{2+}$ 458.[454]



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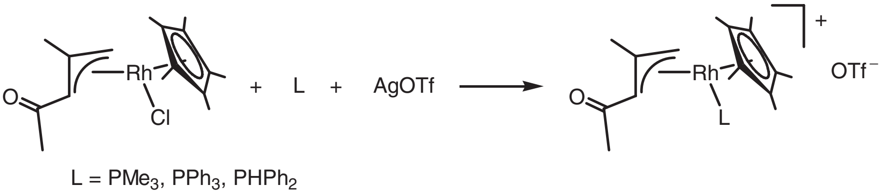
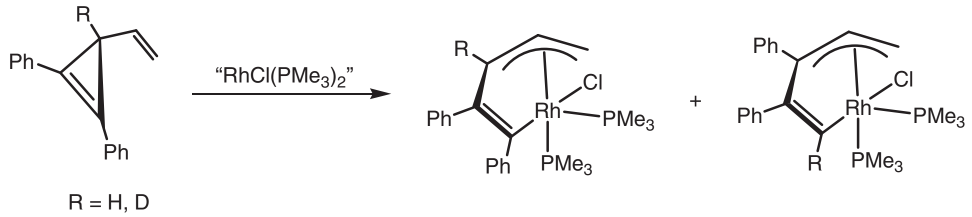
Treatment of $[Cp^{*}RhCl_2]_2$ with lithium produced $Cp^{*}RhCl[(\eta^3\text{-}CH_2C(Me)CHC(Me)(O)]$. Addition of phosphine followed by the addition of AgOTf to the latter compound afforded the preparation of $[Cp^{*}Rh(\eta^3\text{-}CH_2C(Me)CHC(Me)O)(L)]BF_4$ [L = PMe_3, PPh_3, $PHPh_2$] (Scheme 58).[600]

Under conditions of kinetic control, 1,2-diphenyl-3-vinyl-1-cyclopropene underwent ring opening with the "$RhCl(PMe_3)_2$" fragment to give two isomeric $\eta^3{:}\eta^1$-1,3-pentadienediyl compounds: the expected 1,2-diphenyl isomer and the 2,3-diphenyl isomer resulting from an apparent skeletal rearrangement reaction (Scheme 59).[353]

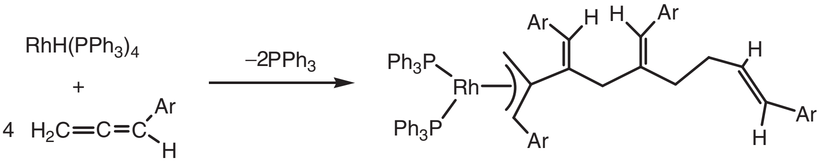
The reaction of $RhH(PPh_3)_4$ at room temperature with excess phenylallene, (4-methylphenyl) allene, (4-methoxyphenyl)allene, (4-*tert*-butylphenyl)allene, (4-chlorophenyl)allene, and (4-fluorophenyl)allene



Scheme 58



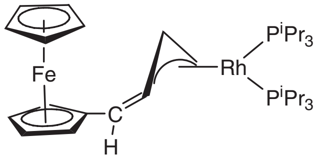
Scheme 59



Scheme 60

resulted in the insertion of four arylallene molecules into the Rh–H bond to afford $Rh\{\eta^3\text{-}CH_2C[CH(Ar)]C({=}CHAr)CH_2C({=}CHAr)CH_2CH_2CH{=}CHAr\}(PPh_3)_2$ ($Ar = C_6H_5$; C_6H_4Me-*p*; C_6H_4OMe-*p*, C_6H_4-*t*-Bu-*p*; C_6H_4Cl-*p*, C_6H_4F-*p*) (Scheme 60).[601]

Using $[Rh(\mu\text{-}Cl)(P^iPr_3)_2]_2$ and ethynylferrocene as starting materials, $[RhCl({=}C{=}CHFc)(P\mathit{i}Pr_3)_2]$ was formed (Fc = ferrocenyl). By treatment of this compound with Grignard reagents, the vinyl and methylrhodium(I) derivatives *trans*-$[Rh(R)({=}C{=}CHFc)(P\mathit{i}Pr_3)_2]$ were generated. These caused further rearrangement to the the π-allyl-ferrocenyl complexes $[Rh(\eta^3$-*trans*-$CH_2CHC{=}CHFc)(P^iPr_3)_2]$ **459** and $[Rh(\eta^3$-*anti*-$CH_2CH{=}CHFc)(P^iPr_3)_2]$ **460**.[309]



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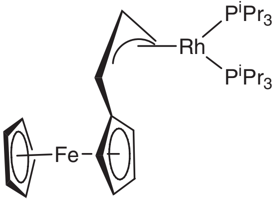

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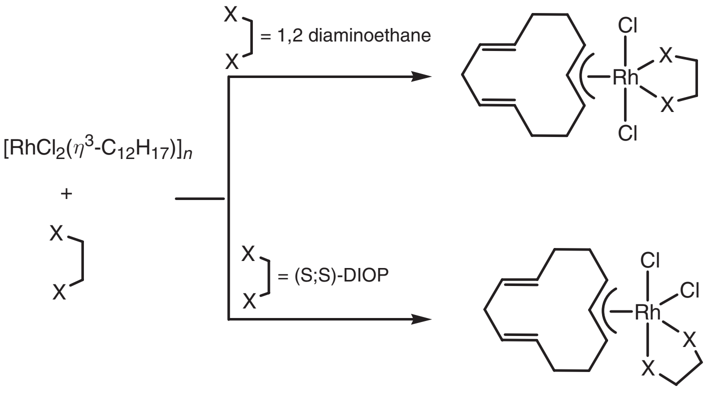
Several works were made on the study of reaction intermediates in catalytic hydroformylation of olefins, some of them regarding π-allylic species. Catalytic hydroformylation of styrene with Rh(I) complexes was proposed to proceed via an η^3-1-phenylethyl species, which would release the unsaturation generated by the related ethylphenyl mono-*hapto* species.[602] η^3-Butenyl rhodium(I) species were also proposed as intermediates for the catalytic hydroformylation of open-chain conjugated dienes.[603] The reaction between the tetrameric cluster $[Rh(\mu\text{-}H)(cod)]_4$ and the bidentate phosphine $Ph_2P(CH_2)_4PPh_2$ (dppb) gave the η^3-cyclooctenyl phosphinerhodium complex $Rh(\eta^3\text{-}C_8H_{13})(dppb)$.[127] A similar η^3-cyclooctenyl complex, $Rh(\eta^3\text{-}C_8H_{13})(dpe)$(dpe = diphenylphosphineethane), was obtained.[533] The reaction of $RhCl_3{\cdot}3H_2O$ with (*EEE*)-1,5,9-cyclododecatriene gave the red polymeric solid $[RhCl_2(\eta^3\text{-}C_{12}H_{17})]_n$, which reacted with diphosphines or diamines to give monomeric η^3-allylic species that could be characterized by means of X-ray diffraction (Scheme 61).[604]



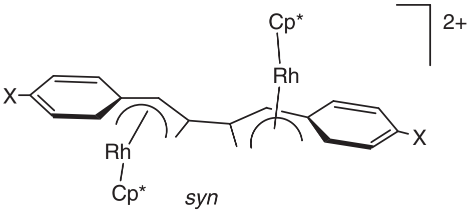
Scheme 61

Monosubstituted allenes such as methoxyallene and phenylallene reacted with $RhH(CO)(PPh_3)_3$ providing stable Rh complexes with π-allylic ligands.[605] The ring slippage in indenyl complexes relates its η^5 and η^3-coordination. The factors affecting the structural and reactivity features of these two types of coordination were theoretically studied and presented in a review.[606]

7.02.3.7 Miscellaneous

7.02.3.7.1 η-Pentadienyl complexes

Complexes $(Cp^*Rh)_2(\mu\text{-}CH_2)_2(C_2C_6H_4X)_2$ reacted with acids to give the unexpected products *syn*- **461** and *anti*-$[(Cp^*)_2Rh_2\{\mu\text{-}\eta^5,\eta^{5'}\text{-}XC_6H_4CH(CH_2)CC(CH_2)CHC_6H_4X\}][BF_4]_2$ **462**, (X = H and *p*-Me). The *syn*-*p*-tolyl complex contains a hydrocarbon skeleton of two linked η^5-allylbenzenes: spectroscopy showed that similar hydrocarbon skeletons were in the other complexes.[249] The synthesis of the oxopentadienyl complex $[Cp^*Rh(\eta^5\text{-}CH_2C(Me)CHC(Me)O)]BF_4$ **463** was reported.[600]



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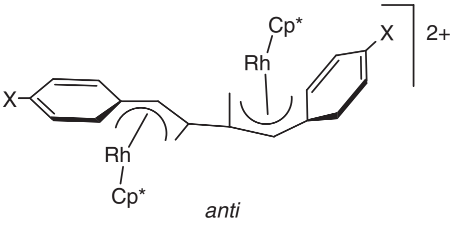

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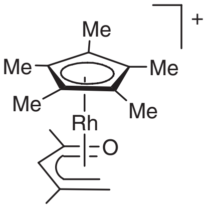

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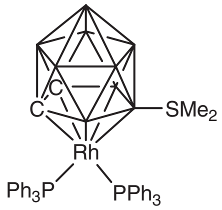
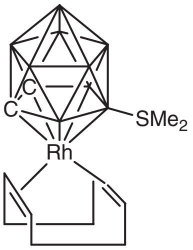
7.02.3.7.2 Rhodacarboranes

A series of new Rh(I) half-sandwich complexes of formulas $[3,3\text{-}(PPh_3)_2\text{-}8\text{-}L\text{-}closo\text{-}3,1,2\text{-}RhC_2B_9H_{10})]$ (L = SMe_2 **464**, SEt_2, $S(CH_2)_4$, SEtPh) and $[1\text{-}Me\text{-}3,3\text{-}(PPh_3)_2\text{-}8\text{-}L\text{-}closo\text{-}3,1,2\text{-}RhC_2B_9H_9)]$ [L = SMe_2, SEt_2] was prepared by the reaction of the respective monoanionic charge-compensated ligands $[10\text{-}L\text{-}nido\text{-}7,8\text{-}C_2B_9H_{10}]^-$ and $[7\text{-}Me\text{-}10\text{-}L\text{-}7,8\text{-}C_2B_9H_9]^-$ with $RhCl(PPh_3)_3$. Complex $3,3\text{-}(cod)\text{-}8\text{-}SMe_2\text{-}closo\text{-}3,1,2\text{-}RhC_2B_9H_{10}$ **465** was also prepared by the reaction of $K[10\text{-}SMe_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_{10}]$ with $[Rh(\mu\text{-}Cl)(cod)]_2$.[607]



$[3,3\text{-}(PPh_3)2\text{-}8\text{-}SMe_2\text{-}\textit{closo}\text{-}3,1,2\text{-}RhC_2B_9H_{10}]$

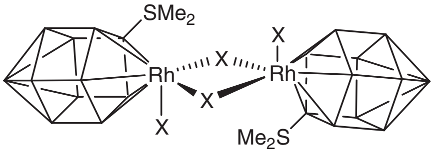
464



$[3,3\text{-}cod\text{-}8\text{-}SMe_2\text{-}\textit{closo}\text{-}3,1,2\text{-}RhC_2B_9H_{10}]$

465

Addition of H_2 to CH_2Cl_2 solutions of $[Rh(diene)(L)_2][\textit{closo}\text{-}CB_{11}H_{12}]$(diene = nbd, cod, L = PCy_3, $P(OMe)_3$, 1/2dppe) resulted in the formation of the *exo–closo* complexes $[Rh(\textit{closo}\text{-}CB_{11}H_{12})(PR_3)_2]$.[608] Addition of $Ag[\textit{closo}\text{-}CB_{11}H_{12}]$ to $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$ afforded the *exo*polyhedrally coordinated complex $[Rh(\textit{closo}\text{-}CB_{11}H_{12})(PPh_3)_2]$. Using the less nucleophilic $[\textit{closo}\text{-}CB_{11}H_6Br_6]^-$ anion, the arene-bridged dimer $[Rh(PPh_3)(PPh_2\text{-}\eta^6\text{-}C_6H_5)]_2[\textit{closo}\text{-}CB_{11}H_6Br_6]_2$ was obtained.[609] (Rhodacarborane)halide complexes of formula $[(\eta^9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})RhX_2]_2$ **466** (X = Cl, Br, I), which are analogous to $[Cp^*RhX_2]_2$, were synthesized by the reaction of $Rh(\eta^9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})(cod)$ with HX. These compounds were used to prepare several sandwich and half-sandwich complexes containing $Rh(\eta^9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})$ fragment. Two-electron ligands destroyed the dimeric structure of $[Rh(\eta^9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})X_2]_2$ to give the adducts $[Rh(\eta^9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})]LX_2$.[610] Reaction of Rh(acac)(cod) with 1 equiv. of $HClO_4$ and subsequent treatment with tetramethylammonium or cesium salts of $[7\text{-}SR\text{-}8\text{-}R^1\text{-}7,8\text{-}C_2B_9H_{10}]^-$ anions afforded $Rh(7\text{-}SR\text{-}8\text{-}R^1\text{-}7,8\text{-}C_2B_9H_{10})(cod)$ **467** (R, R^1 = Ph; R = Ph, R^1 = Me; R = Et, R^1 = Me).[611]



X = Cl, Br, I

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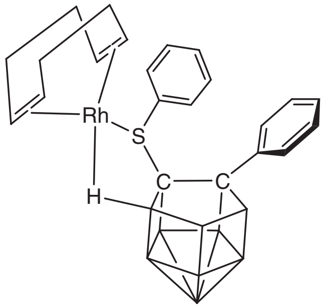

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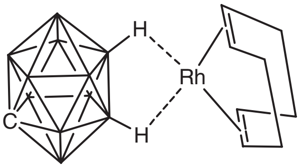
Reaction of $Ag[CB_{11}H_{12}]$ with $[Rh(\mu\text{-}Cl)(cod)]_2$ afforded the complex $Rh(\eta^2\text{-}CB_{11}H_{12})(cod)$ **468**, which was characterized by NMR spectroscopy and X-ray crystallography. The complex $[Rh(cod)(thf)_2][CB_{11}H_{12}]$ was also obtained and characterized.[612] Reaction of $[NMe_4][7\text{-}PPh_2\text{-}8\text{-}R\text{-}7,8\text{-}C_2B_9H_{10}]$ (R = H, Me) with $[Rh(\mu\text{-}Cl)(cod)]_2$ in dichloromethane yielded $Rh(7\text{-}PPh_2\text{-}8\text{-}R\text{-}7,8\text{-}C_2B_9H_{10})(cod)$ [R = H **469**, Me]. The carborane ligand coordinates the Rh through C–PPh$_2$, B(11)–H, and B(2)–H. The Rh(I) atom is pentacoordinated, assuming that cod is bidentate.[613] Rhodium complexes with the eclipsed anionic diphosphine $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ were described. These were prepared from the neutral cod complex $Rh\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}(cod)$ either directly or via the complex $Rh\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}(CO)_2$, which was obtained by bubbling CO through a suspension of $Rh\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}(cod)$ **470**. The CO ligands may be readily replaced by monophosphines, chelating diphosphines, monoamines, and chelating diamines.[614]



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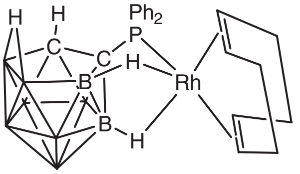

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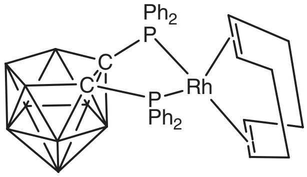
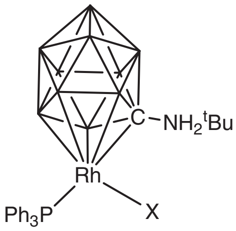


470

The compounds $RhX(PPh_3)_3$ ($X = Br$, Cl) reacted with *nido*-7-NH_2Bu^t-7-$CB_{10}H_{12}$ in toluene to give the 16-electron complexes $RhX(PPh_3)(\eta^5$-7-NH_2Bu^t-7-$CB_{10}H_{10})$ **471**. With $CNBu^t$, by changing the stoichiometry or workup procedures, either the 18-electron complexes $RhX(CNBu^t)(PPh_3)(\eta^5$-7-$NH_2Bu^t$-7-$CB_{10}H_{10})$ **472** or $Rh(CNBu^t)_2(PPh_3)(\eta^5$-7-$NHBu^t$-7-$CB_{10}H_{10})$ **473** were obtained, or the 16-electron complex $Rh(CNBu^t)(PPh_3)(\eta^5$-7-$NHBu^t$-7-$CB_{10}H_{10})$ **474** was formed.[576]



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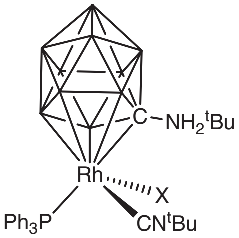

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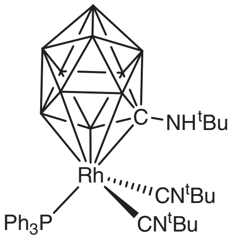

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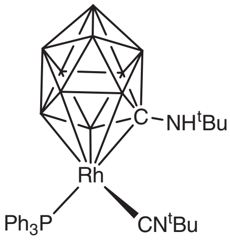

474

The rhodium electrophile $[Cp^*Rh(OCMe_2)_3]^{2+}$ readily reacted with $Cp^*Ru(C_5H_5BMe)$ in acetone to form a labile triple-decker dication $[(\mu$-$C_5H_5BMe)(RuCp^*)(RhCp^*)]^{2+}$.[615] Other rhodium–borole complexes were reported by the same group.[574,616,616a] The reaction of 8,8-$(PPh_2)_2$-*nido*-8,7-$RhSB_9H_{10}$ with a 20-fold excess of $BH_3{\cdot}THF$ afforded the rhodathiaborane 8,8-$(PPh_2PCH_2PPh_2BH_3)$-*nido*-8,7-$RhSB_9H_{10}$. Addition of $Ph_2P(CH_2)_2PPh_2$ (dppe) afforded the preparation of 8,8-(dppe)-*nido*-8,7-$RhSB_9H_{10}$.[617]

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7.03
Application of Rhodium Complexes in Homogeneous Catalysis with Carbon Monoxide

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7.03.1 Introduction

Numerous catalytic reactions that use rhodium as the metal have been reported in the literature. Important examples include carbonylation, asymmetric hydrogenation, alkene dimerization, hydroformylation, hydrosilylation, and asymmetric cyclopropanation. In this chapter, we will confine ourselves to only two applications of organometallic rhodium compounds in homogeneous catalysis, namely hydroformylation of alkenes and carbonylation of methanol. Other applications of rhodium as catalysts in organic synthesis are discussed in Chapters 1.10 and 1.11. These two reactions belong to both the oldest examples and both have found industrial application since the 1970s. Interestingly, research for both has continued and relatively recent advances have led to impressive improvements with the use of new phosphine ligands. In hydroformylation, this will lead to industrial applications, but in methanol carbonylation, this seems less likely because of the inherent instability of phosphines in the iodide-rich carbonylation media; besides, iridium-based systems are competing with the rhodium-based systems. Asymmetric hydroformylation will be discussed in Chapter 1.11 and does not form part of this chapter.

7.03.2 Rhodium-catalyzed Hydroformylation

7.03.2.1 Introduction

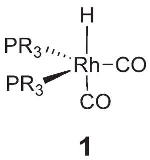
The discovery of triphenylphosphine by Wilkinson and co-workers[1,1a] as the ligand in rhodium-catalyzed hydroformylation has changed the world of hydroformylation. Prior to this, the industrial applications involved cobalt carbonyls, of which only the Shell system, invented by Slaugh,[2,2a,2b] was modified by alkylphosphines as the ligand. The phosphine rhodium catalysts are much faster and more selective, and as a result they can be used at much lower temperatures and pressures. Since the 1970s, commercial applications for propene hydroformylation have been brought on stream by Celanese, Union Carbide Corporation (now Dow Chemical), and Mitsubishi Chemical Corporation. Mitsubishi also operates a process for higher alkenes based on a phosphine-free catalyst system; this is the oldest rhodium-based process, in operation since 1970. In the mid-1980s, a new process came on stream, the Ruhrchemie/Rhone-Poulenc process, which is based on two-phase catalysis using trisulfonated triphenylphosphine as the water-soluble ligand. It can be used for propene and 1-butene and its economics are slightly better than those of the triphenylphosphine process due to energy costs, selectivity, and catalyst stability.[3]

Ligand modification turned out to be extremely useful for rhodium-catalyzed hydroformylation, and a great deal of the more than 6000 publications known today are concerned with this, of which around 30% appeared after COMC (1995). Phosphites, first used by Pruett and Smith,[4] came into focus again when the peculiar behavior of bulky phosphites was reported by van Leeuwen.[5,5a] In particular, diphosphites have been addressed by many authors after their favorable effect on rate and selectivity for many substrates had been discovered by Bryant and co-workers.[6,6a] The effect of backbone and bite angle of bidentate phosphites followed this development, which was first discovered for diphosphines with the introduction of BISBI by Devon (Texas Eastman)[7,7a] and examined by Casey and Whiteker in relation with other ligands and bite angles.[8] The introduction of xantphos-type ligands has enlarged the number of possibilities for variation of the bite angle and the study of its effect on catalysis enormously.[9] In the last decade, understanding of the mechanistic details has grown considerably as well. A monograph on rhodium-catalyzed hydroformylation appeared in 2000,[10] which discusses a large number of representative catalysts, industrial processes,[3] laboratory procedures ranging from reactions of simple alkenes to multistep organic applications, new developments in separation, and issues concerning catalyst preparation and decomposition.

One might wonder if, after all this progress, there is still a quest from an industrial point of view for further improvements, and this is indeed the case. Research in the last decade has been directed toward these new goals. First, the catalysts described above only work for terminal alkenes, and processes for the conversion of 2-butenes and higher alkenes still require cobalt catalysts. For most catalysts, the high selectivities can only be obtained at the cost of lower activities, and more active catalysts are desirable because the rhodium inventory represents a substantial part of the investment. Functionalized substrates leading to diols for polyesters and to nylon intermediates still need better catalysts. Fine chemical applications are potentially interesting provided that high regioselectivities and stereoselectivities can be reached. Separation of catalyst and product for higher alkenes and other products call for better solutions than those that were available a decade ago. Indeed, these have been the targets for hydroformylation research in the last decade. In this chapter we will focus on the advances made for simple alkenes with a view on industrial applications.

7.03.2.2 Computational Studies

Scheme 1 shows the generally accepted reaction sequence for rhodium-catalyzed hydroformylation; the most common catalyst precursors or resting states are structures **1** (bisequatorial or ee isomer), **2** (equatorial-axial or ea), and **3**, the triphosphorus ligand precursor.



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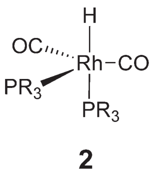

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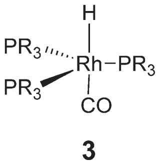

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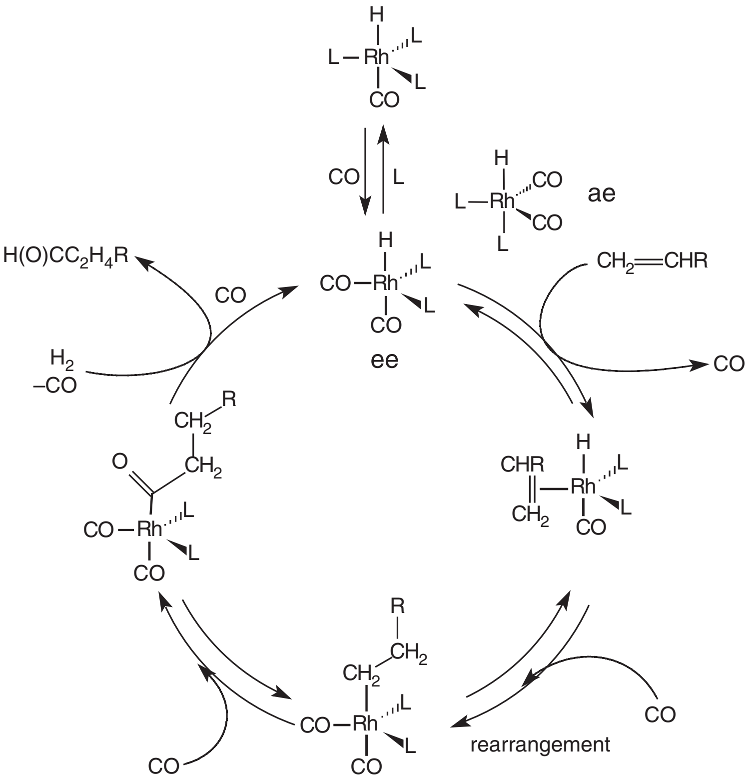
The potential energy profile for the full cycle of olefin hydroformylation catalyzed by $RhH(CO)_2(PH_3)_2$, consisting of olefin coordination and insertion, CO insertion, H_2 oxidative addition, and aldehyde reductive elimination, as well as ligand coordination and dissociation, was studied using the *ab initio* MO method.[11] The coordinatively unsaturated intermediates are strongly coordinated and stabilized by a solvent alkene molecule, while the transition states are not solvated. The energetic and entropic effects of solvation play a critical role in determining the activation free energies. Including the solvent effect, the H_2 oxidative addition step from a solvated intermediate has one of the



Scheme 1 Hydroformylation mechanism.

highest barriers. Kinetic studies show that for most systems this step is not rate determining, and clearly steric effects of ligands and the substrate have to be taken into account.

The equilibrium structures of Rh complexes $HRh(CO)_n(PH_3)_{4-n}$ and $HRh(CO)_n(PH_3)_{3-n}$ were calculated using DFT.[12] The ligand dissociation energies derived from single-point CCSD(T) calculations revealed that MP2 strongly overestimates bond strengths for these systems. Results for PPh_3 complexes show that the phosphine dissociation energies are too low when PH_3 serves as the model phosphine. The situation is improved significantly when PMe_3 was used instead.

Another high-level MO study on the ethene hydroformylation by $HRh(PH_3)_2(CO)$ looked at the effect of the geometry of the complexes having the phosphines in *trans*- or *cis*-positions, stemming respectively from the bisequatorial (ee) and equtorial-apical (ea) trigonal-bipyramidal precursor.[13] They concluded that the *trans*-isomer was the most active one. For this favored pathway, the insertion of CO was found to be the slowest one, which is not supported by kinetic measurements.

To determine the relative transition-state energies of several phosphine systems, a combined QM/MM method with frozen reaction centers was applied by the same authors.[14] Tendencies in regioselectivities of four systems with the bidentate chelating ligands DIPHOS, BISBI, NAPHOS, and the monodentate PPh_3 could be reproduced.

Similar studies for asymmetric hydroformylation were published.[15]

A comparison between experimental and MO data on regioselectivity concerning the hydroformylation of several vinyl substrates (propene, 2-methylpropene, 1-hexene, 3,3-dimethylbutene, fluoroethene, 3,3,3-trifluoropropene, vinyl methyl ether, allyl methyl ether, styrene) with unmodified rhodium catalysts was reported.[16] The activation energies for the alkyl rhodium intermediate formation, computed at either level along the pathways to branched or linear aldehydes, allowed one to predict the regioselectivity ratios. Steric effects may be less important for the unmodified carbonyl complexes and electronic factors dominate, assuming that alkene insertion in Rh–H is irreversible.

Another MO study on $HRh(CO)_3$ concludes that a preference for the formation of branched alkyl species exists ($b:1 = 84:16$), whereas experiments show a slight preference for linear aldehyde formation.[17]

A QM/MM study concerning phosphine ligand on the insertion of ethene into the Rh–H bond of $HRh(PR_3)_2(CO)$ (R = Me, *t*-Bu, Ph, *meta*-SO_3-phenyl, and *para*-SO_3-phenyl) predicts that two reaction channels, one originating from the more stable ea η^2-ethene adduct and the other from the less stable ee η^2-ethylene adduct, will be operative for the ethene insertion reaction with the PMe_3 ligand system, although the latter will be preferred.[18] In the case of the aryl phosphine ligands, a clear preference was found for ethene insertion to proceed from the least stable ee ethylene adduct.

Several hybrid QM/MM computational investigations of propene insertion into the Rh–H bond of $HRh(L)_2(CO)(CH_2{=}CHCH_3)$ were performed to address the issue of regioselectivity in hydroformylation catalysis and the kinetics involved. Cundari[19] reported that for $L = PPh_3$, the ea isomer is more stable than the ee isomer, and and the ea isomer is the one that produces the linear aldehyde while the more active ee isomer produces branched aldehyde. These findings are not in accord with the experimental studies on the bite angle effect.

Carbo *et al.*[20] investigated the origin of regioselectivity in rhodium diphosphine-catalyzed hydroformylation by means of hybrid QM/MM calculations using the IMOMM method. The roles of the diphosphine bite angle and of the non-bonding interactions were analyzed in detail by considering rhodium systems containing xantphos-type ligands, for which a correlation between the natural bite angle and regioselectivity was reported. From the pentacoordinated equatorial–equatorial HRh(CO)(alkene)(diphosphine) key intermediate, eight possible reaction paths were defined and characterized through their transition states. These calculations showed that regioselectivity is governed by the non-bonding interactions between the diphenylphosphino substituents and the substrate, whereas the effects directly associated to the bite angle, which are called orbital effects, seem to have a smaller influence. The trend to higher $l:b$ ratios at wider bite angles was nicely reproduced by the calculations.

Experiments showed that both ee and ea isomers are present in solution for xantphos-type ligands and Landis[21] therefore studied a series of 56 isomers and conformers along the reaction pathway by similar ONIOM methods.

In terms of realistic modeling experiments, the computational results are mixed. In agreement with the experiments, the computations yield a mixture of diequatorial and axial-equatorial isomers of $HRh(xantphos)(CO)_2$ as the catalyst-resting state. Dissociation of CO from these complexes is computed to be barrier-less, leading to a computed free energy for exchange of CO ligands around $15\,kcal\,mol^{-1}$, somewhat lower than the value of ca. $20\,kcal\,mol^{-1}$ derived from experimental data. The computed ratios of rates of propene insertion to form 1-propyl and 2-propyl rhodium (42 : 1) is in good agreement with ratios (52 : 1) for 1-octene hydroformylation. Nonetheless, the computations dramatically overestimate the overall activation free energies for catalytic hydroformylation. Thus, they concluded that at this stage computations do not provide useful insight into the kinetics of hydroformylation. It appears that much of this discrepancy between computed and experimental activation energies originates from the underestimation of propene bonding energies.

The electronic effect of the ligands CO, PMe_3, PH_3, and PF_3 has been studied for the full catalytic cycle of ethene hydroformylation.[22] Predominance of phosphane monocoordination was found, as well as a different sensitivity of unmodified and modified systems toward hydrogen pressure and the early location of the rate-determining step. The crucial first catalytic step, association of ethene to the active species $[HRhL_3]$, may play a key role in the higher activity of systems on less basic phosphines and CO. This association must be fast for CO-based systems, but it has been well established that in carbonyl systems, the hydrogenolysis step of the rhodium-acyl species is rate determining. Most importantly, the study shows that subtle changes in ligand and substrate concentrations play a key role, well in accord with the experiments, and for a full understanding entropy effects should be included. Clearly, computational methods can assist to understand trends and to establish the origin of the trends observed, but they do not give absolute numbers as yet.

7.03.2.3 Carbon Monoxide as the Ligand

For quite some time it has been known that rhodium carbonyls are very active catalysts for hydroformylation, more active than cobalt catalysts, and depending on the circumstances, also more active than the phosphine-modified rhodium catalysts. Above, we have already mentioned that the first industrial application of rhodium-catalyzed hydroformylation was based on rhodium carbonyls. As is to be expected, CO dissociation from $HRh(CO)_4$ is faster than that from donor ligand-substituted complexes, while insertion reaction rates are not that much influenced, and thus carbonyl catalysts are potentially fast. Oxidative addition of H_2 is slower on the less electron-rich rhodium carbonyls than on the phosphorus donor-substituted complexes, and this is now the rate-determining step of the overall process. In the last decade, this has been demonstrated for a large number of substrates under mild conditions by Garland and co-workers. The key factor diminishing the overall effectiveness of these catalysts (apart from selectivity) is the position of equilibrium between $HRh(CO)_4$ and $Rh_4(CO)_{12}$ and/or $Rh_6(CO)_{16}$, which is strongly in favor of the latter clusters, thus diminishing the initial rate of reaction of such a system. Since the resting state under mild conditions is the rhodium-acyl species, potentially all rhodium participates in the catalytic cycle, and depending on the rates of equilibration between the carbonyl complexes and the competing rate of insertion of alkene, there may be no rhodium residing in the $Rh_4(CO)_{12}$ sink. Thus, even for a simple carbonyl system, in the absence of modifying phosphorus ligands, the kinetics can be complicated.

Mixed clusters of Co and Rh carbonyls, for example, $CoRh(CO)_7$, were reported by Garland to be fast initiators for the hydroformylation of 3,3-dimethylbut-1-ene at room temperature and 40 bar of *syn*-gas.[23]

Hydroformylation of 2,4,4-trimethyl-1-pentene, catalyzed by the high-nuclearity carbonyl cluster $[Rh_{12}(CO)_{30}]^{2-}$ at higher temperatures and pressures, also proceeded via cluster fragmentation driven by CO pressure, as shown by IR spectroscopy.[24]

Lazzaroni and co-workers studied the rhodium carbonyl-catalyzed hydroformylation of a variety of functional substrates. Hydroformylation and deuterioformylation of open-chain unsaturated ethers revealed that at low temperatures (293 K) the insertion of alkene into Rh–H bonds is irreversible, but that at higher temperatures (393 K) the insertion is reversible.[25] Interestingly, ^2H NMR investigation of the rhodium-catalyzed deuterioformylation of 1,1-diphenylethene gave evidence for the formation of a tertiary alkylmetal intermediate, a relatively rare phenomenon.[26] The conclusion stems from the incorporation of deuterium, as no tertiary aldehyde product was formed; apparently the tertiary alkyl undergoes β-hydride elimination rather than CO insertion. Similar results were obtained for 2-phenylpropene, 2-methylpropene, and 2,3,3-trimethylbutene via deuterioformylation experiments at 373 K, and 100 atm, and $Rh_4(CO)_{12}$.[27]

A method for the potential commercial synthesis of isovaleraldehyde is hydroformylation of isobutene, which was considered by Solodar and co-workers at Monsanto.[28] However, the low production volume excluded the possibility of a continuous process, and it was felt that catalyst-handling losses would make a traditional rhodium phosphine system too costly in the batch mode. This dilemma was solved by developing a batch process for the hydroformylation of isobutene, which employed a non-phosphine $Rh(CO)_2$-acetylacetonate system at such low levels that Rh could be considered a “throwaway” ingredient in the process.

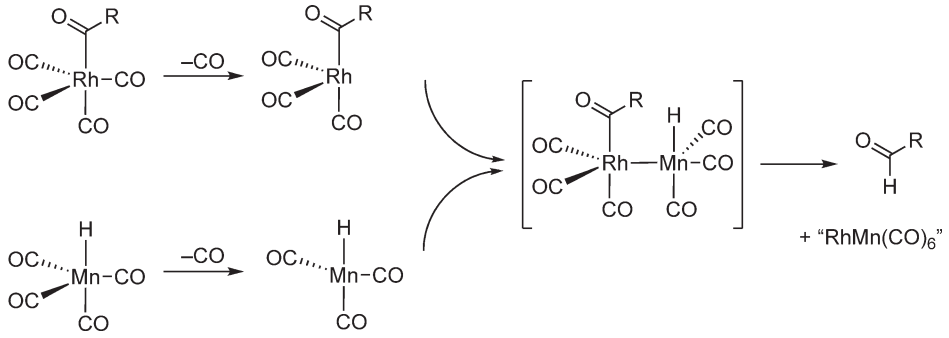
Garland studied as many as 20 alkenes,[29] starting with $Rh_4(CO)_{12}$ as catalyst precursor in *n*-hexane as solvent, using high-pressure *in situ* IR spectroscopy as the analytical tool. Five categories of alkenes were studied, namely, cycloalkenes, symmetrical internal linear alkenes, terminal alkenes, methylenecycloalkanes, and branched alkenes. The typical reaction conditions were 293 K, and hydrogen and carbon monoxide pressures of 20 bar. In most experiments, the precursor $Rh_4(CO)_{12}$ was converted in good yield but different rates, to the corresponding observable mononuclear acyl Rh-tetracarbonyl intermediate $RCORh(CO)_4$, of which 15 have been observed. To a first approximation, the primary differences in rates of hydroformylation are due to the conversion of $Rh_4(CO)_{12}$ and are not real TOFs. For cyclohexene, complete conversion of the precursor $Rh_4(CO)_{12}$ to the intermediate $C_6H_{11}CORh(CO)_4$ was never observed during the 8 h experiments. Instead, after approximately 30 min, a pseudo-steady state was achieved between the species $Rh_4(CO)_{12}$ and $C_6H_{11}CORh(CO)_4$ (298 K, 20 bar H_2 pressure, 60 bar CO pressure). There is no statistically significant contribution to aldehyde formation from a monometallic, catalytic, binuclear elimination (Rh-acyl + RhH) in the Rh-catalyzed hydroformylation reaction under these conditions.[30] Styrene showed rate-limiting hydrogenolysis of the two acyl species as the rate-determining step at temperatures 298–313 K.[31] During hydroformylation of ethene at 293 K, both propionylrhodium and ethylrhodium tetracarbonyl species were observed by IR spectroscopy.[32] Dienes are poisonous for 1-alkene hydroformylation using rhodium carbonyl catalysts, due to their higher activity and the formation of less reactive allylic rhodium species. Nevertheless, butadiene can be slowly hydroformylated and several intermediates have been characterized.[33]

A computational tool was developed to unravel large amounts of spectral data in order to obtain accurate spectra of the individual species.[34,34a] Among other observations, it allowed the spectral identification of $HRh(CO)_4$ and $RCORh(CO)_3(\pi\text{-}C_2H_4)$.[35]

An interesting and long sought for finding was the bimetallic elimination of aldehyde from metal hydrides and acylrhodium complexes, see Scheme 2. Both cyclopentene and 3,3-dimethylbut-1-ene underwent bimolecular elimination at 298 K with $HMn(CO)_5$ as the hydrogen source. On a molar basis, manganese hydride was more active than dihydrogen for this reaction under these conditions.[36,36a]

7.03.2.4 Phosphites as Ligands

Very soon after the discovery of Wilkinson that PPh_3 led to active catalysts, phosphites were also used successfully.[37,37a] A survey of phosphites has been reported recently, showing that until the late 1980s, only a few phoshites showed remarkable results; as for most phosphites, selectivities for any product did not exceed 80%.[38] Two



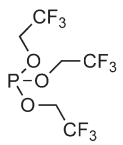
Scheme 2 Bimetallic aldehyde elimination.

examples are worth mentioning, both from Shell; one concerns an electronic effect on linear/branched (*l*/*b*) ratio with the use of ligand **4**,[39] while the bulky *o*-Bu^t-phenyl phosphite **5** gave rise to extremely fast catalysts.[40] The latter were thought to lead to mono-ligand complexes under hydroformylation conditions. A recent spectroscopic study has shown that also a bis-ligand complex occurs.[41] Ligand **4** gives a *l*/*b* ratio of 24, and a low percentage of isomerization can be obtained; at low phosphite concentrations, it is also a good isomerization catalyst, and now internal heptenes give linearities as high as 60%.

Phosphites are easier to make and may be more stable than phosphines (provided that water and alcohols are absent). Interestingly, the breakthroughs in the area of phosphites originate from industry. Pursuing the effect of bulky phosphite ligands reported by van Leeuwen,[40] Bryant and co-workers at Union Carbide Corporation (UCC, now Dow) turned to bidentates such as **6**, **7**, and **9**,[42,42a] which has led to an impressive number of ligands tested, first by them, and later by numerous chemical companies **8**, **10** with an interest in hydroformylation, as the results with the bidentates were astounding. Several bidentates have been reported that give very high *l*/*b* ratios and high rates in the hydroformylation of terminal and internal alkenes, with or without functional groups. Typical examples taken from the patent literature have been collected in the book that appeared on rhodium-catalyzed hydroformylation.[43] A more readily accessible example can be found in the work of Cuny and Buchwald, who used one of the most successful UCC ligands **6** for the hydroformylation of a range of different α-alkenes,[44,44a] and in the work by van Rooy *et al.* who focused on 1-octene, styrene, and cyclohexene as the substrates and several diphosphites.[45]

The solution structures of such selective catalysts have been studied, and it is most likely that all the selective catalysts $HRh(L–L)(CO)_2$ contain the bidentate phosphite in the equatorial plane;[46,46a] in particular, bulky ligands lead to high *l*/*b* ratios.[47] The reverse is not true; not all bisequatorial complexes are selective catalysts for making linear aldehyde. The bisphenol backbone is usually highly effective; it is the same structural motif as that of BISBI (see Section 07.02.02.2.3.2), the diphosphine analog of the bisphenol-based diphosphites. Other phosphorus ligands containing this basic structure often retain the high selectivity, and the list of phosphonites, phosphoramidites **11**,[48,48a] etc., is still limited, leaving room for more variations. Pyrroles as substituents at phosphorus were found to result in strongly electron-withdrawing phosphorus ligands, and they were used in hydroformylation.[49,49a] When used as a bidentate with a bisphenol, wide-bite-angle backbone an extraordinary behavior was found, as in **12**;[50] the catalyst formed is as fast as a bulky monophosphite catalyst and it produces 1-aldehyde only. Yet, the selectivity is not 100% as an additional ~10% of 2-alkene is formed which does not react under the circumstances tested. Thus, in addition to the bite angle effect, which has a steric origin, there is an electronic effect, as was mentioned above also for trifluoroethyl phosphite **4**,[39] although this is still relatively rare for rhodium-catalyzed hydroformylation. So far, theoretical studies have not been able to explain this electronic effect;[20] most likely, it should not be explained by a selective insertion reaction but by a kinetic effect in the rates of reactions of the secondary alkyl species.

Calix[4]arenes have been used extensively as scaffolds for phosphines or phosphinites and their complexes with many metals, or as aryl phosphites, suitable as ligands in hydroformylation.[51] In particular the work by Paciello stands out as high *l*/*b* ratios were obtained for diphosphites based on one calix[4]arene and bulky substituents.[52,52a] In these systems, the four oxygen atoms of calix[4]arene are used to bind two P–OAr groups, where OAr is a bulky phenol group, 2,6-di-*tert*-butyl-4-methoxyphenol, for example, **13**. Most likely, the steric constraints allowed the formation of the linear rhodium-alkyl only, while rates were still relatively high, as is typical of bulky phosphites. A disadvantage is that the highest selectivities for linear product are accompanied by formation of alkanes up to 27%. Phosphites **14** utilizing three phenol groups of one calix[4]arene led to less exciting results.[53,53a–53c] Other structures **15** having $P(OAr)_2$ or PAr_2 groups connected to two adjacent or two alternate oxygen atoms of a calix[4]arene also gave moderate results.[54,54a–54c]



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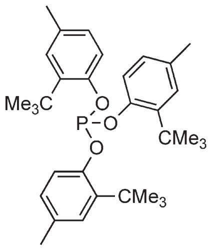

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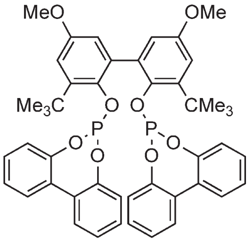

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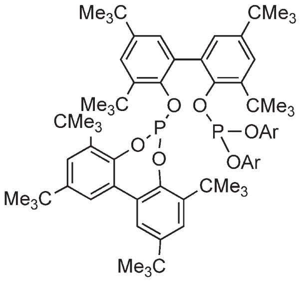
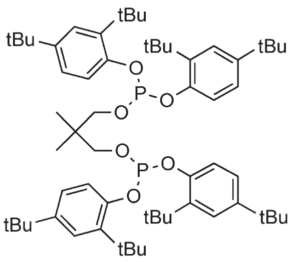


7 Ar = 4-C_6H_4Cl



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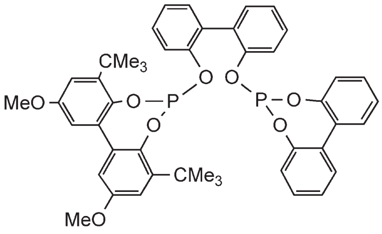

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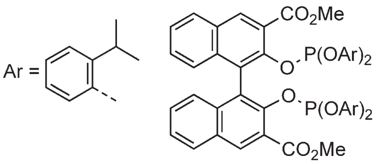

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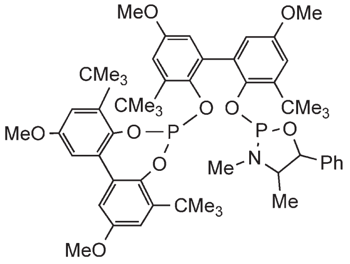

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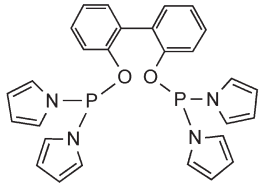

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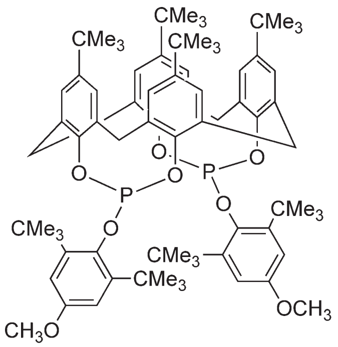

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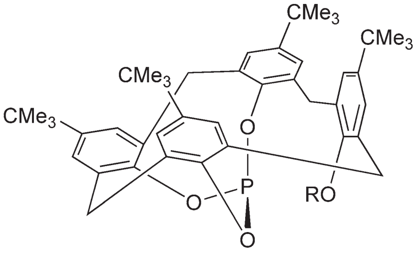

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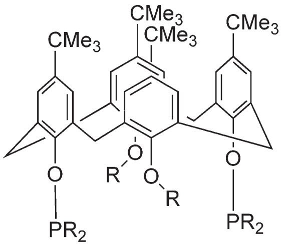


15

7.03.2.5 Arylphosphines as Ligands

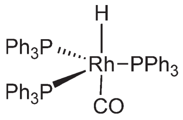
7.03.2.5.1 Monophosphines

Triphenylphosphine and trisulfonated triphenylphosphine continue to be the most important monodentate phosphine ligands in rhodium-catalyzed hydroformylation, both in industrial processes and in applications in organic syntheses. The precursor introduced by Wilkinson was the complex $RhH(PPh_3)_3CO$, 16 with structure 3, which actually was first reported by Bath and Vaska,[55] but its hydroformylation activity was only discovered five years later. At moderate pressures of carbon monoxide and high phosphine concentrations (100 mM), the tris-phosphine species is the resting state of the catalyst. Since they are all in the equatorial plane of the trigonal bipyramid, dissociation of one of them always leads to a species having the two phosphines *trans* to one another.[56] It is thought that this leads to the high *l*/*b* ratio in the Union Carbide (now Dow)/Johnson Matthey process (which uses PPh_3) and the Ruhrchemie/Rhone-Poulenc system (using tppts, tris-sulfonated PPh_3 in the *meta* positions). At lower PPh_3 (10 mM) concentrations, typically *l*/*b* ratios of around 2 are obtained and now the resting state is $RhH(PPh_3)_2(CO)_2$, as a mixture of bisequatorial and equatorial-apical species **1** and **2**.[57] These observations inspired a number of groups to search for bidentate ligands that might enhance bisequatorial coordination of the diphosphine, and these results will be the subject of Section 07.02.02.2.3.2. *In situ* studies using ^{31}P NMR spectroscopy confirm the presence of $RhH(PPh_3)_2(CO)_2$ during a hydroformylation reaction of 1-hexene when $RhH(PPh_3)_3CO$ is used as the precursor.[58] Other intermediates were not observed. The inhibiting effect of CO pressure, known from kinetic studies, was also demonstrated in these studies. In complexes of the type $HRh(CO)_x(L)_{4-x}$, the hydride usually occupies an apical position in the trigonal bipyramid. One exception has been reported by Neibecker *et al.*,[59] who found that in $HRh(CO)_2(TPP)_2$ (TPP = 1,2,5-triphenyl-1H-phosphole), the resting state of the catalytic system for the hydroformylation of styrene by the Rh/TPP mixture, this complex consists in solution of two stereoisomers in equilibrium. The major isomer is a bisequatorial species, which is favored because of the large cone angle of the ligand. The minor isomer was best explained as a geometry where the hydride ligand occupies an equatorial position. An alternative explanation (unpublished) might be that this species contains equatorial-apical phosphines, accompanied by fast exchange of the hydride from one face of the pseudo-tetrahedral complex to the most accessible other face, *trans* to the other phosphine, without passing through a bisequatorial species.

Steric effects have been studied, but the results are not as spectacular as those for phosphites. Compared to triphenylphosphane, when more bulky arylphosphines are used in the Rh-catalyzed hydroformylation of propene and 1-hexene, the formation of branched aldehydes increased.[60] Functional groups in the *ortho*-position of a phenyl group such as thioethers give additional coordination possibilities and several exceptions to the general rule of higher branching were encountered.[61] In general, it remains an interesting target to find ligand systems that lead preferentially to branched aldehydes for normal 1-alkenes, as opposed to aryl and heteroatom-substituted alkenes that give branched products with most ligands.

When the steric bulk in the group R of the alkene $R{-}CH{=}CH_2$ is increased, the preference for linear product increases without much loss of velocity, provided that no direct substitution at the vinyl group is involved.[62] This was carried out both with triphenylphosphine and with *o*-Bu^t-phenyl phosphite, **5**. The selectivity toward the linear aldehyde increases progressively with substitution, from 66% for 1-octene up to 100% for 3,3-dimethyl-1-butene.

Usually, the intermediates of the hydroformylation reaction cannot be isolated, and further intermediate alkylrhodium or acetylrhodium complexes result in loss of CO and/or alkene. This can be circumvented by connecting the alkene to a phosphine ligand. Several examples are known and here we will mention the ones reported by Dickson and co-workers, which interestingly contain bridging phosphido group connected to a group 3 metal, $M(CO)_4(PPh_2)_2$, M = Cr, Mo, W.[63] Several heterobimetallic acyl- and μ-acyl-rhodium complexes have been isolated from reactions of the phosphido-bridged complexes $(OC)_4M(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$ with the phosphinoalkenes $Ph_2P(CH_2)_nCH{:}CH_2$ where $n = 1$–3. Several of the complexes have been characterized, and their potential role as intermediates in the catalytic hydroformylation of the parent phosphines has been investigated. Structure **17** is an example of an acyl intermediate of which the crystal structure has been determined.



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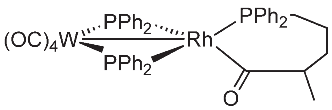

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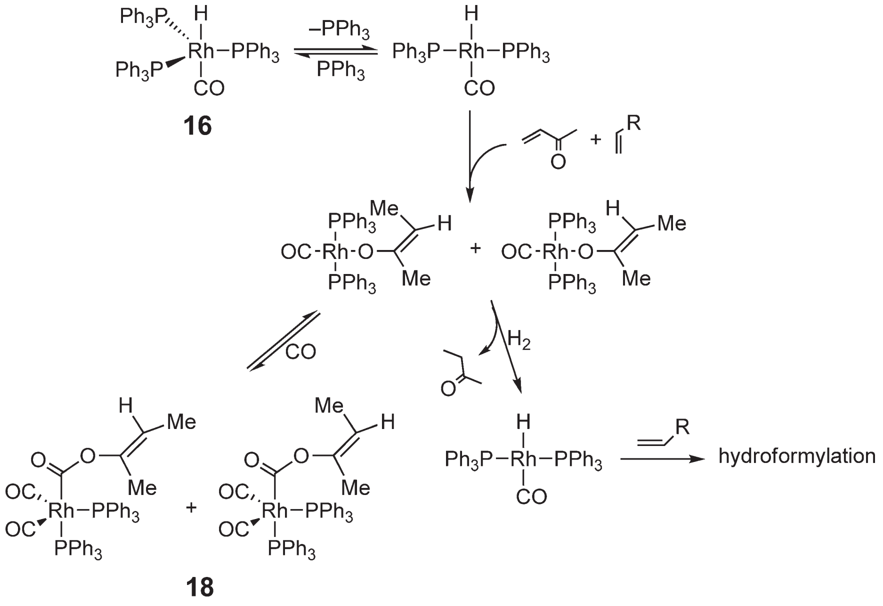
Very often, the kinetics of rhodium-catalyzed hydroformylation do not follow the expected first order in alkene concentration and the minus one order in CO pressure.[10] Severe or slight incubation has also been observed. To those skilled in the art, it is known that impurities such as 1,3-alkadienes, enones, and terminal alkynes may be the cause of such behavior. In a mixture of 1-alkenes and butadiene for instance, the latter is much more reactive and will react preferentially with the rhodium hydride catalyst. The allylic rhodium species formed, however, reacts much more sluggishly with carbon monoxide than alkyl rhodium complexes, and thus the catalyst is tied up in this inactive sink.

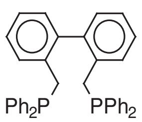


Scheme 3 Enone inhibition mechanism.

Detailed studies were not known until recently although several workers in the field took preventions to make sure that the 1-alkene substrates were not contaminated with enones, dienes, or alkynes. In an *in situ* IR study combined with high pressure NMR studies, Walczuk has shown how this temporary inhibition takes place and what intermediates are formed.[64] *In situ* IR clearly showed the disappearance of rhodium hydride catalyst when these "poisons" were added; the dormant states were slowly depopulated and after all impurities were converted, the hydroformylation of 1-octene started, while simultaneously the hydride-resting state of the catalyst was recovered. Enones gave rise to stable alkoxycarbonyl species **18** (Scheme 3) that were slowly converted to ketones after deinsertion of CO. The degree of inhibition depends both on the structure of the inhibitor and on the ligand; as yet, the latter has not been fully exploited.

7.03.2.5.2 Diphosphines

In the UCC process, one uses $RhH(PPh_3)_3CO$ **16** as the catalyst in the presence of an excess of PPh_3. Under such circumstances, the precursor is also the resting state of the catalyst, which is relatively slow, that is, turnover frequencies of a few hundred at 120 °C and 30 bar of *syn*-gas pressure, but it gives a high linear-to-branched product aldehyde ratio ($l/b = 12–16$). As mentioned above, dissociation of one of the phosphines always leads to a *trans*-like species, and this was held responsible for the high regioselectivity; the precursor $RhH(PPh_3)_2(CO)_2$ gives rise to several intermediate isomers and the selectivity is low ($l/b = 2–3$). Until 1987, all known bidentate phosphines gave *cis*-complexes in square-planar complexes and apical-equatorial complexes in trigonal bipyramids, as rhodium hydride seems to prefer. Perhaps it was for this reason that none of them seemed to give interesting results in rhodium-catalyzed hydroformylation of 1-alkenes as concerns regioselectivity. Brown and Kent[57] studied the intermediates occurring in the reaction of precursor **16** with decene-1 and styrene, and several intermediates were identified. Their studies suggested that bidentate diphosphines should perhaps be sufficiently flexible to allow wider bite angles during the catalytic cycle. At the time of this publication, the important breakthrough with BISBI in bidentate ligands had already been obtained by Devon and co-workers at Eastman Kodak.[65] The introduction of BISBI, **19**, started a new era in rhodium-catalyzed hydroformylation. One cannot tell from the patent literature whether BISBI was an accidental discovery or a matter of "design" following the ideas that were inexplicitly present in the literature. BISBI showed unprecedented selectivity toward the linear aldehyde at satisfactory rates; linear/branched ratios are $l/b = 50$ and more recently, values as high as 300 were reported.[66] In later studies, Casey and Whiteker proved that the key to this invention was the bisequatorial mode of coordination of the diphosphine in trigonal-bipyramid complexes **1**. In the early 1990s, Casey, Whiteker,[67] and Yamamoto *et al.*[68] designed several other ligands that might prefer wider bite angles, for example, **23** natural bite angle (126°), but the success was moderate and apparently the "calculated" bite angle is not the only criterion for a high selectivity. Note, however, that the successful bisphenol diphosphites have the same structure as a backbone: their bite angles are very similar. The natural bite angle β_n was introduced by Casey and Whiteker, and it is obtained from molecular mechanics calculations on a complex of the bidentate ligand and a dummy metal atom, with certain distances and force constants but with the P–M–P bending force constant put to zero. Thus, it is the ligand-preferred angle of coordination, without angular preference of the metal.



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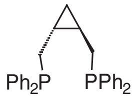

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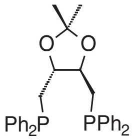

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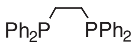

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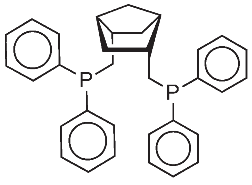
Structure	*Bite angle* (deg)	*Ratio l/b*
19	113	66
20	107	12
21	102	8.5
22	85	2.1

While calculated bite angles[69] are still a matter of debate,[70] and measured bite angles are not useful for this purpose, Casey *et al.*[8] found a trend between calculated bite angle and the linearity of the product of 1-alkene hydroformylation. In hindsight, we can extend the list with a number of ligands that were tested long before these studies and it is seen that they fit quite nicely in the series.[10,71] DIOP[72] has been reported as early as 1973 by Consiglio to give *l*/*b* ratios of 12 and dppf[73] in 1981 by Unruh with *l*/*b* ratios of 5, clearly higher than PPh_3 systems. We have not included xantphos which will be discussed later.

To investigate electronic effects of equatorial and apical phosphines, analogs of chelating diphosphines of BISBI, *trans*-dppm-cyp, and dppe having electron-withdrawing substituents on the aryl rings were synthesized and used in hydroformylation[74] (see 24–26). The introduction of electron-withdrawing substituents on the aryl rings of the diequatorial chelate 24 leads to an "increase" in linear aldehyde selectivity as well as rate. In contrast, introduction of electron-withdrawing substituents on the aryl rings of the apical-equatorial chelate 26 resulted in a "decrease" in linear aldehyde selectivity when compared with the phenyl-substituted dppe. Interestingly, electron-withdrawing groups in equatorial and apical positions had opposite effects on *l*/*b* regioselectivity. Hydroformylation results with the electron-withdrawing "diequatorial"-coordinated ligands 24 and 25 showed an increase in the *n*/*i* ratio, while "apical-equatorial"-coordinated ligand 26 showed a decrease in the *l*/*b* ratio. Thus, electron-withdrawing aryl substituents in the equatorial position lead to higher *l*/*b* regioselectivity and in the apical position to lower regioselectivity.

Beller *et al.* used NAPHOS 27, a BISBI analog backbone, substituted with 3,5-bistrifluoromethylphenyl groups as the ligand in rhodium-catalyzed hydroformylation of internal alkenes and obtained high selectivities to the linear product.[75]



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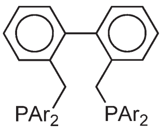

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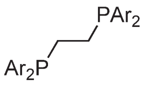

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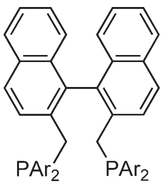

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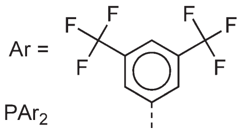
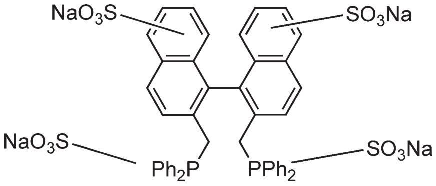


Although water-soluble catalysts are not the topic of this chapter, a few highlights will be mentioned. The sulfonated analog of NAPHOS, named BINAS, has been developed by Herrmann and co-workers.[76] It affords one of the most effective systems for propene hydroformylation in a two-phase system; the commercial process using tppts is the most effective process to date in terms of energy consumption, feedstock efficiency, and catalyst stability. In the Ruhrchemie/Rhone-Poulenc process, a large excess of tppts is needed in order to obtain a high *l*/*b* ratio, but clearly for BISBI-type ligands this is not the case. In addition, the bidentate-based systems are much more reactive, because they require dissociation of a carbonyl ligand, while in the monophosphine systems dissociation of a phosphine from a trisphosphine complex is involved. The BINAS system based on 28 is about ten times faster than the tppts system under comparable conditions.



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The success of the BISBI ligand has stimulated the design of new ligands with wider bite angles. Molecular mechanics has proved to be a useful tool in the development of new bidentate diphosphines. The natural bite angle (β_n) and flexibility range of a bidentate ligand, introduced by Casey and Whiteker,[69] are useful parameters that can be calculated using molecular modeling. In the actual calculation, a "dummy"-type metal atom is used that has no defined geometry and a typical M–P bond length, known from X-ray structures of similar complexes. The force constant for P–M–P bending is defined to be zero and consequently, the structure of the complex is determined by the organic ligand only. The outcome of the calculations is dependent on the defined M–P distance, which is influenced by the metal of choice. In this way, the natural bite angle can be calculated easily since the parameters for the metal are not needed in the actual calculations. Other unknown parameters, such as dihedral and bending force constants, in which the metal is involved, may strongly influence the result, but usually these are ignored.

van Leeuwen and co-workers applied this method for the design of a new range of xanthene-based ligands, the parent ligand being coined "xantphos".[77] By varying the bridge in the 10-position, small variations in the bite angle were introduced. According to molecular mechanics calculations (Table 1), these ligands have natural bite angles ranging from 102° to 121°, and a flexibility range of ca. 35°. It should be noted that the absolute values of the calculations will be dependent on the used force field, but the relative results and, therefore, the observed trends will be the same.

The X-ray crystal structure of the free xantphos ligand shows that only very little adjustment of the structure is necessary to form a chelate; the orientation of the diphenyl–phosphine moieties is nearly ideal. The observed P···P distance in the free ligand is 4.08 Å, while MM studies indicate that a decrease of the P···P distance to 3.84 Å is necessary for chelation with a P–Rh–P angle of 112°, a decrease of only 0.24 Å. The P atoms are brought together by means of a slight decrease of the angle between the two phenyl planes in the backbone of the ligand from ca. 166° to 158°. As a consequence, these xantphos-type ligands do not form bimetallic species, whereas the oxygen atom in the backbone prevents metallation of the ligand.

7.03.2.5.2.(i) 1-Alkenes

The ligands 29–38 have been applied in a variety of catalytic reactions, but their initial purpose was to serve in rhodium-catalyzed hydroformylation. The selectivity of the xantphos ligands in the rhodium-catalyzed hydroformylation was tested with the use of 1-octene (Table 2). DPEphos, having a calculated natural bite angle of 102°, induced an enhanced, though moderate selectivity (compared to most diphosphines), but no isomerization was detected. The

Table 1 Natural bite angles (β_n) and the flexibility range calculated for the xantphos ligands

X, in bridge	*Ligand*	β_n (deg)	*Flexibility range*
H,H;	29	102	86–120
C_2H_4	30	102	92–120
PhP	31	108	96–127
$Si(CH_3)_2$	32	109	96–130
S	33	110	96–133
$C(CH_3)_2$	34	111	97–133
$C{=}C(CH_3)_2$	35	113	98–139
NBz	36	114	99–139
NH	37	114	99–141
"benz"	38	121	102–146

Table 2 Hydroformylation of 1-octene using xantphos ligands

Ligand	β_n (deg)	*l* : *b* ratio[b]	*Linear aldehyde*[b] (%)	*Isomer*[b] (%)	*tof*[b,c]
29[d]	102	6.7	87.0	0	250
30	102	8.5	88.2	1.4	37
31	108	14.6	89.7	4.2	74
32	109	34.6	94.3	3.0	81
33	110	50.0	93.2	4.9	110
34	111	52.2	94.5	3.6	187
35	113	49.8	94.3	3.8	162
36	114	50.6	94.3	3.9	154
37	114	69.4	94.9	3.7	160
38	121	50.2	96.5	1.6	343
39[d]	131	3.0	71.0	5.5	125
19[d]	123	80.5	89.6	9.3	850

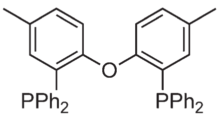
[a] Conditions: CO/H_2 = 1, *P*(CO/H_2) = 20 bar, ligand/Rh = 5, substrate/Rh = 637, [Rh] = 1.00 mM, number of experiments = 3. In none of the experiments was hydrogenation observed.

[b] Linear over branched ratio, percent linear aldehyde, percent isomerization to 2-octene, and turnover frequency were determined at 20% alkene conversion.

[c] Turnover frequency = (mol of aldehyde)(mol of Rh)$^{-1}$ h^{-1}.

[d] *P*(CO/H_2) = 10 bar.

ligands with a one-atom bridge between the aromatic rings of the backbone **31**–**38** have calculated natural bite angles near 110° and showed a very high regioselectivity and a very low rate of isomerization to internal alkenes. DBFphos **39** (dibenzofuran backbone),[78] having a calculated natural bite angle of 131°, proved not to be very selective, probably because the bite angle was too large to form a chelating complex. The ultimate test for a catalyst to check its selectivity toward the linear aldehyde is the hydroformylation of styrene, since this is a substrate with a distinct preference for the formation of the branched aldehyde due to the stability of the 2-alkyl-rhodium species, induced by the formation of an η^3-benzyl complex. The rhodium-catalyzed hydroformylation of styrene using **34** (the most selective catalyst) resulted in relatively high selectivity for the linear aldehyde (a *l*/*b* ratio of up to 2.35 was obtained, whereas for monophosphines this may be as low as 0.01).



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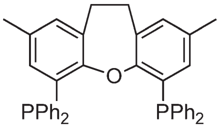

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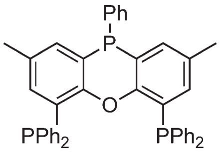

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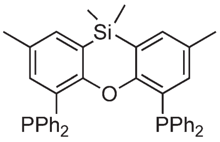

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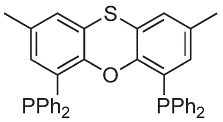

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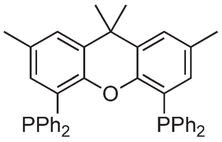
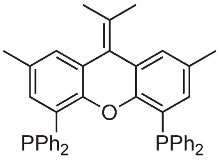


34 Xantphos



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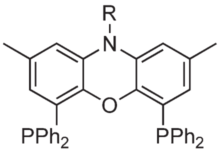
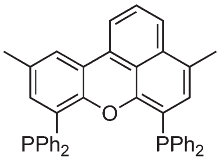


36: R = Bz
37: R = H



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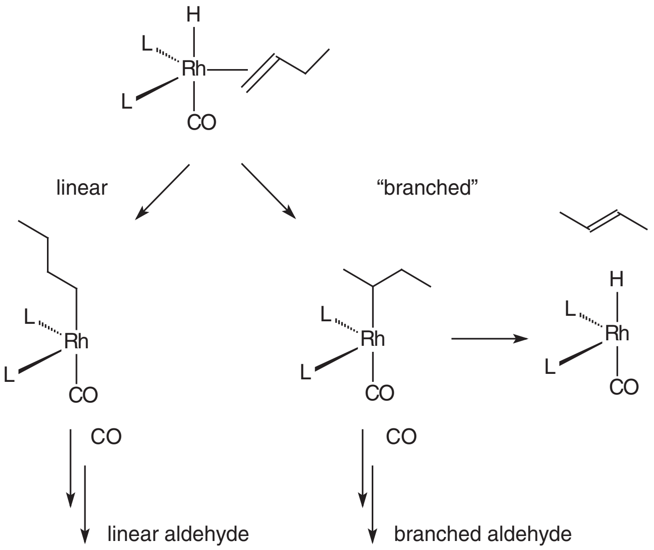
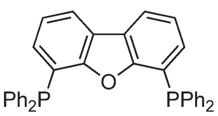


Scheme 4 Formation of 2-alkene.

Under these mild reaction conditions, the selectivities toward the linear aldehyde observed for 32–38, and especially 38, are higher than that observed for BISBI, 19. This is mainly due to the very low amount of isomerization of 1-octene. The *l*/*b* ratios of the ligands are very close to that of BISBI. Furthermore, no hydrogenation was observed. Even though the *l*/*b* ratio is 80.5 for BISBI, the selectivity toward the linear aldehyde amounts to only 89.6% due to the relatively high isomerization of 1-octene to 2-octene (under these conditions, as at lower temperatures BISBI shows no isomerization) (Scheme 4).

The catalytically active complexes could be synthesized by facile exchange of PPh_3 in $(PPh_3)_3Rh(H)(CO)$ with the diphosphines. Subsequent bubbling of CO through a solution of (diphosphine)Rh(H)(CO)(PPh_3) led to displacement of the remaining PPh_3. *In situ* high-pressure IR experiments (*vide infra*) have shown that ligands 29–38 form mixtures of bisequatorial and equatorial-apical isomers, which rapidly equilibrate. Especially for ligands having small bite angles and electron-donating substituents, the proportion of the "unwanted" ea isomer can be substantial, but the preference for linear aldehyde remains relatively high for such systems.



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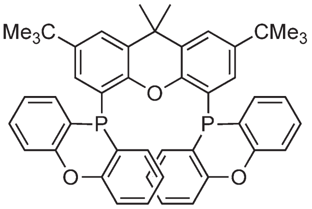


40

7.03.2.5.2.(ii) 2-Alkenes

Xantphos ligands having still wider bite angles are obtained when rigid, cyclic substituents are used, as in 40. In the hydroformylation of 1-octene, the introduction of the phosphacyclic moieties leads to higher reaction rates. More importantly, the dibenzophospholyl- and phenoxaphosphino-substituted xantphos ligands exhibit an unprecedented high activity and selectivity in the hydroformylation of *trans*-2- and 4-octene to linear non-anal. The high activities of the phosphacyclic xantphos ligands are explained by the lower phosphine basicity and the wider natural bite angles of the phosphacyclic ligands. The extraordinary high activity of the phenoxaphosphino-substituted xantphos ligand can be attributed to the 4–6-fold higher rate of CO dissociation compared to the other xantphos ligands. The effect of the phosphacyclic moieties on the coordination chemistry in the (diphosphine)$Rh(CO)_2H$ complexes was studied using NMR and IR spectroscopy. Both NMR and IR spectroscopy showed that the phosphacyclic xantphos ligands exhibit an enhanced preference for diequatorial (ee) chelation compared to the diphenylphosphino-substituted parent compound. CO dissociation rates from the (diphosphine)Rh$(CO)_2$H complexes were determined using ^{13}CO labeling in rapid-scan IR experiments. This was the first rhodium catalyst containing phosphines giving such high selectivity for linear aldehydes from internal alkenes.

7.03.2.5.2.(iii) Mechanistic studies

The detailed mechanism governing the higher linearity for wider bite angles is still unclear. The rate-determining step in the hydroformylation of 1-octene with xantphos-type ligands is in an early stage in the catalytic cycle. Dissociation of CO, alkene coordination, and migratory insertion are relevant for the determination of the rate. So far, only the first step has been studied separately.[79,80] An experimental set-up was introduced, enabling the measurement of the rate constants for CO dissociation from the (diphosphine)Rh$(CO)_2$H complexes. By changing the ^{12}CO ligands for isotopically pure ^{13}CO ligands, the carbonyl absorptions in the IR spectra of the (diphosphine)Rh$(CO)_2$H complexes shift 30–40 cm^{-1} to lower energy.

The rate constants k_1 for the dissociation of ^{13}CO from the (diphosphine)Rh$(^{13}CO)_2$H complexes were determined by monitoring the exchange of ^{13}CO for ^{12}CO by exposing the ^{13}CO labeled complexes to a large excess of ^{12}CO, so any dissociated ^{13}CO will be replaced quantitatively by ^{12}CO.

To investigate the possible effect of the natural bite angle on the rate of CO dissociation from the (diphosphine)Rh$(CO)_2$H complexes, ^{13}CO exchange was measured for complexes containing ligands **31, 33,** and **35**. The exchange of ^{13}CO for ^{12}CO in the (diphosphine)Rh$(^{13}CO)_2$H complexes was monitored by rapid-scan HP IR spectroscopy at 40 °C. The ^{13}CO/^{12}CO exchange was initiated by adding a large excess of ^{12}CO. The difference between the reactivity of the ee and ea isomers **1** and **2** of the (diphosphine)Rh$(^{13}CO)_2$H complexes cannot be determined, since the exchange between **1** and **2** isomers is several orders of magnitude faster than the rates of ^{13}CO dissociation, as is evident from the NMR spectra. The observed rate constants, k_1, are listed in Table 3.

It is commonly accepted that CO exchange in (diphosphine)Rh$(CO)_2$H complexes proceeds via the dissociative pathway. The decay of the carbonyl resonances of the (diphosphine)Rh$(^{13}CO)_2$H complexes indeed follows simple first-order kinetics. This clearly confirms that reformation of the (diphosphine)Rh$(^{13}CO)_2$H complex via k_{-1} pathway is suppressed effectively, and all dissociated ^{13}CO is replaced by ^{12}CO. The experiments with ligand **35** at different ^{12}CO partial pressure show that the rate of CO displacement is independent of the CO pressure. Furthermore, the rate is also independent of the (diphosphine)Rh$(^{13}CO)_2$H complex concentration, as demonstrated by the experiments with ligand **33**. It can therefore be concluded that CO dissociation for these complexes proceeds by a purely dissociative mechanism and obeys a first-order rate-law.

Table 3 shows that there is only a weak correlation between the rate of CO dissociation and the natural bite angle. The rate constants k_1 for ligands **31, 33,** and **35** do not differ significantly and cannot explain the trend in observed hydroformylation activities. Ligand **40** gives both the fastest CO exchange as well as the rate of hydroformylation. The comparison of the k_1 values for ligand **31, 33, 35**, and **40** with the turnover frequencies depicted in Table 3, reveal that the rates of CO dissociation, measured at 40 °C, are higher than the hydroformylation rates at 80 °C. Since reaction rates increase approximately at most an order of magnitude with a temperature rise of 20 degrees, the CO dissociation rate at 80 °C is at most 100 times as fast as the hydroformylation reaction, that is, CO dissociation represents a considerable part of the activation barrier.

Table 3 Kinetics of ^{13}CO dissociation of (diphosphine)Rh$(^{13}CO)_2$H complexes[a]

Ligand	β_n (deg)	P (^{12}CO)(bar)	k_1 (h^{-1})	*Rate*[c]
31	108	25	177	74
33	110	25	206	110
33[b]		25	200	
35	113	20	182	162
35		25	185	
35		30	181	
40	123	25	1200	1560

[a] Reaction conditions: [(diphosphine)Rh$(^{13}CO)_2$H] = 2.00 mM in cyclohexane, $P(^{13}CO) = 1$ bar, $P(H_2) = 4$ bar, $T = 40$ °C, diphosphine/Rh = 5.

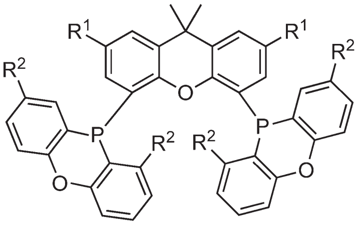
[b] [(Diphosphine)Rh$(^{13}CO)_2$H] = 3.00 mM.

[c] Rate of hydroformylation at 80 °C, 20 bar.

In this study no influence of the natural bite angle on the rate of formation of the (diphosphine)Rh(CO)H complexes (k_1) was found, implying that the activation energy for the formation of these complexes is not affected significantly. Therefore, the increase in hydroformylation rate with increasing bite angle must originate from an increase in the concentration of these four-coordinate complexes, or from a decrease in the activation energy for alkene coordination (if this step were rate-determining), or a lower energy of the alkene complex, or a faster migratory insertion.

It is not likely that increasing the bite angle would lower the activation energy for alkene coordination. Increasing the bite angle results in increased steric congestion around the rhodium center and consequently in more steric hindrance for the alkene entering the coordination sphere. What kind of electronic effect the widening of the bite angle has on the activation energy for alkene coordination is unclear, since it depends on the bonding mode of the alkene. Rhodium-to-alkene backdonation is promoted by narrow bite angles, while alkene-to-rhodium donation is enhanced by wide bite angles.

The wide bite angle of **40** leads to a high propensity to isomerization, while the high selectivity to linear product is retained. As a result, internal alkenes can now be hydroformylated to linear aldehydes.[81] For octene-2, the *l*/*b* ratio is 9, and for octene-4, this value is 4.4 (conditions: 120 °C, 2 bar CO/H_2, ligand/Rh = 5, octene/Rh = 637, [Rh] = 1 mM). At higher pressures of CO, less linear aldehyde is formed, because the rate of isomerization decreases. Further exploration of ligand **40** led to catalyst systems with good selectivity and rates for the hydroformylation of internal alkenes.[82,83] These catalysts received industrial interest as they were potential catalysts for the hydroformylation of butene mixtures, as they come from the cracker ("raffinate II"). For industrial applications, the solubility of the ligand **40** in common solvents (the product, or heavy ends formed thereof) was too low.[84] The solubility was increased easily by adding alkyl chains R^1 and R^2 to ligand **40** to give **41** which did not deteriorate the catalytic performance. For 1-octene, *l*/*b* ratios >100 were obtained, and for internal octenes, average rates >145 (mol aldehyde)·(mol Rh)$^{-1}$ h^{-1} and high regioselectivities up to 91% toward the linear product were obtained (pressure = 3.6–10 bar, T = 120 °C, [Rh] = 1 mM, [alkene] = 640–928 mM).



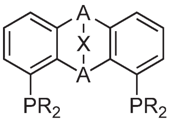
R^1 = H, Me, $CHMe_2$, CHMeEt, CMe_3, $CMe_3CH_2CH_2$, C_6H_{13}, $CMe_3CH_2CMe_2$, $C_{10}H_{21}$

R^2 = H, Me, $CMe_3CH_2CH_2$, C_6H_{13}

41

Compared to other wide-bite-angle diphosphine ligands, xantphos-type ligands can be modified easily while retaining their favorable properties, especially in hydroformylation, and as a result many derivatives have been synthesized by several groups and used in fluorous-phase hydroformylation catalysis,[85] aqueous phase catalysis,[86,87] one-phase hydroformylation and catalyst extraction,[88] catalysis in ionic liquids,[89,90] hydroformylation with immobilized catalysts,[91,92] and catalysis in supercritical CO_2.[93]

Ligands structurally related to the xanthene backbone such as generic **42** and triptycene derived **43** were shown to be just as effective as xantphos in hydroformylation by Ahlers *et al.*[94] Ligand **43** gave *l*/*b* ratios as high as 100 in the hydroformylation of 1-octene (100 °C, 5 bar). Amide groups as substituents at phosphorus are close to carbon-based susbstituents, but when the amide group is substituted with a phenyl sulfone group (or tosyl group), the nitrogen substituent becomes much more electron withdrawing, and the effect mentioned before comes into play and high *l*/*b* ratios can be obtained. For instance, **44**, a diphosphine or phosphoramide with a four-atom bridge is a highly selective ligand in hydroformylation, with *l*/*b* ratios up to 20 (60 °C, 7 bar).[95]



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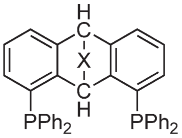

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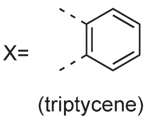
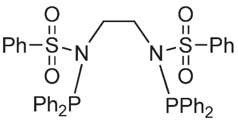




44

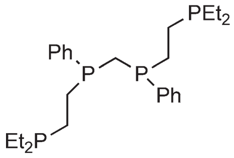
7.03.2.6 Alkylphosphines as Ligands

7.03.2.6.1 Monophosphines

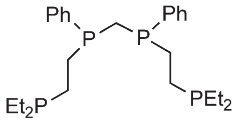
Electron-rich phosphines were not expected to be good ligands in hydroformylation, because the complexes they form of the type $HRh(CO)_x(L)_{4-x}$ are very stable toward dissociation of either CO or L (L = alkylphosphine) due to a "push–pull" effect of the donor- and acceptor-ligand combination. Cole-Hamilton and co-workers[96] did find activity for alkylphosphine complexes when $RhH(PEt_3)_3$ was used as the precursor at higher temperatures, as expected. Under the reaction conditions, $RhH(CO)(PEt_3)_3$ is the major species present. When the reactions are carried out in alcohols, the product of the reaction is the alcohol rather than the aldehyde. Deuteration studies show that the alcohol is the primary product and the reaction sequence is not the common one for hydroformylation. A new mechanism for this direct hydrocarbonylation is proposed in which the key acyl intermediate becomes protonated by the alcohol solvent because of the high electron density it bears as a result of the presence of the electron-donating trialkylphosphines. High pressure NMR studies showed that a rhodium carbene-like intermediate $[Rh\{C(O\cdots HOEt)Et\}(CO)_2(PEt_3)_2]$ is present during catalytic hydrocarbonylation of ethene in ethanol. Ethene gave rates as high as 54 000 turnovers per hour.

7.03.2.6.2 Dirhodium tetraphosphine

The majority of rhodium-based hydroformylation catalysts have the general structure $HRh(CO)_x(L)_{4-x}$ for the key intermediate, and no ionic intermediates are found. If under acidic conditions Rh^+ is formed, this usually leads to hydrogenation of the alkene and the aldehyde as a side reaction.[92] Stanley and co-workers[97] discovered a new type of catalyst, which also contains electron-rich phosphines, but which is a tetraphosphine-giving bimetallic catalyst. This system involves cationic rhodium species, which due to the strong donor phosphines, are sufficiently electron rich for CO binding and hydroformylation activity.[98] Several potential intermediates have been identified spectroscopically in the complex catalyst mixture, and several may have close metal–metal distances and bridging CO's. For the catalyst precursor $Rh_2(nbd)_2$(*rac*-45)$(BF_4)_2$, the X-ray structure determination shows that the two rhodium atoms have a square-planar geometry forming five-membered rings with the ligand and a metal–metal distance of 5.5 Å. The catalytic activity in 1-hexene hydroformylation of the bimetallic species was compared with several mononuclear complexes of ligands such as 47, which is one-half of ligands 45 and 46 and lacks the propensity for the formation of dimeric species. The results are surprising, as $Rh_2(nbd)_2$(*rac*-45)$(BF_4)_2$ forms a catalyst superior to all other systems; a tof of 600 (mol of aldehyde)·mol of $Rh)^{-1}\cdot h^{-1}$ (at 6 bar, 90 °C) and a *l*/*b* ratio of 27 was found in the aldehyde product (selectivity to aldehyde 85%). Surprisingly, *meso*-46 was 10 times less active and gave a *l*/*b* of 14. All other ligands (such as 47) gave tof's of 1–6 only and "normal" *l*/*b* ratios of 2–3. The large difference in activity between the bimetallic $Rh_2(nbd)_2$(*rac*-45)$(BF_4)_2$ and monometallic $Rh(nbd)^+$47 strongly suggests that the former reacts via a bimetallic mechanism. Most likely the intermediates are dicationic species, of which 48 is the key one of the bimetallic mechanism.

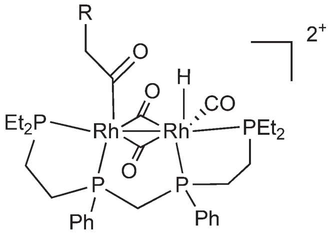


45 (*rac*)



46 (*meso*)

47



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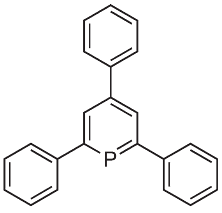
7.03.2.7 New Developments

New developments include new ways for separating catalyst and product, such as fluorous-phase hydroformylation catalysis, aqueous phase catalysis, one-phase hydroformylation and catalyst extraction, catalysis in ionic liquids, hydroformylation with immobilized catalysts, and catalysis in supercritical CO_2.[85–93] Two types of new ligands that attract attention will be mentioned here, namely phosphabenzene-type ligands and bidentate ligands constructed via supramolecular interactions. A variety of phosphabenzene ligands was synthesized by Breit *et al.*;[99] 49 represents a typical example. The phenyl substituents have been replaced by methyl groups and a variety of electronically varied aryl groups. As is to be expected, 49 is a very bulky ligand and its behavior in catalysis confirms this. The electronic properties are in between those of arylphosphines and phosphates, being closer to the latter. The performance in rhodium-catalyzed hydroformylation resembles that of the bulky phosphite 5. It provides a very fast catalyst for 1-octene, most likely with a precursor of the formula $HRh(CO)_3$**49**, as was proposed for **5**. Hydroformylation of internal alkenes was also found to be relatively fast. Remarkably, even tetra-substituted alkenes reacted with the phosphabenzene catalyst. Addition of benzyne to **49** gives phosphabarrelenes **50**. The rhodium complexes of these ligands are highly active for the hydroformylation of internal alkenes, but they give less isomerization than **5** under similar conditions.[100]



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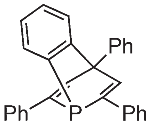

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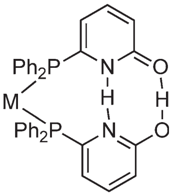
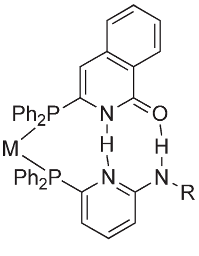


51

Two ways of assembling bidentate ligands by non-covalent interactions have been introduced in recent years, namely by hydrogen bonding and by the use of another assembly metal. Only the examples relevant to hydroformylation will be mentioned here. Breit *et al.* used hydrogen bonding to assemble the bidentate diphosphine ligand **51** which contains 2-pyridone/2-hydroxypyridine as the binding unit.[101] A bidentate ligand forms, which potentially has a wide bite angle resembling BISBI and xantphos, although it should be mentioned that the hydrogen bond is relatively weak, and the major part of the bonding energy between the two monodentates stems from the bonding of the phosphines to the metal. The performance in hydroformylation is excellent and *l*/*b* ratios up to 30 have been reported (70 °C, 10 bar). The system is less selective than xantphos but several times faster. A more stable bidentate was obtained with the use of the A–T binding motif of DNA, as shown in **52**.[102] Interestingly, the dissimilar parts can now be used separately and each gives a normal monophosphine selectivity; the *l*/*b* ratio is ~3. The combined supramolecular system led to high selectivity, mimicking the wide-bite-angle bidentate effect; the *l*/*b* ratio is ~25. The advantage of this approach is that a small number of monodentate ligands can lead to a quadratic number of new bidentate ligands. The second way to assemble bidentate ligands or more bulky ligands is the use of metal templates, which was explored by Reek and van Leeuwen and co-workers. In these studies, the assembly metal complex is a zinc porphyrin which has been exploited in several ways. Pyridylphosphines were reported previously as ligands in rhodium-catalyzed hydroformylation.[103] They behave as triphenylphosphine, but they are slightly weaker σ-electron donors (or better π-acceptors), and thus provide somewhat faster catalysts. The pyridyl group is still available for complexation to another metal complex. They were successfully ligated to zinc porphyrins to give encapsulated rhodium catalysts **53**.[104,105] In part, the system behaves as a more bulky catalyst albeit with a higher selectivity to branched aldehyde. The encapsulated phosphines lead exclusively to monoligated transition metal complexes, and in the Rh-catalyzed hydroformylation of 1-octene, the encapsulation of the catalysts resulted in a 10-fold increase in activity. The branched aldehyde was formed preferentially (*l*/*b* = 0.6), a selectivity that is highly unusual for this substrate, which is attributed to the encapsulation of the transition metal catalysts. Bis-zinc-porphyrin templates were used to make bidentate ligands **54**[106]; the phosphine derivative gave *l*/*b* ratios of 3 but a pyridyl phosphite analog gave *l*/*b* ratios of 16, and apparently they form bisequatorial complexes as a result of the bis-porphyrin template.



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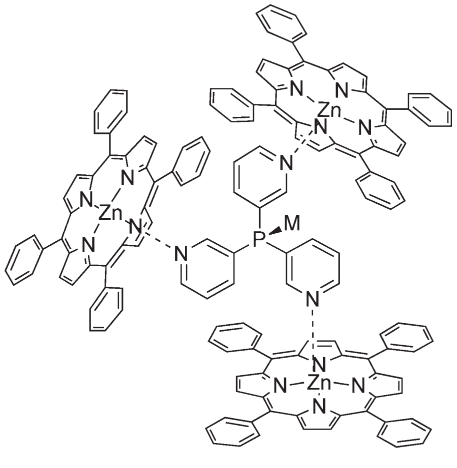

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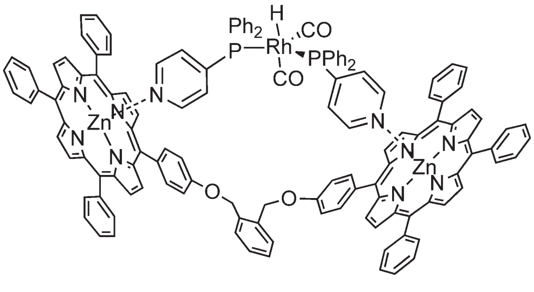
In another approach bidentates were assembled via a mixed covalent and supramolecular bonding. In **55**, one phosphite is connected covalently to the zinc porphyrin moiety and the second ligand is a pyridylphosphine. A complex $HRh(CO)_2$ **55** has been characterized showing bisequatorial coordination. Addition of PPh_3 did not interfere with this complex.[107] Combination in this way leads easily to libraries of new, bidentate ligand systems.



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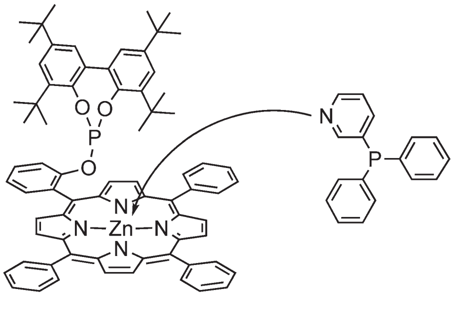

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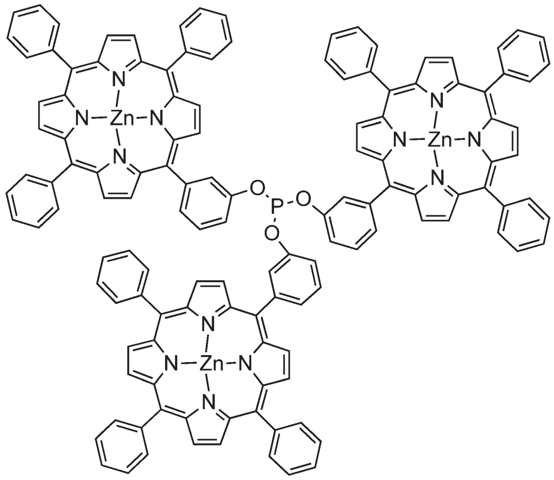
Phosphite **56** equipped with three zinc porphyrins reacts with 1,4-diazabicyclo[2.2.2]octane as the templating agent to give selectively **57** as a bis-phosphite rhodium metal complex.[108] In the absence of the templating diamine, the *l*/*b* ratio is 2–3 in the rhodium-catalyzed hydroformylation, but after addition of the template, it raised to 15–23, similar to covalently bonded bidentate phosphates with a wide bite angle.



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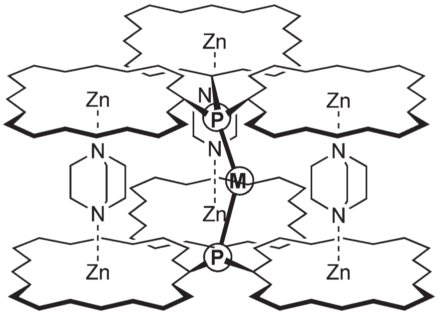

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7.03.3 Rhodium-catalyzed Methanol Carbonylation

7.03.3.1 Introduction

Acetic acid is a bulk chemical commodity industrially used for a wide range of applications, not only as a solvent, but also in the manufacture of cellulose acetate (for cigarette filters and photographic films) and vinyl acetate (paints, adhesives and textiles), as a bleach activator, or in the manufacture of food, pharmaceuticals, pesticides, etc.[109]

In 1966, the rhodium-iodide process for the catalytic production of acetic acid was initiated at the Monsanto laboratories.[110,110a] The first production plant based on this technology started operating in 1970 in Texas City with an initial capacity of 135 000 ton year^{-1}. In 1986, BP Chemicals (British Petroleum) acquired and further developed the technology while extending it all over the world. Nowadays, the global production of acetic acid reaches eight million ton year^{-1}, and it is led by two companies, Celanese (using "Monsanto" technology) and BP Chemicals, with processes based on both, rhodium and iridium.[111]

The high price of the rhodium and its complex recovery process have continuously driven the development of new systems that overcome these disadvantages. Increasing the activity and the stability of the catalyst, or immobilizing it to facilitate rhodium recuperation, are still current challenges.

7.03.3.2 Mechanism and Side Reactions

Mechanistically, the Monsanto process actually involves two interrelated catalytic cycles, one organometallic-based on rhodium ionic species, and an organic one where iodide should be considered as the true catalyst (Scheme 5). The two main components (rhodium and iodide) can be added in many forms. Under the reaction conditions RhI_3 is reduced by H_2O and CO to monovalent rhodium active species **58**, and methanol is converted to the iodo form, MeI.

The organometallic cycle comprises oxidative addition of MeI to $[RhI_2(CO)_2]^-$ **58** (generated *in situ*), which is considered to be the rate-limiting step of the Monsanto process, ligand migration to generate the acetyl complex **60**, CO coordination and reductive elimination of acetyl iodide to regenerate the rhodium active species **58**. Acetyl iodide enters the "organic" cycle where it is hydrolyzed to give acetic acid and HI, which transforms MeOH into the more electrophilic MeI that comes into the organometallic cycle.

It is important to notice that the two "organic" reactions ((1) and (2)) involving iodide show complete conversion. As a result, all of the iodide in the system occurs as a methyl iodide, and due to reaction (1), the rate of the catalytic cycle is independent of the methanol concentration.[112]

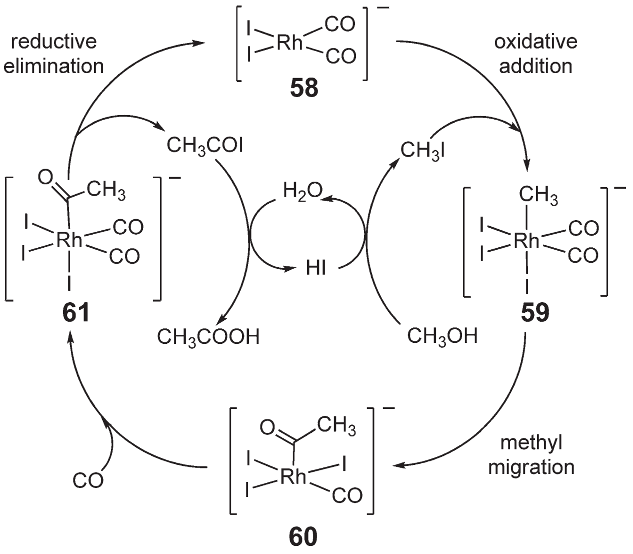
$$CH_3OH + HI \rightarrow H_2O + CH_3I \tag{1}$$

$$CH_3COI + H_2O \rightarrow CH_3COOH + HI \tag{2}$$

One of the main drawbacks of the process is the loss of the expensive metal due to the formation of Rh(III) inactive species, which, in areas of low CO pressure at the end of the reaction, precipitate as RhI_3. The inactive species $[RhI_4(CO)_2]^-$ can be produced by reaction of compounds **58** and **59** with HI according to reactions (3) and (4):

$$[Rh(CH_3)I_3(CO)_2]^- + HI \rightarrow CH_4 + [RhI_4(CO)_2]^- \tag{3}$$

$$[RhI_2(CO)_2]^- + 2\,HI \rightarrow H_2 + [RhI_4(CO)_2]^- \tag{4}$$



Scheme 5 Monsanto catalytic cycle.

In the Monsanto process, this problem is solved by keeping the water content relatively high, because it inhibits Rh precipitation by regenerating the Rh(I) active species from the labile $[RhI_4(CO)_2]^-$:

$$[RhI_4(CO)_2]^- + H_2O + CO \rightarrow [RhI_2(CO)_2]^- + 2\,HI + CO_2 \tag{5}$$

H_2 can also accomplish this goal (reaction (6)), and it can be generated in the reactor at high water concentrations through the water-gas shift reaction (7). In the absence of water, added H_2 could also perform this role, as it does in the related Eastman acetic anhydride process.[113,114]

$$[RhI_4(CO)_2]^- + H_2 \rightarrow [RhI_2(CO)_2]^- + 2\,HI \tag{6}$$

In fact, the presence of water is controversial; it is needed to maintain the rhodium in the active Rh(I) form, but there are also several problems associated with keeping it at high concentrations:

(i) The reaction of H_2O with CO through the water-gas shift reaction causes the loss of one of the feedstocks. Even if the selectivity of the overall process in MeOH is in the high nineties, the selectivity in CO can be as low as 90%.

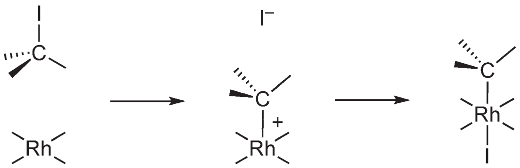
$$CO + H_2O \rightarrow H_2 + CO_2 \tag{7}$$

(ii) For the synthesis of acetic anhydride, water needs to be removed from the product by distillation at the end of the reaction, increasing the production costs considerably.

In the late 1980s, major technological advance was developed by Celanese, in order to circumvent the water problem.[115,115a] It consists of the use of salts (LiI or LiOAc) as promoters to maintain the reaction at low water levels. When using low water concentrations, the reduction of Rh(III) back to Rh(I) is slower, but so is the formation of $[RhI_4(CO)_2]^-$ due to the lower HI content available for reactions (3) and (4). The promotional effect of Li salts is attributed to the coordination of either acetate or iodide to **58** forming a highly nucleophilic intermediate dianion, $[Rh(CO)_2I_2X]^{2-}$ (X = I or OAc) and also to the kinetic and thermodynamic parameters of this new organic cycle, in which water has been replaced by LiOAc.[116,117]

7.03.3.3 Oxidative Addition of MeI; the Rate-limiting Step

The oxidative addition of MeI to **58** is considered to be the rate-determining step of the rhodium iodide-catalyzed process. It is generally accepted that it follows a two-step S_N2 mechanism; nucleophilic attack by the metal on the methyl carbon to displace iodide, presumably with inversion of configuration at the carbon atom, and a subsequent iodide coordination to the five-coordinate rhodium complex to give the alkyl-complex **59** (Scheme 6).[118,119] The product of this reaction has been fully characterized spectroscopically.[110a,120–122] Observations that support this mechanism are the second-order rate-law observed (first-order in both MeI and **58**) and the large negative activation entropies calculated that indicate highly organized transition states. Although there is general agreement on the mechanism, the theoretical calculations with respect to the geometry of the TS are still controversial.[117,123,124]



Scheme 6 MeI oxidative addition mechanism.

Table 4 ν(CO)-IR of the complexes [RhI(CO)L], and their reactivity towards MeI

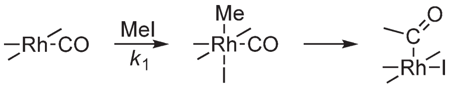
References	*Added ligand* (*L*)	ν(*CO*) (cm^{-1}) [RhI(CO)L]	$10^3 k_1$ (M^{-1}s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})
120,122	–[a]	2055, 1985	0.0293	50 ± 1	−165 ± 4
128	2PEt$_3$	1961	1.37	56 ± 13	−112 ± 44
126	**62**	1981	no reaction		
125	**63a**	1970	no reaction		
127	2 **64a**[b]	1943	0.0441	36 ± 1	−189 ± 3
134,135	dppms **66**	1987	1.19	47 ± 1	−144 ± 2
134,133	dppmo **67**	1983	1.14	34 ± 4	−188 ± 13
134,135	dppe **68**	2011	1.41	40 ± 1	−167 ± 2
142	**80a**	1994	12.0	35 ± 1	−162 ± 4
142	**80b**	1993	1.02	42 ± 1	−160 ± 2
142	**80c**	1993	0.145	41 ± 1	−182 ± 2
142	**80d**	1989	140	25 ± 2	−176 ± 6
142	**80e**	1988	88.5	27 ± 1	−175 ± 4
142	**80f**	1987	8.34	25 ± 3	−201 ± 10
142	**80g**	1977	206	18 ± 1	−199 ± 4
143	**81**[c]	1980	1660	19 ± 1	−179 ± 4

[a] Neat MeI.
[b] [MeI] = 1.6M, CH$_2$Cl$_2$, data concerning only the forward reaction.
[c] Complex [Rh(CO)**81**].

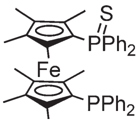
A general approach to facilitate the oxidative addition of MeI to the active rhodium species is to increase the nucleophilicity of the metal center by means of donor ligands. In order to get an insight into the activity of the related ligand-modified systems, independent kinetic studies pertaining only to this elementary step can be performed by using IR spectroscopy. Table 4 presents the values of second-order rate constants and activation parameters for MeI oxidative addition to rhodium complexes when using several ligands. They have been calculated by measuring pseudo first-order constants (k_{obs}) (using at least 10-fold excess of MeI in CH$_2$Cl$_2$) at different temperatures and MeI concentrations.

In all the cases, a first-order dependence on both MeI and rhodium complex is observed for the reactions. Depending on the relative rates of oxidative addition/methyl migration, sometimes the directly corresponding acetyl compound is observed, but occasionally (*vide infra*), the alkyl intermediate, the product of the oxidative addition, can be detected by IR spectroscopy or even isolated as the sole product of the reaction (Scheme 7).

The frequency of the IR stretch vibration ν(CO) of the catalytically active complex [RhI(CO)L] is usually considered as a measure of the electron density on the metal center, and consequently its nucleophilicity and reactivity toward MeI. It is generally accepted that the larger the electron density on the metal, the lower the ν(CO), due to electron back-donation on the π^*-orbital of the coordinated CO. Nevertheless, some examples provide evidence that a direct correlation between the frequency of the IR stretch vibration of the coordinated CO and the reactivity of the rhodium complex versus MeI cannot be established, but several other factors need to be taken into account. First, the relative disposition of the ligands around the rhodium center plays a role. If we compare [RhI(CO)dppe] with [RhI(CO)(PEt$_3$)$_2$], which each exhibit similar reactivity toward MeI, the frequencies of the corresponding ν(CO) differ by ca. 50 cm^{-1}. This can be attributed to the fact that a carbonyl trans to iodide experiences considerably more back-donation than one trans to a phosphine. Secondly, not only electronic, but also steric effects play an important role in this elementary step. Ligands **62** and **63** (SPANphos) represent extreme cases.[125,126] The corresponding metal complexes [RhI(CO)**62**], and *trans*-[RhI(CO)**63**] show ν(CO) frequencies similar to other active systems (see Table 4), but they do not react with MeI via oxidative addition. This difference in reactivity is attributed to the fact that the backbone of the ligand eclipses one of the axial coordination sites of the rhodium center, inhibiting oxidative addition.



Scheme 7 Kinetic scheme.



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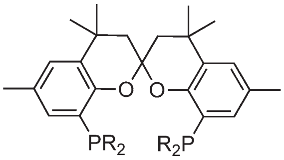
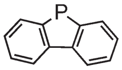
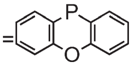


63a: $PR_2 = PPh_2$
63b: $PR_2 = PCy_2$
63c: $PR_2 =$ 
63d: $PR_2 =$ 

64a: R = Me
64b: R = Et
64c: R = CH_2Ph
64d: R = 4-pentenyl
64e: Mesityl

In the case of ligands **64**,[127] despite the higher nucleophilicity of the corresponding Rh-biscarbene complex that could be envisaged due to the low value of their corresponding ν(CO), they display a very low reactivity versus MeI (see Table 4). In this case, it should be also attributed to the characteristic ligand disposition in which the NCN plane is perpendicular to the Rh(I) coordination plane, and therefore the R substituents partially block the rhodium axial sites inhibiting nucleophilic attack on MeI. When using ligand **64a**, the corresponding Rh(III) acetyl compound is obtained at the end of the reaction, but it is unstable and decomposes to [RhI(CO)**64**$_2$] by elimination of MeI. The thermodynamic parameters for the forward reaction are similar to those of more active systems. When these carbene ligands are applied in methanol carbonylation, they show no activity enhancement compared to the Monsanto process, and they dissociate from the rhodium center to generate $[RhI_2(CO)_2]^-$.

In order to accelerate the rate of MeI oxidative addition (and consequently the rate of the overall process), electron-donating ligands need to be used. The IR stretch vibration of the CO coordinated to the metal can be indicative of the electron density on the rhodium center, but steric effects play a key role when relating it to reactivity versus MeI.

7.03.3.4 Ligands Design

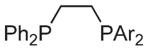
In the last 20 years, many efforts have been directed to develop ligands able to increase the activity of the rhodium-iodide based Monsanto system. In some cases, even if they do not contribute with a significant reaction improvement, they are crucial for a better understanding of the reaction mechanism, and constitute basic pillars for further developments. Some of the most representative examples are mentioned in this section.

In 1997, Ranking *et al.* reported a PEt_3-rhodium modified system,[128,128a] and when employing this basic phosphine, the rate of oxidative addition of MeI to $[RhI(CO)(PEt_3)_2]$ is ca. 47 times higher than the one reported for **58** at 25 °C. The corresponding alkyl compound $[RhI_2(CO)(CH_3)(PEt_3)_2]$ was isolated and crystallographically characterized, exhibiting a *trans*-configuration of the phosphine ligands about the metal center. Although in comparison to the Monsanto system there is a large increase in the rate of oxidative addition, it represents only an increase in activity of 1.8 under catalytic conditions (150 °C). At this temperature, loss of activity is observed after ca. 10 min, due to degradation of the catalytically active system to $[Rh(CO)_2I_2]^-$. Decomposition proceeds via reaction of $[RhI_2(CO)(CH_3)(PEt_3)_2]$ with HI to generate $[RhI_3(CO)(PEt_3)_2]$, which reductively eliminates $[PEt_3I]^+$ leading to $OPEt_3$.

Chelating symmetrical and unsymmetrical ligands have been introduced in order to overcome the instability of the monophosphines under the harsh conditions of the process.

The use of symmetrical diphosphines has been covered by the patent literature,[129,130,130a] and when using xantphos derivatives **29**–**38** as ligands for methanol carbonylation, they are stable systems that show a slightly higher activity than the one obtained with the Monsanto catalyst. Nevertheless, in this case, a terdentate P–O–P coordination of the ligand is claimed.

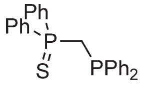
Carraz *et al.*[131,131a] reported the use of asymmetrically substituted 1,2-ethanediyl diphosphines **65** that are very stable under the reaction conditions, although they do not represent an improvement on the catalytic activity when compared with the Monsanto process. At the end of the reaction, a mixture of diphosphine Rh(III) carbonyl complexes can be isolated and characterized, and a second run can be performed without loss of activity.



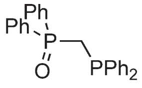
65a: Ar = C_6H_4OMe-4
65b: Ar = C_6H_4F-3
65c: Ar = $C_6H_4CF_3$-3
65d: Ar = $C_6H_3F_2$-3,5
65e: Ar = $C_6H_2F_3$-3,4,5
65f: Ar = $C_6H_3(CF_3)_2$-3,5

An alternative strategy to increase the activity and stability of the systems is the use of hemilabile phosphine ligands (PX; X = P, O, S). They are supposed to stabilize the complex via the chelate effect and to increase the nucleophilicity of the rhodium by coordination of a heterodonor atom.

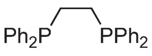
A comparative study of PS, PO, and PP ligands able to form 5-membered chelate rings 66,[132] 67,[133] 68 shows that the corresponding [RhI(CO)(PX)] complexes react between 35 and 50 times faster with MeI than 58, an activity similar to the one observed with PEt_3.[134,135] This enhancement in activity is attributed to the good donor properties of the ligands. Unlike dppe and PEt_3 systems, for which the corresponding alkyl intermediate can be isolated, dppms 66 undergoes a fast subsequent migratory insertion to give the corresponding acetyl compound.



dppms **66**

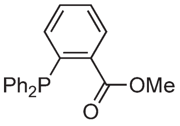


dppmo **67**



dppe **68**

Another example of this family of ligands using oxygen as a heteroatom is methyl 2-diphenylphosphinobenzoate 69.[136] Depending on the stoichiometry of the reaction with $[Rh(CO)_2Cl]_2$, the corresponding rhodium species [RhCl(CO)69], 70, and $[RhCl(CO)69_2]$, 71, are formed. In complex 70, the ligand acts as a chelate through the P and O atoms, whereas in 71, two phosphines coordinate in a *trans*-fashion, and secondary Rh–O interactions are suggested. Due to the increased nucleophilicity of the rhodium center, both systems show an activity that is ca. 1.5 times higher than Monsanto's system under the same catalytic conditions. This increase in nucleophilicity is in agreement with the low values of ν(CO) observed (1979 and 1949 cm^{-1}, respectively). Nevertheless, complex 71 shows slightly lower reaction rates, which is attributed to the increase in steric hindrance about the metal center on account of the presence of two ligands.



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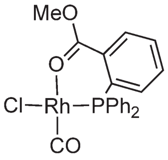

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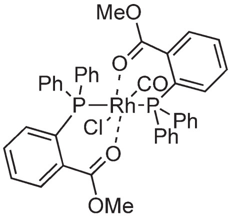

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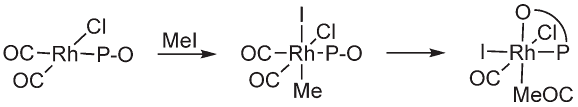
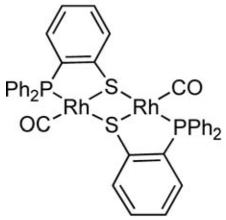
Hemilabile ether-phosphine ligands Ph_2PCH_2OMe **72** and $PPh_2(CH_2)_2OEt$ **73** react with 0.5 equiv. of $[Rh(CO)_2Cl]_2$ to form the corresponding complexes $[RhCl(CO)_2\mathbf{72}]$ and $[RhCl(CO)_2\mathbf{73}]$, with the ligands coordinating only through the phosphorus atom (κ(P)).[137] These rhodium complexes undergo oxidative addition with MeI to yield the six-coordinate acetyl species in which the ligand acts as a chelate with the oxygen bound to the metal trans to the acetyl moiety. Under catalytic conditions, ligands **72** and **73** show an activity ca. 1.2 and 3.3 (respectively) times higher than the Monsanto system. The difference in activity is attributed to the higher basicity and stability of the five-membered chelate ring of the acetyl complex formed when using **73**, in comparison to the four-membered chelate ring obtained with **72**. In both cases, a "closing–opening" mechanism is proposed and a catalytic cycle, involving species in which the ligands act in both monodentate κ(P) and bidentate κ(P)–κ(O) manners, has been proposed (see Scheme 8).

When using dppeo,[133] $Ph_2P(CH_2)_2P(O)Ph_2$ **74**, a ligand quite active for methanol carbonylation under mild conditions (80 °C, 50 psig CO, tof = 400 mol mol^{-1} h^{-1}), the same type of "closing–opening" mechanism is supposed to be operative. This is in contrast with dppmo, which forms a five-membered chelate ring, and the ligand acts as a bidentate during the whole catalytic cycle.



Scheme 8

Also, several P–S (phosphino-thiolate) anionic ligands which form five- and six-membered chelate rings have been evaluated as catalysts for the methanol carbonylation.[138,138a,139] When using these ligands, the catalyst precursors are the dinuclear rhodium compounds with bridging thiolates **75–77**. In the case of complexes **75** and **76**, the reaction with MeI leads to S-methylation of the ligand and formation of the mononuclear rhodium halide–carbonyl phosphine thioether complexes **78** and **79**, respectively. Systems **75–77** catalyze methanol carbonylation ca. 3–4 times faster than $[Rh(CO)_2I_2]^-$, and only slightly lower activities are observed for systems **78** and **79**. A catalytic cycle involving mononuclear phosphine-thioether species was proposed.



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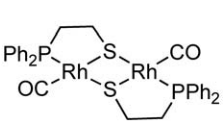

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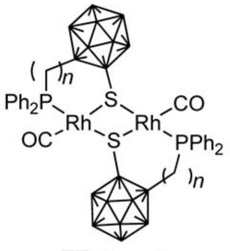
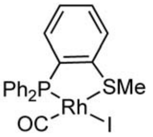


77a: *n* = 0
77b: *n* = 1



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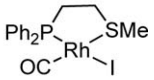
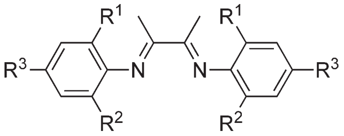


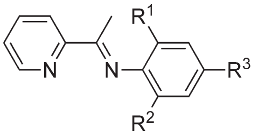
79

Mono-coordinating nitrogen donor ligands (i.e., *ortho*-, *meta*-, and *para*-amino benzoic acids and pyridine aldehydes) have also been tested in the carbonylation of methanol.[140,141] The corresponding rhodium complexes with the ligand coordinated by the nitrogen atom $[Rh(CO)_2ClL]$ have been characterized, and additional coordination of the oxygen atom to generate a bidentate ligand is not observed in any of the cases. The reaction with MeI to yield directly the acetyl derivatives $[Rh(CO)(COCH_3)ClL]$ is evidence that fast migration occurs after oxidative addition has taken place. The activities observed under catalytic conditions are ca. 2 times more than those obtained when employing $[Rh(CO)_2I_2]^-$, and in the case of aminobenzoic acids, the catalyst can be recycled without an important decrease in the activity, proving its thermal stability.

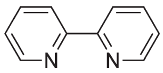
Chelating α-diimine ligands have been used to evaluate the importance of steric effects on the rate of oxidative addition/migratory insertion.[142] In the case of the less bulky ligands **80a, 80d, 80e, 80g**, the reaction of the corresponding [RhI(CO)**80**] complexes with MeI renders the Rh(III) methyl compounds and, in the best case, it presents a rate enhancement of ca. 70 000 times when compared to **58**. The ligands exerting greater steric hindrance, **80b** and **80c**, show a much lower rate of oxidative addition, and the Rh(III) alkyl complexes immediately form the acetyl compounds, due to faster migratory insertion.



Str	*R*1	*R*2	*R*3
80a	H	*i*Pr	H
80b	Me	Me	Me
80c	*i*Pr	*i*Pr	H

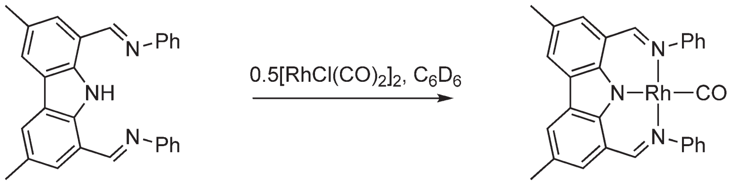


Str	*R*1	*R*2	*R*3
80d	H	H	H
80e	H	*i*Pr	H
80f	*i*Pr	*i*Pr	H



80g: bipy

In order to increase even further the nucleophilicity of these bis-imine systems, Gaunt *et al.*[143] described also a terdentate anionic bis(imino)carbazolide ligand **81**. In the corresponding rhodium complex [Rh(CO)**81**], the soft iodide ligand has been replaced by the harder *N*-carbazolide moiety (Scheme 9). When this complex is tested for the oxidative addition of MeI, it showed a rate increase of 7000 with respect to the best bis-imine complex [RhI(CO)**80g**]. It represents a reaction rate 50 000 times higher than the value reported for the original $[RhI_2(CO)_2]^-$ Monsanto catalyst, and to date, it is the fastest system reported for the oxidative addition of MeI. Unfortunately, the catalytic performance of this very promising system has not been published yet.



81

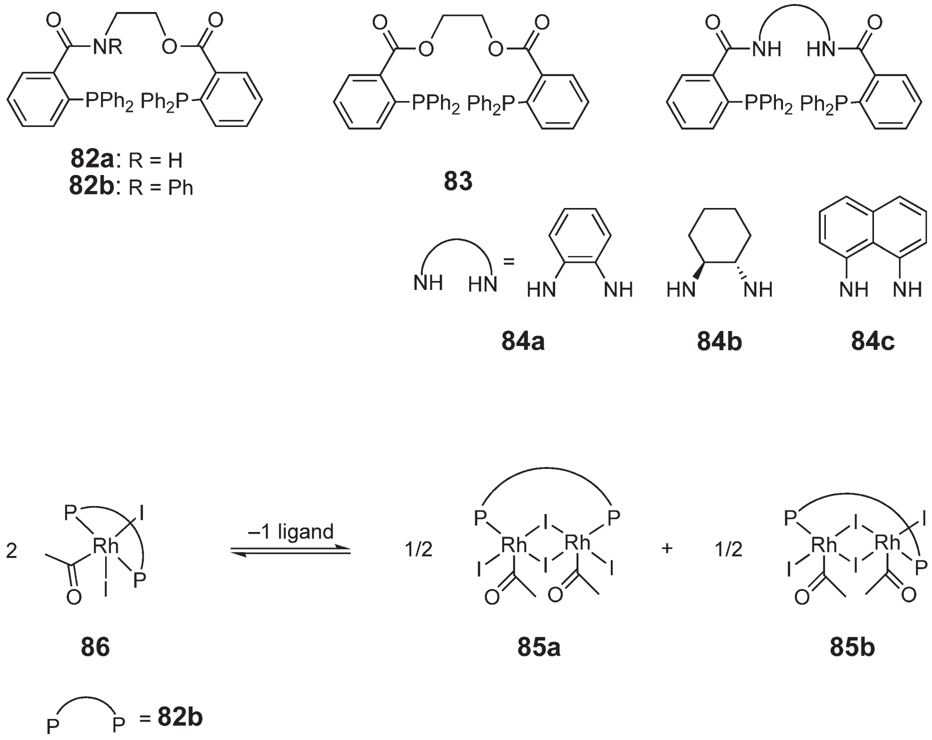
Scheme 9

7.03.3.5 *Trans*-diphosphines in Methanol Carbonylation; Dinuclear Systems?

Phosphorus-based systems constitute an important family of ligands in homogeneous catalysis. Even though the use of basic phosphines, which increases the nucleophilicity of the rhodium center, was initially considered a very promising strategy,[128] their instability under the harsh conditions of the process constituted a major drawback for their application. Attempts to circumvent the decomposition were undertaken by using bidentate diphosphines, which stabilize the active rhodium species by the chelate effect (*vide supra*).

In an effort to develop new systems able to combine both stability and activity, Süss-Fink and co-workers reported a family of trans-spanning, but flexible diphosphines.[144,145,146] These ligands form stable complexes, due to the chelate effect, which resemble the ones obtained with PEt_3, (*trans*-$[RhI(CO)(PEt_3)_2]$), with the two phosphorus atoms in a *trans*-disposition. These ligands, as benzoic acid diphenylphosphine derivatives, are supposed to increase the electron density on the rhodium center due to a weak Rh–O interaction.

When the corresponding rhodium complexes are tested in methanol carbonylation, the activity obtained is ca. 2.5 times higher than the one obtained with the Monsanto system under the same conditions. The stability of the systems is evident by the ability to perform several runs without any noticeable loss in activity. From the residue of the reaction, when ligand **82b** is employed, apart from the corresponding [RhI(CO)**82b**] complex, the dinuclear isomeric compounds **85a** and **85b** were isolated and characterized by X-ray diffraction (Scheme 10).



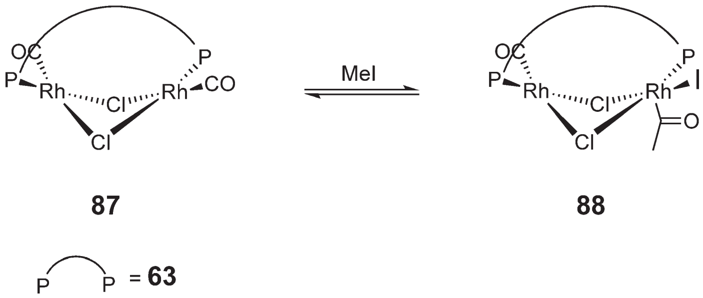
82a: R = H
82b: R = Ph

83

84a **84b** **84c**

86 **85a** **85b**

Scheme 10 Monomer-dimer equilibrium.



Scheme 11 Oxidative addition with dinuclear complexes.

The proposed catalytic cycle is analogous to Monsanto's one, but it involves neutral species with a *trans*-chelating diphosphine. Presumably, the isolated dinuclear compounds 85a and 85b act as resting states for the acetyl complex [RhI_2(COMe)82b] 86, which arises from it by loss of diphosphine.

Another family of diphosphines displaying a *trans*-coordination mode, SPANphos 63a–d, has also been tested in this reaction.[125] Surprisingly, even if the corresponding *trans*-[RhI(CO)63] render systems as active as the Süss-Fink analogs, when tested in an elementary step, they show no reaction in the oxidative addition of MeI (*vide supra*). The observed catalytic activity has been attributed to dinuclear species formed under catalytic conditions. The dinuclear compounds [$Rh_2(\mu\text{-Cl})_2(CO)_2$63a], 87, react with MeI at 25 °C with a k_1 value of ca. 0.025 $s^{-1}M^{-1}$, and currently they represent the fastest phosphine-based systems reported for methanol carbonylation. According to spectroscopic and GC-MS analysis, the products of the MeI oxidative addition are dinuclear monoacetyl derivatives 88 (Scheme 11).

The reactivity of dinuclear rhodium compounds toward MeI has been a subject of study since the late 1970s.[147,148] Unfortunately, no kinetic data are available, but the corresponding mono- and bis-acetyl derivatives have been detected. The fact that the oxidative addition/migration on the second metal center becomes more difficult after the first one has taken place is a common observation, especially when the "open-book" conformation of the complexes is forced by the (bridging) ligands.[149]

In fact, the possible involvement of dinuclear species in the Monsanto process was proposed already in the earliest studies, where the dimerization equilibrium of the acetyl derivative $[RhI_3(COMe)(CO)]^-$ 60 was considered.[120] The corresponding dinuclear species $[Rh_2I_6(CO)_2(COMe)_2]^{2-}$ was isolated in the form of its trimethylphenylammonium salt and characterized by X-ray diffraction. The possibility that neutral dinuclear methyl and acetyl Rh(III) species play an important role in the Monsanto process has very recently been reconsidered.[150] These neutral species should lead to faster CO migratory insertions and reductive eliminations than their anionic analogs, and surely in the future new ligands able to generate more active dinuclear systems for methanol carbonylation will be developed.

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7.04
Iridium Organometallics

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7.04.1 Introduction

7.04.1.1 Perspective and Scope

Following a general trend which is common to most different areas of organometallic chemistry, fundamental and applied studies focused on iridium organometallic compounds have had a tremendous expansion in the decade that separates the preparation of this review from COMC (1995) which reviewed the scientific literature from 1982 to the end of 1994. A perusal of the available scientific databases addressing the topic "iridium" associated with the common lemmas and keywords of organometallic chemistry disclosed a huge amount of scientific literature dealing with iridium organometallic compounds and their application in different disciplines, mainly in homogeneous catalysis. Due to the readily available source of information via search engines on the World Wide Web, rather than attempting to organize a comprehensive account on organoiridium chemistry, the authors have decided to emphasize a few specific sections reflecting their own opinions and interests among the many possibilities available in the broad field offered by iridium organometallic compounds.

Although the development of iridium organometallic chemistry cannot compare with the importance assumed by its light congener, rhodium, iridium organocompounds have faced a tremendous growth including both fundamental and applied chemistry. Iridium has become a popular transition metal in the chemical community doing research in homogeneous catalysis. Worthy of mention to underpin the importance of organoiridium compounds are the successful industrial application of simple iridium halocarbonyl complexes to the manufacture of acetic acid via catalytic carbonylation of methanol (CATIVA™ process) and the use of simple iridium salts and complexes in a great variety of catalytic reactions including asymmetric processes which are brought about with high conversions and enantioselectivities. Even more importantly, these often complement the performance obtained by catalysts based on "classic" active metals such as rhodium, ruthenium, and palladium.

7.04.1.2 Organization of the Material

The chapter has been divided into six sections with the material organized in a different way with respect to both COMC (1982) and COMC (1995) which surveyed the literature up to 1982 and 1994, respectively. Thus, while the first two editions of COMC organized the chapter "iridium" following the criterion of grouping organoiridium species as a function of the iridium nuclearity (COMC (1982)) or the coordination number exhibited by the metal center (COMC (1995)), we decided to follow a different approach.

This chapter begins with a section dealing with iridium carbonyl complexes, organized by following the increasing metal nuclearity of the compounds. Section 2 summarizes iridium organometallic compounds featuring single Ir–C bonds. Alkyl, aryl, alkenyl, and alkynyl iridium species are therefore described in this section which ends with the specific uses of these complexes for the construction of C–C bonds via homogeneous catalytic processes. Section 7.04.3 summarizes the important field of organoiridium complexes with multiple Ir–C bonds. Carbenes, vinylidenes, allenylidenes, and higher cumulenilidenes are described in this section together with the few known carbyne species in which a formal $Ir{\equiv}C$ triple bond is present. Next, we consider the organoiridium complexes presenting π-type ligands, mainly cyclopentadienyls, indenyls, and arenes, which are ubiquitous throughout the organoiridium chemistry and have found spectacular applications in homogeneous catalysis, and have allowed unraveling the mechanism of many fundamental organometallic reactions. Section 6 reviews organoiridium compounds containing fullerene as ligand and precedes the final section of this review which summarizes the chemistry of iridium hydrides. Although hydrides cannot be formally enrolled among organometallic compounds as they do not possess any Ir–C bond, their importance in mediating fundamental organometallic processes and their significance in understanding structural and bonding issues of organometallic chemistry justify their presence in a review devoted to highlight the development of organoiridium chemistry in the last decade.

We are well conscious that different choices in the systematization of this chapter would have been possible, all with identical dignity and scientific importance. Occasionally, although compounds which are relevant to different aspects of iridium organometallic chemistry appear in different chapters of this review, we do not think this is a limit of the work; rather, a clear indication that a comprehensive summary of "iridium organometallic chemistry" may have different interpretations and multiple viewpoints to both readers and authors.

7.04.2 Carbonyl Iridium Complexes

In the last decade, iridium carbonyl complexes have found many applications in homogeneous and heterogeneous catalysis, as well as in photoluminescent and optoelectronic devices. These aspects will be described in the corresponding sections. Here are summarized the main developments in the synthesis, characterization, and some, although brief, descriptions of use of the most remarkable iridium mono-, di-, polycarbonyl and cluster complexes. Specific reactivity of alkyl, aryl iridium carbonyl complexes are dealt with in the appropriate paragraph in this chapter.

7.04.2.1 Monocarbonyl Complexes

7.04.2.1.1 Vaska's complex: recent analogs and reactivity studies

Some interesting modifications of Vaska's complex $[IrCl(CO)(PPh_3)_2]$[1] **1** have appeared in the literature since the publication of COMC (1995). Apart from the multitude of analogs obtained with different phosphines, such as *trans*-$[IrCl(CO)(PCy_3)_2]$,[2,2a] an improved, high-yield general synthesis for *trans*-$[IrCl(CO)(PR_3)_2]$ ($PR_3 = PPh_3$ **1**, PPh_2Me **2**, $PPhMe_2$ **3**, PEt_3 **4** and PMe_3 **5**) was reported.[3]

Water-soluble analogs of **1** were prepared using the water-soluble phosphine ligands sodium di- or triphenyl(*m*-sulfonatophenyl)phosphine (TPPMS, TPPTS) and 1,3,5-triaza-7-phosphaadamantane (PTA). The water-soluble Ir complexes *trans*-$[IrX(CO)L_2]$ (X = Cl, OH; L = $PPh_2(m\text{-}C_6H_4SO_3K)$ (TPPMS), $P(m\text{-}C_6H_4SO_3Na)_3$ (TPPTS)) were used to examine the effect of pH changes on the rate of H_2 addition to an organometallic center. The kinetic isotope effect, $k_H/k_D = 1.1$ (L = TPPMS) and 1.2 (L = TPPTS), for addition of H_2O to *trans*-$[IrCl(CO)L_2]$ in H_2O is the same as that observed for **1** in toluene and indicates a common mechanism. Polar solvents accelerate the rate of H_2 addition to *trans*-$[IrCl(CO)L_2]$ in accordance with a polar transition state. Increasing the pH causes a decrease in the rate of H_2 addition for *trans*-$[IrCl(CO)(TPPMS)_2]$ **6** and *trans*-$[IrCl(CO)(TPPTS)_2]$ **7** in H_2O.[4]

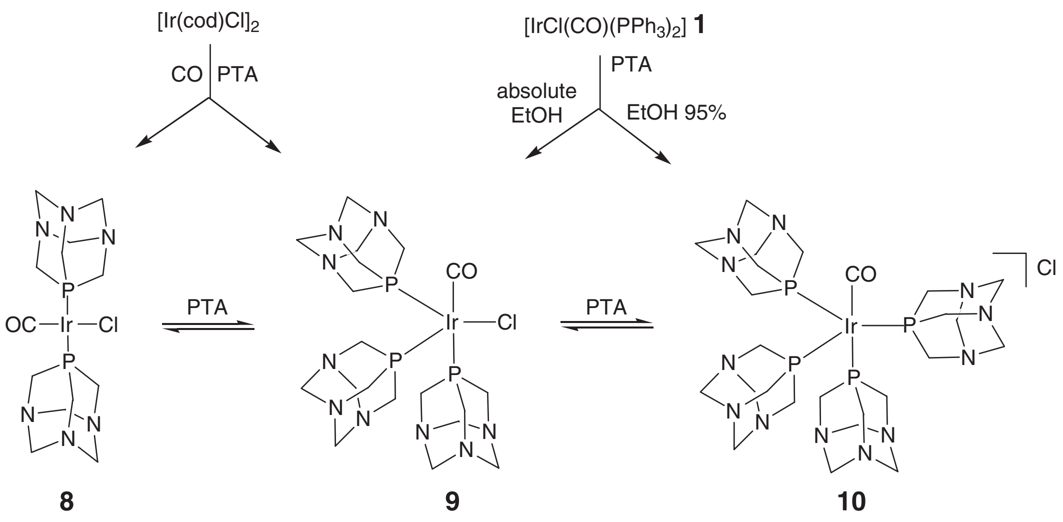
The structural parameters in **6** closely resemble those found in the parent complex, as shown by X-ray crystallography.[5] The oxygen adduct $[(O_2)IrCl(CO)(TPPMS)_2]$ was isolated and identified by IR spectroscopy ($\nu_{CO} = 2012\ cm^{-1}$ and $\nu_{O2} = 854\ cm^{-1}$) and ^{31}P NMR (δ 12.8 ppm). The solution behavior of **6** in water is markedly different from that of Vaska's complex in organic solvents as reactions with O_2 and H_2 are irreversible due to the formation of the strongly hydrated proton and chloride ions. Furthermore, complex **6** is an active catalyst for the hydrogenation of C=C double bonds in short-chain unsaturated acids in aqueous solution. Complex **7** H_2O was prepared from the reaction of the water-soluble $[IrCl(cod)(TPPTS)_2]\cdot 6H_2O$ and found to catalyze the hydration of terminal alkynes to give ketones in aqueous solutions at room temperature.[6]

An important water-soluble compound is the PTA version of Vaska's complex *trans*-$[IrCl(CO)(PTA)_2]$ **8**.[7,7a] A related compound $[IrCl(CO)(PTA)_3]$ **9** was synthesized by either refluxing *trans*-$[IrCl(CO)(PPh_3)_2]$ with 3 equiv. of PTA in absolute ethanol or by combining 3 equiv. of PTA with $[Ir(cod)Cl]_2$ under CO.[5] The tris-PTA derivative **9** reacts with water converting into the tetrakis cationic adduct $[Ir(CO)(PTA)_4]Cl$ **10**. The latter is also formed by heating *trans*-$[IrCl(CO)(PPh_3)_2]$ with PTA in H_2O at 60 °C for 4 h or by refluxing **1** with excess PTA in 95% EtOH (Scheme 1).

Another water-soluble phosphine ligand, amphos (amphos = $[PPh_2CH_2CH_2NMe_3]I$), was used for the synthesis of *trans*-$[Ir(CO)X(amphos)_2]$ (X = Cl **11a**, I **11b**), $[Ir(CO)(H)(amphos)_3]$ **12** and $[Ir(CO)_3(amphos)_2]^+$ **13**, which were further reacted with H_2 and CO. Structures of *trans*-$[Ir(CO)(Cl)(PPh_2CH_2CH_2NMe_2)_2]$ and **11a**·2DMSO were compared to each other and to **1**. The amphos ligand changes the solubility of Ir complexes without affecting the nature of the metal center.[8]

Time-resolved IR absorption spectroscopy was used to investigate the photolysis of **1**. Upon 308 nm photolysis, an intermediate dimeric species was formed that regenerated **1** on a millisecond timescale. This intermediate was not formed at the laser flash, but was generated over the course of ca. 10 μs without decrease of the C–O stretching of **1** upon photolysis.[9]

Fluorous analogs of Vaska's complex were also described. The tris(pentafluorophenyl) phosphine complexes $[IrX(CO)\{P(C_6F_5)_3\}_2]$ (X = Cl, **14a**, Br, **14b**), formed by reaction between IrX_3 and $P(C_6F_5)_3$ in 2-methoxyethanol,



Scheme 1

were synthesized by Hope and co-workers and the crystal structure of **14b** was reported.[10] The reaction of $[IrCl(cod)]_2$ with $P\{CH_2CH_2(CF_2)_5CF_3\}_3$ and CO (1 atm) gave the perfluoro analog of **1**, namely *trans*-$IrCl(CO)[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ **15**, for which the X-ray crystal structure was also determined (Figure 1).[11]

The νCO stretching value for **15** (1975 cm^{-1}) shows that the CH_2CH_2 spacers do not protect the metals from the influence of the perfluoroalkyl groups completely. Compound **15** is soluble in $CF_3C_6F_{11}$, $CF_3C_6H_5$, ether, THF, and acetone but insoluble in hexane, toluene, $CHCl_3$, and CH_2Cl_2. Reactions of **15** with RI, H_2, and $^3O_2$ or $^1O_2$ in $CF_3C_6F_{11}$ gave $[IrI(Cl)(R)\{P(CH_2CH_2(CF_2)_5CF_3)_3\}_2]$ [**16**, R = $CH_2CH_2(CF_2)_7CF_3$, CH_3, $CHMeCH_2CH_3$], $[IrCl(CO)(H)_2\{P(CH_2CH_2(CF_2)_5CF_3)_3\}_2]$, **17** and $[IrCl(CO)(O_2)\{P(CH_2CH_2(CF_2)_5CF_3)_3\}_2]$, **18** respectively. Additions of RI occur by free-radical chain mechanism as evidenced by reaction inhibition in the presence of duroquinone and slower reactions in the dark.[12]

7.04.2.1.2 Ligand substitution reactions

Several N-based ancillary ligands were used in the recent literature in ligand substitution reactions with monocarbonyl iridium complexes. The reaction of **1** with indolyllithium reagents gave the σ-N-coordinated indolyl complexes *trans*-$[Ir(CO)(PPh_3)_2(L)]$[L = indolyl **19**, 2,3-dimethylindolyl **20**]. Complex **20** was characterized by X-ray diffraction. The indolyl ligand behaves as a σ-donor to the metal ion, the Ir–N bond being stable to protic acids. This stability is reflected in the reaction of **20** with triflic acid resulting in protonation at the 3-position of the heterocycle and formation of an indolenine complex. Reaction of **19** with $NaBH_4$ forms $[Ir(PPh_3)_2(CO)H_3]$ **21** as a mixture of isomers, but does not react with CO (3 atm) at room temperature over 18 h (Scheme 2).[13]

Condensation of *Z*-$PPh_2CH_2C(Bu^t){=}NNH_2$ with salicylaldehyde or 4,6-dimethoxysalicylaldehyde gave the azine phosphines *Z,E*-$PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_5H_4OH)$ (L_1) or *Z,E*-$PPh_2CH_2C(Bu^t){=}N{-}N{=}CH[C_6H_2(OH)\text{-}(4,6\text{-}OMe)_2]$ (L_2), respectively. Reaction of L_2 with $[IrCl(CO)_2(p\text{-}MeC_6H_4NH_2)]$ or 0.5 equiv. of $[Rh_2Cl_2(CO)_4]$ in the presence of NEt_3 gave the square-planar complexes $[M(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH[C_6H_2O\text{-}(4,6\text{-}OMe)_2]\}]$ (M = Ir **22** or Rh **23**). The carbonyliridium(I) complex **22** oxidatively adds MeI, allyl chloride, acetyl chloride or propargyl chloride to yield the halocarbonyliridium(III) complexes $[IrX(R)(CO)\{PPh_2CH_2CH_2C(Bu^t){=}N{-}N{=}CH[4,6\text{-}C_6H_2O(OMe)_2]\}]$ **24a–d** respectively, whereas the reaction of the rhodium(I) analog **23** with allyl chloride affords the π-allylrhodium(III) complex $[RhCl(\eta^3\text{-}C_3H_5)\{PPh_2CH_2CH_2C(Bu^t){=}N{-}N{=}CH[4,6\text{-}C_6H_2O\text{-}(OMe)_2]\}]$ **25**.[14]

The use of similar functional phosphines in selective catalytic hydrogenation of saturated and unsaturated ketones and aldehydes in the presence of $[Ir(CO)(PPh_3)(2\text{-}Ph_2PC_6H_4NR\text{-}\kappa^2\text{–}N,P)]$ (R = H, **26a**; R = Me, **26b**) and $[Ir(CO)(PPh_3)(2\text{-}Ph_2PC_6H_4N\{C(O)camph\text{-}(1S)\}\text{-}\kappa^2\text{–}N,P)]$ **27**, C(O)camph-(1S) = (1S)-camphanoyl) was studied. Only **26a** showed significant activity for the reduction of the carbonyl group, by formation of the *cis*-dihydride $[IrH_2(CO)(PPh_3)(2\text{-}Ph_2PC_6H_4NH\text{-}\kappa^2\text{–}N,P)]$ **28** which was observed by ^1H NMR at 45 bar H_2. The homogeneous hydrogenation of α,β-unsaturated carbonyl compounds such as crotonaldehyde, ethylvinyl ketone, 2-cyclohexen-1-one,

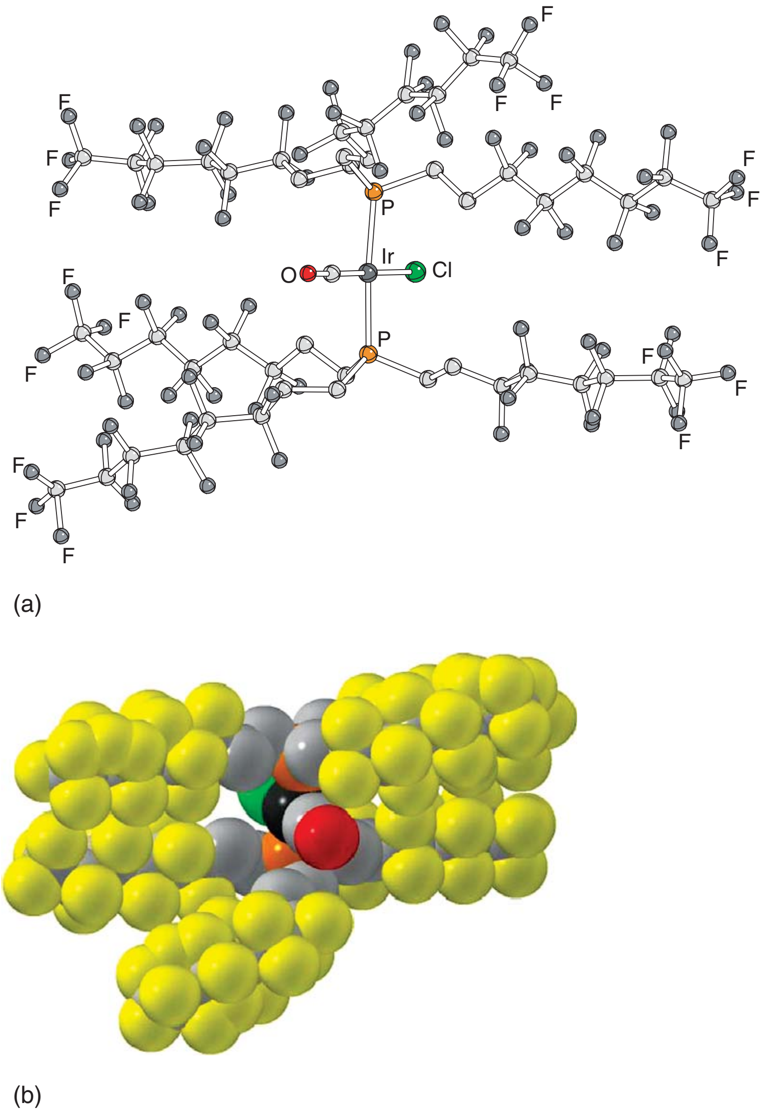
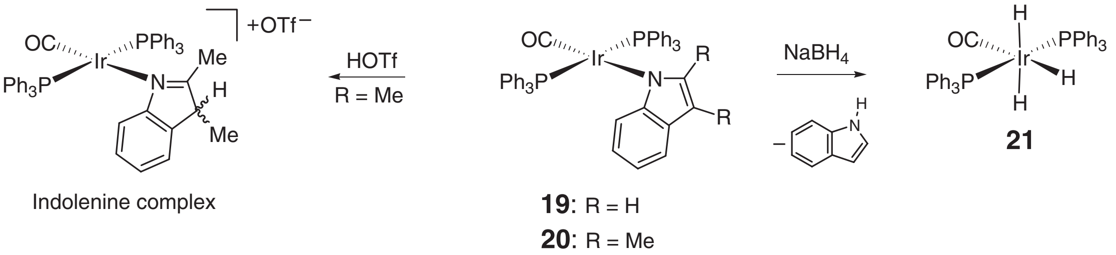


Figure 1 (a) X-ray crystal structure of **15** and (b) space filling diagram of **15**.



Scheme 2

benzylideneacetone, and benzylideneacetophenone in the presence of **26a** proceeded with chemoselectivities for the corresponding allylic alcohols varying between zero for EtC(O)CH=CH_2 and 77–78% for PhCH=CHC(O)Me and MeCH=CHCHO, respectively.[15]

The syntheses and characterizations of terminal Ir(I)-amido complexes containing trialkylphosphines were described. The anilide complexes, *trans*-[Ir$(PR_3)_2$(CO)(NHPh)] [$PR_3 = PMe_3$ **29a** and PEt_3 **29b**], undergo CO insertion followed by C–H activation to produce [Ir$(PR_3)_2$(CO)(H){C(O)NH(C_6H_4)}] **30a** and **30b**. It was also possible to synthesize an alkylamide complex, *trans*-[Ir$(PEt_3)_2$(CO)(NHCMe$_3$)], **31**, which readily converts to an amido-bridged dimeric species [Ir(PEt_3)(CO)(μ-NHCMe$_3$)]$_2$ **32**. Complex **31** resulted to be a suitable precursor for further reaction with CO to produce a trigonal-bipyramidal carbamoyl complex, [Ir$(PEt_3)_2$(CO)$_2${C(O)NHCMe$_3$}], **33**, with the carbamoyl ligand in an axial position and the phosphine ligands distributed between axial and equatorial positions. An alkyne adduct was formed between **31** and PhC≡CPh, whereas PhC≡CH produces a monoalkynyl complex. Addition of two or more equivalents of PhC=CH ultimately affords the bis(alkynyl) complex, *trans*-[Ir$(PEt_3)_2$(CO)(H)(C≡CPh)$_2$], **34**.[16]

2-(2′-Thienyl)pyridine (Hthpy) reacts with [Ir(CO)(MeCN)$(PPh_3)_2$]PF_6 **35** in CH_2Cl_2 at room temperature to give [Ir(CO)(Hthpy)$(PPh_3)_2$]PF_6 **36**, featuring an N-bound Hthpy. Direct cyclometallation occurs when the chelating ligand reacts with **35** under reflux conditions in a dichloromethane/2-methoxyethanol mixture. [Ir(H)(thpy)(CO)$(PPh_3)_2$]PF_6 **37** can also be obtained through thermal rearrangement of **36**. The structures of **36** and **37** were determined by single crystal X-ray diffraction studies (Figure 2).[17]

The coordination chemistry of the polyfunctional phosphine 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine (dpnapy) with Ir(I) complexes was studied. The phosphine, dpnapy, reacts with *cis*-[IrCl(CO)$_2$(*p*-toluidine)] in 1 : 2 and 1 : 1 molar ratios giving the κ^1-*P* complexes *trans*-[IrCl(CO)(dpnapy)$_2$] **38** and *cis*-[IrCl(CO)$_2$(dpnapy)] **39**, respectively.[18]

Treatment of **1** with the Li salts of the bidentate ligands 2-$Ph_2PC_6H_4N$(R)H [‘PN(R)H’; R = H, Me] produced the chelate complexes [Ir(CO)(PPh_3)(‘PNR’)] [NR = NH **40a**, NMe **40b**] containing the CO ligand and the NR substituent in mutual *trans*-arrangement. Oxidative addition of H_2 to **40b** reversibly formed *cis*-[IrH_2(CO)(PPh_3)(‘PNMe’)], with H_2 perpendicular to the N–Ir–CO axis. Reactions of **40** with SO_2 reversibly formed pentacoordinate SO_2 adducts [Ir(SO_2)(CO)(PPh_3)(‘PNR’)] [NR = NH **41a**, NMe **41b**], with M–S-bonded pyramidal MSO_2 units as established by an X-ray structure analysis of **41a**. Complex **41b** reacted with O_2 to form the sulfato derivative [Ir(O_2SO_2)(CO)(PPh_3)(‘PNMe’)] **42**. The reaction of **40a** with HCl in $CHCl_3$ at −60 °C resulted in protonation of both the Ir and the N atoms to give an ionic chelate complex, [IrHCl(CO)(PPh_3)(‘PNH_2’)]Cl **43**, having an NH group H-bonded to Ir–Cl (Scheme 3).[19]

Reductive aminations of *ortho*- and *meta*-(diphenylphosphino)benzaldehydes with N,N′-bis(2-pyridyl-2-ethyl)-amine (bpea) or 1,4-diisopropyl-1,4,7-triazacyclononane (tacn*) afforded four novel ditopic N_3P-donor ligands each

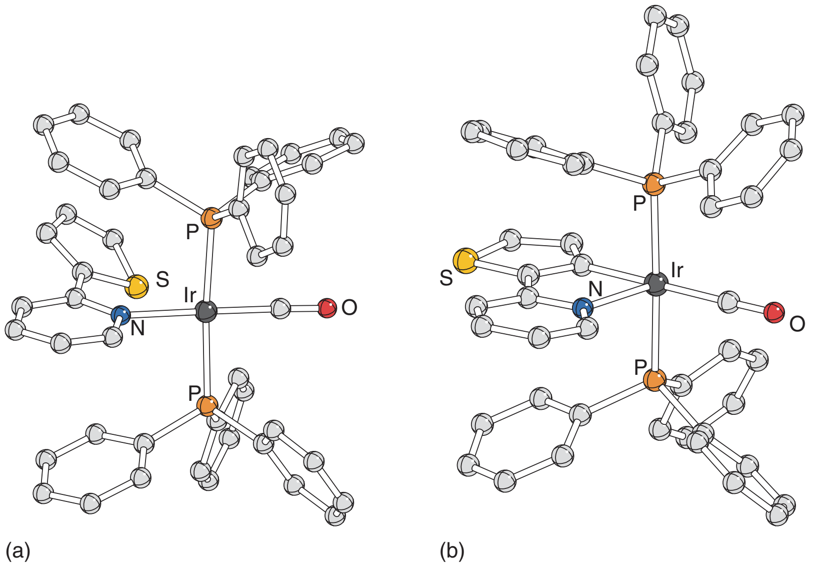
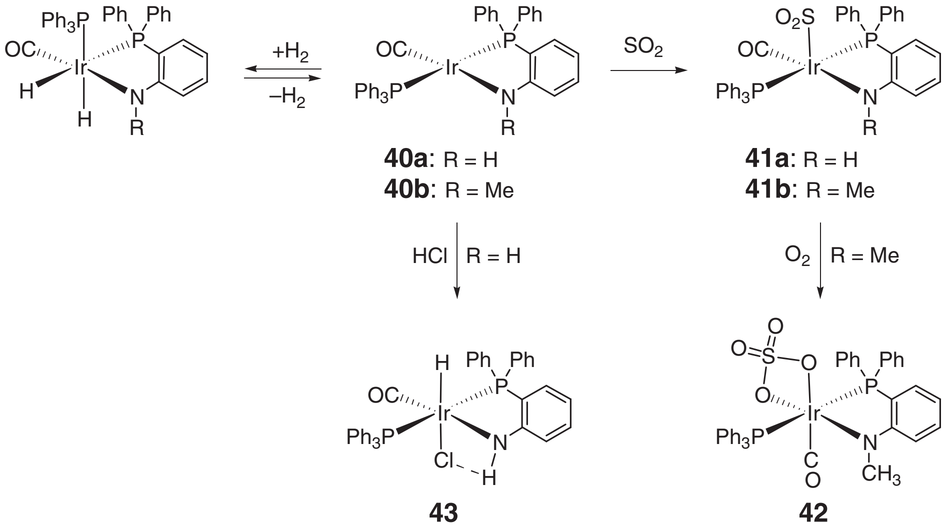


Figure 2 X-ray crystal structure of (a) **36** and (b) **37**.



Scheme 3

bearing 2- or 3- (diphenylphosphino)phenylmethyl tethered to bpea (L_1, L_3) or tacn* (L_2, L_4). Six complexes with the phosphine of L_1–L_4 coordinated to a soft metal center sincluding Ir(I) and with dangling, metal-free N_3-donor moiety were prepared. *trans*-[$IrCl(CO)(L_3)_2$] reversibly forms a dioxygen adduct. An $Ir^{III}Cu^{II}_2$ heterometallic complex was obtained by adding hard Cu(II) ions to the Ir(I) complex with metal-free N_3-donor domains. An inhibition effect of submolar quantities of heterometallic complexes on the aerobic oxidation of styrene in methylethyl ketone was observed, with strong dependence of conversion and product selectivity on the nature of the metal(II) ion.[20]

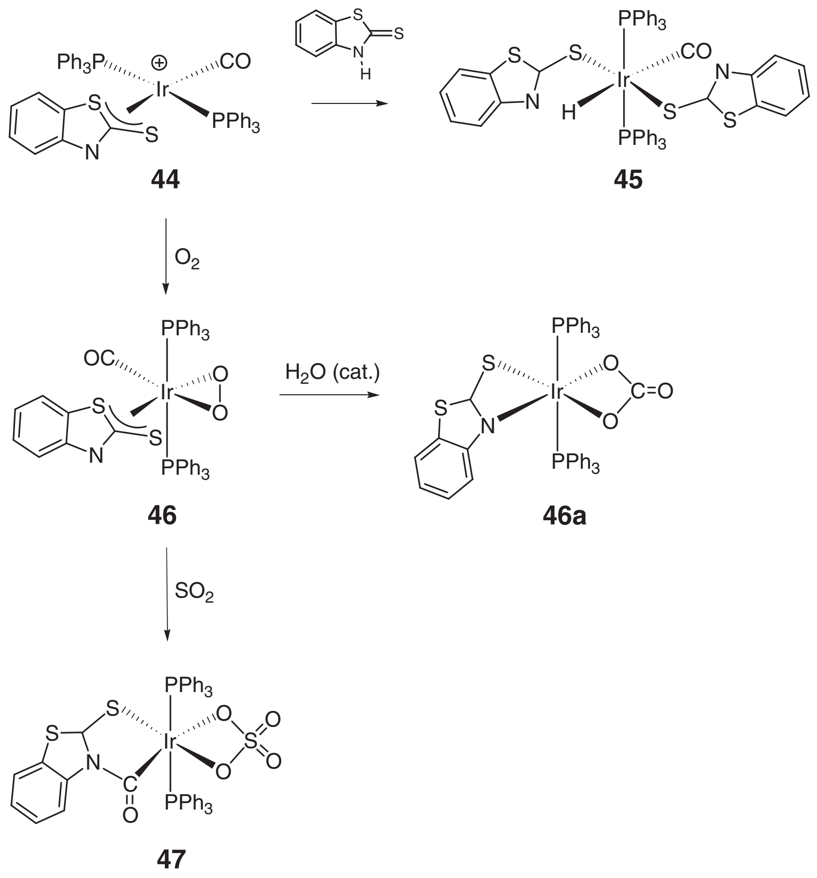
A well-represented class of monocarbonyl Ir complexes includes S-based ligands. The square-planar complex [$Ir(C_7H_4NS_2)(CO)(PPh_3)_2$] **44** was obtained in high yield from the reaction of lithium benzothiazole-2-thiolate ($LiC_7H_4NS_2$) with **1**. Protonation reactions with HBF_4 gave the hydridoiridium(III) complex [$IrH(C_7H_4NS_2)(CO)(PPh_3)_2$]$BF_4$. The neutral ligand $C_7H_5NS_2$ reacts with **44** to give [$IrH(C_7H_4NS_2)_2(CO)(PPh_3)_2$] **45**. Complex **44** adds dihydrogen, MeI, and O_2. The peroxo species [$Ir(C_7H_4NS_2)(O_2)(CO)(PPh_3)_2$] **46** undergoes an intramolecular oxidation of the carbonyl ligand catalyzed by H_2O to yield the carbonato complex [$Ir(C_7H_4NS_2)(CO_3)(PPh_3)_2$] **46a**. The reaction of the dioxygen complex **46** with SO_2 gave the unprecedented incorporation of CO into the benzothiazole-2-thiolate ligand through the heterocyclic N atom, accompanied by oxidation to sulfate, yielding [$Ir\{C(O)NC(S)SC_6H_4\}(SO_4)(PPh_3)_2$] **47** (Scheme 4).[21,22]

Hidai and co-workers reported on the chemistry of dinuclear thiolato species and a few examples of this work are described below in Scheme 5.[23] The diaryl disulfide ligand in the thiolato-bridged diiridium(III) complexes [$\{Ir(\mu\text{-}SC_6H_{4-n}Me_nCH_2)Cl(PPh_3)\}_2(\mu\text{-}ArSSAr)$] (**48a**, $n=1$, Ar = *o*-Xyl; **48b**, $n=2$, Ar = Mes) is readily substituted by CO to yield the bis(carbonyl) complexes [$Ir(\mu\text{-}SC_6H_{4-n}Me_nCH_2)Cl(PPh_3)(L)$]$_2$ **49a**, $n=1$, L = CO; **49b**, $n=2$, L = CO). Reaction of **48b** with MeLi resulted in reductive cleavage of the disulfide bond to give the coordinatively unsaturated diiridium(III) complex [$Ir(\mu\text{-}SC_6H_2Me_2CH_2)(SMes)(PPh_3)$]$_2$, which is further converted into the bis(carbonyl) complex [$Ir(\mu\text{-}SC_6H_2Me_2CH_2)(SMes)(PPh_3)(CO)$]$_2$ **50** upon addition of CO.

[$IrH(CO)(\eta^1\text{-}SpyH)_2(PPh_3)_2$]$(BF4)_2$ **51** was obtained from the reaction of [$IrH_3(CO)(PPh_3)_2$] with HBF_4 in the presence of pyridinethione (SpyH). The reaction of the trihydride *mer*-[$IrH_3(PPh_3)_3$] with HBF_4 in the presence of SpyH was investigated by Morris and co-workers (see Section 7.04.7.4). The reaction affords a dihydrido SpyH complex [$IrH_2(\eta^1\text{-}SpyH)(PPh_3)_3$]$BF_4$ which undergoes a substitution of one phosphine by another SpyH to yield [$IrH_2(\eta^1\text{-}SpyH)_2(PPh_3)_2$]$BF_4$.[24]

Thiobenzamide reacted with *mer*-[$IrH_3(PPh_3)_3$] in boiling toluene to afford [$IrH_2\{S(NH)CPh\}(PPh_3)_2$]. The reactions of thiobenzoic acid with *mer*-[$IrH_3(PPh_3)_3$] under forcing conditions gave [$IrH_2\{S(O)CPh\}(PPh_3)_3$], [$IrH\{S(O)CPh\}_2(PPh_3)_2$], and [$Ir\{S(O)CPh\}_3(PPh_3)_2$], the last two of which on carbonylation afforded [$IrH\{S(O)CPh\}_2(CO)(PPh_3)_2$] **52** and [$Ir\{S(O)CPh\}_3(CO)(PPh_3)_2$] **53**, respectively.[25]

Ligands with two sulfur atoms directly connected to the carbon framework of monoanionic 7,8-dicarba-*nido*-undecaborate were reacted with **1** in the presence of $AgNO_3$ in EtOH to form stable metal complexes. Each Ir(I) atom is four-coordinated to two P atoms of the PPh_3 groups and the two S atoms of the 7,8-dicarba-*nido*-undecaborate



Scheme 4

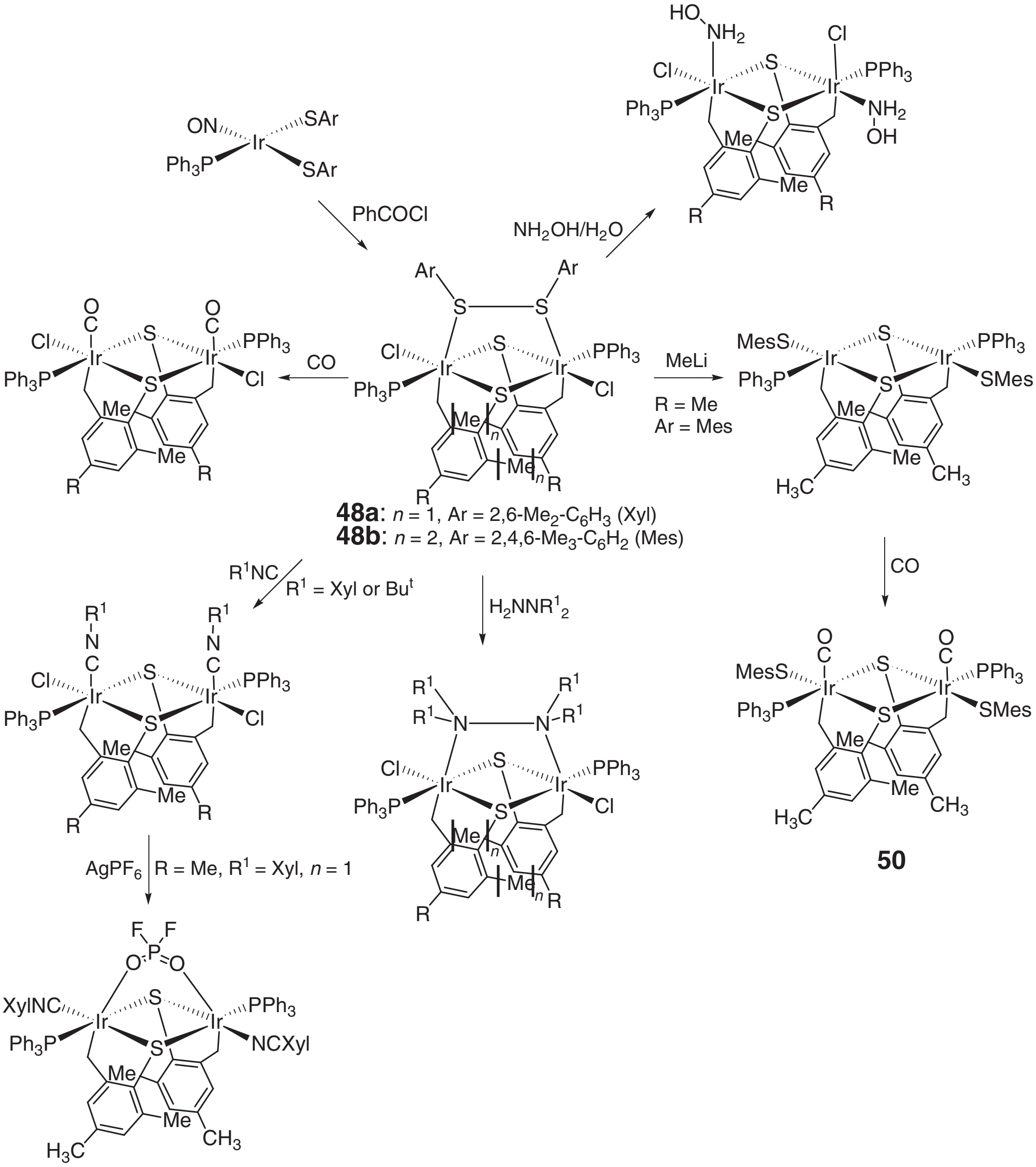
ligand. The influence of the S,S′ outer chain was studied by reacting these Ir(I)–dithioether complexes with O_2. The crystal structure of $[IrO_2(Ls2n)(PPh_3)_2]\cdot Me_2CO$ **54** was obtained (Figure 3), showing the presence of O_2 as peroxo ligand (Scheme 6).[26]

The X-ray diffraction analysis of the iridium complex $[\{Ir(CO)Cl(PPh_3)(\mu\text{-}P_4S_3)\}_2]$ **55** originally prepared by Midollini *et al.*[27] by reaction of P_4S_3 with **1** was characterized by X-ray crystallography (Figure 4).[27a] Each activated P_4S_3 ligand coordinates as bidentate, binding to the two Ir centers through oxidative addition and the cleavage of a basal P–P bond.

A rare thiazyl difluoride complex $[IrCl(F)(CO)(NSF_2)(PPh_3)_2]$ **56** was prepared by the reaction of **1** and NSF_3 and its X-ray crystal structure was determined.[28]

The synthesis of Rh(I) and Ir(I) complexes of functionalized carborane ligands were studied by Lee *et al.* who described both *P*,*S*-[29] and *N*,*S*-[30] chelate ligands. With $[SC_2B_{10}H_{10}(CH_2)_nPPh_2]$ ($n = 0$, Cab*P*,*S*; $n = 1$, $CabCH_2$*P*,*S*), two new phosphinothiolato complexes [M(Cab*P*,*S*)(cod)] (M = Rh **57a**, Ir **57b**) were synthesized by the reaction of $[MCl(cod)]_2$ with 2 equiv. of the corresponding lithium phosphinothiolato ligand LiCab*P*,*S*. Carbonylation of **57** yields the dinuclear $[M(\mu\text{-S-Cab}P,S)(CO)]_2$ [M = Rh **58a**, Ir **58b**]. The molecular structures reveal that the two metal atoms are bridged by the two thiolato ligands, and the carbonyls complete the coordination of the metal atoms. The same complexes could also form upon reaction of carbonyl dimers $[M(\mu\text{-Cl})(CO)_2]_2$ with 2 equiv. of Cab*P*,*S*. Bridge cleavage of the dinuclear complexes **58** with triethylphosphine give the monosubstituted mononuclear metal complexes $[M(\text{Cab}P,S)(CO)(PEt_3)]$ (M = Rh **59a**, Ir **59b**). Complexes **58** and **59** were tested as catalysts for the carbonylation of methanol to acetic acid. In particular, the dinuclear rhodium carbonyl complex **58a** showed higher activity than the previously known catalyst $[RhI_2(CO)_2]^-$.[29]

The similar reaction of $[MCl(cod)]_2$ (M = Rh, Ir) with 2 equiv. of the lithium *ortho*-carboranethiolate derivative LiCab*N*,*S* [LiCab*N*,*S* = closo-2-(dimethylaminomethyl)-1-(lithiumthiolato)-*ortho*-carbora] produced the four-coordinated



Scheme 5

metallacyclic compounds, [(Cab*N*,*S*)M(cod)], and upon subsequent carbonylation reactions the corresponding dicarbonyl N,S-chelates [(Cab*N*,*S*)M$(CO)_2$] [M = Rh **60a**, Ir **60b**]. The metal atom is coordinated by nitrogen and sulfur atoms of the amino-*ortho*-carboranethiolate ligand, and two carbonyl ligands complete the coordination sphere.[30]

Alkylidene carbonyl iridium complexes are also known. The reactions of **1** and the Rh(I) analog *trans*-$RhCl(CO)(PPh_3)_2$ with bis- and tris[phenyl(iodonium)] di- and triyne triflate salts [PhI–C≡C–RC≡C–IPh]$(OTf)_2$ (R = *p*-C_6H_4, *p*-$Me_4C_6H_4$, 4,4′-$C_6H_4C_6H_4$, *o*-C_6H_4) and [1,3,5-(PhI–C≡C)$_3C_6H_2$]$(OTf)_3$ in acetonitrile afforded high yields of the corresponding iridium(III) and rhodium(III) σ-acetylide complexes as stable, crystalline solids. The reaction of [PhI–C≡C$(C_6R_4)_n$C≡C–IPh]$(OTf)_2$ (R = H, Me, $n = 1$; R = H, $n = 2$) with **1** in MeCN gave 73–90% acetylide complexes **61** shown in Scheme 7.[31]

Alkyl complexes [$IrCl_2(\eta^1$-$CH_2Ar)(CO)(PPh_3)_2$] [Ar = Ph **62a**, *p*-Tol **62b**] were synthesized by the reaction of *mer*-[$IrHCl_2(PPh_3)_3$] with terminal alkynes ArC≡CH in the presence of water. The X-ray crystal structure of **62b** was

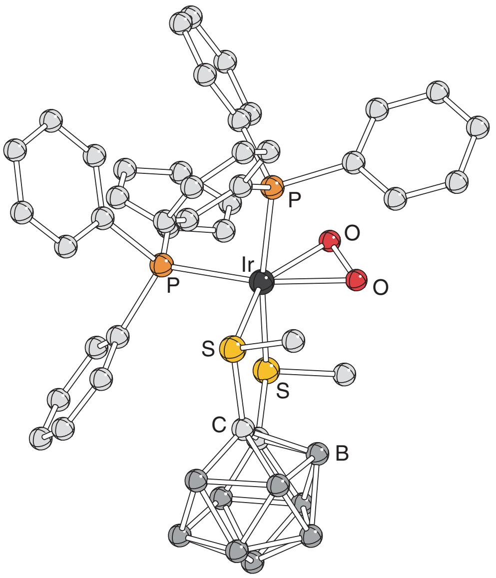
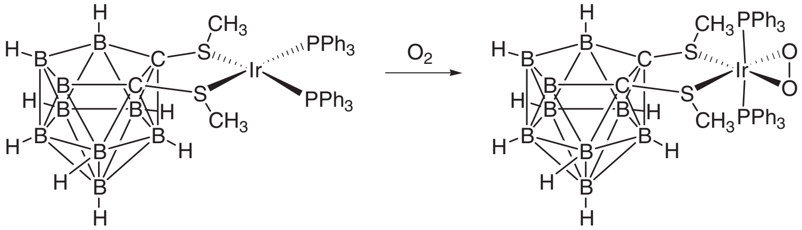


Figure 3 X-ray crystal structure of 54.



54

Scheme 6

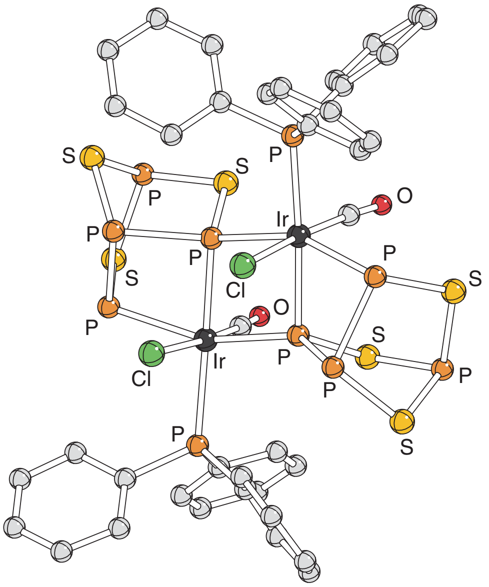
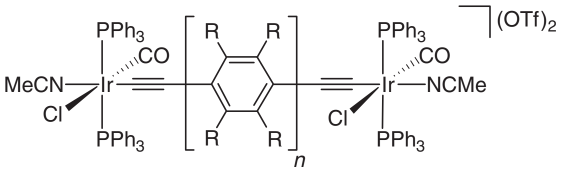


Figure 4 X-ray crystal structure of **55**.



R = H, Me, *n* = 1; R = H, *n* = 2

61

Scheme 7

obtained. The acyl complex $[IrCl_2\{C(O)CH_2C(CH_3)_3\}(PPh_3)_2]$ **62c** was obtained by reacting *mer*-$[IrHCl_2(PPh_3)_3]$ with *tert*-butylacetylene in the presence of H_2O, via hydration of terminal alkyne giving cleavage of the $C\equiv C$ triple bond.[32]

Compound *trans*-$[IrCl({=}C{=}C{=}C{=}CPh_2)(PPr^i_3)_2]$ was prepared by Werner and co-workers in good yield from $[IrH_2Cl(PPr^i_3)_2]$ and $HC\equiv CC(OTf){=}CPh_2$ in the presence of NEt_3. Salt metathesis with KI, KOH, and NaN_3 led to the formation of the substitution products *trans*-$[IrX({=}C{=}C{=}C{=}CPh_2)(PPr^i_3)_2]$ of which the hydroxo derivative reacts with phenol to give *trans*-$[Ir(OPh)({=}C{=}C{=}C{=}CPh_2)(PPr^i_3)_2]$. By contrast, the reaction with methanol afforded the octahedral dihydridoiridium(III) complex $[IrH_2(CH{=}C{=}C{=}CPh_2)(CO)(PPr^i_3)_2]$ **63** by fragmentation of the alcohol. In the presence of CO, the methyl compound *trans*-$[Ir(CH_3)({=}C{=}C{=}C{=}CPh_2)(PPr^i_3)_2]$ and the azido complex *trans*-$[Ir(N_3)({=}C{=}C{=}C{=}CPh_2)(PPr^i_3)_2]$ undergo migratory insertion reactions to yield the four-coordinate iridium(I) carbonyls *trans*-$[Ir(C(C\equiv CCH_3){=}CPh_2)(CO)(PPr^i_3)_2]$ **64** and *trans*-$[Ir(C\equiv CC(N_3){=}CPh_2)(CO)(PPr^i_3)_2]$ **65**, respectively (Figure 5). Compound **65** rearranges to the thermodynamic product *trans*-$[Ir(C(N_3){=}C{=}C{=}CPh_2)(CO)(PPr^i_3)_2]$ **66**.[33]

The syntheses of $[\{CpW(CO)_3\}C\equiv C{-}C\equiv C\{M(CO)(PPh_3)_2\}]$ **67**, M = Rh, Ir) from $[CpW(C\equiv CC\equiv CH)(CO)_3]$ and $[M(OTf)(CO)(PPh_3)_2]$ were described. Reactions with iron carbonyls gave $[\{CpW(CO)_3\}C\equiv C{-}C_2\{Fe_2M(CO)_8(PPh_3)\}]$ and $[\{CpW(CO)_8Fe_2\}C_2C_2\{Fe_2M(CO)_8(PPh_3)\}]$, in which $Fe_2(CO)_6$ moieties add to a $C\equiv C$ group and the adjacent metal center. The X-ray structure of $[\{CpW(CO)_8Fe_2\}C\equiv C{-}C\equiv C\{Fe_2Ir(CO)_8(PPh_3)\}]$ **68** was determined (Figure 6).[34]

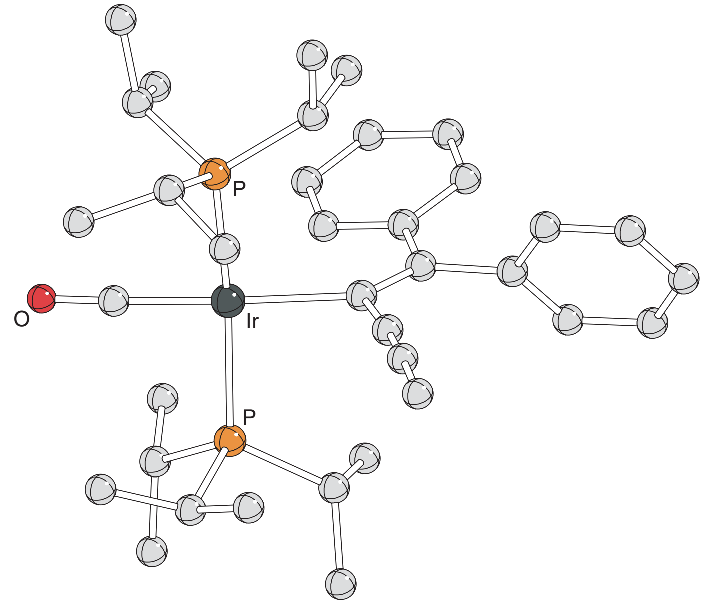


Figure 5 X-ray crystal structure of **64**.

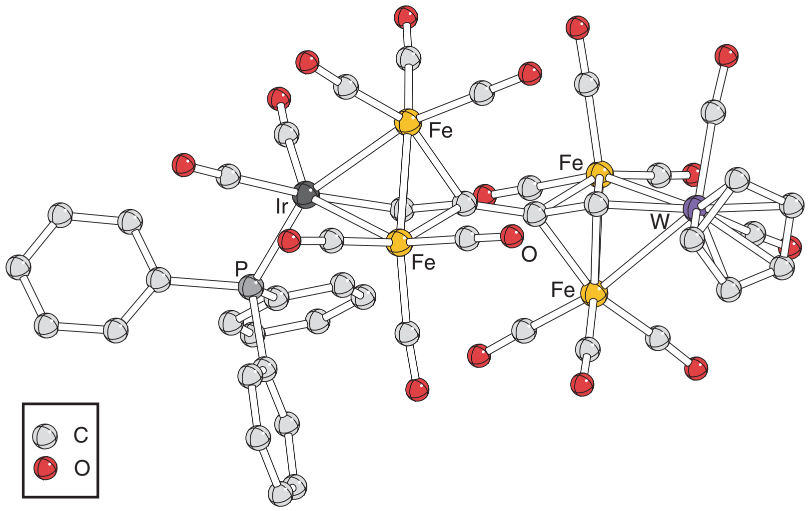
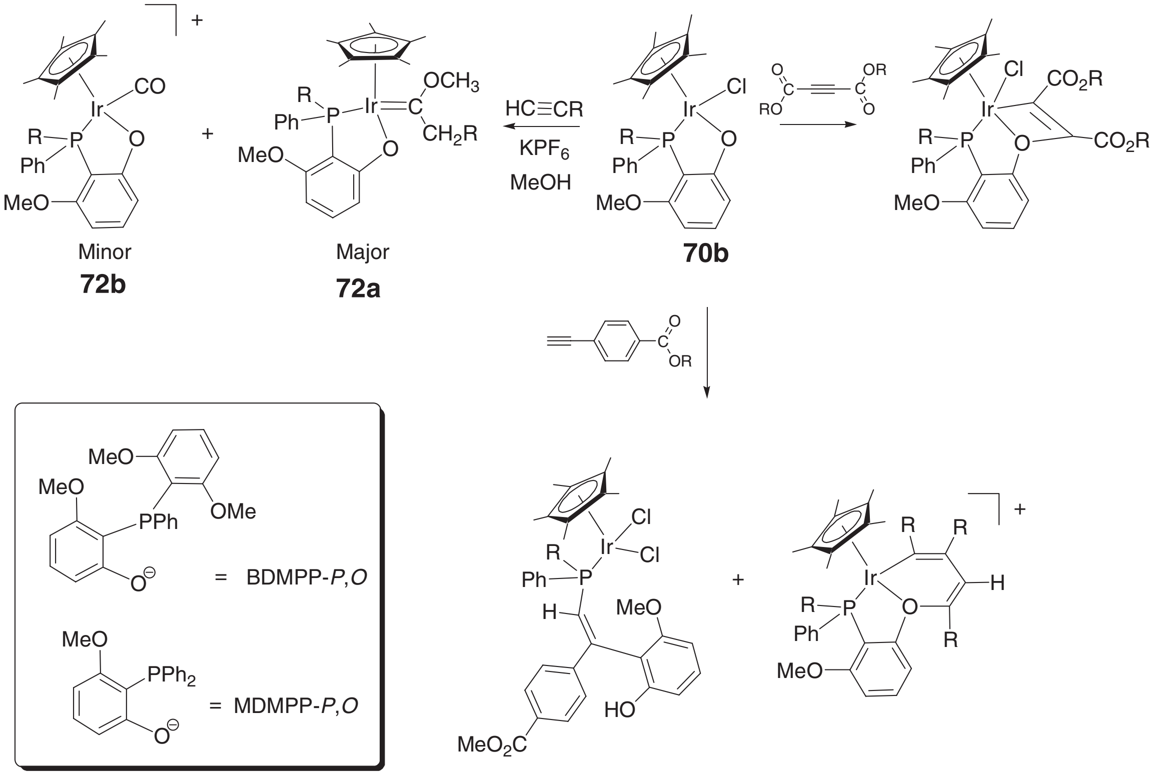


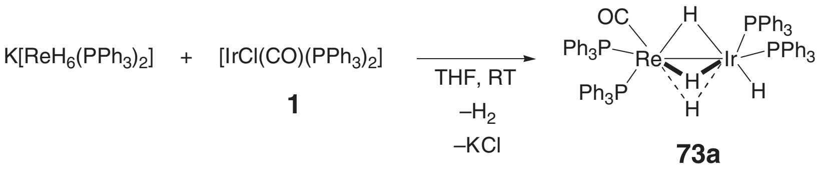
Figure 6 X-ray crystal structure of **68**.

Reactions of the water-soluble precursors [Cp*IrCl$_2$(PAr$_3$)](PAr$_3$ = TPPMS) with alkynes HC≡CR in H$_2$O/C$_6$H$_6$ gave the new water-soluble alkyl–carbonyl complexes, [Cp*Ir(CH$_2$R)(CO)(PAr$_3$)]$^+$ [R = Ph **69a**, Bz **69b**, Bu^t **69c**, *p*-Tol **69d**], by cleavage of the C≡C bond of the alkynes. The C≡C bond of ethene is also cleaved in the reaction of the Ir precursor with ethene in the presence of Ag$^+$ in water to give [Cp*Ir(CH$_3$)(CO)(PAr$_3$)]$^+$.[35]

The chemistry of the P,O mononegative ligands MDMPP-P,O [PPh$_2$(C$_6$H$_3$-2-MeO-6-O)] and BDMPP-P,O [PPh{C$_6$H$_3$-2,6-(MeO)$_2$}(C$_6$H$_3$-2-(MeO)-6-O)] with iridium and rhodium has been investigated by Yamamoto *et al.* and is presented in Scheme 8.[36] Thus, reactions of [Cp*MCl(MDMPP-P,O)] (M = Rh **70a**, Ir **70b**) or



Scheme 8



Scheme 9

[Cp*MCl(BDMPP-P,O)] (M = Rh **70a**, Ir **71b**) with l-alkynes were carried out in the presence of KPF$_6$. Complex **70a** reacted with HC≡CR (R = Ph, *p*-Tol) to give [Cp*Rh{PPh$_2$(C$_6$H$_3$)-2-(MeO)-6-(O-CR═CHCH═CR)}]PF$_6$ bearing the (*P,O,C*) tridentate ligand derived from a head-to-head dimerization of 1-alkynes, whereas reaction with Bu^{n}C≡CH gave a head-to-tail double insertion complex. Conversely, the reactions of **70b** in MeOH gave the carbene complexes [Cp*Ir{PPh$_2$(C$_6$H$_3$-2-(MeO)-6-O)}{═C(OMe)CH$_2$R)}]PF$_6$ **72a** and a minor amount of the carbonyl complex [Cp*Ir(CO){PPh$_2$(C$_6$H$_3$-2-(MeO)-6-O)}]PF$_6$ **72b**. The reaction with activated internal and terminal alkynes, such as dialkyl propiolates and *p*-RO$_2$CC$_6$H$_4$C≡CH, which affords interesting products deriving from C–C and C–O bond-forming steps, is also reported in Scheme 8.

The reaction of K[ReH$_6$(PPh$_3$)$_2$] with **1** gives the bimetallic bridging trihydride [(CO)(PPh$_3$)$_2$Re(μ-H)$_3$IrH(PPh$_3$)$_2$] **73a** in moderate yield (Scheme 9).[37]

A hexanuclear rhenium cluster encapsulated by six iridium(I) moieties, [Re$_6$Te$_8$(CN)$_6$][{Ir(CO)(PPh$_3$)$_2$}$_6$](OTf)$_2$ **73b**, behaves as an effective catalyst for the hydrogenation of *p*-CH$_3$C$_6$H$_4$C≡CH to *p*-CH$_3$C$_6$H$_4$CH═CH$_2$. This polynuclear species was obtained by Kim *et al.* and its structure was determined by X-ray crystallographic methods (Figure 7). Reaction of **73b** with H$_2$ afforded the dihydridoiridium(III) complex [Re$_6$Te$_8$(CN)$_6$]-[{Ir(CO)(H)$_2$(PPh$_3$)$_2$}$_6$](OTf)$_2$ **73c** without affecting the core structure of the cluster. The Ir(III) polynuclear dihydride also catalyzes the alkyne to alkene hydrogenation.[38]

Iridabenzenes possessing aromatic character and incorporating CO ligands have been studied by Haley and co-workers who prepared these intriguing compounds via intramolecular metal-promoted cyclopropene

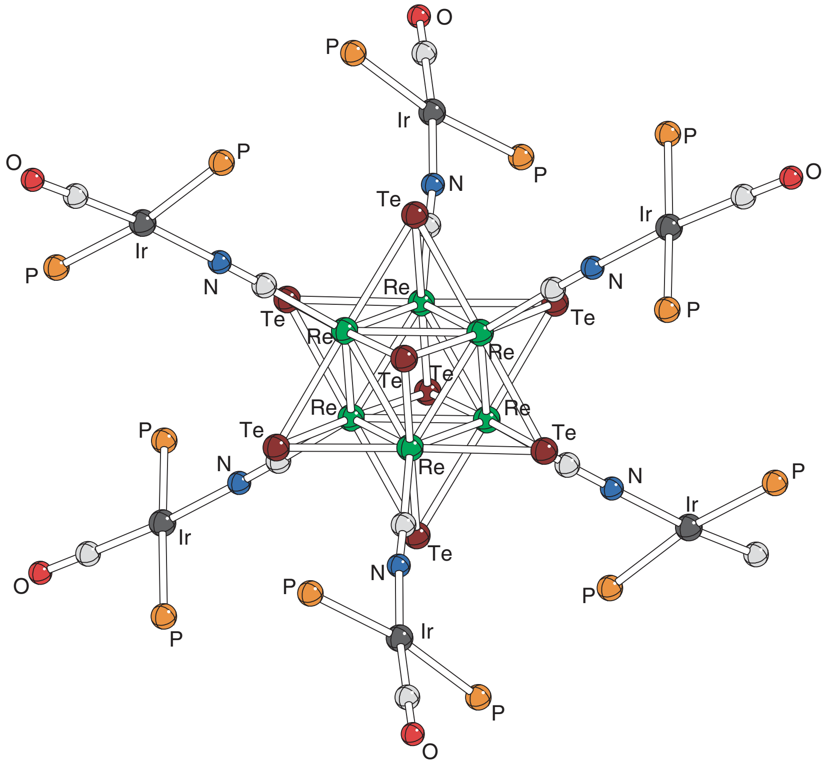
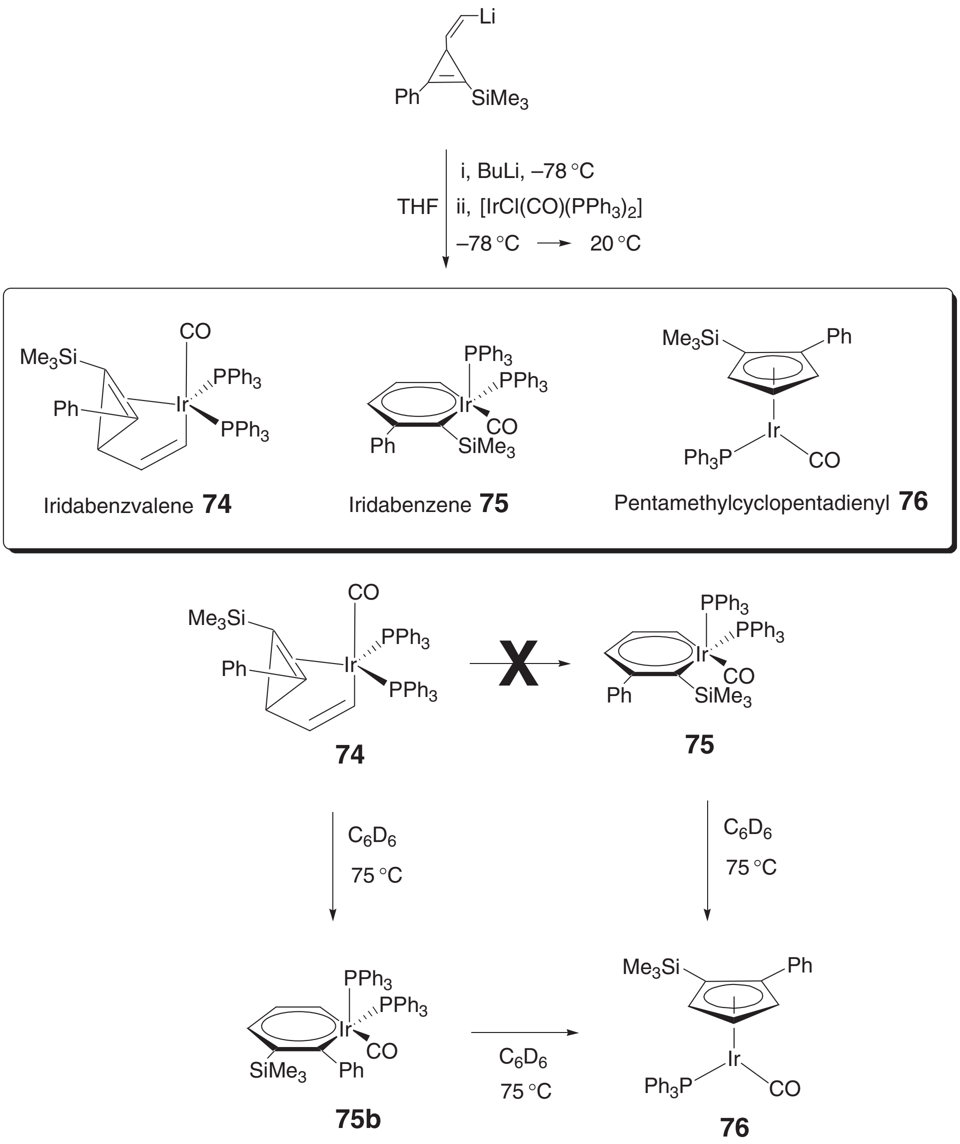


Figure 7 X-ray crystal structure of **73b**. The phenyl groups of the PPh$_3$ ligands have been omitted for clarity.

rearrangement.[39,39a,39b] The reaction of a lithiated cyclopropene derivative, that is, (*Z*)-1-phenyl-2-(trimethylsilyl)-3-(2-lithiovinyl)cyclopropene, with **1** at −78 °C generates the iridabenzavalene **74**, the iridabenzene **75**, and cyclopentadienyl derivative [Ir{η^5-1-Ph-2-(SiMe$_3$)C$_5$H$_3$}(CO)(PPh$_3$)] **76** in a 10 : 2 : 3 ratio. NMR studies in C_6D_6 show that different conversion pathways are active also resulting in apparently unpredictable rearrangements. Thus, samples containing pure **74** kept at 75 °C over a 24 h period do not isomerize to **75** but to a different regioisomer **75b** differing in the relative position of Ph and SiMe$_3$ substituents in the iridabenzene ring. Further heating shows that both **74** and **75b** completely transform to **76** which represents the first example of iridabenzene rearrangement to a π-cyclopentadienyl ring. Compound **76**, which forms independently from **74**, also rearranges to **76** after heating in benzene. Scheme 10 shows these intriguing transformations.[39b]

The phenylmethoxy carbonyl complex [Ir(CO)(OCH$_2$Ph){P(*p*-Tol)$_3$}$_2$] **77** was synthesized and characterized by X-ray crystallography. The *p*-cresolate derivative [Ir(CO)(OC$_6$H$_4$CH$_3$){P(*p*-Tol)$_3$}$_2$]·CH$_3$C$_6$H$_4$OH and the hydroxy analog [Ir(CO)(OH)(PCy$_3$)$_2$] were characterized by X-ray crystallography. The latter structure is disordered with a scrambled image of the carbonyl and hydroxide ligands, implying that the Ir–CO and Ir–OH distances may suffer from systematic errors.[40]



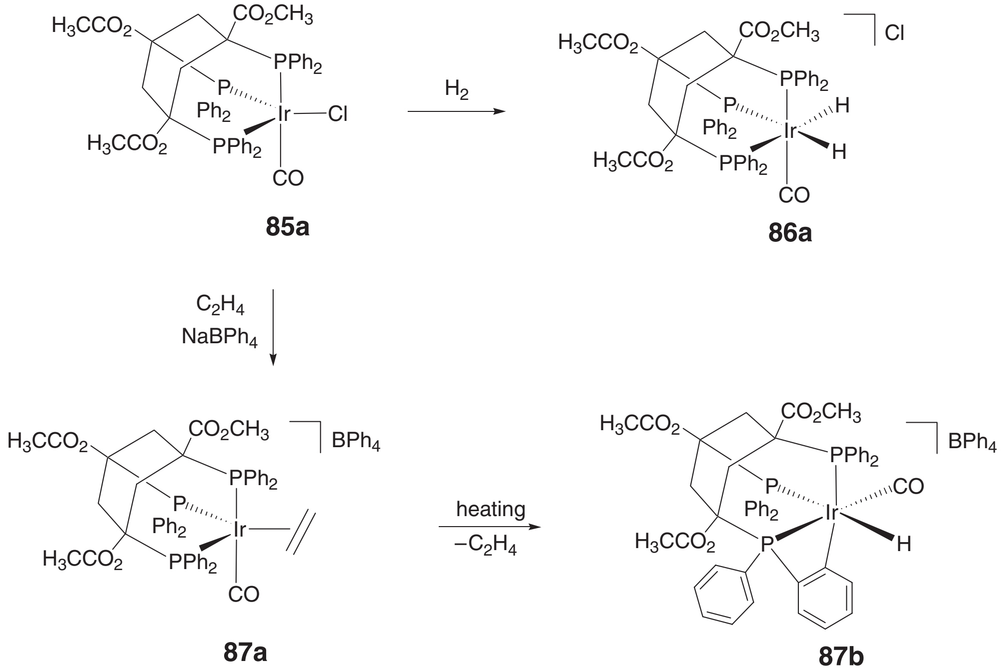
Scheme 10

$[IrCl(coe)_2]_2$ reacts with 4 equiv. of diallyl(*tert*-butyl)phosphine in $CHCl_3$ at low temperature (LT) producing two isomers of $[\{Me_3C(C_3H_5)PCH_2CH{=}CH\}IrHCl(coe)\{P(CMe_3)(C_3H_5)_2\}]$ **78a**, which at 40 °C gives hydride transfer from the metal to cyclooctene yielding the complex $[\{Me_3C(C_3H_5)PCH_2CH{=}CH\}IrCl(C_8H_{15})\{P(CMe_3)(C_3H_5)_2\}]$ **78b**. By bubbling CO into a $CHCl_3$ solution of **78b** at RT produces the carbonyl complex $[\{Me_3C(C_3H_5)PCH_2CH{=}CH\}$-$Ir(CO)Cl(C_8H_{15})\{P(CMe_3)(C_3H_5)_2\}]$ **78c**.[41]

Mayer and co-workers have developed the coordination chemistry of tripodal-like ligands based on 1,3,5-trisubstituted cyclohexane scaffolds. Typical ligands of this class are *cis,cis*-1,3,5-tris[(diphenylphosphanyl)methyl]-cyclohexane (tdppmcy) and *cis,cis*-1,3,5-tris(diphenylphosphino)cyclohexane (tdppcy).[42,43] The reaction of tdppmcy with **1** in toluene gives trinuclear $[\{Ir(CO)Cl\}_3(tdppmcy)_2]$ **79** with the tripodal ligand behaving as a trismonodentate ligand. Complex **79** was converted into trinuclear $[\{Ir(CO)(Cl)H\}_3(tdppmcy)_2]_3{}^+$ **80**, $[Ir(CO)(Cl)H_2]_3(tdppmcy)_2$ **81**, and $[Ir(CO)H_3]_3(tdppmcy)_2$ **82** by treatment with H^+, H_2, and H^-, respectively.[42]

The reaction of tdppcy with **1** yielded the TBP complex [IrCl(tdppcy)(CO)] **83**.[43] This was further transformed into either [IrH(tdppcy)(CO)] **84** or $[Ir(tdppcy)(CO)(H)_2]^+$ by treatment with $NaBH_4$ in refluxing THF. CH_2Cl_2 or Cl_2 oxidized **83** to $[Ir(tdppcy)Cl_3]$, which was converted into $[IrCl(tdppcy)(H)_2]$, by treatment with $NaBH_4$ in THF. Similarly, treatment of the analogs *cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxymethyl)cyclohexane (tdppcymome)[44] and *cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane (tdppcyme)[45] with **1** leads to the trigonal-bipyramidal complex $[Ir(\eta^3\text{-}L)(CO)Cl]$ (L = tdppcymome **85a**, tdppcyme **85b**). Complex **85a** gave $[Ir(\eta^3\text{-}tdppcymome)(CO)(H)_2]Cl$ **86a** via oxidative addition of H_2 and chloride abstraction. Under the same conditions a phosphine arm dissociation from **85b** occurs to form the dihydride $[IrCl(\eta^2\text{-}tdppcyme)(CO)(H)_2]$ **86b**. In a CO atmosphere, complexes **85** form the dicarbonyl derivatives $[IrCl(\eta^3\text{-}L)(CO)_2]Cl$ **87**, whereas under ethene in the presence of $NaBPh_4$ they give the ethene complexes $[Ir(\eta^3\text{-}L)(CO)(C_2H_4)]BPh_4$ **87a**, which for the case of L = tdppcymome, lose ethene at high temperature and undergoes orthometallation yielding the *ortho*-metallated hydrido carbonyl complex **87b** shown in Scheme 11. Interestingly, NMR studies proved a dynamic equilibrium between a square-planar and a trigonal-bipyramidal complex with two and three phosphine groups coordinated to Ir, respectively, for L = tdppcyme. This is in contrast to the behavior of **83** which only exists in the TBP form. The carbonyl chloro complexes are readily protonated by the strong acid HBF_4 to give the octahedral cations $[IrCl(\eta^3\text{-}L)(CO)H]BF_4$. The weaker acid NH_4PF_6 is only able to protonate the most basic complex **83**.

The syntheses of the octahedral complexes $[Ir(tetas)X_2]X$ (X = Cl, Br or I), containing the tetradentate tripodal polyarsine $As(o\text{-}C_6H_4AsMe_2)_3$ (tetas), were described by Hill *et al.* Cyclic voltammetry revealed irreversible reduction



Scheme 11

waves to Ir(I). The reaction of **1** with tetas gave the Ir(III) carbonyl [Ir(tetas)(CO)Cl]$(BF_4)_2$ **88**, which was characterized by a single crystal X-ray study.[46]

7.04.2.1.3 Reactivity of monocarbonyl complexes

Monocarbonyl iridium complexes were reacted with noble gas halogenides. XeF_2 behaves as an efficient fluorurating reagent toward Ir(I) and, for example, reacts with [Ir(CO)X$(PEt_3)_2$] (X = Cl, Br, I) to give the *cis*-addition difluoride product, [M(CO)F_2X$(PEt_3)_2$] **89**, which was characterized by NMR spectroscopy.[47]

[IrH(CO)$Cl_2$$(PR_3)_2$] ($PR_3$ = PPh_3 **90a**, PMe_3 **90b**) complexes were characterized by X-ray crystallography as octahedral Ir(III) complexes with *trans*-trimethylphosphine and *cis*-chloride ligands.[48,48a] The reactions of [MH(CO)$(PPh_3)_3$] **91**; M = Rh or Ir) with anhydrous HF or $HBF_4 \cdot Et_2O$ lead to completely different products. With an excess of acid, when M = Ir, oxidation gives [IrH_2(CO)$(PPh_3)_3$]X (X = HF_2 **92a**, BF_4 **92b**), whereas, when M = Rh dissociation of a ligand and elimination of H_2 give a 1 : 1 mixture of [Rh(CO)$(PPh_3)_2$(solv)]X and [$HPPh_3$]X (X = HF_2, BF_4).[49] In the presence of [IrH(CO)$(PPh_3)_3$], activated nitriles undergo dimerization to give the corresponding cyano enamines.[50]

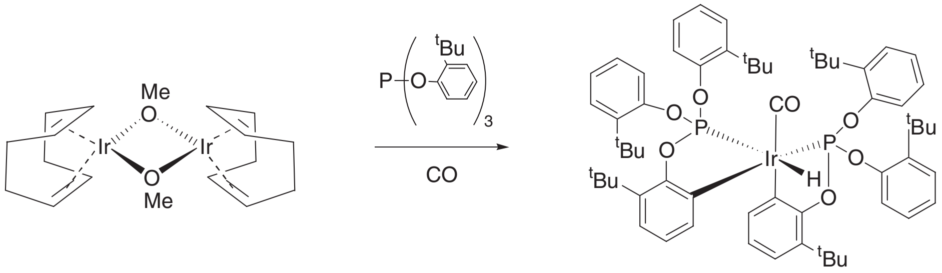
The interaction of the complex [IrH_2(CO)Cl$(PPh_3)_2$] **93** with various proton donors of increasing acidity, such as 2,2,2-trifluoroethanol (TFE), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), perfluoro *tert*-butylalcohol (PFTB), and trifluoroacetic acid (TFA), has been investigated by Aime *et al.* The intermolecular H···Cl hydrogen bond affects the reactivity of the complex and particularly the H/D exchange process. The [Ir(η^2-HD)(CO)Cl$(PPh_3)_2$] isotopomer obtained by reacting **93** with D_2 in dichloromethane is formed in greater amount when one of the proton donors is added to the reaction, depending on the acid strength.[51]

The first example of a mononuclear iridium carbonyl hydride complex with two orthometallated phosphite ligands *cis*-[IrHCO{P(O-*o*-$Bu^tC_6H_3$)(O-*o*-$Bu^tC_6H_4$)$_2$}$_2$] **94** was described by Claver *et al.* by treating [Ir(μ-OMe)(cod)]$_2$ with tris-*ortho-tert*-butylphenyl phosphite under carbon monoxide (Scheme 12). The complex shows great stability even under high pressures of hydrogen and carbon monoxide.[52]

The chemistry of iridium pyrrolyl derivatives was studied by Hartwig and Driver.[53] *trans*-[Ir(CO)$(PPh_3)_2$(NC_4H_4)] **95** undergoes reaction with a variety of substrates at the metal center rather than at the pyrrolyl N, allowing for the study of reactions between the pyrrolyl group and accompanying ancillary ligands yielding N-substituted pyrroles, X–NC_4H_4 [X = C(O)CH_3, C(O)$C_6H_4CH_3$, H, $SnMe_3$, $SiMe_3$, $SiEt_3$, Bcat (HBcat = 1,3,2-benzodioxaborole)]. Complex **95** reversibly oxidatively adds hydrogen to form the stable Ir(III) pyrrolyl product [IrH_2(CO)$(PPh_3)_2$(NC_4H_4)] **96**. Reductive elimination of pyrrole is observed upon prolonged heating of **96** in the presence of PPh_3, accompanied by the formation of [IrH$(PPh_3)_3$(CO)].

The coordination of sulfur dioxide to iridium(I) centers, together with sulfur dioxide insertion into a methoxy–metal bond was investigated. For *trans*-[IrX(CO)L_2] (L = PPh_3, P(*p*-Tol)$_3$, PCy_3; X = Cl, Me), the equilibrium constants for SO_2 binding were noticed to decrease with increasing size of the phosphine. Reactions of SO_2 with [Ir(OR)(CO)L_2] (R = H, Me, CMe_3; L = PPh_3, P(*p*-Tol)$_3$) result in insertion of the SO_2 to form an *O*-coordinated sulfite ligand. For R = H, further decomposition of the HSO_3 ligand occurs. The product of SO_2 insertion into the Ir–OMe bond, [Ir(CO){OS(O)OMe}(SO_2)$(PPh_3)_2$] **97**, was also characterized by X-ray crystallography as toluene adduct (Figure 8). The metal is in a square-pyramidal coordination environment with the SO_2 ligand in the apical site and the methyl sulfite unit bonded to the metal via one oxygen atom.[54]

trans-[IrCl(CO)$(Ph_2PPy)_2$] **98**; Ph_2PPy = 2-(diphenylphosphino)pyridine) was obtained in good yield from the reaction of [IrCl$(CO)_2$(*p*-toluidine)] with the short-bite ligand Ph_2Ppy, featuring two monodentate Ph_2PPy ligands



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Scheme 12

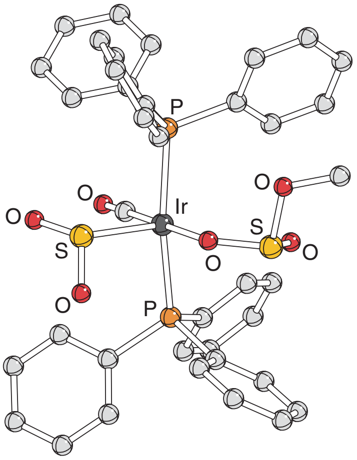
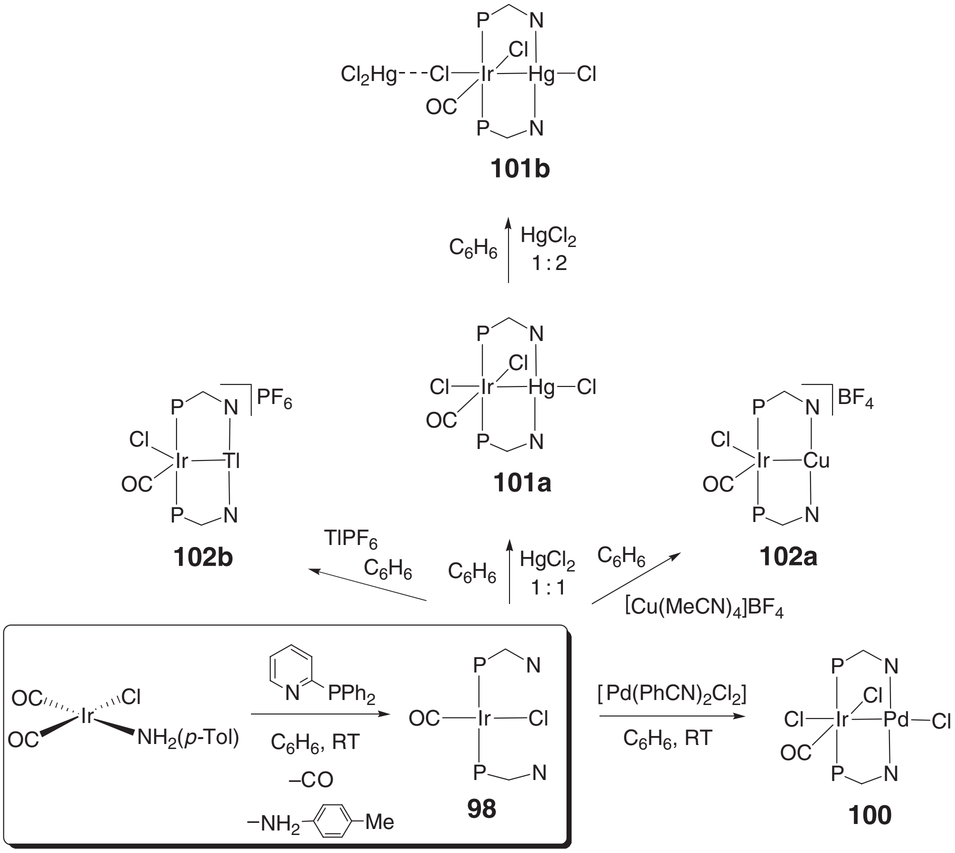


Figure 8 X-ray crystal structure of **97**.

P-bonded to the Ir(I) center, and reacts with SO_2, halogens, HCl, and CH_3I similarly to **1**. Addition of HCl to **98** initially occurs at the pyridine N atoms of the pendant Ph_2PPy and subsequently at the Ir(I) center, affording $[IrHCl_2(CO)(Ph_2PPyH)_2]Cl_2$ **99**.[55] The chemistry of this system was thoroughly investigated by Faraone and co-workers and is summarized in Scheme 13. An interesting reactivity was shown by addition of a benzene solution of $[Pd(PhCN)_2Cl_2]$ to **98** in the same solvent giving the bimetallic complex $[IrPd(CO)Cl_3(\mu\text{-}Ph_2PPy)_2]$ **100**. Similarly,



Scheme 13

the reaction with $HgCl_2$, in a 1:1 molar ratio, afforded binuclear $[Ir(CO)Cl_2(\mu\text{-}Ph_2PPy)_2HgCl]$ **101a**, whereas with a 1 : 2 molar ratio $[Ir(CO)Cl_2(HgCl_2)(\mu\text{-}Ph_2PPy)_2HgCl]\cdot 2CH_2Cl_2$ **101b** was obtained. With $[Cu(MeCN)_4]BF_4$, **98** afforded the ionic orange solid $[Ir(CO)Cl(\mu\text{-}Ph_2PPy)_2Cu]BF_4$ **102a**, and $[Ir(CO)Cl(\mu\text{-}Ph_2PPy)_2Tl]PF_6$ **102b** from the reaction with $TIPF_6$. Complex **98** was used as a pre-catalyst in the hydroformylation of styrene at 80 °C and under 80 atm of CO/H_2 (1 : 1) pressure, giving higher rates than with Vaska's complex, due to a favorable effect of the pendant Ph_2PPy ligand, albeit with low process chemoselectivity.[55]

The synthesis and reactivity of electrophilic iridium(III) complexes containing dppe was studied by Eisenberg and co-workers. Reaction of [IrI(CO)(dppe)] **103a** with RI ($R = CH_3$ and CF_3) results in the formation of the Ir(III) complexes $[IrI_2R(CO)(dppe)]$ ($R = CH_3$ **104a** and CF_3 **104b**) which were converted into the triflate analogs $[IrR(CO)(dppe)(OTf)_2]$ [$R = CH_3$ **105a** and CF_3 **105b**], by reaction with AgOTf. These latter undergo anion metathesis with the Brookhart salt $NaBAr^F$ ($BAr^F = B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$) in the presence of 1,2-diiodobenzene (DIB) forming the dicationic $[IrR(CO)(dppe)(DIB)](BAr^F)_2$ ($R = CH_3$ **106a** and CF_3 **106b**). Complex **106a** reacts with ethene forming the fluxional cationic iridium(I) product $[Ir(C_2H_4)_2(CO)(dppe)]BAr^F$ **107**. Variable-temperature NMR studies showed that **107** undergoes three dynamic processes corresponding to ethene rotation, Berry pseudorotation, and intermolecular ethene exchange in order of increasing temperature as deduced from NMR line shape analyses which were also used to determine the thermodynamic parameters for the processes.[56]

The activation of C–F bonds was also observed in the presence of Ir–dppe carbonyl complexes. The cationic Ir(III) complex **106b** undergoes reaction in the presence of dihydrogen to form $[IrH_2(CO)_2(dppe)]BAr^F$ **108** as the major product. Through labeling studies and ^1H and $^{31}P\{1H\}$ NMR including parahydrogen measurements, the mechanism of conversion of the coordinated CF_3 ligand into carbonyl via initial heterolytic activation of dihydrogen, leading to proton generation which promotes C–F bond cleavage, was elucidated. Polarization occurs in the final product **108** by the reaction of H_2 with the Ir(I) species $[Ir(CO)_2(dppe)]^+$ that is generated in the $CF_3 \rightarrow CO$ conversion.[57]

Methane and $[IrH(CO)(dppe)](OTf)_2$ **109** are formed when a CH_2Cl_2 solution of **105a** is reacted with 1 atm of hydrogen. Complex **109** is an effective hydrogenation catalyst for ethene and 1-hexene while acetone hydrogenation is inhibited by the formation of $[IrH_2(HOCHMe_2)(CO)(dppe)]OTf$ **110**. Linear dimerization and polymerization of styrene occurs via a carbocationic mechanism initiated by HOTf elimination from **109**. Carbonyl insertion was obtained in MeCN yielding $[Ir(AcO)(NCMe)_3(dppe)](PF_6)_2$ **111** which readily undergoes deinsertion in CH_2Cl_2 to form $[IrMe(CO)(NCMe)_2(dppe)](PF_6)_2$ **112**.[58]

The behavior of Ir alkyl complexes **104a** and **104b** was studied upon complexation with DIB as labile chelating ligand. These complexes showed catalytic activity in olefin isomerization, that is, for 1-pentene, C=C double bond isomerization occurs over several days at room temperature giving a product distribution of 2% 1-pentene, 14% *cis*-2-pentene, and 84% *trans*-2-pentene. For isobutylene, β-pinene, and styrene, exothermic reactions were obtained with conversion of the monomers to polymerized/oligomerized olefins in all cases. Polymerizations proceed via a cationic mechanism with the complex working as initiator, rather than by a coordination/insertion mechanism, as indicated by the wide polydispersity.[59]

The oxidative addition of catecholborane (1,3,2-benzodioxaborole) to [IrX(CO)(dppe)] [X = I **103a**, Br **103b**, H **103c**, $BO_2C_6H_4$ **103d**] proceeds stereoselectively under kinetic control. Of the four complexes that can be formed by *cis*-oxidative addition of the B–H bond to **103b**, the one having hydride *trans* to P and B *trans* to bromide is formed in >99% yield, while addition to **103a** occurs similarly but with only 90% stereoselectivity. The oxidative addition reactions of catecholborane to **103c** and **103d** also occur in a *cis*-fashion with 99% stereoselectivity yielding Ir(III) products with hydride *trans* to CO and B *trans* to P. Therefore, the observed stereoselectivity for catecholborane addition to **103a** and **103b** is reversed with respect to **103c** and **103d** and is due to electronic factors involving the π-basicity of the halide ligands.[60]

Following these aspects, the effects of steric and electronic properties of chelating P–S, P–P, and P–O ligands on the reactivity of Rh and Ir complexes toward alkyl halides have been studied by Haynes and co-workers. Kinetic studies of the reactions of [M(CO)(L–L)I] [L–L = $Ph_2PCH_2P(S)Ph_2$ (dppms), dppe, and $Ph_2PCH_2P(O)Ph_2$ (dppmo); M = Rh, Ir] with MeI have been undertaken. Oxidative addition was promoted in all cases by factors of between 30 and 50 compared to $[M(CO)_2I_2]^-$ complexes, due to good donor properties. Migratory CO insertion in $[Rh(CO)(L\text{–}L)I_2Me]$ leads to acetyl complexes $[Rh(L\text{–}L)I_2(COMe)]$ for which X-ray crystal structures were obtained for L–L = dppms and dppe. Unexpectedly, Me migration is faster by a factor of ca. 1500 for $[Rh(CO)(dppms)I_2Me]$ than for $[Rh(CO)(dppe)I_2Me]$. For M = Ir, alkyl iodide oxidative addition gives stable alkyl complexes $[Ir(CO)(L\text{–}L)I_2R]$. Migratory insertion (induced at high temperature by CO pressure) was faster for $[Ir(CO)(dppms)I_2Me]$ **113a** than for its dppe analog **104b**. Reaction of Me triflate and ethyl iodide with [Ir(CO)(dppms)I] **114** yielded the dimer $[\{Ir(CO)(dppms)(\mu\text{-}I)Me\}_2]^{2+}$ **113b**, which was characterized by X-ray crystallography along with **113a** and $[Ir(CO)(dppms)I_2Et]$ **115** respectively (Figure 9).

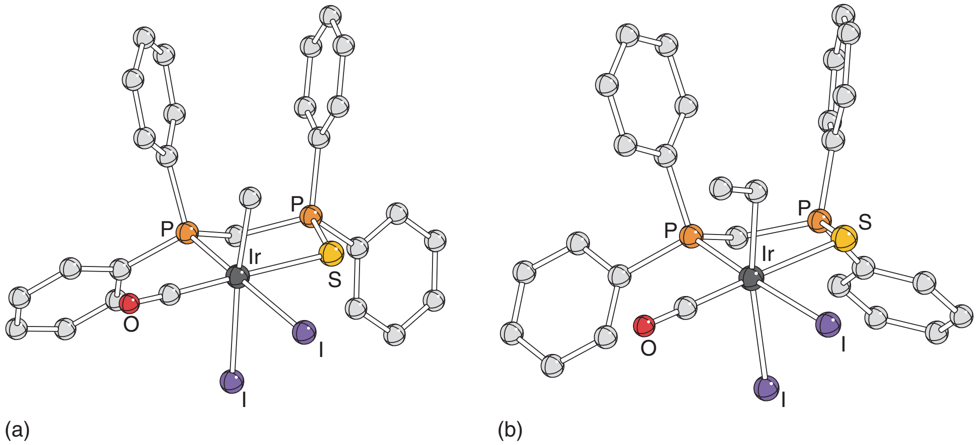


Figure 9 X-ray crystal structures of (a) **113a** and (b) **115**.

Analysis of the X-ray crystal structures showed that dppms adopts a conformation which creates a sterically crowded pocket around the alkyl ligands of **113** and **115** (Figure 10). It is proposed that this steric strain can be relieved by migratory insertion, to give a five-coordinate acetyl product in which the sterically crowded quadrants flank a vacant coordination site, exemplified by the crystal structure of $[Rh(CO)(dppms)I_2Me]$. *Ab initio* calculations suggest an electronic contribution to the migratory insertion barrier, with a sulfur atom *trans* to CO stabilizing the transition state compared to systems with phosphorus *trans* to CO.[61,61a]

Neutral four-coordinate Ir(I) complexes $[Ir(L)(L^1)(Et_2dtc)]$ ($L = L^1 = CO$, PPh_3, $P(OPh)_3$; $L = CO$, $L^1 = PPh_3$; $L + L^1 =$ dppe, cod, 1,2-bis(di(pentafluorophenyl)phosphino)ethane; $Et_2dtc =$ N,N′-diethyldithiocarbamate) were synthesized and characterized by NMR, IR, and electronic spectroscopies. A distorted square-planar coordination geometry is confirmed by a single crystal structure determination of $[Ir(CO)(PPh_3)(Et_2dtc)]$ **116**. All of the complexes exhibit emission in the solid state and in frozen glass media at 77 K. Furthermore, **116**, $[Ir(dppe)(Et_2dtc)]$, and $[Ir\{P(OPh)_3\}_2(Et_2dtc)]$ display emission in CH_2Cl_2 at RT. The latter undergoes intramolecular C–H activation in benzene giving the orthometallated product $[IrH\{P(OPh)_2(OC_6H_4)\}\{P(OPh)_3\}(Et_2dtc)]$ **117**. Complex **116** reacts with H_2 in benzene, forming several different dihydride products $[IrH_2(CO)(PPh_3)(Et_2dtc)]$ **118**, including an isomer with a kinetic preference for the formation of 170 : 1 as determined using PHIP NMR effect at 300 K. PHIP is also observed in H_2 oxidative addition to $[Ir\{(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2\}(Et_2dtc)]$. Benzene solutions of **116** and $[Ir(dppe)(Et_2dtc)]$ react with O_2 to form the stable adducts $[Ir(O_2)(CO)(PPh_3)(Et_2dtc)]$ **119a** and $[Ir(O_2)(dppe)(Et_2dtc)]$ **119b**, respectively, and both lose O_2 upon simple irradiation.[62]

The luminescent alkyl complexes $[IrR(CO)(PAr_3)_2(mnt)]$ (mnt = maleonitriledithiolate; R = Me, Et, Pr, CH_2CN) were synthesized and characterized. The complexes possess octahedral coordination geometries with the phosphine ligands in mutually *trans*-positions, as confirmed by a crystal structure analysis of the Me derivative

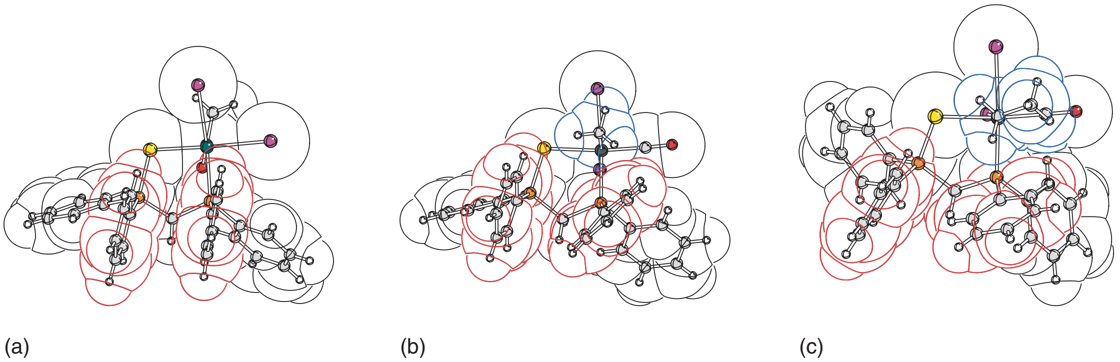


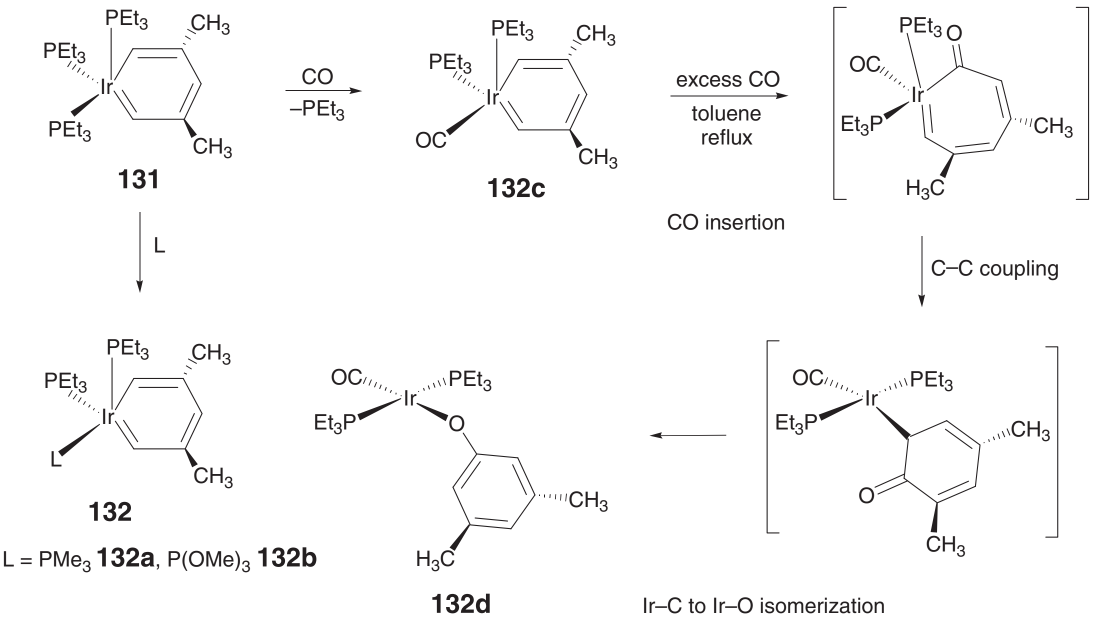
Figure 10 Space filling models for (a) $[Rh(CO)(dppms)I_2R]$, (b) **113a** (R = Me), and (c) **115** (R = Et).

[IrMe(CO)$(PPh_3)_2$(mnt)] **120**. Photolysis of **120** in the presence of H-atom sources and radical traps leads to products consistent with Ir–alkyl bond homolysis favored strongly over CO photodissociation as proved by ^{13}CO NMR probe. Photochemical activation of [IrR(CO)$(PPh_3)_2$(mnt)], where R contains β-hydrogens, produces only the β-elimination products of olefins and the hydride complex [IrH(CO)$(PPh_3)_2$(mnt)] **121** even in the presence of large excesses of phosphine, CO, or different radical trapping agents.[63]

An interesting class of Ir carbonyl complexes is represented by "A frame" bimetallic species mainly studied by Cowie and co-workers. The reactivity of the alkyl substituents often associated with these systems is detailed elsewhere in this chapter (*vide infra*). In some cases, an interesting behavior was observed where the CO ligand is concerned. For example, the Me complex $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2]$OTf **122** reacts readily with alkynes containing electron-withdrawing substituents giving the alkyne-bridged products, $[Ir_2(CH_3)(CO)_2(\mu\text{-}alkyne)(dppm)_2]$OTf **123**, with formal replacement of the bridging ligand. With other 1-alkynes (HC≡CR, R = Me, Ph), reaction at −80 °C results in oxidative addition to give acetylide hydrides $[Ir_2H(CH_3)(CO)_2(\mu\text{-}C_2R)(dppm)_2]$OTf **124**, which upon warming undergo transfer of the hydride ligand to the β-carbon of the acetylide to give the vinylidene-bridged products. At ambient temperature CH_4 elimination occurs, giving the acetylide-bridged products $[Ir_2(CO)_2(\mu\text{-}C_2R)(dppm)_2]$OTf **125**. Under a CO atmosphere, exchange of a vinylidene hydrogen and the Me ligand occurs to give a methylvinylidene-bridged hydride $[Ir_2(H)(CO)_3(\mu\text{-}CCHMe)(dppm)_2]$[OTf] **126**.[64]

In case of heterobimetallic Ir/Rh analogs, reaction of $[RhIr(CH_3)(CO)_3(dppm)_2]$OTf **127** with several phosphines and phosphites yields the carbonyl-substitution product $[RhIr(CH_3)(PR_3)(CO)_2(dppm)_2]$OTf **128**, in which the added phosphine and the Me ligands are coordinated to Ir. At −80 °C, an intermediate in this reaction, $[RhIr(CH_3)(PR_3)(CO)_3(dppm)_2]$OTf **129**, is observed with PR_3 bound to Rh. Similar reactions with the dicarbonyl compound $[RhIr(CH_3)(CO)_2(dppm)_2]$OTf **130** suggest that attack occurs directly at Ir in this case. The structure of **129** is slightly different in solution, having the carbonyls both terminally bound one to each metal in solution, but having one bridging in the solid.[65]

A rare example of a stable metallabenzene complex was synthesized in three steps from $[IrCl(PEt_3)_3]$ by Bleeke *et al.* by treatment with potassium 2,4-dimethylpentadienide yielding [cyclic] *mer*-$[CH{=}C(Me)CH{=}C(Me)CH_2IrH(PEt_3)_3]$ **131** via C–H bond activation, followed by reaction with MeOTf and deprotonation (Scheme 14). This compound reacts with a variety of small σ-donor ligands under mild conditions to produce monosubstituted metallabenzenes [cyclic] $[CH{=}C(Me)CH{=}C(Me)CH{=}Ir(PEt_3)_2L]$ (L = PMe_3 **132a**, $P(OMe)_3$ **132b**, CO **132c**), in which L resides preferentially in a basal coordination site. Treatment with excess CO in refluxing toluene leads to carbonyl insertion and C–C coupling involving the iridabenzene ring, ultimately yielding via an intramolecular rearrangement the phenoxy species [(3,5-dimethylphenoxy)Ir$(PEt_3)_2$(CO)] **132d**.[66]



Scheme 14

Although a whole paragraph is dedicated to Ir complexes bearing extended Huckel systems, some remarkable examples of (substituted) cyclopentadienyl Ir monocarbonyl complexes featuring unexpected reactivity are summarized below.

Heating $[\mathrm{Cp}^*\mathrm{Ir}(\mathrm{PMe}_3)(\mathrm{H})\{\mathrm{C(O)CF}_3\}]$ leads to the quantitative formation of $[\mathrm{Cp}^*\mathrm{Ir}(\mathrm{CO})(\mathrm{PMe}_3)]$ **133** and $\mathrm{CF_3H}$ instead of inducing reductive elimination of aldehyde, or decarbonylation to give a trifluoroalkyl hydride. The mechanism (see also Scheme 45) involves dissociation of trifluoromethyl anion to give the transient ion-pair intermediate $[\mathrm{Cp}^*\mathrm{IrH(CO)(PMe}_3)]^+[\mathrm{CF}_3]^-$. Three additional acyl hydrides, $[\mathrm{Cp}^*\mathrm{Ir(H)(PMe}_3)\{\mathrm{C(O)R_F}\}]$ ($\mathrm{R_F = CF_2CF_3}$, $\mathrm{CF_2CF_2CF_3}$, or $\mathrm{CF_2(CF_2)_6CF_3}$), undergo $\mathrm{R_F}$–H elimination to give **133** at a faster rate than $\mathrm{R_F = CF_3}$.[67,67a]

Reaction of the neutral dihydride complexes $[\mathrm{Cp^RIr(L)H_2}]$ ($\mathrm{L = P(OPh)_3}$, CO; R = H, Me) with triflic acid at ambient temperature or above has been studied by Heineckey. The reaction affords $\mathrm{H_2}$ and the dimeric hydride-bridged species $[\{\mathrm{Cp^RIr(L)H}\}_2(\mu\text{-H})]\mathrm{OTf}$. Deprotonation of the cationic complexes gives the neutral dimers $[\mathrm{Cp^RIr(L)H}]_2$. Thermolysis of the carbonyl complex $[\mathrm{Cp^RIr(CO)H}]_2$ **134** affords $[\mathrm{Cp^RIr(CO)}]_2$ **135** and dihydrogen. The crystal structures of the related $\mathrm{Cp^{Et}}$ derivative $[\mathrm{Cp^{Et}Ir(CO)H}]_2$ **136** were also reported.[68]

Reactions between $[\mathrm{Cp^*Ir(PMe_3)(Me)(OTf)}]$ and aldehydes (RCHO) proceed with high selectivity to give the hydrocarbyl carbonyl salts $[\mathrm{Cp^*Ir(PMe_3)(R)(CO)}]\mathrm{OTf}$ (**137**, R = Me, Et, Pr, Ph, 1-ethylpropyl, *p*-Tol, Mes, (*Z*)-1-phenyl-1-propen-2-yl, vinyl, $\mathrm{Bu^t}$, 1-adamantyl). The tandem C–H bond activation/decarbonylation reaction afforded the first isolated tertiary alkyl complexes of Ir. X-ray diffraction studies were carried out on Mes, $\mathrm{Bu^t}$, and 1-adamantyl derivatives. Hydride reduction of the *p*-Tol complex provided an example of a rare transition metal formyl complex, $[\mathrm{Cp^*Ir(PMe_3)}(p\text{-Tol})(\mathrm{CHO})]$.[69]

The reaction of $[\mathrm{Ir(CO)}(\eta^2\text{-coe})(\eta^5\text{-C}_9\mathrm{H}_7)]$ ($\mathrm{C_9H_7}$ = indenyl) with excess $\mathrm{C_2R_2}$ (R = Ph, Tol) in benzene at reflux leads to a mixture containing $[\mathrm{Ir(CO)}(\eta^2\text{-C}_2\mathrm{R}_2)(\eta^5\text{-C}_9\mathrm{H}_7)]$ [R = Ph **138a**, *p*-Tol **138b**] and $[\mathrm{Ir_2(CO)_2}(\mu\text{-C}_2\mathrm{R}_2)(\eta^5\text{-C}_9\mathrm{H}_7)_2]$ [R = Ph **139a**, Tol **139b**]. Complex **139a** contains a dimetallacyclobutene framework with the CO ligands adopting a *trans*-orientation with respect to the $\mathrm{Ir_2C_2}$ mean plane. The indenyl ligands take positions opposite the carbonyls at each Ir center.[70]

Finally, an interesting behavior was observed by Morales-Morales *et al.* during the transfer dehydrogenation of primary and secondary alcohols catalyzed by the PCP pincer complex, $[\mathrm{IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}}]$ (*vide infra*). Whereas dehydrogenation normally occurs across the C–O bond rather than the C–C bonds and the corresponding aldehydes or ketones are obtained as the sole products, methanol is an exception to this pattern of reactivity and undergoes only stoichiometric dehydrogenation to give the carbonyl complex, $[\mathrm{Ir(CO)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}}]$ **140**.[71]

7.04.2.2 Dicarbonyl Complexes

Among the most studied dicarbonyl iridium(I) complexes are the anionic $[\mathrm{IrX_2(CO)_2}]^-$ (X = Cl **141a**, Br, **141b**, I **141c**) due to their implications in catalytic processes such as methanol carbonylation See for example Refs: 72, 72a–72g. (*vide infra*), both from experimental and theoretical[73] viewpoint, as for derivatives such as *cis*-$[\mathrm{Ir(CO)_2(py)_2}]\mathrm{PF_6}$ **142** which was found to catalyze the WGS reaction.[74] From the synthetic point of view, it is worth mentioning here a few examples of systems derived from $[\mathrm{IrX_2(CO)_2}]^-$.

The anionic complexes $[\mathrm{RhCl_2(CO)_2}]^-$, $[\mathrm{IrCl_2(CO)_2}]^-$, or $[\mathrm{RuCl_3(CO)_2(DMF)}]^-$ were obtained by Kalck and co-workers in high yields (up to 85%) by refluxing DMF solutions of commercial hydrate chlorides $\mathrm{MCl_3{\cdot}3H_2O}$ (M = Rh, Ir, Ru). Depending on the metal, it was observed that the presence of small amounts of $\mathrm{H_2O}$ and/or HCl greatly accelerates the reduction step.[75,75a]

The active Ir species in the MeOH carbonylation reaction was crystallized as $[\mathrm{PPN}][\mathrm{IrI_2(CO)_2}]$ **143** and the X-ray structure solved, showing a *cis*-geometry and a square-planar environment. Iodidric acid reacts very quickly with this compound to provide $[\mathrm{PPN}][\mathrm{IrHI_3(CO)_2}]$ **144**, the X-ray crystal structure of which was also determined. The two CO ligands remain in mutual *cis*-position in a pseudo-octahedral environment. The same *cis*-arrangement was observed from the X-ray structure for $[\mathrm{PPN}][\mathrm{IrMeI_3\ (CO)_2}]$ **145** resulting from the slower oxidative addition of $\mathrm{CH_3I}$ to $[\mathrm{PPN}][\mathrm{IrI_2(CO)_2}]$ (Figure 11). By iodide abstraction with $\mathrm{InI_3}$, the anionic Me complex gave rise to the dimeric neutral complex $[\mathrm{Ir(CO)_2I}(\mu\text{-I})\mathrm{Me}]_2$. An X-ray structure showed that the Me ligands are in the equatorial positions of the two octahedrons sharing an edge, formed by the two bridging iodide ligands.[76]

The OCT anion $[\mathrm{Ir(CO)_2I_4}]^-$ **146** was isolated and characterized as the isoquinolinium salt during carbonylation of EtOH and higher alcohols using $\mathrm{IrCl_3{\cdot}3H_2O}$ as a catalyst precursor with HI as a promoter. X-ray analysis shows discrete cationic $[\mathrm{C_{11}H_{12}N}]^+$ and *cis*-$[\mathrm{Ir(CO)_2I_4}]^-$ with a distorted octahedral environment around Ir and average Ir–I and Ir–C distances of 2.702(2) and 1.86(4) Å, respectively. Spectral and electrochemical studies on the intermediates

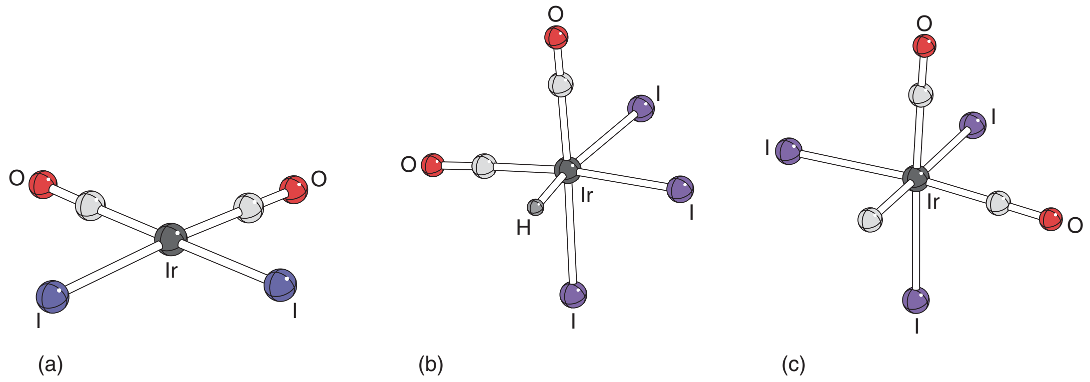


Figure 11 X-ray crystal structures of (a) **143**, (b) **144**, and (c) **145**.

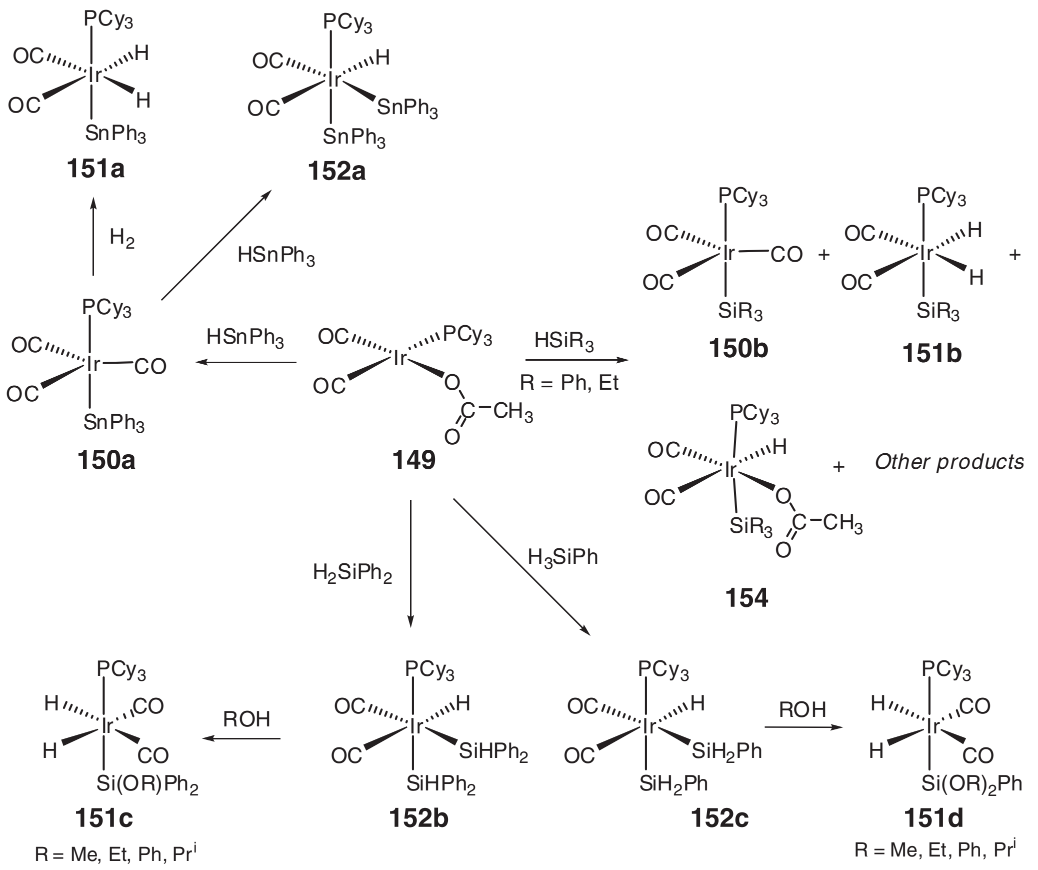
isolated during carbonylation of other higher alcohols revealed a strong influence of the counter cation on the electron-transfer processes in these halocarbonyl complexes of Ir(III).[77]

The structure and reactivity of anionic complexes $[M(CO)_2I_2]^-$ (M = Rh, Ir) supported on ion exchange resins based on quaternized poly(4-vinylpyridine-co-styrene-co-divinylbenzene) have been investigated using a variety of techniques. The reactivity toward MeI of $[M(CO)_2I_2]^-$ supported on thin polymer films was probed directly *in situ* by IR spectroscopy. For M = Ir oxidative addition gave a stable Me complex, $[Ir(CO)_2I_3Me]^-$, as observed in solution chemistry. The kinetic measurements represent a rare example of quantitative rate data for fundamental reaction steps of a heterogenized transition metal catalyst.[78]

Activation of dihydrogen by $(Bu_4N)[IrBr_2(CO)_2]$ **141b** and tin dibromide was studied by Eisenberg using PHIP allowing the detection of transient dihydrides not observable in conventional ^1H NMR spectra. Tin dibromide reacts with iridium(I) complex **141b** in acetone forming equilibrium mixtures of *cis*- and *trans*-tribromostannyl derivatives $[IrBr_n(SnBr_3)_{2n}(CO)_2]^-$, **147**, $n = 0, 1$). The σ-donating effect of the $SnBr_3^-$ ligand facilitates the oxidative addition to the iridium center. The structures of the dihydrides are assigned from hydride chemical shifts and values of $^2J(^1H\text{-}^{117,119}Sn)$. The only dihydride observed in conventional ^1H NMR spectra is *cis–trans–cis*-$[IrH_2(SnBr_3)_2(CO)_2]^-$ **148**, the identity of which was confirmed using the ^{13}C labeled Ir(I) precursor. Both **141b** and its tribromostannyl derivatives catalyze *cis*-pairwise addition of dihydrogen to phenylacetylene.[79]

The reactivity of the $[Ir\{\eta^1\text{-}OC(O)Me\}(CO)_2(PCy_3)]$ **149** toward $HSnPh_3$, $HSiPh_3$, $HSiEt_3$, H_2SiPh_2, and H_3SiPh was described. Complex **149** reacts with $HSnPh_3$ to afford $[Ir(SnPh_3)(CO)_3(PCy_3)]$ **150a** for which the molecular structure was determined by X-ray studies. The coordination polyhedron around the Ir atom can be described as a TBP with the triphenylstannyl group and the tricyclohexylphosphine ligand occupying the axial positions, while the three carbonyl groups define the equatorial plane. Complex **150** reacts with H_2 and $HSnPh_3$, yielding $[IrH_2(SnPh_3)(CO)_2(PCy_3)]$ **151a** and $[IrH(SnPh_3)_2(CO)_2(PCy_3)]$ **152a**, respectively. The reactions of **149** with $HSiR_3$ (R = Ph, Et) have been investigated by Esteruelas *et al.* (Scheme 15). The reaction gave mixtures of products, including $[Ir(SiR_3)(CO)_3(PCy_3)]$ (**150b**, R = Ph, Et), $[IrH_2(SiR_3)(CO)_2(PCy_3)]$ (**151b**, R = Ph, Et), $[IrH(\mu\text{-}OAc)(CO)(PCy_3)]_2$ **153**, and $[IrH\{\eta^1\text{-}OC(O)Me\}(SiR_3)(CO)_2(PCy_3)]$ (**154**, R = Ph, Et). The reaction of **149** with 1 equiv. of H_2SiPh_2 gives $[IrH_2\{Si(OC(O)Me)Ph_2\}(CO)_2(PCy_3)]$ **155** along with small amounts of **153** and $[Ir(SiHPh_2)(CO)_3(PCy_3)]$. In the presence of 2 equiv. of H_2SiPh_2 and H_3SiPh, **149** affords $[IrH(SiHPh_2)_2(CO)_2\text{-}(PCy_3)]$ **152b** and $[IrH(SiH_2Ph)_2(CO)_2(PCy_3)]$ **152c**, respectively. Complexes **152b** and **152c** react with MeOH, EtOH, 2-propanol, and phenol to give $[IrH_2\{Si(OR)Ph_2\}(CO)_2(PCy_3)]$ (**151c**, R = Me, Et, Pr^i, Ph) and $[IrH_2\{Si(OR)_2Ph\}(CO)_2(PCy_3)]$ (**151d**, R = Me, Et, Pr^i), respectively. The key intermediates of these alcoholysis processes are postulated to be silylene species of Ir(III).[80]

The iridasilylacyle *fac*-$[IrH(PMe_3)_3(o\text{-}C_6H_4SiMe_2)]$ **156** results from the orthometallation of the transient $[Ir(PMe_3)_3(SiMe_2Ph)]$, generated from $[Ir(PMe_3)_4Cl]$ and $PhMe_2SiLi$ at ambient temperature. The same complex can also be obtained from *fac*-$[IrH(CH_3)(PMe_3)_3(SiMe_2Ph)]$, upon reductive elimination of methane. The reaction of the iridacycle with CO allows trapping of the iridium(I) species and provides a synthetic route to $[Ir(PMe_3)_2(CO)_2(SiMe_2Ph)]$ **157**. Complex **157** was identified by spectroscopy and by X-ray crystallographic methods. Metallation of silyl ligands can be, therefore, a facile reversible process under mild conditions and iridasilacycles can be used as a masked form of electron-rich Ir(I) silyl complexes, which are not readily accessible species.[81]



Scheme 15

The addition of I_2 to $[Ir_2\{\mu\text{-HN}(p\text{-Tol})\}_2(CO)_4]$ **158** produces the dimer $[Ir_2I_2\{\mu\text{-NH}(p\text{-Tol})\}_2(CO)_4]$ **159**, where the two Ir centers are connected by a metal–metal single bond of length 2.591(1) Å. Complex **159** undergoes substitution of only one CO with phosphines (PPh_3 and PPh_2Me), even when an excess of the phosphines is used.[82]

Pyrazolyl-bridged iridium dimers represent an interesting class of bimetallic carbonyl complexes. The synthesis in high yields and the dissociative behavior, in the solid state and in solution, of mononuclear *cis*-$[M(CO)_2Cl(pyz)]$ (M = Rh **160a**, Ir **160b**; pyz = pyrazine) have been reported. The mononuclear complexes of Rh and Ir are relatively labile with respect to pyrazine release. Particularly in the case of Rh they generate, even in the solid state, the corresponding dinuclear complexes *cis,cis*-$[\{M(CO)_2Cl\}_2(\mu\text{-pyz})]$ [M = Rh **161a**, Ir **161b**] with the pyrazine ligand as tethering unit between two MCl(CO) moieties. The ^1H NMR spectra of these mononuclear Rh and Ir complexes in $CHCl_3$ show at 25 and 60 °C, respectively, fast and reversible metal dissociation from the bridging pyrazine, which can be avoided by lowering the temperature. The solid-state structure of **160b** was determined via single crystal X-ray diffraction (Figure 12).[83]

A rare example of mixed valence Ir(III)/Ir(I) dimer, namely $[Ir_2(\mu\text{-pz})_2Me(CO)_2(PPr^i_3)_2]ClO_4$ **162** was prepared by Oro and co-workers as intermediate species for the S_N2 oxidative addition of MeI to dinuclear $[Ir(\mu\text{-pz})(CO)(PPr^i_3)]_2$ **163**. The complex features a weak metal–metal bond interaction.[84]

Slow uptake of dihydrogen by the diiridium(I) complex $[Ir(\mu\text{-pz})(PPh_3)(CO)]_2$ **164** is accompanied by the formation of the diiridium(II) adduct $[IrH(\mu\text{-pz})(PPh_3)(CO)]_2$ **165**. Reaction with CCl_4 effects hydride replacement in **165**, affording the monohydride $[Ir_2H(Cl)(\mu\text{-pz})_2(PPh_3)_2(CO)_2]$ **166a** in which Ir–Ir distance is 2.683 Å. At one metal center, H is equatorial and PPh_3 is axial, while at the other, Cl is axial as is found in the symmetrically substituted product $[Ir(\mu\text{-pz})(PPh_3)(CO)Cl]_2$ **167** (Ir–Ir = 2.754 Å) that is formed by the action of CCl_4 on **164**. Treatment of **164** with I_2 yields the diiodo analog **167**, which reacts with $LiAlH_4$ to afford the iodo complex $[Ir_2H(I)(\mu\text{-pz})_2(PPh3)_2(CO)_2]$ **166b** (Ir–Ir = 2.684 Å). Protonation of **164** with HBF_4 gave the binuclear cationic complex $[Ir_2H(\mu\text{-pz})_2(PPh_3)_2(CO)_2]BF_4$ **166c**, which crystallizes as an axially symmetrical unit in which Ir–Ir = 2.834 Å. Reaction of **166b** with water or wet methanol gives the cationic diiridium(III) products $[Ir_2H_2(\mu\text{-OX})(\mu\text{-pz})_2(PPh_3)_2(CO)_2]BF_4$ (**168**, X = H, Me).[85]

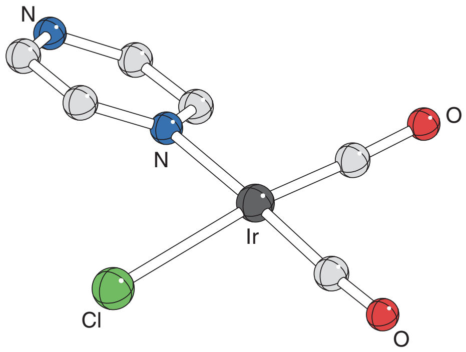


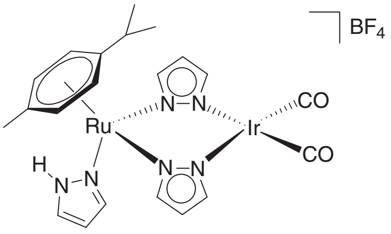
Figure 12 X-ray crystal structure of **160b**.

The metal–metal bonded dicarbonyl complexes [(*p*-cymene)M(μ-pz)$_2$IrCl(CO)$_2$] (M = Ru **169a**, Os **169b**) react stereospecifically with PPh$_3$ to yield an enantiomeric pair of carbonyl compounds [(*p*-cymene)M(μ-CO)(μ-pz)$_2$IrCl(CO)(PPh$_3$)] [M = Ru **170a**, Os **170b**] in which the Cl ligand is *trans* to the bridging CO group. Under similar conditions, the nonmetal–metal bonded [(*p*-cymene)RuCl(μ-pz)$_2$M(CO)$_2$] **171** eliminate CO forming the monosubstitution products [(*p*-cymene)RuCl(μ-pz)$_2$M(CO)(PPh$_3$)] [**172**, M = Ir, Rh]. Removal of the Cl ligand affords [(*p*-cymene)Ru(pz)$_2$Ir(CO)$_2$(PPh$_3$)]BPh$_4$ **173** as two isomers. The related OsIr compound [(*p*-cymene)Os(μ-CO)(μ-pz)$_2$Ir(CO)(PPh$_3$)]BPh$_4$ **174** was prepared from [(*p*-cymene)Os(CO)(η-pz)$_2$Ir(CO)$_2$]BPh$_4$ **175a** and PPh$_3$.[86] Complex **175a** was also obtained via reaction of the cationic compounds [(*p*-cymene)OsCl(Hpz)$_2$]X (Hpz = pyrazole; X = Cl **a**, BF$_4$ **b**), which are suitable precursors to the heterobinuclear complex [(*p*-cymene)OsCl(μ-pz)$_2$Ir(cod)], which upon carbonylation produces the dicarbonyl [(*p*-cymene)OsCl(μ-pz)$_2$Ir(CO)$_2$] or, in the presence of NaBPh$_4$, the cationic tricarbonyl [(*p*-cymene)Os(CO)(μ-pz)$_2$Ir(CO)$_2$]BPh$_4$. Complex **175a** in methanol isomerizes to the metal–metal-bonded complex [cyclic] [(*p*-cymene)Os(μ-pz)$_2$IrCl(CO)$_2$] **175b**.[87]

Heterodinuclear [(*p*-cymene)(pz)Ru(μ-pz)$_2$Ir(CO)$_2$] **176a** was prepared by treating [(*p*-cymene)Ru(pz)$_2$(Hpz)] with [Ir(acac)(CO)$_2$]. The carbonyl complexes **176a** reacted with mono- or diphosphines, rendering [(*p*-cymene)(pz)Ru(μ-pz)$_2$IrL$_2$] (L$_2$ = CO, PPh$_3$ **177a**, dppm **178a**, dppe **178b**). Protonation of **176a** or **177a** with HBF$_4$ afforded the corresponding cationic complexes [(*p*-cymene)(Hpz)Ru(μ-pz)$_2$IrL$_2$]BF$_4$ (L$_2$ = (CO)$_2$ **176b**, CO, PPh$_3$ **177b**). The molecular structure of complex **176b** was determined by X-ray diffraction methods, exhibiting two bridging pyrazolate groups between the metals without direct intermetallic interaction, the Ru–Ir distance being 3.6770(6) Å (Scheme 16).[88]

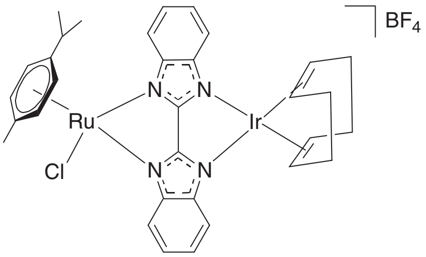
The cationic ruthenium complex [(*p*-cymene)Ru(HBbzim)(PPh$_3$)]BF$_4$ (H$_2$Bbzim = 2,2′-bibenzimidazole) reacts with [Ir(acac)(cod)] yielding the cationic binuclear complex [(*p*-cymene)(PPh$_3$)Ru(μ-Bbzim)Ir(cod)]BF$_4$ **179**. Carbonylation of **179** afforded [(*p*-cymene)(PPh$_3$)Ru(μ-Bbzim)Ir(CO)$_2$]BF$_4$ **180** for which a molecular structure was determined by diffractometric methods (Scheme 17). The cation consists of a Ru and an Ir atom connected by a Bbzim^{2-} anion that chelates both metals through four N atoms.[89]

The energetics of the oxidative additive of I$_2$ to [Ir(μ-L)(CO)$_2$]$_2$ [L = SBu^t **181a**, 3,5-dimethylpyrazolate (**181b**, 3,5-Me$_2$pz) and 7-azaindolate (**181c**, 7-aza)] was studied by Ciriano and co-workers by using calorimetric measurements, X-ray structure determinations, and extended Hückel MO calculations. The addition of 1 molecule of iodine



176b

Scheme 16



180

Scheme 17

to 1 molecule of **181** in toluene leads to $[Ir(\mu\text{-}L)(I)(CO)_2]_2$ [L = SBu^t **182a**, 3,5-dimethylpyrazolate (**182b**, 3,5-Me$_2$pz) and 7-azaindolate (**182c**, 7-aza)] with the formation of two Ir–I bonds and one Ir–Ir bond. The following enthalpies of reaction were obtained for this process: −125.8 ± 4.9 kJ mol^{-1} **182a**, −152.0 ± 3.8 kJ mol^{-1} **182b**, and −205.9 ± 9.9 kJ mol^{-1} **182c**. These results are consistent with a possible decrease of the strain caused by formation of three-, four-, and five-membered rings in the corresponding products, as suggested by EHMO calculations, which also indicate a slightly stronger Ir–Ir bond for **182b** than for **182a** despite the fact that the Ir–Ir bond lengths are identical for both complexes. The reaction of **181a** with 2 molecules of iodine yielded $[Ir(\mu\text{-}SBu^t)I_2(CO)_2]_2$ **183**. The X-ray structures of **182a** and **182b** were determined (Figure 13). In both complexes, the overall structure can be described as two square-planar pyramids, one around each iridium atom, with the iodine atoms in the apical positions, and the equatorial positions occupied by two CO groups and the two sulfur atoms of the SBu^t ligands, or two N atoms of the pyrazolyl ligands. In the case of L = SBu^t the pyramids share a common edge defined by the two bridging sulfur atoms while for L = 3,5-Me$_2$pz they are connected through the two N–N bonds of the pyrazolyl ligands.[90]

Polymetallic carbonyl iridium complexes have also been described in the literature mainly thanks to the work done in Zaragoza by Oro and co-workers. Reaction of $[Rh(\mu\text{-}Cl)(cod)_2]$ with $[Cp^{Bu}{}_2Zr(\mu\text{-}S)_2\{Ir(CO)_2\}]^-$ **184**, which was in turn prepared from $[Cp^{Bu}{}_2Zr(\mu\text{-}SH)_2]$ with $[Ir(CO)_2Cl_2]^-$, gave heterotrimetallic complex $[Cp^{Bu}{}_2Zr(\mu\text{-}S)_2\{Ir(CO)_2\}\{Rh(cod)\}]$ **185** which subsequently underwent carbonylation to give $[Cp^{Bu}{}_2Zr(\mu\text{-}S)_2\{Ir(CO)_2\}\text{-}\{Rh(CO)_2\}]$ **186**. Complex **185** was also characterized by X-ray crystallography.[91]

The reactions of the early–late trinuclear complex $[Cp(acac)Ti(\mu_3\text{-}S)_2\{Ir_2(CO)_4\}]$ **187** with electrophiles occur on the iridium atoms with no other involvement of the early metal than in electronic effects. The reaction with iodine gave two isomers of the diiridium(II) complex $[Cp(acac)Ti(\mu_3\text{-}S)_2\{Ir_2I_2(CO)_4\}]$ **188a** differentiated by the relative positions of the iodo ligands on the iridium atoms. In contrast, the reactions with iodoalkanes RI are highly stereoselective yielding only one isomer of formula $[Cp(acac)Ti(\mu_3\text{-}S)_2\{Ir_2(R)I(CO)_4\}]$ **188b** (R = CH$_3$, CH$_2$I, CHI$_2$) with a carbonyl and the iodo ligand *trans* to the metal–metal bond. The structures of the symmetrical isomer

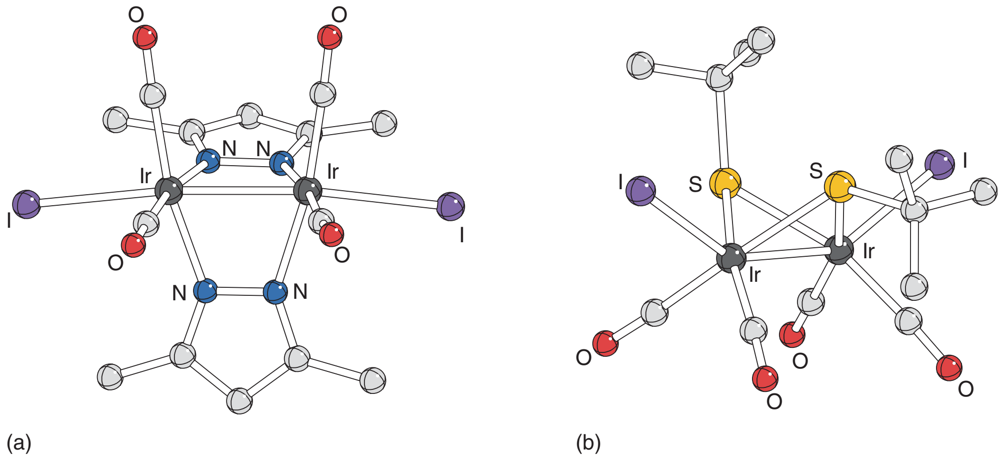
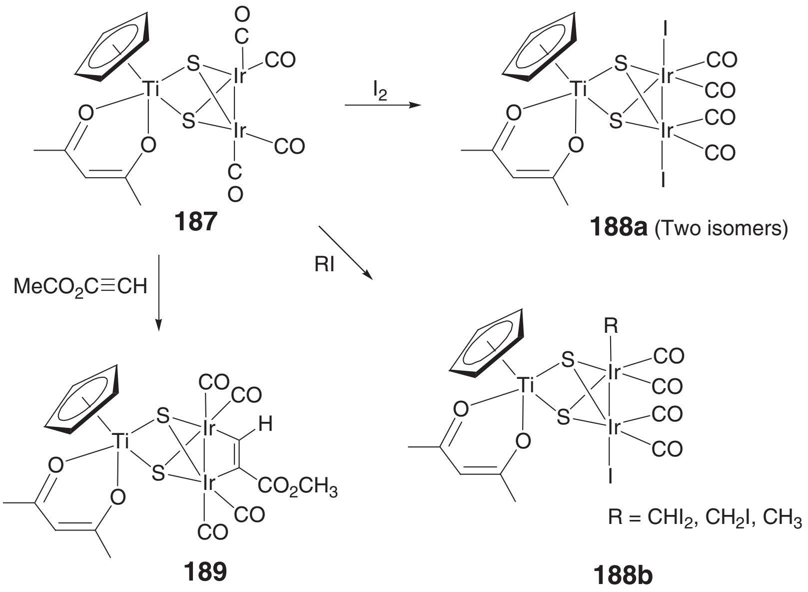


Figure 13 X-ray crystal structures of (a) **182a** and (b) **183**.



Scheme 18

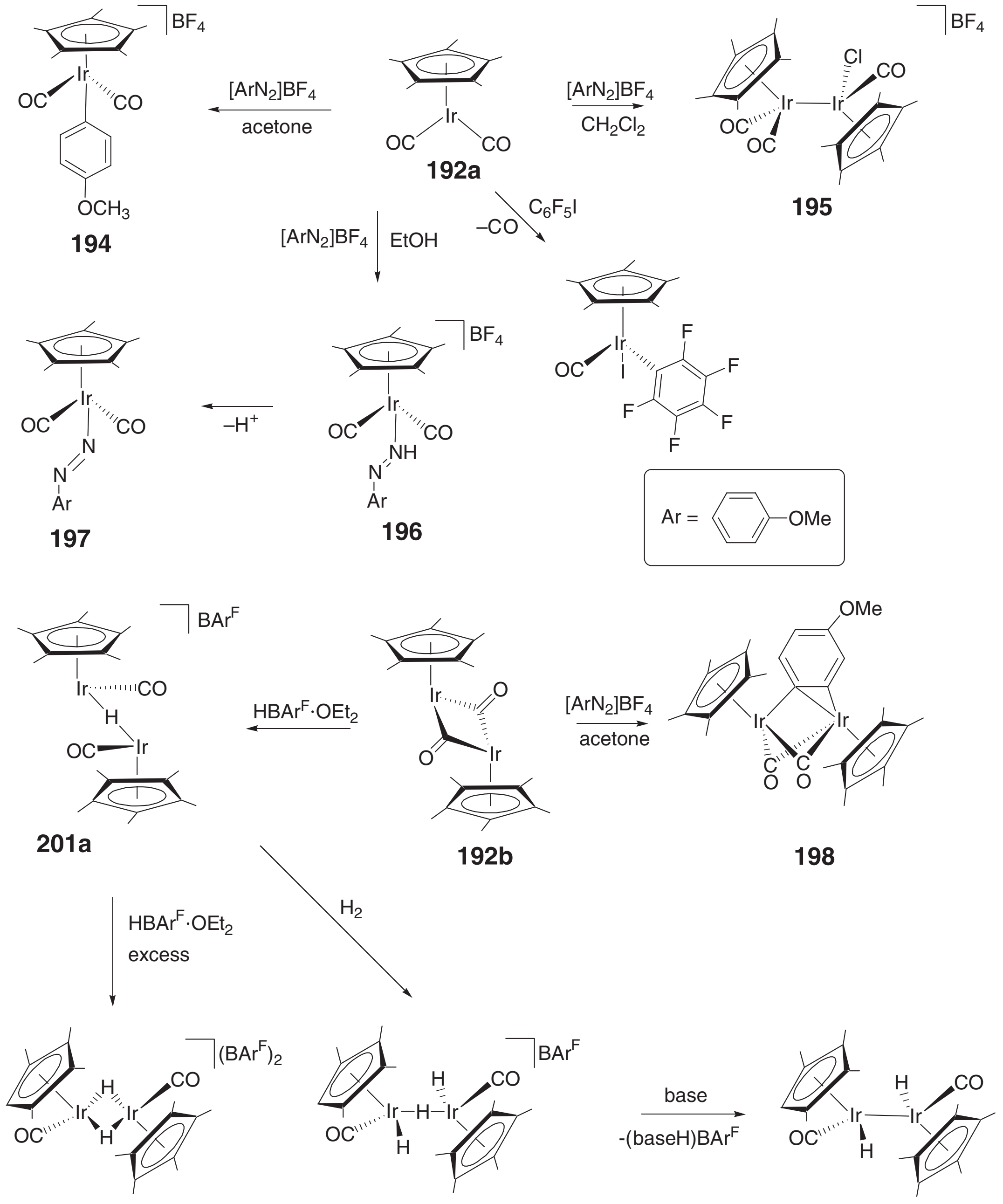
with the iodo ligands *trans* to the metal–metal bond and that of the compound with R = CHI$_2$ have been solved by X-ray diffraction methods. The stereoselectivity of the oxidative addition reactions were rationalized assuming the influence of steric effects of the groups on the titanium center and a radical-like mechanism. Alkyne insertion across the Ir–Ir bond was also reported, giving, in case of methylpropiolate, the cluster [Cp(acac)Ti(μ_3-S)$_2${Ir$_2$(μ-HC=CCO$_2$Me)(CO)$_4$}] **189** (Scheme 18).[92]

Reaction of the zirconium–sulfide metallocene anion [Cp$^{Bu}{}_2$ZrS$_2$]$^{2-}$ (Cptt = η^5-1,3-di-*tert*-butylcyclopentadienyl) with [{Ir(μ-Cl)(cod)}$_2$] gave the unusual early/late d^0–d^8 complex [Cp$^{Bu}{}_2$Zr(μ_3-S)$_2${Ir(cod)}$_2$] with a triangular ZrIr$_2$ core capped by two symmetrical μ_3-sulfido ligands. The reaction of [Cp$^{Bu}{}_2$Zr(SH)$_2$] with [Ir(acac)(cod)] gave the complex [Cp$^{Bu}{}_2$(acac)Zr(μ^3-S)$_2${Ir(cod)}$_2$] and, upon carbonylation, the tetracarbonyl [Cp$^{Bu}{}_2$(acac)Zr(μ_3-S)$_2${Ir(CO)$_2$}$_2$] **190**, while [Cp$^{Bu}{}_2$Zr(μ_3-S)$_2${Ir(CO)$_2$}$_2$] **191** resulted also from the reaction of [Cp$^{Bu}{}_2$Zr(SH)$_2$] with (PPh$_3$Bz)[IrCl$_2$(CO)$_2$] in the presence of triethylamine.[93]

Other common Ir(I) dicarbonyl precursors are the complexes [Cp*Ir(CO)$_2$] **192a**, [Cp*Ir(μ-CO)]$_2$ **192b**, and [CpIr(CO)$_2$] **192c**. The latter has been used as a 2e donor ligand, for example, in the synthesis of mixed hetero-bimetallic polycarbonyl derivatives such as [Cp(OC)$_2$Ir{W(CO)$_5$}] **193a**, [Cp(CO)$_2$IrRu(CO)$_3$(SiCl$_3$)$_2$] **193b**, [Cp(CO)$_2$IrOs(CO)$_3$(GeCl$_3$)Cl] **193c**, [Cp(CO)$_2$IrOs(CO)$_3$Br$_2$] **193d**. The crystal structures of **193a, 193b**, and **193d** reveal that all contain an unbridged metal–metal bond. With the exception of **193b**, all the complexes dissociate in solution at room temperature. Only in the case of **193d** an equilibrium was observed, indicating that CpIr(CO)$_2$ is a weak ligand.[94]

Functionally substituted compounds bearing **192c** were prepared from reactions of the corresponding substituted Cp^{R}Na, -Li, or -Tl reagents with [IrCl(CO)$_2$(py)]. Ring-substituted compounds synthesized by this route include chloro, benzyl, pentabenzyl, acetyl, carbomethoxy, Me, benzoyl, trimethylsilyl, cyano, dimethylamino, tetraphenyl, dimethylaminoethyl, (tetramethyl)dimethylaminoethyl, methoxyethyl, and pentamethyl. The symmetrical and asymmetrical CO stretching frequencies as well as the ^{13}C NMR chemical shifts of the carbonyl substituents were correlated with various Hammett substituent parameters.[95,95a]

Reaction of **192a** with [N$_2$Ar]BF$_4$ (Ar = *p*-C$_6$H$_4$OMe) in acetone at −78 °C affords the N$_2$ extrusion product [Cp*Ir(CO)$_2$(Ar)]BF$_4$ **194**, whereas in CH$_2$Cl$_2$ it yields dinuclear [Cp*(CO)$_2$Ir–IrCl(CO)Cp*]BF$_4$ **195**, and in EtOH the aryldiazene product [Cp*Ir(CO)(OEt)(NHNAr)]BF$_4$ **196** (Scheme 19). Deprotonation of **196** gives quantitatively the neutral doubly bent aryldiazenido complex [Cp*Ir(CO)(OEt)(N$_2$Ar)] **197**. The IR ν(CO) frequencies observed for **195** indicate no bridging carbonyl. ^{13}C NMR study shows that **195** is stereochemically non-rigid at ambient temperature and the CO ligands are all involved in a fast exchange process which is frozen at −86 °C. By reaction of [N$_2$Ar]BF$_4$ with **192b** in acetone, [{Cp*Ir(CO)}$_2$(1-η^1-1,2-η^2-*p*-C$_6$H$_4$OMe)]BF$_4$ **198** with a rare *s,p*-bridging aryl group was obtained and crystallized.[96]



Scheme 19

[Cp*Ir(CO)(C$_6$F$_5$)I] **199** was prepared by oxidative addition of iodopentafluorobenzene to **192a** after prolonged refluxing in benzene (40 h). Subsequent CO displacement from **199** with PMe$_3$ afforded [Cp*Ir(PMe$_3$)(C$_6$F$_5$)I].[97]

The reaction of 1-(ferrocenyl)indenyllithium, generated from (3-ferrocenyl)indene and BuLi in THF, with the dimers [IrCl(cod)]$_2$ and [IrCl(coe)$_2$]$_2$ afforded the heterobimetallic [(η^5-1-(ferrocenyl)indenyl)Ir(cod)], [(η^5-1-(ferrocenyl)indenyl)Ir(coe)$_2$], and [(η^5-1-(ferrocenyl)indenyl)Ir(CO)$_2$] **200**, the latter obtained from the COE derivative by substitution reaction with CO at RT. In contrast, the carbonylation of the Ir–cod complex at low temperature produces the intermediate [(η^1-1-(ferrocenyl)indenyl)Ir(cod)(CO)$_2$] stable up to room temperature. The crystal structure of **200** showed that iron and iridium are disposed in a cisoid configuration favored by a stabilizing weak

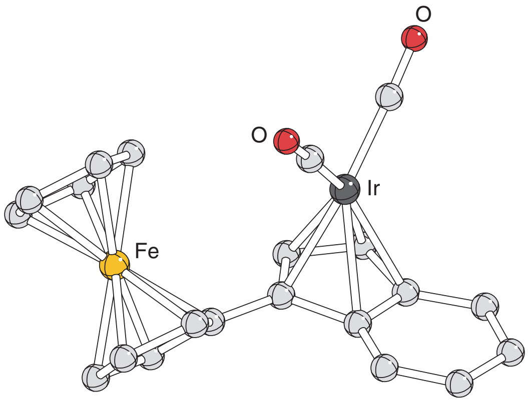


Figure 14 X-ray crystal structure of **200**.

bond interaction between the hydrogens of the Cp ring and iridium and its carbonyls (Figure 14). The results of the electrochemical oxidation of **200** support the existence of a significant interaction between the two metals.[98]

Protonation of the carbonyl-bridged dimer **192b** with 1 equiv. of the strong acid $HBAr^F \cdot 2Et_2O$ generated the hydride-bridged species $[\{Cp^*Ir(CO)\}_2(\mu\text{-}H)]BAr^F$ **201a** (see Scheme 19). Addition of excess acid gave the dihydride dication $[\{Cp^*Ir(CO)\}_2(\mu\text{-}H)_2]^{2+}$ **202a**. Complex **201a** reacts rapidly with CO or H_2 to afford $[\{Cp^*Ir(CO)\}_2(\mu\text{-}CO)(\mu\text{-}H)]^+$ **201b** and $[\{Cp^*Ir(CO)H\}_2(\mu\text{-}H)]^+$ **202b**. Deprotonation of complex **202b** generates the neutral dihydride dimer $[\{Cp^*Ir(CO)H\}_2]$ **203**, a compound with an unsupported Ir–Ir bond for which an X-ray diffraction analysis reveals an Ir–Ir bond length of 2.730(1) Å.[99]

Finally, $[Cp^*Ir(CO)(EPh)_2]$ **204**, E = S, Se) were prepared by the photo-induced reaction of **192a** with the diphenyl dichalcogenides E_2Ph_2 and used as neutral chelating ligands in carbonylmetal complexes such as $[Cp^*Ir(CO)(\mu\text{-}EPh)_2\{Cr(CO)_4\}]$, $[Cp^*Ir(CO)(\mu\text{-}EPh)_2\{Mo(CO)_4\}]$, and $[Cp^*Ir(CO)(\mu\text{-}EPh)_2\{Fe(CO)_3\}]$. The heterodimetallic complexes were characterized by IR and NMR spectroscopy, and the geometry of $[Cp^*Ir(CO)(\mu\text{-}SePh)_2\{Mo(CO)_4\}]$ was determined by a single crystal X-ray structure analysis, showing the absence of metal–metal interaction according to the long Ir···Mo distance [3.953(1) Å].[100]

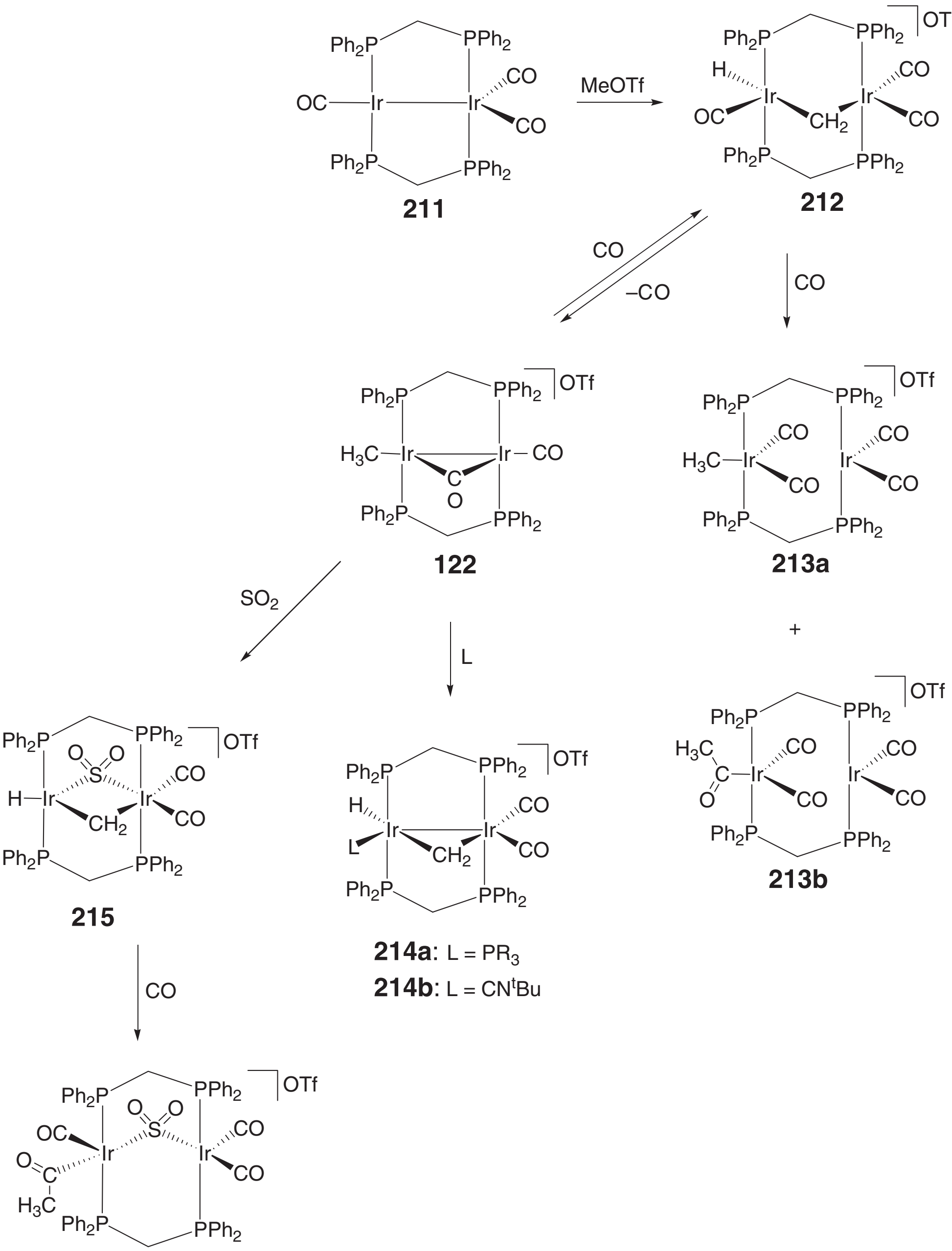
7.04.2.3 Polycarbonyl Complexes

A theoretical study of the carbonyl complexes $[M_2(CO)_8]$ of the group 9 metals (M = Co **205a**, Rh **205b**, Ir **205c**) has been published by Aullon and Alvarez.[101] Three isomers were found for each metal, with the relative stabilities and energies differing from one metal to another, and two transition states corresponding to their interconversion processes were identified. The minima in the potential energy surface have been fully characterized through a vibrational analysis and the Raman-active metal–metal stretching frequencies, as well as IR-active carbonyl stretching frequencies.

The dimer $[Ir(CO)_2I(\mu\text{-}I)Me]_2$ **206** reacts with CO to give the tricarbonyl *fac*-$[Ir(CO)_3I_2Me]$ **207** identified by high pressure IR and NMR spectroscopy and isotopic labeling. Kinetic data for the migratory CO insertion reaction to give *mer*-$[Ir(CO)_3I_2(COMe)]$ **208** indicates its nature as a key intermediate in Ir-catalyzed methanol carbonylation.[102]

Reduction of $Na[Ir(CO)_4]$ by Na in $(Me_3N)_3PO$, followed by treatment with liquid ammonia, provided high yields (90%) of unsolvated $Na_3[Ir(CO)_3]$ **209**, a thermally stable, pyrophoric orange solid with iridium in its lowest known formal oxidation state of −3. The iridate salt was characterized by IR spectroscopy, elemental analyses, and by its conversion to the triphenylgermyl and triphenylstannyl complexes, *trans*-$[Ir(CO)_3(EPh_3)_2]^-$ **210**, E = Ge, Sn). Single crystal X-ray structures of the Et_4N^+ salts of these species show the TBP nature of the anions, as predicted from their IR spectra in the carbonyl stretching frequency region.[103]

The reaction of the A-frame bimetallic complex $[Ir_2(CO)_3(dppm)_2]$ **211** with MeOTf yields the methene-bridged hydride $[Ir_2H(CO)_3(\mu\text{-}CH_2)(dppm)_2]OTf$ **212**, in which the hydride and methene hydrogens are rapidly scrambling at ambient temperature (Scheme 20). Under CO this species yields the Me and acyl products $[Ir_2(R)(CO)_4(dppm)_2]OTf$ [R = CH_3 **213a**, COMe **213b**]. Removal of one carbonyl from **212** yields the fluxional methyl complex **122** in which the methyl group readily migrates from metal to metal. Addition of CO, PR_3, $CNBu^t$, or SO_2 to **122** results in C–H bond cleavage of the Me group yielding the methene-bridged hydride species $[Ir_2H(CO)_2L(\mu\text{-}CH_2)(dppm)_2]OTf$ (L = CO **212**; PR_3 **214a**; $CNBu^t$ **214b**) or $[Ir_2H(CO)_2(\mu\text{-}CH_2)(\mu\text{-}SO_2)(dppm)_2]OTf$ **215**. Both the carbonyl and SO_2



Scheme 20

adducts are fluxional, having the hydrogens of the hydrido ligand and the methene group exchanging rapidly at ambient temp. X-ray structures of compounds **213, 214a**, and **215** have been also determined confirming the proposed structures.[104]

Reaction of CO with 7 in DMSO/H_2O gave reversibly $[Ir(CO)_3(TPPTS)_2]Cl$ **216** in H_2O and DMSO and $Ir(CO)_2Cl(TPPTS)_2$ **217** in DMSO only. In H_2O, further reactions occur slowly, including WGS reaction and formation of $[Ir(CO)_2(TPPTS)_3]^+$ **218**. In DMSO, reaction with CO readily forms $[Ir(CO)_3(TPPTS)_2]^+$ **219**; no reaction with CO is observed in H_2O. Reaction of **218** with H_2 occurs through TPPTS dissociation giving $[Ir(CO)_2(H)_2(TPPTS)_2]^+$ **220** initially before reaction with free TPPTS gives $[Ir(CO)(H)_2(TPPTS)_3]^+$ **221** as the final product.[105]

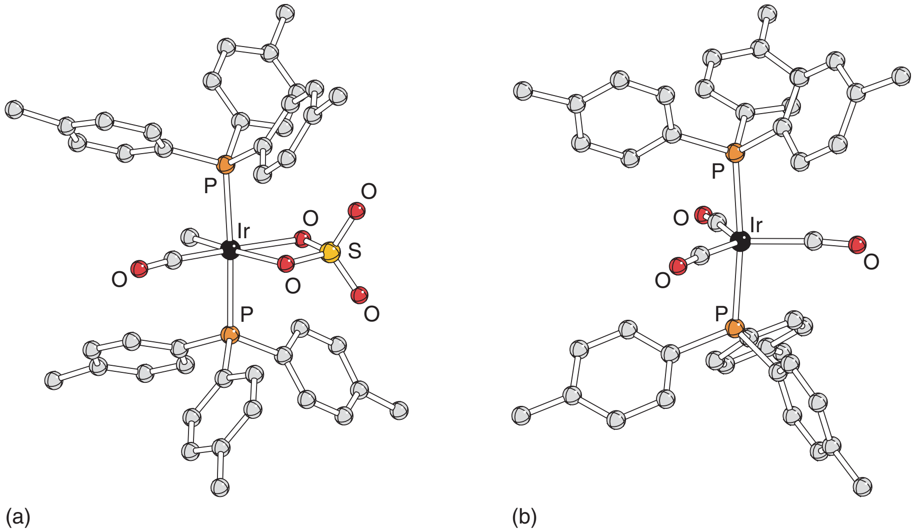


Figure 15 X-ray crystal structure of (a) **222** and (b) **223**.

Carbonylation of $[Ir(CO)(Me)(SO_4)\{P(p\text{-}Tol)_3\}_2]$ **222** leads to two products, $[Ir(CO)_3\{P(p\text{-}Tol)_3\}_2]^+$ **223** and $[Ir(CO)_3(COMe)\{P(p\text{-}Tol)_3\}_2]$ **224** by two different pathways. Structures of **222** and **223**·$[HSO_4]$ were determined (Figure 15). The $Ir(CO)_3P_2$ core of the cation has a geometry slightly distorted from D_3h symmetry, with Ir–P = 2.363(5) and 2.374(5) Å and Ir–CO = 1.921(21)–2.012(28) Å.[106]

Cationic Ir(III) carbonyl complexes $[Ir(CO)_6](Sb_2F_{11})_3$ **225** and $[Ir(CO)_5Cl](Sb_2F_{11})_2$ **226** were prepared and characterized. Complex **226** was identified by X-ray single crystal diffraction analysis.[107]

The reactions of either $[Rh(CO)_2(\mu\text{-}Cl)]_2$ or $[Ir(CO)_3Cl]_n$ with superacid HF–SbF_5 in a CO atmosphere produce $[M(CO)_5Cl](Sb_2F_{11})_2$ (M = Ir **227a**, Rh **227b**) where SbF_5 functions as an oxidizing agent. Single crystals of **227a** are obtained from *mer*-$[Ir(CO)_3(SO_3F)_3]$ in "magic acid," that is, HSO_3F–SbF_5 (Figure 16). The cations (point group C_4v) feature unusually long M–C bonds and correspondingly short CO bonds, as well as high CO stretching frequencies. The $[Sb_2F_{11}]^-$ anions are not symmetry related, and their dihedral and bridge angles differ slightly in both salts.

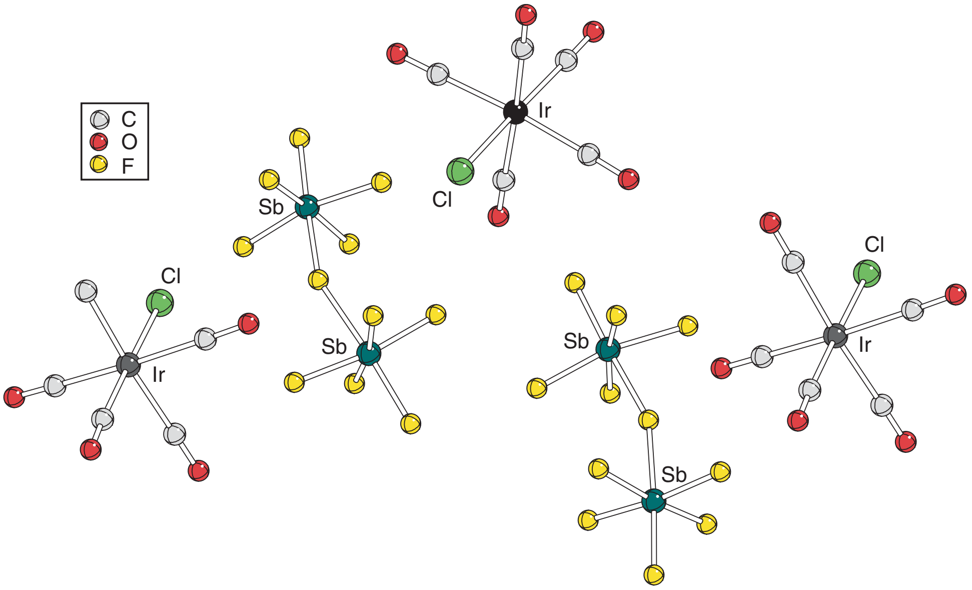


Figure 16 X-ray crystal structure packing of **227a**.

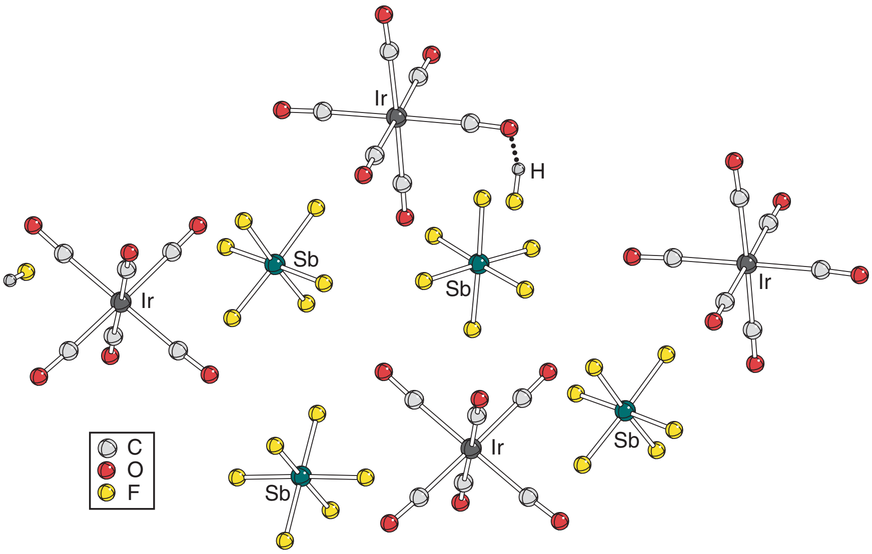


Figure 17 X-ray crystal structure packing of **228a**.

There are significant interionic contacts in $[Ir(CO)_5Cl](Sb_2F_{11})_2$ exclusively of the C–F type resulting in extended structures.[108]

The reductive carbonylation of IrF_6 in a dilute solution of SbF_5 in anhydrous HF produces CO complex $[Ir(CO)_6](SbF_6)_3{\cdot}4HF$ **228a** at room temperature and 1.5 atm, while $[Ir(CO)_6](Sb_2F_{11})_3$ **228b** is obtained in liquid SbF_5 under similar conditions. The average ν(CO) was measured at 2269 cm^{-1}, representing the highest average stretching frequency observed for octahedral metal carbonyl cations. The molecular structure of **228a** was determined by single crystal X-ray diffraction (Figure 17). The average Ir–C bond length in the octahedral $[Ir(CO)_6]^{3+}$ cation at 2.029(10) Å is the longest observed for iridium carbonyl derivatives, consistent with the absence of Ir–CO π-backbonding. Also remarkable is the structure of the anion. The four solvate HF molecules form a tetrahedron via long, asymmetric, and partly delocalized hydrogen bonds with F–F edge lengths of 2.857 and 2.914 Å, representing an unprecedented example of polyhedral $(HF)_n$ cluster. Moreover, the four F atoms of the $(HF)_4$ cluster are coordinated to the C atoms of the CO ligands, again in an unprecedented fashion.[109]

The reaction of the *anti*-$[Cr(CO)_3$-$\mu,\eta^{1:1}$-indenyl–Ir(cod)] complex with an excess of CO in CH_2Cl_2 at −70 °C produces quantitatively the [η^1-{η^6-$Cr(CO)_3$–indenyl}Ir(cod)$(CO)_2$] intermediate **229** which above 0 °C converts into the fully carbonylated complex [η^1-{η^6-$Cr(CO)_3$–indenyl}$Ir(CO)_4$], **230a**, stable up to 40 °C. Complex **230a** is also produced directly by carbonylation of the COE derivative *anti*-[$Cr(CO)_3$-$\mu,\eta^{1:1}$-indenyl-$Ir(coe)_2$]. The rearomatization of the cyclopentadienyl ring in iridium complexes to give the unstable *anti*-[$Cr(CO)_3$-μ,η:η-indenyl-$Ir(CO)_2$] **230b** is a difficult process which takes place only on bubbling Ar through the solution. When the carbonylation is carried out using a blanket of CO the scarcely soluble diridium complex [η^6-$Cr(CO)_3$-indenyl-η^3-$Ir(CO)_3]_2$ was obtained.[110]

The spectacular iridium compound HH,HT,HH-$[Ir_6(\mu\text{-}OPy)_6(I)_2(CO)_{12}]$ **231** containing an unprecedented almost linear metal chain made up of six iridium atoms has been prepared by Tejel *et al.* by oxidation of $[Ir_2(\mu\text{-}OPy)_2(CO)_4]$ with iodine at 0 °C in toluene. The formal oxidation state of the iridium atoms is 1.33. The new hexairidium compound has been characterized by X-ray diffraction analysis showing a linear array of iridium-bonded atoms with an HT-$[Ir_2(\mu\text{-}OPy)_2(CO)_4]$ complex sandwiched in between two HH-$[Ir_2(\mu\text{-}OPy)_2(I)(CO)_4]$ units (Figure 18).[111] Complex **231** represents the longest polyiridium chain complex so far know. Other polyiridium species with as many as four iridium atom chain have been reported, see Ref: 112,112a,112b

7.04.2.4 Carbonyl Cluster Complexes

Substitution reactions of cluster $[Ir_4(CO)_{12}]$ **232** have been reported in the literature, together with studies on the reactivity of the parent and obtained compounds.

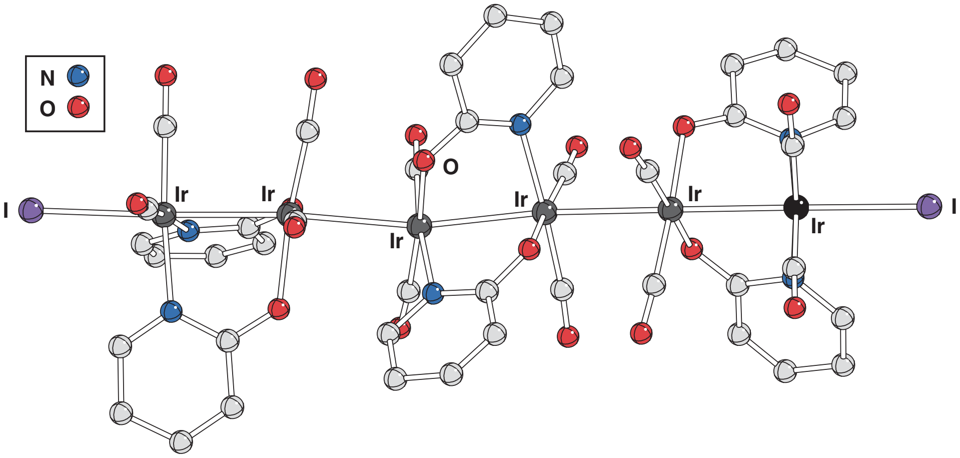


Figure 18 X-ray crystal structure of **231**.

The isomerization of the red isomer of $[Ir_6(CO)_{16}]$ **233** with four face-bridging carbonyl ligands was studied. At room temperature it affords a mixture of this red isomer and of the black isomer which has four edge-bridging carbonyl ligands. Mild thermal treatment of the solution under N_2 or air causes cluster decomposition to **232**. This behavior is in contrast with that of the Rh analog with four face-bridging carbonyl ligands, which is stereochemically rigid even at 70 °C and because metal carbonyl clusters usually increase their nuclearity by thermal treatment. The unusual decrease of the observed nuclearity here might be explained by the high stability of **232** in a neutral reaction medium.[113]

The uncoordinated phosphine group of $[Fe(CO)_3\{(Ph_2P)_2CHCH_2PPh_2\}]$ reacts with **232** to give mono, di-, and trisubstituted heterobimetallic cluster complexes, $[Ir_4(CO)_{12-x}\{Ph_2PCH_2CH(PPh_2)_2Fe(CO)_3\}_x]$ (**234**, $x = 1–3$). The complexes were characterized by IR and $^{31}P\{^1H\}$ NMR spectra.[114]

Reactions of **232** with $Ph_2PCH{=}CHPPh_2$ (dppen) and $Ph_2PN(H)PPh_2$ (dppa) gave $[Ir_4(CO)_{12-n}(L)_{n-2}]$ (**235**, L = dppen or dppa and $n = 2$ or 4) depending upon the reaction conditions. The structures of the cluster complexes were determined from IR, ^{31}P NMR spectroscopic data, and FAB mass spectra. The structure of the disubstituted species $[Ir_4(CO)_8(dppa)_2]\cdot 3THF$ (**235a**, L = dppa, $n = 4$) was also determined by X-ray crystallographic methods (Figure 19).[115]

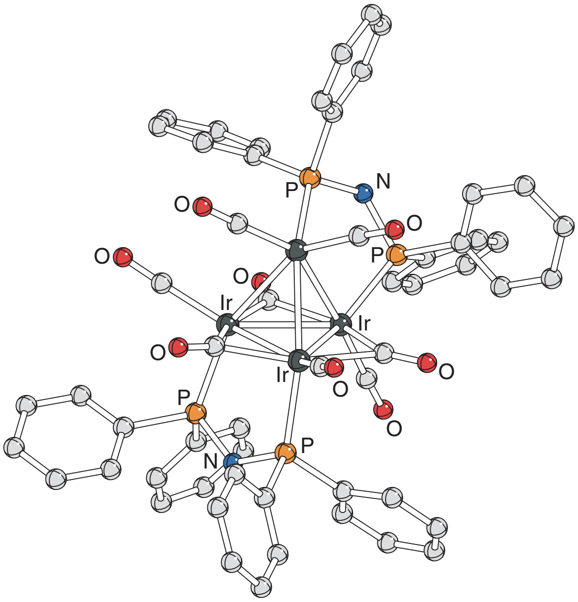


Figure 19 X-ray crystal structure of **235a**.

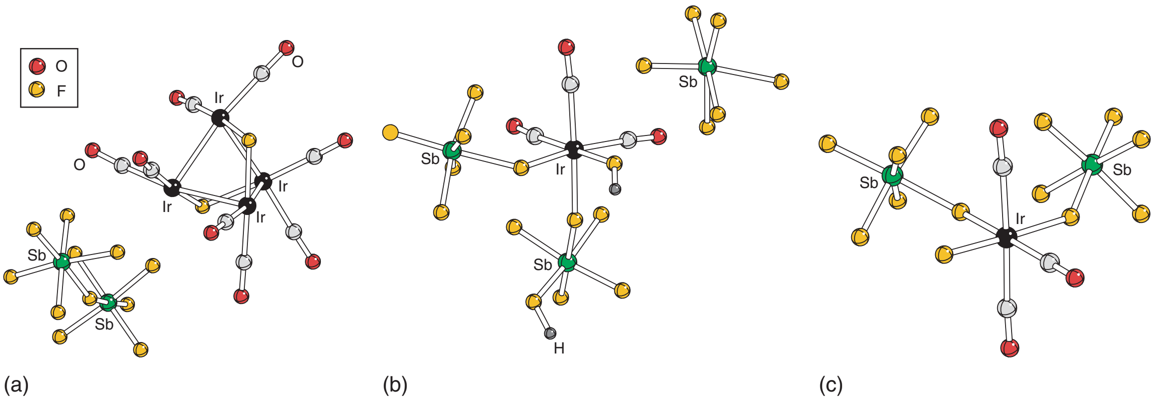


Figure 20 X-ray crystal structures of (a) **238a**, (b) **238b**, and (c) **238c**.

Complex **232** was shown to react with pyridylphosphines to give $[Ir_4(\mu\text{-}CO)_3(CO)_5(\mu\text{-}PPh_2pyl)(PPh_2pyl)_2]$ **236a**, $[Ir_4(\mu\text{-}CO)_3(CO)_5(\mu\text{-}PPhpyl_2)(PPhpyl_2)_2]$ **236b**, and $[Ir_4(\mu\text{-}CO)_3(CO)_5(\mu\text{-}Ppyl_3)(Ppyl_3)_2]$ **236c** (pyl = 2-pyridyl), in which one of the phosphine ligands bridges through coordination of P and N atoms. Clusters **236** were characterized by ^1H, ^{31}P NMR, and IR spectroscopy.[116]

The reaction of **232** with Ph_3SnH yielded the new Ir–Sn cluster complexes $[Ir_3(CO)_6(\mu\text{-}SnPh_2)_3(SnPh_3)_3]$, **237**. The product contains triangular Ir_3 clusters with three bridging $SnPh_2$ and three terminal $SnPh_3$ ligands. The Ir–Ir bonds are unusually long due to the importance of Ir–Sn bonding and weak direct Ir–Ir interactions.[117]

Fluorination of **232** in HF/SbF_5 produced three different compounds, namely $[Ir_4(CO)_8(\mu\text{-}F)_2(Sb_2F_{11})_2]$ **238a**, *fac*-$[Ir(CO)_3(FSbF_5)_2(FH)]SbF_6{\cdot}HF$ **238b**, and *mer*-$[Ir(CO)_3F(FSbF_5)_2]$ **238c** (Figure 20). The tetranuclear iridium complex **238a** crystallizes with two of the six edges of the Ir_4 tetrahedron in $[Ir_4CO_{12}]$ replaced by bridging fluorine atoms, and it may be better formulated as $[Ir_4(CO)_8(\mu\text{-}F)_2]^{2+}(Sb_2F_{11}{}^-)_2$ since the Sb–F bond is only slightly elongated and the Ir···F–Sb contact is long. In compound **238b** the Ir_4 tetrahedron from **232** is completely broken down, but the facial $Ir(CO)_3$ configuration is retained.[118]

The reactions of the cluster $[HIr_4(CO)_{10}(\mu\text{-}PPh_2)]$ **239** with phosphines, PMe_3, and PPh_3, and diphosphines such as dppm, dppe, dppb, and dppen were studied. Reaction of **239** with PMe_3 yielded the mono- and disubstituted derivatives $[HIr_4(CO)_{10-n}(PMe_3)_n(\mu\text{-}PPh_2)]$ **240**, $n = 1$, 2 and $n = 2$, 3). ^1H and ^{31}P NMR data showed that $[HIr_4(CO)_8(L)_2(\mu\text{-}PPh_2)]$ (L = PMe_3, PPh_3) exist in solution in three isomeric forms at −60 °C. Cluster **239** also reacts with diphosphines to give CO substitution products, whose composition depends on the length of the methene chain. While reaction with dppm and dppen yields only the disubstituted species $[HIr_4(CO)_8(dppm)(\mu\text{-}PPh_2)]$ **241a** and $[HIr_4(CO)_8(dppen)(\mu\text{-}PPh_2)]$ **241b**, with dppb both dimeric $[\{HIr_4(CO)_9(\mu\text{-}PPh_2)\}_2(dppb)]$ **242a** and monomeric $[HIr_4(CO)_8(dppb)(\mu\text{-}PPh_2)]$ **242b** are formed, and with dppe only dimeric $[\{HIr_4(CO)_9(\mu\text{-}PPh_2)\}_2(dppe)]$ **243** was obtained. The dppm complex exists in solution as two interconverting isomers differing in the mode of coordination of the dppm and CO ligands. Isomerization is proposed to involve intramolecular migration of dppm and carbonyl ligands.[119]

The reaction of $[Ir_4(CO)_{10}(\mu\text{-}dppm)]$ **244a** with anhydrous KOH forms $[Ir_4(CO)_{10}(\mu\text{-}dppm)]^-$ **244b** which subsequently converts into $[Ir_4(CO)_9(\mu_3\text{-}dppm)]^-$ **245**, a rare example of an Ir cluster with an Ir–C bond [2.274(8) Å] (Figure 21). The same reaction with the weaker base 1,8-diazobicyclo[5.4.0]undec-7-ene or with K_2CO_3 in wet CH_2Cl_2 under CO affords $[HIr_4(CO)_9(\mu\text{-}dppm)]^-$, a hydride cluster with an unusually long Ir–H distance [2.08(6) Å]. $[PPN][Ir_4(CO)_9(\mu^3\text{-}dppm)]$ and $[PPN][HIr_4(CO)_9(\mu\text{-}dppm)]$ were characterized by X-ray crystallography.[120]

Disubstituted clusters $[Ir_4(CO)_{10}(\mu\text{-}L\text{–}L)]$ with one edge-bridging ligand (L–L = $(MeS)_2CHMe$, **246a**) or with three edge-bridging CO's (L–L = $(Ph_2P)_2CHMe$, **246b**, dppp, **246c**) have been prepared. A comparative ^{13}C NMR study suggests the presence of fluxional processes consisting of a merry-go-round of six CO's about a unique triangular face and the rotation of terminal CO's about one Ir atom. The factors affecting the activation energy of the merry-go-round process result from the relative bite angles of the bidentate ligands in the ground-state geometry.[121]

The carbonyl cluster $[Ir_4(CO)_{11}(SnX_3)]^-$ [X = Cl **247a** or Br **247b** was obtained by insertion of SnX_2 in the Ir–Br bond of $[Ir_4(CO)_{11}Br]^-$ **248** or by substitution of bromine with $[SnCl_3]^-$ in THF at room temperature. The

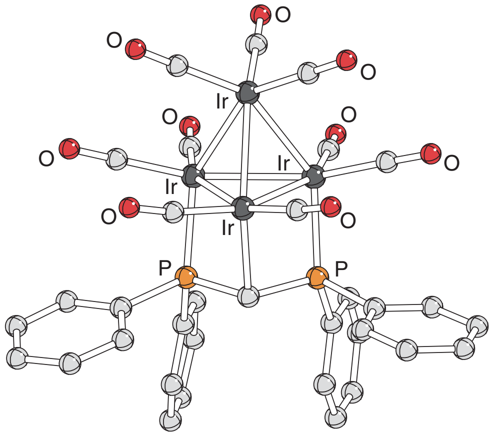


Figure 21 X-ray crystal structure of **245**.

disubstituted cluster $[Ir_4(CO)_{10}(SnCl_3)_2]^{2-}$ **249** was obtained in 50% yields by double substitution on **248** in THF at 60 °C, whereas $[Ir_6(CO)_{15}(SnCl_3)]^-$ **250** could be prepared by carbonyl substitution of **233** with an excess of $[SnCl_3]^-$ in refluxing THF. The $SnCl_3$ units act as a one-electron donor, displaying terminal (in **247**), edge-bridging (in **247** and **249**), and face-bridging coordination (in **250**).[122]

The mixed metal cluster $[Cp_2Mo_2Ir_2(CO)_{10}]$ **251** has been synthesized either by reacting $[CpMo(CO)_3H]$ with $[IrCl(CO)_2(p\text{-toluidine})]$ under a CO atmosphere in the presence of zinc, or by combining $[CpMo(CO)_3]^-$ with $[IrCl(CO)_2(p\text{-toluidine})]$. In contrast to $[Cp_2W_2Ir_2(CO)_{10}]$ **252**, complex **251** behaves as a tetrahedral cluster with all edges bridged by CO, with an unusual "semi-face-capping" carbonyl ligand. Carbonyl bridging and hence steric crowding increase on proceeding from tungsten to molybdenum, so that **251** can be classified amongst the most crowded metal clusters.[123]

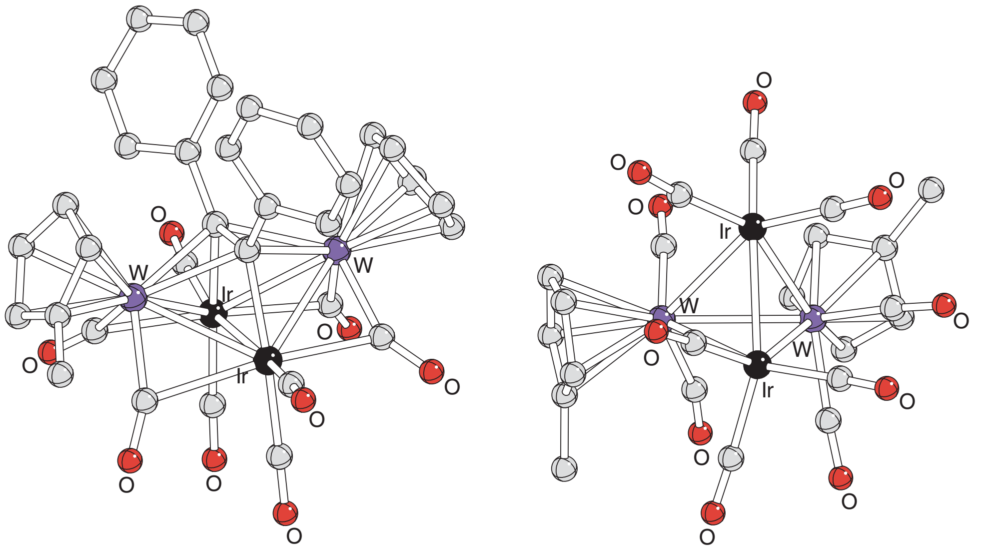
The syntheses and structural determinations of complexes $[Ir_4(CO)_{11}L]$ $\{L = [Fe(\eta^5\text{-}P_3C_2Bu^t{}_2)(\eta^5\text{-}P_2C_3Bu^t{}_3)]$ **253a**, or $[CpFe(\eta^5\text{-}P_3C_2Bu^t{}_2)]$ **253b**$\}$ and $[HIr_4(CO)_{10}\{\mu\text{-}CpFe(\eta^5\text{-}P_3CH_2(CMe_2)CBu^t)\}Ir_4(CO)_{11}]$, with one iridium for each Ir_4 cluster coordinated to one P atom of the triphosphadicarba ring, were described by Benvenutti *et al.* and characterized by X-ray methods.[124,124a]

Reactions of $[CpWIr_3(CO)_{11}]$ **254** with stoichiometric amounts of phosphines afford $[CpWIr_3(\mu\text{-}CO)_3(CO)_{8-x}L_x]$ (**255**, L = PPh_3, PMe_3; $x = 1$–3) in moderate yields. These products exhibit ligand fluxionality in solution, resolvable at low temperature into the constituent interconverting isomers. Ligand substitution induces a rearrangement in the cluster coordination sphere from the all-terminal carbonyl ligand geometry of **254** to one in which the three edges of a WIr_2 face of the tetrahedral core contain bridging carbonyls or one in which the three edges of the triiridium face are bridged by carbonyl ligands.[125]

The crystal structure of the mixed metal cluster with a butterfly metal core $[Cp^{Me}{}_2W_2Ir_2(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)(\mu\text{-}CO)_4(CO)_4]$ **256** has been determined. The W atoms are situated at the wingtip sites and Ir atoms at the hinge positions. A diphenylacetylene ligand is μ_4-η^2-coordinated with the C–C bond parallel to the Ir–Ir vector, then completing a pseudo-OCT $W_2Ir_2C_2$ unit. The two tungsten atoms are each ligated by a methylcyclopentadienyl ligand, and the Ir atoms bind two terminal carbonyls, with the coordination completed by four bridging carbonyls, each of which lies across a W–Ir bond.[126] Similarly, crystals of $[Cp^{Me}{}_2W_2Ir_2(CO)_{10}]$ **257** feature the tungsten atoms ligated by a methylcyclopentadienyl ligand and two carbonyl ligands, and the Ir atoms bearing three carbonyl ligands (Figure 22).

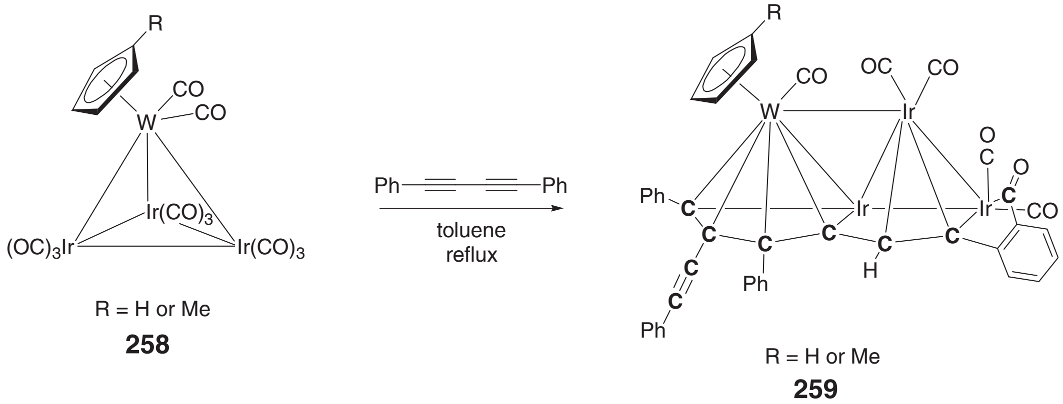
Reactions of $[Cp^RWIr_3(CO)_{11}]$ (**258**, $Cp^R = Cp$, Cp^{Me}) and excess diphenylbuta-1,3-diyne in refluxing toluene gave a mixture of products, one of which ($Cp^R = Cp$) has been identified as $[CpWIr_3\{\mu^4\text{-}\eta^7\text{-}C(Ph)C(C{\equiv}CPh)C(Ph)CC(H)C\text{-}o\text{-}C(O)C_6H_4\}(CO)_7]$ **259** by single crystal X-ray diffraction. The structure of **259** reveals a unique 10-electron-donating ligand which has formed from merging of two diphenylbuta-1,3-diyne units and one carbonyl group (Scheme 21). Similarly, the combination resulting in the C_9Ph_4 ligand follows from orthometallation of one phenyl group, followed by formal insertion of the carbonyl into the Ir–Ph bond.[127]

Condensation of $[Ir(CO)_4]^-$, $[Ir(cod)(thf)_2]^+$, and $[Rh(cod)(thf)_2]^+$ followed by saturation with CO (1 atm) in THF afforded the first synthetic route to pure $[Ir_3Rh(CO)_{12}]$ **260**. The substitution chemistry of this intriguing hetero-tetrametallic carbonyl was studied by Laurenczy *et al.* and is partially summarized in Scheme 22.[128] Substitution of



(a) (b)

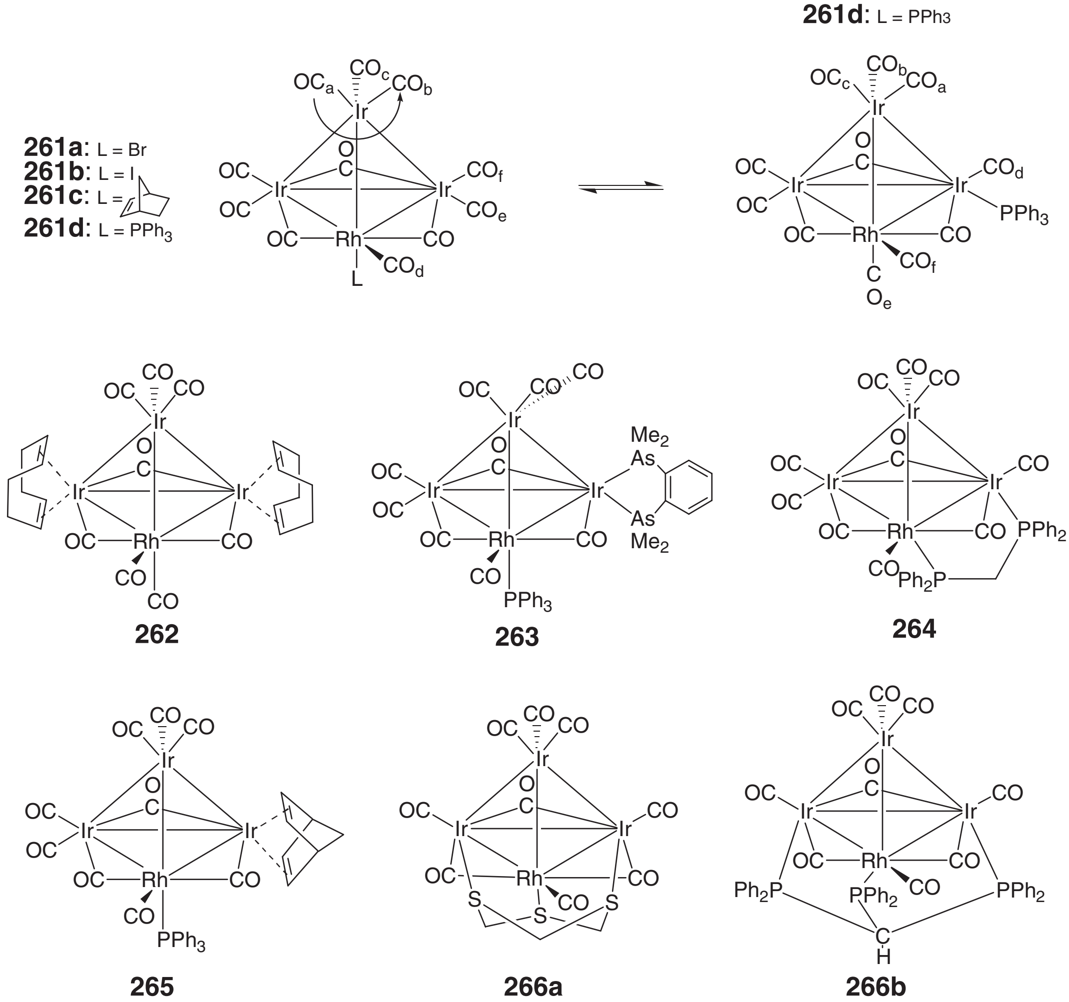
Figure 22 X-ray crystal structures of (a) **256** and (b) **257**.



Scheme 21

CO by monodentate ligands gave $[Ir_3Rh(CO)_8(\mu^2\text{-}CO)_3L]$ (L = Br **261a**, I **261b**, bicyclo[2.2.1]hept-2-ene **261c**, PPh_3 **261d**). All clusters have C_s-symmetry with the ligand L bound to the basal Rh atom in axial position and are fluxional in solution on the NMR timescale due to the occurrence of two CO scrambling processes: the merry-go-round of basal CO's and changes of basal face. Additionally, intramolecular migration of PPh_3 from the Rh to a basal Ir atom takes place in **261d** above RT. Substitution of CO by polydentate ligands gave $[Ir_3Rh(CO)_{7-x}(\mu\text{-}CO)_3(\eta^4\text{-}L)_x]$ (**262**, L = NBD, COD; $x = 1,2$), $[Ir_3Rh(CO)_6(\mu\text{-}CO)_3(\eta^2\text{-diars})]$ **263**, $[Ir_3Rh(CO)_7(\mu\text{-}CO)_3(\eta^4\text{-}L)]$ (**264**, L = dppm, bonded to two basal Ir atoms or one Ir and one Rh atom), $[Ir_3Rh(CO)_6(\mu\text{-}CO)_3(\eta^4\text{-nbd})PPh_3]$ **265**, and $[Ir_3Rh(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}L)]$ [L = 1,3,5-trithiane **266a**, $CH(PPh_2)_3$ **266b**.

Reactions of $[CpMoIr_3(\mu\text{-}CO)_3(CO)_8]$ **267** with stoichiometric amounts of the isocyanide Bu^tNC afford the ligand substituted clusters $[CpMoIr_3(\mu\text{-}CO)_3(CNBu^t)_n(CO)_{8-n}]$ **268**, $n = 1$–3. In contrast, **267** reacts with PPh_3 to afford a single unexpected product, $[CpMoIr_3(\mu\text{-}CO)_3(CO)_6(PPh_3)_2]$ **269**. A single crystal X-ray study of **269** reveals that the phosphines occupy coordination sites adjacent to the plane of bridging carbonyls in a radial–radial–axial conformation previously unobserved in structural studies of $MoIr_3$ or WIr_3 clusters. Reactions of $[Cp_2Mo_2Ir_2(\mu\text{-}CO)_3(CO)_7]$ **270** with Bu^tNC or diphenylacetylene proceed cleanly in high yield to afford $[Cp_2Mo_2Ir_2(\mu\text{-}CO)_2(CNBu^t)_2(CO)_6]$ **271** or $[Cp_2Mo_2Ir_2(\mu_4\text{-}\eta^2\text{-}PhCCPh)(\mu\text{-}CO)_4(CO)_4]$ **272**. Reacting **271** with diphenylacetylene or **272** with ButNC results in a



Scheme 22

more complex mixture of products from which [$Cp_2Mo_2Ir_2(\mu^4$-η^2-PhCCPh)(μ-CO$)_4$(CNBu^t)(CO$)_3$] **273** can be isolated in low yield.[129]

Polycarbonyl clusters combining early transition metals with iridium were studied by Oro and co-workers.[91,92,130,131] Replacement of cod by CO in [CpTi(μ^3-S$)_3Ir_3$(cod$)_3$] gives the carbonyl derivative [CpTi(μ^3-S$)_3Ir_3(CO)_6$] **274**. Further reactions of the carbonyl iridium complex with tertiary phosphine and phosphite ligands produce the 62e valence clusters [CpTi(μ^3-S$)_3Ir_3$(μ-CO)(CO$)_3(PR_3)_3$] **275**, $PR_3 = PPh_3$ **275a**, PMe_3, P(OMe$)_3$, $PMePh_2$). A delocalized bonding picture was proposed for the Ir triangle involving an interaction between the tetrahedral Ir and the Ti atom. Complex **275** quickly exchange all their carbonyl ligands with ^{13}CO to give labeled complexes fluxional at low temperature. The reaction of **275a** with HBF_4 gave the unsymmetrical and non-fluxional hydride [CpTi(μ_3-S$)_3Ir_3$(μ-CO)(H)(CO$)_3(PPh_3)_3]BF_4$.[130]

Deprotonation of [$Cp_2Ti(SH)_2$] with the mononuclear carbonyl complexes [Ir(acac)(CO$)_2$] yields the ion-pair complex [Cp_2Ti(acac)][$Ir_3(\mu_3$-S$)_2(CO)_6$] **276** with complete transference of the sulfido ligands to the d^8-metal centers. Carbonylation of the complexes [Cp(acac)Ti(μ_3-S$)_2${Ir(cod)}$_2$] or [Cp(quinol)Ti(μ_3-S$)_2${Ir(cod)}$_2$] yields [Cp(acac)Ti(μ_3-S$)_2${Ir(CO$)_2$}$_2$] **277** and [Cp(quinol)Ti(μ_3-S$)_2${Ir(CO$)_2$}$_2$] **278**, respectively. Substitution of the carbonyl complexes with PPh_3 gave the disubstituted complexes [Cp(acac)Ti(μ_3-S$)_2${Ir(CO)(PPh$_3$)}$_2$] **279** or [Cp(quinol)Ti(μ_3-S$)_2${M(CO)(PPh$_3$)}$_2$] **280**, which were obtained as mixtures of *cis-* and *trans*-isomers.[131]

The reaction of [$Ir_3(\mu$-CO$)_3Ind_3$] **281** with various metal electrophiles yield the cationic tetranuclear clusters [Ir_3{M(PPh$_3$)}(CO$)_3Ind_3]PF_6$ (M = Cu **282a**, Ag **282b**, Au **282c**), [$Ir_3Tl(\mu$-CO$)_3Ind_3]PF_6$ **283**, and

$[Ir_3(HgR)(CO)_3Ind_3]PF_6$ **284**, R = Ph; $CpW(CO)_3$). The structures of compounds **282b** and **283** were determined by X-ray diffraction and consist of a triangle of Ir atoms, each edge of which has a bridging carbonyl oriented out of the plane in the same direction and each vertex of which has an η^5-indenyl ligand oriented toward the opposite side of the plane. The Tl atom in **283** adopts a face-capping mode of coordination on the same side of the triiridium plane as the three indenyl ligands and is encapsulated by the phenylene portions of the indenyl groups. The molecular structure of **282b** consists of an $AuIr_3$ butterfly framework with a hinge angle of 153.63(3)° and the Au atom in a wingtip position. The indenyl ligands take up positions opposite those of the CO ligands at each Ir center.[132]

The base-induced condensation of **232** at room temperature has yielded $[Ir_9(CO)_{20}]^{3-}$ **285** and $[Ir_9H(CO)_{19}]^{4-}$ **286**, featuring a face-sharing bioctahedral metallic framework. Oxidation of **285** produced $[Ir_{10}(CO)_{21}]^{2-}$ **287** after addition of a butterfly-capping Ir atom; these clusters were compared with known compounds of Ru, Rh, and Ir, which together model the building-up process of the closed-shell trigonal-bipyramidal polyhedron; step-by-step growth shows irregularities in the number of valence electrons, since the larger clusters require more filled orbitals than predicted by the capping principle.[133]

The cluster $[Ir_{11}(CO)_{23}]^{3-}$ **288** was obtained by reaction of **287** and $[Ir(CO)_4]^-$ in refluxing MeCN, and its solid-state structure was determined on $[NEt_4]_3[Ir_{11}(CO)_{23}]$. The metallic framework of D_{3h} symmetry is composed by three face-fused octahedra, all sharing a common edge. The cluster contains nine edge-bridging and 14 terminal carbonyl ligands. Naked clusters of non-transition metals, found in binary and ternary materials, such as $Cs_{11}O_3$, display very similar trioctahedral polyhedra. The synthesis of **287** was also reinvestigated.[134]

7.04.3 Iridium–Carbon Single-Bonded Complexes

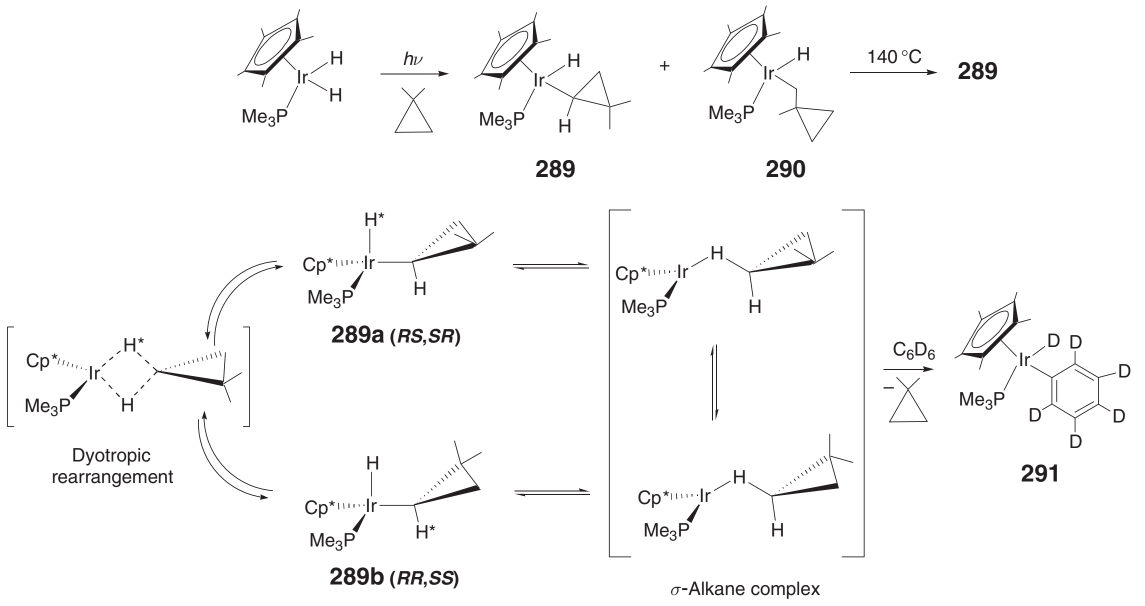
During the past several years, the number of iridium complexes containing single metal–carbon bonds have increased enormously paralleling the growing applications of iridium complexes in homogeneous and heterogeneous catalysis. A perusal of the data available in literature archives shows a great number of patents indicating a concrete interest of industry for iridium-catalyzed organic reactions. Topics such as the selective C–H activation of unactivated hydrocarbons, which were central during the 1980s in the chemistry of iridium, still represent a challenging task for organometallic chemists and several important advancements have been done.[135] However, the lack of complete success in finding a really efficient and applicable protocol to achieve the homogeneous catalytic functionalization of the natural feedstock of hydrocarbons has caused a progressive disaffection from this subject.

Interest in iridium hydrocarbyl complexes has been fueled by the higher thermodynamic stability of both Ir–C and Ir–H bonds in comparison to related compounds of rhodium. Therefore, iridium alkyl and aryl complexes have been frequently and successfully used as kinetically inert models for a variety of rhodium-catalyzed reactions allowing to collect intriguing mechanistic information on important industrial processes and organometallic reactions of academic interest.

As it is not the aim of this chapter to describe in detail the numerous catalytic processes promoted by organoiridium derivatives, we have not attempted to be really comprehensive in reviewing the organometallic compounds of iridium with single carbon–metal bond. In keeping with this view, many iridium hydrocarbyl complexes that are not mentioned in this section may have been discussed in other sections due to the ubiquitous role played by metal alkyls and aryls in fundamental and applied organometallic chemistry. A section at the end of this chapter will nonetheless attempt to critically summarize the most intriguing breakthroughs in iridium catalysis which, since the publication of COMC (1995), has become a mature field of research and applied interest. Finally, among the compounds containing Ir–C single bonds, we have deliberately omitted any mention to iridium carbonyls which have been described in the previous section of this chapter.

7.04.3.1 Alkyl and Aryl Complexes

Iridium σ-alkyl and σ-aryl complexes have played a major role in highlighting important mechanistic issues of organometallic chemistry. Worth to be mentioned here are a number of selected articles published by Bergman and co-workers which address the remarkable question of the mechanism of C–H oxidative addition and reductive elimination of C–H bonds in non-activated alkanes.[136] For example, the study of the diastereomeric complexes $[Cp^*Ir(PMe_3)(H)\{(RS,SR)\text{-}(2,2\text{-dimethylcyclopropyl})\}]$ **289a** and $[Cp^*Ir(PMe_3)(H)\{(RR,SS)\text{-}(2,2\text{-dimethylcyclopropyl})\}]$ **289b**, formed by photolysis in neat 1,1-dimethylcyclopropane, provided mechanistically important details. Although the reaction also produced $[Cp^*Ir(PMe_3)(H)\{CH_2C(CH_3)CH_2CH_2\}]$ **290** as a side-product via C–H activation of one methyl substituent of cyclopropane, thermolysis at controlled temperature transforms **290** completely into



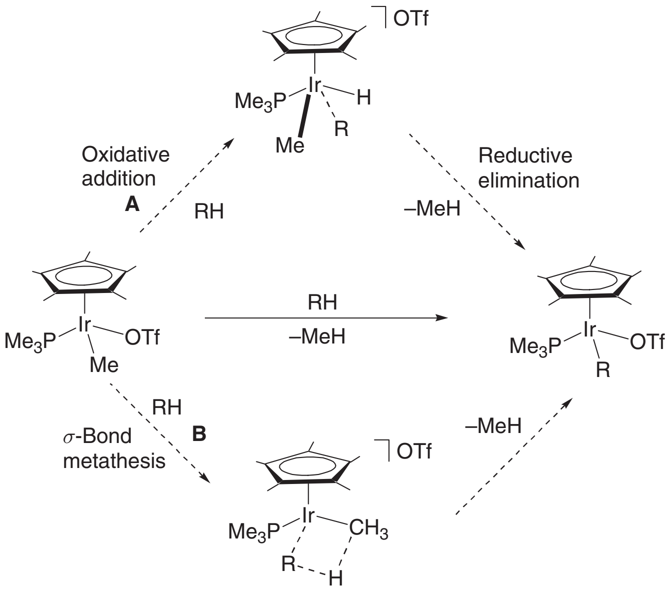
Scheme 23

the diastereomeric mixture **289a** and **289b**. From this mixture, the pure diastereomers were separated by low temperature chromatography (Scheme 23).[137] Combined kinetic investigations of the interconversion of this diastereomeric pair and analysis of the deuterium scrambling undergone by their α-deuterated isotopomers in C_6D_6 showed that both processes take place at a rate comparable with the reductive elimination of cyclopropane in benzene-d_6 to afford the perdeuterated $[Cp^*Ir(PMe_3)D(Ph\text{-}d_5)]$ **291** via C–D oxidative addition of the solvent. A perusal of these kinetic data allowed to hypothesize the formation of an alkane intermediate complex to account for the observed rearrangements. This latter mechanism was preferred over a dyotropic rearrangement which was also considered.

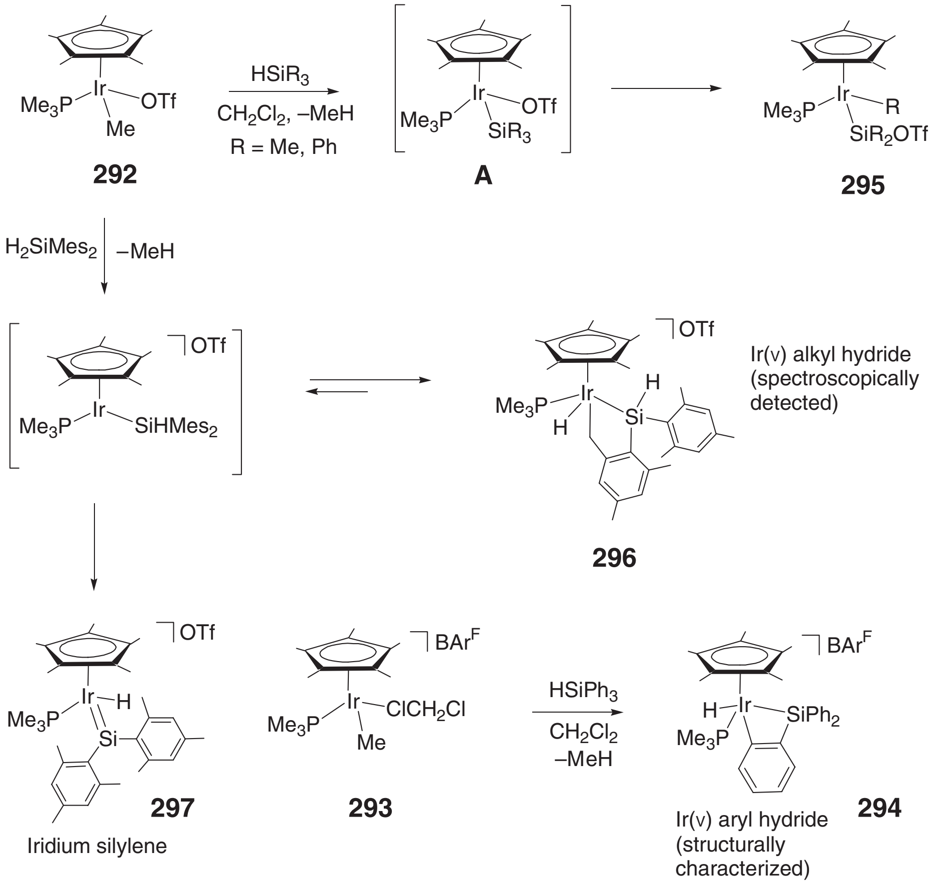
In contrast to this report, a surprising result was obtained by Chen and co-workers by studying with electrospray tandem mass spectrometry the C–H activation in *n*-pentane, cyclohexane, and benzene by Bergman's catalyst $[Cp^*Ir(PMe_3)Me]^+$.[138] Neither the oxidative addition/reductive elimination nor the concerted σ-bond metathesis mechanism was found to be operative. Rather, an elimination/addition mechanism through Ir(III) intermediates was proposed and confirmed by isotopic labeling.

The electrophilic Ir(III) complexes $[Cp^*Ir(PMe_3)(Me)(OTf)]$ **292** and $[Cp^*Ir(PMe_3)(Me)(CH_2Cl_2)]BAr^F$ **293** have been extensively used by Bergman and Arndtsen to activate C–H bonds of methane and other hydrocarbons under extremely mild reaction conditions.[139] A report highlighting the work done in the area of C–H activation by cationic iridium(III) complexes has been published.[140] The energy profile of intermolecular versus intramolecular carbon–hydrogen bond activation has been theoretically modeled in $CpIr(PH_3)(Me)(H)$ by *ab initio* methods.[141] Further theoretical studies support the occurrence of an oxidative addition mechanism for the C–H activation of hydrocarbons proceeding through Ir(V) intermediates (path A in Scheme 24)[142] but these species were not directly observed,[143] then suggesting that the alternative σ-bond metathesis (path B) pathway would better account for the C–H activation reaction.

Supporting evidence for the C–H oxidative addition mechanism was provided by Klei *et al.* who described the first stable and isolable example of Ir(V) aryl hydride by studying the reaction of **292** and **293** with silanes.[144] Scheme 25 highlights this chemistry while Figure 23 shows the molecular structure of the first structurally characterized Ir(V) aryl hydride species, $[Cp^*Ir(PMe_3)(H)\{\kappa^2\text{-}Si,C\text{-}Si(C_6H_4)Ph_2\}]$ **294**. The reaction of **292** with $HSiR_3$ (R = Me, Ph) affords $[Cp^*Ir(PMe_3)(R)(SiR_2OTf)]$ **295** likely via an undetected $[Cp^*Ir(PMe_3)(OTf)(SiR_3)]$ (A) from which **295** may form by 1,2-migration with coordination to iridium of one of the hydrocarbyl groups originally linked to silicon. Using the bulky H_2SiMes_2, the cyclometallated complex $[Cp^*Ir(PMe_3)(H)\{\kappa^2\text{-}Si,C\text{-}SiH(Mes)(C_6H_2Me_2CH_2)\}]OTf$ **296** is immediately formed before converting over 9 h to the silylene complex $[Cp^*Ir(PMe_3)(H)(SiMes_2)]OTf$ **297**. The formation of **296** requires oxidative addition of a C–H bond of one of the mesityl methyl groups to the Ir(III) center to produce an unprecedented Ir(V) alkyl hydride. Even more convincing, in favor of the oxidative mechanism, is the



Scheme 24



Scheme 25

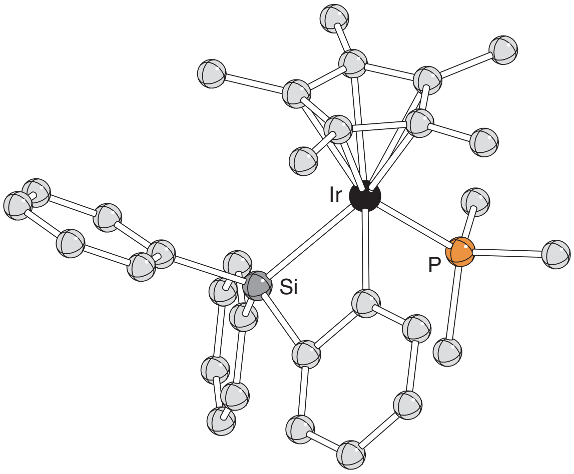


Figure 23 X-ray crystal structure of **294**.

reaction of **293** with $HSiPh_3$ which brought to the isolation of **294**. Although the presence of silyl ligand is thought to contribute to the overall stability of the Ir(V) species,[145(145a,145b)] the synthesis of **297** and the characterization of **296** represent compulsory arguments to the validity of the C–H oxidative addition path.

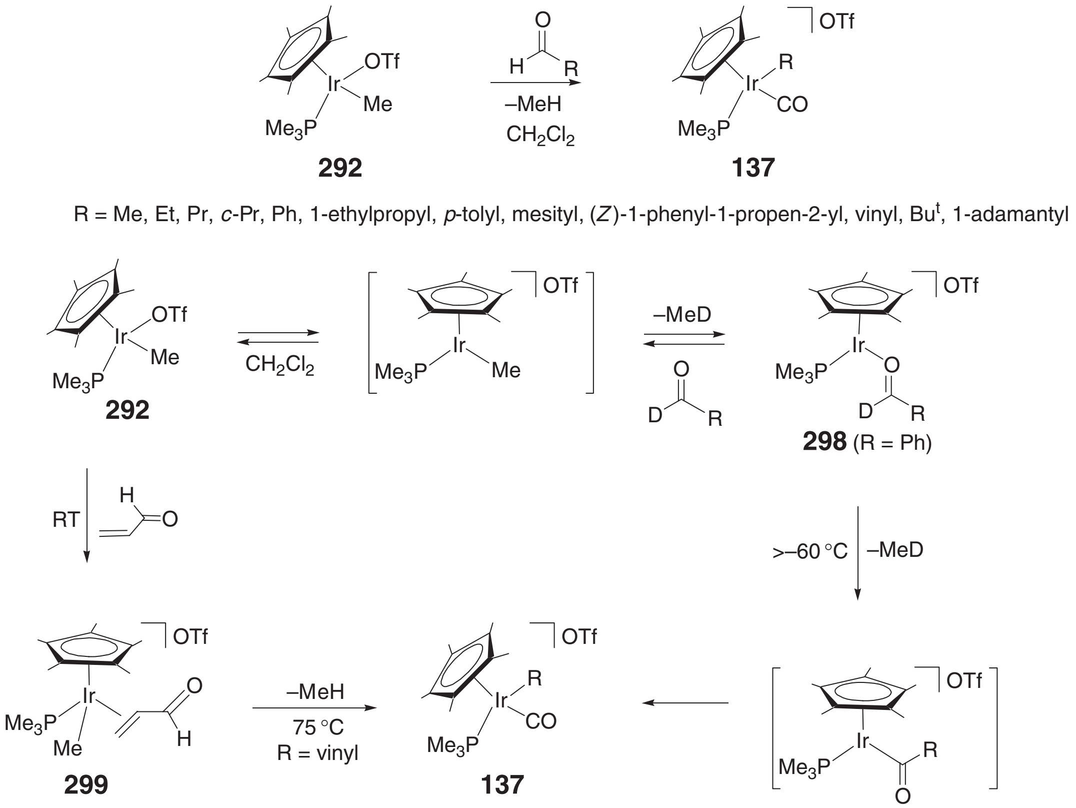
A general synthetic method to prepare iridium alkyl and aryl complexes containing sterically demanding organic groups, including tertiary alkyls, has been developed based on the reaction of **292** with aldehydes.[146,69] The reaction (see Scheme 26) affords methane and alkyl or aryl(carbonyl) cationic complexes of formula $[Cp^*Ir(PMe_3)(R)(CO)]OTf$ **137** (R = Me, Et, Pr, *c*-Pr, Ph, 1-ethylpropyl, *p*-Tol, mesityl, (*Z*)-1-phenyl-1-propen-2-yl, vinyl, Bu^t, 1-adamantyl) with complete selectivity toward the aldehyde C–H hydrogen. X-ray diffraction analyses of a few tertiary alkyl complexes were carried out and a view of the complex cation $[Cp^*Ir(PMe_3)(1\text{-adamantyl})(CO)]^+$ is given below in Figure 24.

This tandem C–H bond activation/decarbonylation reaction provides useful information concerning the mechanism of aldehyde activation at iridium. The reaction goes through preliminary OTf dissociation, followed by aldehyde coordination. The formation of the coordinatively unsaturated 16e cation $[Cp^*Ir(PMe_3)(Me)]^+$ was also demonstrated by kinetic measurements and labeling experiments and is considered a prerequisite along the pathways leading to C–H activation of organic molecules.[147]

Monitoring the reaction between **292** and PhCHO at −78 °C indicates the formation of the η^1-*O*-bound aldehyde complex $[Cp^*Ir(PMe_3)(Me)\{\eta^1\text{-OC(H)PhCO}\}]OTf$ **298** from which methane is easily eliminated (only MeD is produced from acetaldehyde-d_1) on increasing the temperature. Decarbonylation from an undetected acyl ligand results in the formation of the alkyl(carbonyl) derivative **137**. The possibility that an Ir(V) intermediate may be responsible for the decarbonylation step has been also considered. In the case of acrolein, the tandem process is preceded by π-alkene coordination leading to $[Cp^*Ir(PMe_3)\{\pi\text{-}CH_2{=}CHC(O)H\}]OTf$ **299** which undergoes C–H activation/decarbonylation only after prolonged thermolysis in CH_2Cl_2.

The dimethyl complex $[Cp^*Ir(PMe_3)Me_2]$ **300** was used by Diversi *et al.* to promote C–H bond activation in hydrocarbons by electron-transfer catalysis.[148(148a,148b)] Thus, **300** and other related phosphino derivatives $[Cp^*Ir(PR_3)Me_2]$ ($PR_3 = PPh_3$, $PMePh_2$, PMe_2Ph) react with different arenes, in the presence of catalytic amounts of $[Cp_2Fe]PF_6$ or $AgBF_4$ as one-electron oxidants, to give methane and the corresponding methyl aryl species $[Cp^*Ir(PR_3)Me(Ar)]$ **301** (Scheme 27). C–H activation does not occur in pyridine, where the cationic $[Cp^*Ir(PR_3)Me(py)]$ **302** is formed or when using $NOBF_4$, due to formation of cationic alkylnitrosyl derivatives such as $[Cp^*IrMe_2(NO)]BF_4$ **303** or $[Cp^*Ir(PR_3)Me(NO)](BF_4)_2$ **304**.[149] The proposed mechanism, entailing the formation of an Ir(IV) radical following the one-electron oxidation of **300** has been confirmed by EPR measurements,[149(a)] but questioned by Bergman and co-workers on the basis of labeling experiments with deuterium.[140] The reactivity of **300** with monoelectronic oxidants was later extended to silanes.[150]

SO_2 inserts into the iridium methyl bond in **292** to yield the methylsulfinate complex $[Cp^*Ir(PMe_3)(OTf)\{\eta^1\text{-}S\text{-}SO_2Me\}]$ **305** (Scheme 28).[151] The structure of the acetonitrile complex $[Cp^*Ir(PMe_3)(NCMe)\{\eta^1\text{-}S\text{-}SO_2Me\}]OTf$ **306** has been determined.



R = Me, Et, Pr, *c*-Pr, Ph, 1-ethylpropyl, *p*-tolyl, mesityl, (*Z*)-1-phenyl-1-propen-2-yl, vinyl, Bu^t, 1-adamantyl

Scheme 26

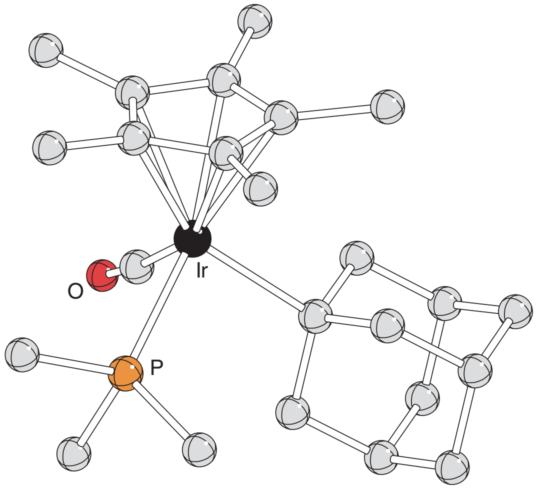
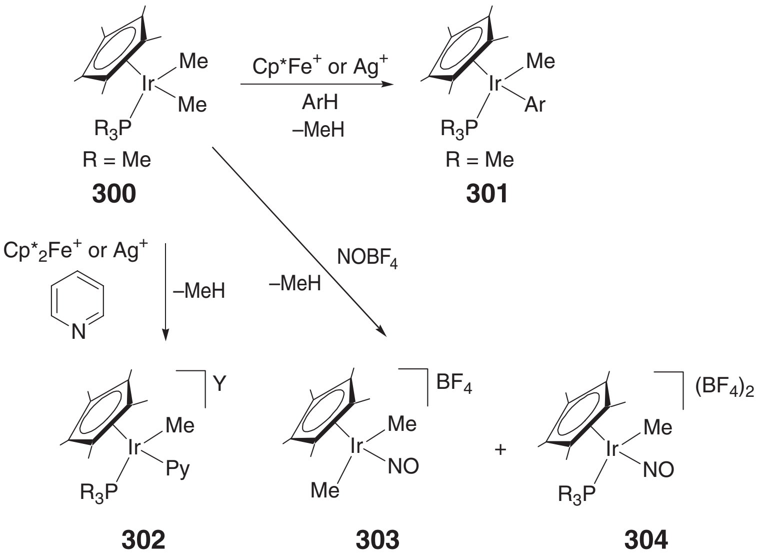
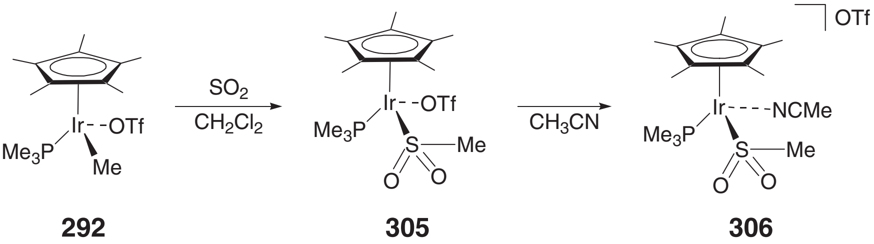


Figure 24 X-ray crystal structure of 137 (R = adamatyl).

Substituted cyclopentadienyl ligands have been extensively used to influence the stereochemistry of reactions occurring at iridium with respect to conventional Cp and Cp* systems.[152] Alkylphosphine- and aniline-substituted cyclopentadienides have been prepared and their basic organometallic iridium chemistry explored in detail to recognize the effect of their planar chirality in controlling the stereochemistry at the metal and in affecting the

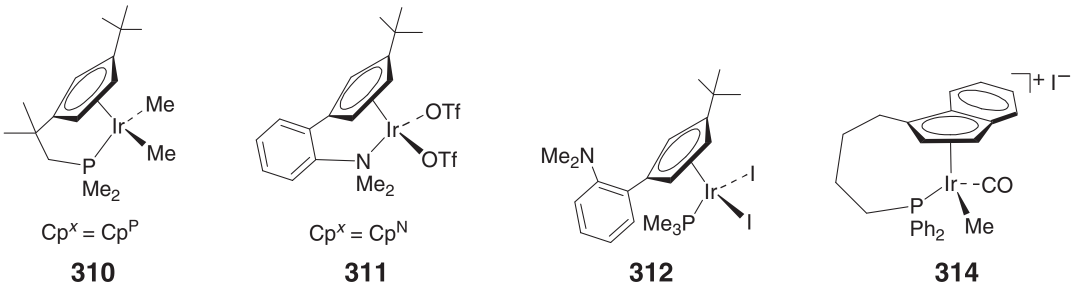


Scheme 27



Scheme 28

iridium reactivity (Scheme 29).[153] Complexes such as [Cp^{x}IrI$_2$] **307**, [Cp^{x}IrH$_2$] **308**, [Cp^{x}Ir(I)Me] **309**, [Cp^{x}IrMe$_2$] **310**, [Cp^{N}Ir(OTf)$_2$] **311** have been synthesized and characterized [Cp^x = 1-(2-dimethylphosphino-1,1-dimethylethyl)-3-*tert*-butylcyclopentadienyl (Cp^P) or 1-(2-dimethylamino)phenyl-3-*tert*-butylcyclopentadienyl (Cp^N)]. The presence of the chelating Cp^N and Cp^P ligands rouses steric congestion and affects the electronic and steric character at the metal center compared to that of achiral iridium analogs. While the dialkylphosphino end forms stable chelate rings, dechelation readily occurs in the case of the pending *N*-donor group. As an example, addition of PMe$_3$ to [Cp^{N}IrI$_2$] removes the weakly coordinated nitrogen donor and affords the unchelated [Cp^{N}Ir(PMe$_3$)I$_2$] **312**. The structure of [Cp^{N}Ir(C$_2$H$_4$)$_2$] **313** shows a symmetric side-on coordination of two ethene molecules while the aniline arm remains uncoordinated (Figure 25).[153]



Scheme 29

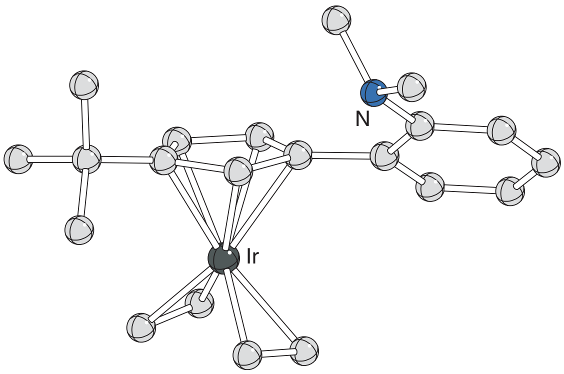
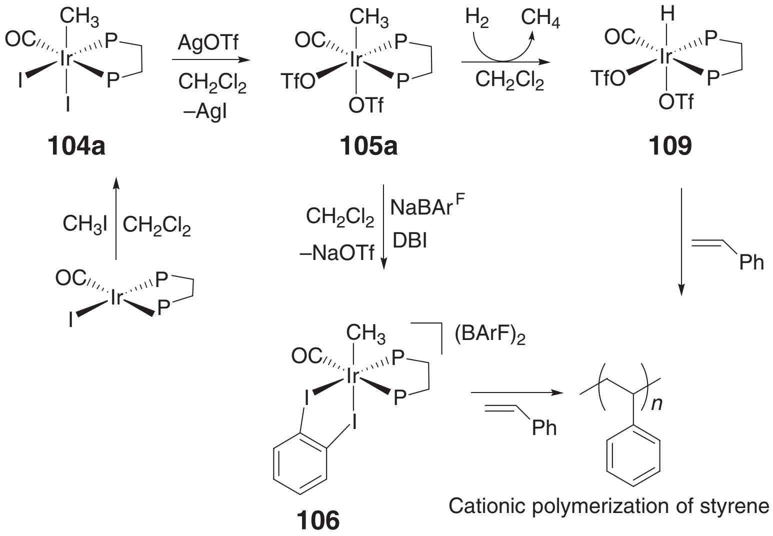


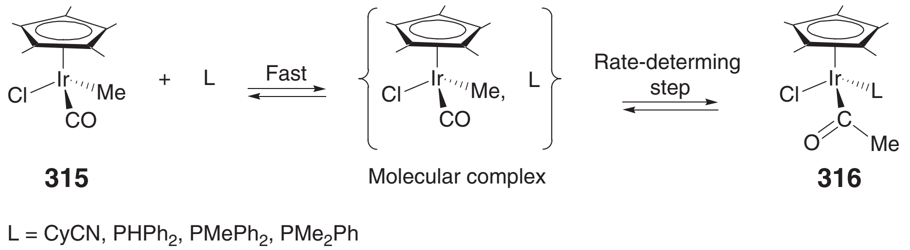
Figure 25 X-ray crystal structure of **313**.

A similar concept has inspired the work of Kataoka *et al.* who designed substituted Cp and Ind ligands bearing tertiary phosphines[154] or optically active oxazoline rings[155] connected by an alkylene chain. In a series of rhodium carbonyl complexes, a remarkable control of the stereoselectivity of the oxidative addition of alkyl halides was found to be governed by the length of the spacer connecting the PR_2 group with the indenyl ligand. Iridium was successfully employed to get mechanistic information on the reaction and the cationic iridium(III) complex $[\{\eta^{5:1}$-$Ind(CH_2)_4PPh_2\}Ir(CO)(Me)]I$ **314** was synthesized.[154]

Apart from the cyclopentadienyl iridium(III) alkyl and aryl complexes described above, an interesting class of electrophilic Ir(III) compounds, $[(diphosphine)Ir(CH_3)(OTf)_2(CO)]$ (**105a**; diphosphine = dppe, chiraphos), were straightforwardly prepared (see Section 7.04.2.1.3) by Eisenberg and co-workers by treatment of $[(diphosphine)Ir(CH_3)I_2(CO)]$ **104a** with AgOTf in dichloromethane.[58] Methane elimination was observed by treatment of **105a** with H_2 at atmospheric pressure giving the hydride $[(diphosphine)IrH(CO)(OTf)_2]$ **109**. The formation of an acidic molecular hydrogen complex capable of protolyzing the Ir–CH_3 bond was assumed, but not demonstrated (Scheme 30). In the presence of 1,2-diiodobenzene, $[(dppe)Ir(CH_3)(OTf)_2(CO)]$ and its trifluoromethyl analog undergo a clean metathesis with $NaBAr^F$ to give the dicationic halocarbon adducts $[(dppe)IrR(CO)(DIB)](BAr^F)_2$ (**106**; R = CH_3, CF_3). These complexes behave as efficient electrophilic initiators to promote the oligomerization/polymerization of several alkenes,[56,59] and the Nazarov cyclization of aryl vinyl and divinyl ketones.[156]



Scheme 30



L = CyCN, $PHPh_2$, $PMePh_2$, PMe_2Ph

Scheme 31

Isonitriles and phosphines promote the alkyl migratory insertion in [Cp*IrCl(CO)Me] **315** to give the acyl derivatives [Cp*IrCl{C(O)Me}(L)] (L = CyNC, $PHPh_2$, $PMePh_2$, PMe_2Ph; **316**).[157] The reaction has been studied by Monti *et al.* by kinetic methods which suggested a two-step process involving the fast formation of a molecular complex, that is, [{Cp*Ir(Cl)(CO)(Me)},{L}], maintaining the molecular structure of the adduct **315**, followed by the rate-determining step via migration of the methyl group to the close CO ligand (Scheme 31).

Homo- or heterodinuclear "A-frame" complexes stabilized by a pair of bridging dppm ligands were used by Cowie and co-workers to synthesize iridium alkyl compounds.[158,158a] Then, alkylation of $[RhIr(CO)_3(dppm)_2]$ **317** with MeOTf yields $[RhIrMe(CO)_3(dppm)_2]OTf$ **127**, having the Me group terminally bound to iridium as confirmed by X-ray diffraction analysis (Figure 26).[158]

Complex **127** adds H_2 evolving one molecule each of methane and CO to give the trihydride $[RhIr(H)(CO)_2(\mu\text{-}H)_2(dppm)_2OTf$ **318**. Repeating the reaction at 0 °C affords the dihydrido(methyl) complex intermediate $[RhIr(H)(Me)(CO)_2(\mu\text{-}H)(dppm)_2]OTf$ **319** which transforms into the trihydride **318** and methane after further hydrogenation at RT (Scheme 32). Migratory insertion of the methyl ligand takes place when **127** is treated with isonitriles. Thus, reaction with C≡NBu^t affords the iminoacyl product $[RhIr(CO)_2(\mu\text{-}Bu^tN{=}CMe)(dppm)_2OTf$ **320** which also requires a loss of one CO ligand. Insertion of SO_2 does not occur when **127** is treated with sulphur dioxide. Nonetheless, 1 equiv. of SO_2 is taken up leading to $[RhIr\{C(O)Me)\}(CO)_2(\mu\text{-}SO_2)(dppm)_2]OTf$ **321**. Apart from a

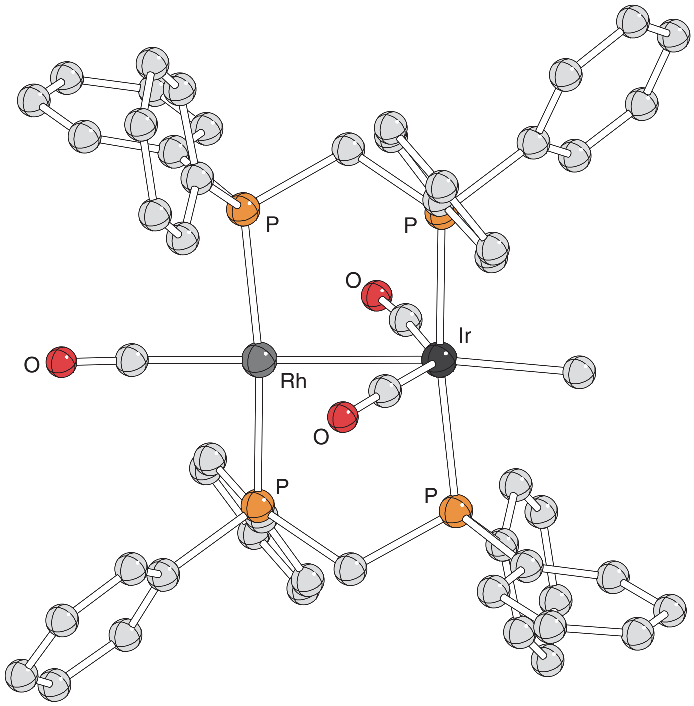
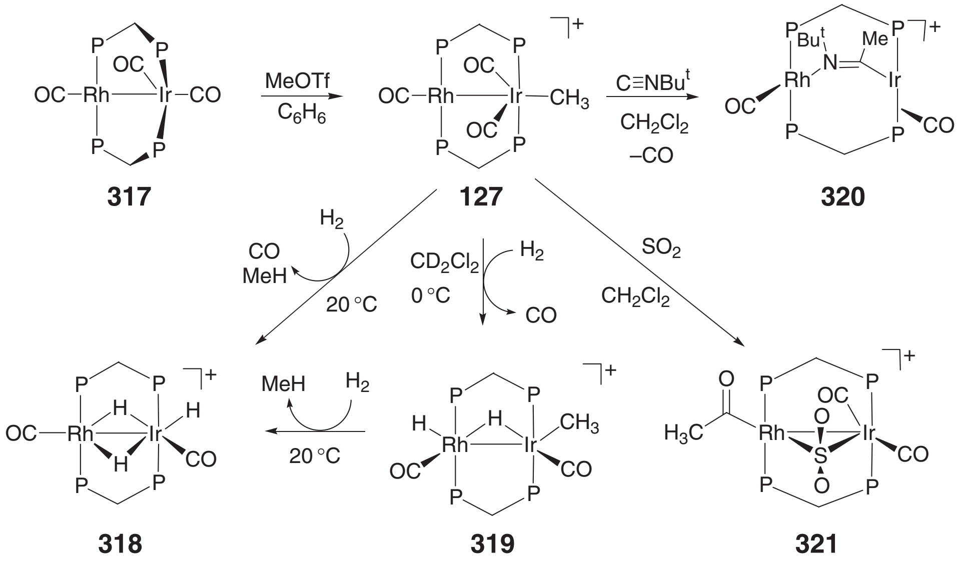


Figure 26 X-ray crystal structure of **127**.



Scheme 32

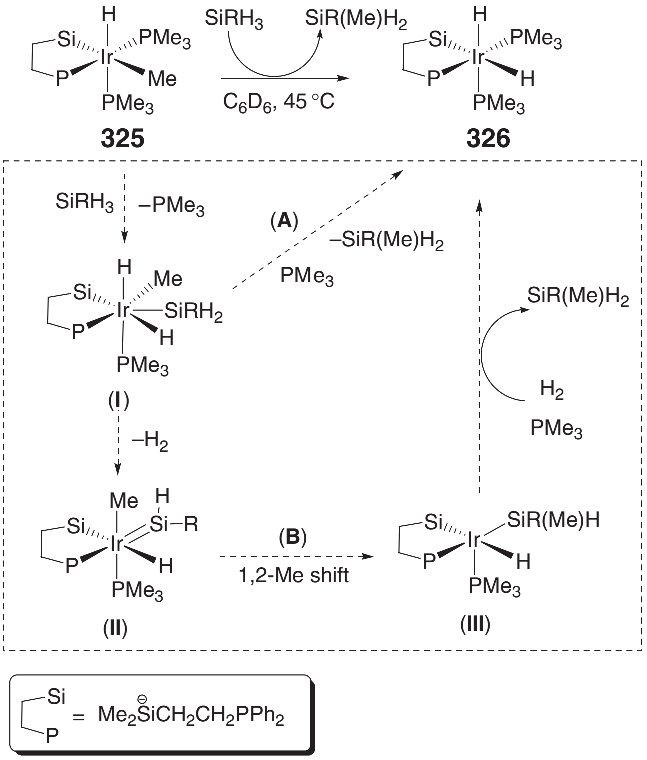
bridging SO_2, the complex features a rhodium-bonded acetyl ligand which noticeably forms, via methyl migration to rhodium followed by migratory insertion to one carbonyl ligand.

Alkylation of the dinuclear complex $[Ir_2(CO)_3(dppm)_2]$ **211** with CH_3I and CH_3OCH_2I gives the oxidative addition products $[Ir_2(R)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (R = CH_3 **322a**), CH_2OCH_3 **322b**).[158(a)] The reactivity of the cationic $[Ir_2(Me)(CO)(\mu\text{-}CO)(dppm)_2]OTf$ **122** with ethene and fluorurated alkenes has been also investigated.[159] In the case of C_2H_4, the reaction starts at low temperature with ethene coordination inducing the C–H bond activation of the methyl ligand. As a result, the μ-methene derivative $[Ir_2(H)(CO)_2(\eta^2\text{-}C_2H_4)(\mu\text{-}CH_2)(dppm)_2]OTf$ **323** is obtained. On warming, **323** transforms into $[Ir_2(Me)(CO)(\eta^2\text{-}C_2H_4)(\mu\text{-}CO)(dppm)_2]OTf$ **324** where simple alkene coordination is found. While 1,1,-difluoroethene behaves identically to ethene, other floururated alkenes, $C_2H_{4-n}F_n$ ($n = 1$–4), yield only the η^2-adducts similar to **324**.[159]

Functionalization of organic molecules by stoichiometric conversion of (hydrido)alkyl organometallic compounds represents an important goal for research as it has been considered preliminary to the development of any transition metal-catalyzed alkane functionalization reaction.[136] A step forward in such chemistry has been achieved by Okazaki *et al.* who studied the thermal behavior of alkyl(hydrido)(hydrosilyl) iridium(III) complexes in the presence of silanes.[160,160a–160c] Thus, co-thermolysis of $[IrMe(H)\{\kappa^2\text{-}P,Si\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2]$ **325** with $SiRH_3$ (R = Bu^n, pentyl, hexyl) in C_6D_6 at 45 °C leads to selective transfer of the methyl ligand from iridium to silicon affording $SiR(Me)H_2$ and the dihydride $[IrH_2\{\kappa^2\text{-}P,Si\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2]$ **326**.[35] Scheme 33 highlights this nice example of silane stoichiometric functionalization and shows the two suggested mechanisms both involving preliminary PMe_3 dissociation and formation of an Ir(V) intermediate **I**.[145,161,161a] Mechanism A entails a classic oxidative addition/reductive elimination pathway in which elimination of Si–C over C–H or C–C bonds is preferred to account for the formation of $SiR(Me)H_2$. Mechanism B claims an intriguing intramolecular H_2 elimination leading to a methylsilylene intermediate **II** from which the –SiR(Me)H unit is formed by 1,2-Me shift from iridium to silicon **III**. H_2 addition and silane elimination complete the process.

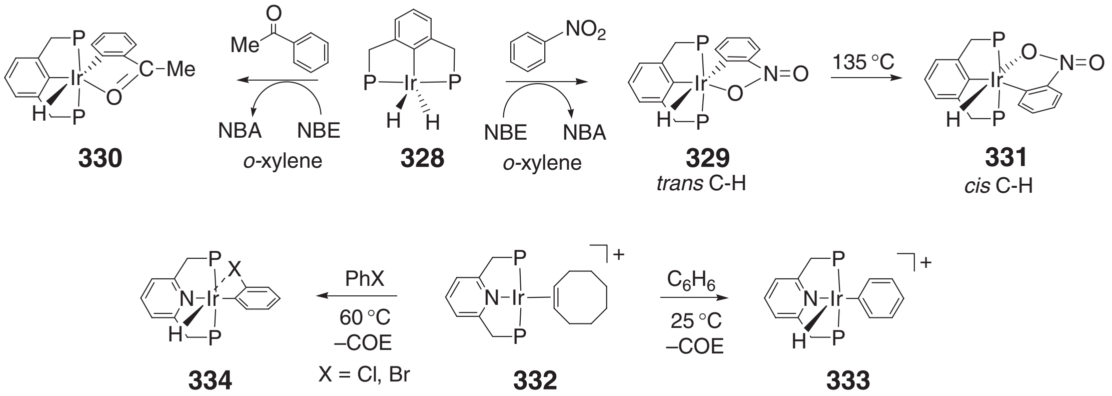
A careful study of the thermal reactivity of the related $[IrMe(H)\{\kappa^2\text{-}P,Si\text{-}MesSi(H)(CH_2)_2PPh_2\}(PMe_3)_2]$ **327** with MeOH strongly supports the occurrence of a 1,2-H shift from the silyl silicon atom to the iridium center to generate a hydrido(silylene)iridium(I) intermediate species, and then points to validate mechanism B for these classes of iridium-mediated C–Si bond-forming processes.[160a,160b]

PCP iridium pincer complexes are a well-studied and attractive class of compounds which promote important catalytic and stoichiometric processes. Although this class of compounds are also briefly discussed in the sections describing iridium hydrides (Section 7.04.6) and iridium catalyzed C–C bond-forming processes (Section 7.04.3.5), a few notes addressing their relevance in the chemistry of hydrocarbyl iridium complexes are here necessary. Both the neutral (PCP)Ir [PCP = 3-C_6H_3-2,6-$(CH_2PBu^t_2)_2$] and the cationic $(PNP)Ir^+$ [PNP = 2,6-bis-(di-*tert*-butyl phosphino methyl)pyridine] systems add aryl C–H bonds to give isolable aryl hydrides.[162,162a] Important mechanistic

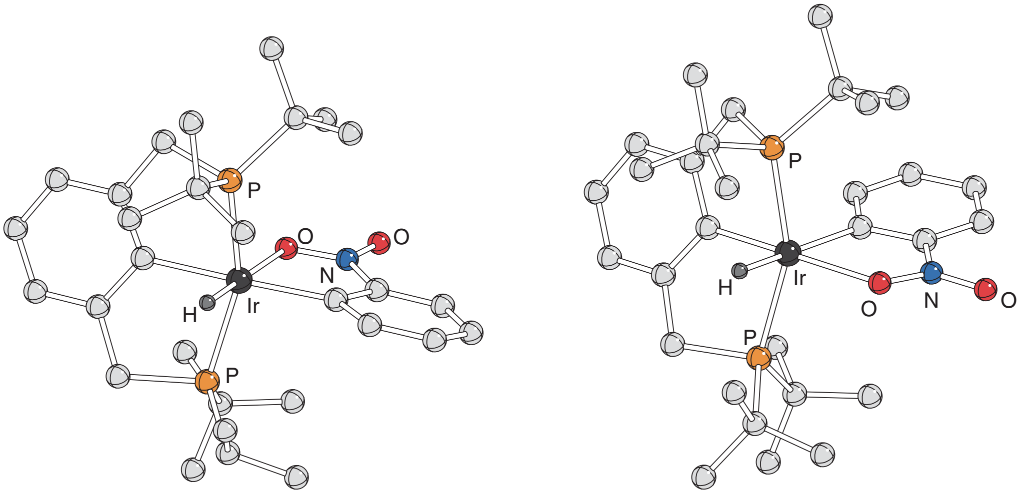


Scheme 33

information about the C–H activation process has been obtained by Goldman and co-workers by studying the reaction of [(PCP)IrH_2] 328 with nitrobenzene and acetophenone.[163b] Both reactions take place at RT in the presence of NBE, assisting the dehydrogenation of 328, to give κ^2-*O,C*-chelated complexes by oxidative addition of an aryl C–H bond and coordination of a nitro 329 or acetyl oxygen 330 (Scheme 34). In the case of PhNO_2, the cyclometallated iridium(κ^2-*O,C*-nitrophenyl)hydride, [(PCP)Ir(H)(κ^2-*O,C*-ON(O)C_6H_4)] 331, was characterized by X-ray crystallography showing a *trans*-disposition of the hydride and *ortho*-metallated carbon atom (Figure 27a). The incongruity between the actual structure and that expected on the basis of a C–H activation step (with a *cis*-disposed hydride) stimulated a detailed investigation of the reaction mechanism. A low temperature NMR study excluded a mechanism primarily involving coordination of the functional group followed by C–H activation. Rather, a kinetic



Scheme 34



(a) (b)

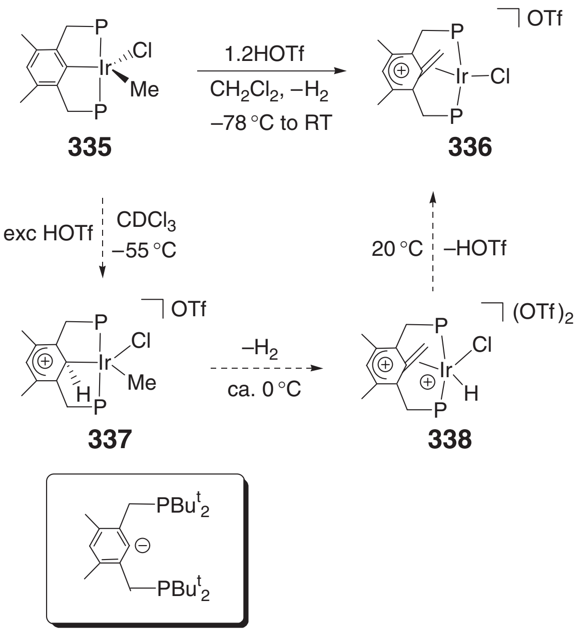
Figure 27 X-ray crystal structures of (a) **331** and (b) **329**.

preference for *meta*- and *para*-positions was observed at LT. In such a picture, the potentially chelating functional group would act as trapping device for the *ortho* C–H activation favoring the formation of **329** at RT. Noticeably, this is not the thermodynamic sink as complete isomerization of **329** to the *cis* C–H complex **331** occurs upon heating to 135 °C (Figure 27b). Correlated results were reported by Milstein who studied the C–H activation of arenes by $[(PNP)Ir(coe)]PF_6$ **332** yielding the thermally robust phenyl hydride $[(PNP)IrH(Ph)]PF_6$ **333** (Scheme 34). He also showed the ortho-selective addition of C–H bonds of PhCl and PhBr to the isoelectronic cationic (PNP)Ir fragment **334** and proposed that this regioselecivity was directed by halogen coordination.[162a]

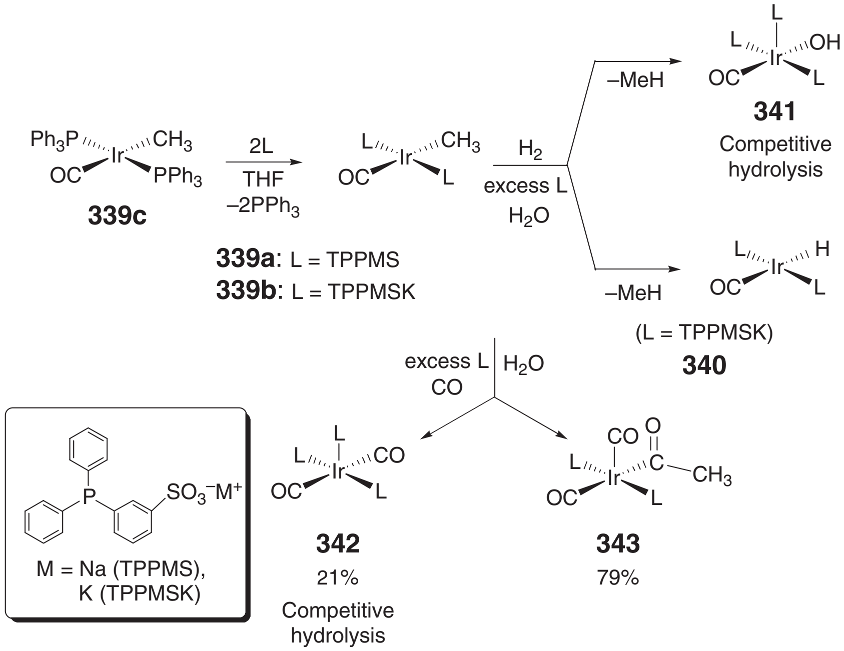
Protonation of the methyl(chloride) pincer iridium complex $[(PCP)Ir(Me)Cl]^+$ **335**[163a] by HOTf affords the methene arenium iridium complex $[IrCl\{CH_2{=}C_6H(CH_3)_2(CH_2PBu^t{}_2)_2\}]OTf$ **336** via a dearomatization process taking place under exceedingly mild conditions.[164] The low temperature study of this process has allowed to spectroscopically detect and characterize two intermediates, that is, a Wheland-type σ-arenium complex $[IrMe(Cl)\{C_6H_2(CH_3)_2(CH_2PBu^t{}_2)_2\}]OTf$ **337** and a dicationic hydrido bistriflate $[Ir(H)Cl\{CH_2{=}C_6H(CH_3)_2(CH_2PBu^t{}_2)_2\}](OTf)_2$ **338** from which **336** may form by elimination of HOTf. A cascade of events including attack of proton to the metal or *ipso*-carbon, 1,2-methyl shift, β-hydride elimination, and hydride abstraction by deprotonation, may well account for the formation of the Milstein's methene arenium species. Scheme 35 summarizes this chemistry.

Water-soluble iridium(I) alkyls have been prepared by Paterniti and Atwood.[165] The reactivity of *trans*-$[Ir(CH_3)(CO)(TPPMS)_2]$ **339a** and *trans*-$[Ir(CH_3)(CO)(TPPMSK)_2]$ **339b** in water has been explored and compared with that of *trans*-$[Ir(CH_3)(CO)(PPh_3)_2]$ **339c**. Hydrogenation of **339b** affords methane and the water-soluble hydride *trans*-$[Ir(H)(CO)(TPPMSK)_2]$ **340**. Hydrolysis of Ir–C bond is however a strong competitive reaction resulting in the formation of MeH and *trans*-$[Ir(OH)(CO)(L)_3]$ (**341**, L = TPPMS, TPPMSK). More intriguing is the water carbonylation of both **339a** and **339b** that have been proposed as a possible model for the carbonylation of $[Rh(H)(CO)(TPPTS)_3]$ which catalytically converts propene to butanal in the well-known Ruhrchemie/Rhône–Poulenc process.[166,166a] Carbonylation in water of **339a** or **339b** in the presence of a slight excess of L affords, apart from the hydrolysis product $[Ir(CO)_2L_3]$ (**342**, 21%), the acetyl derivative *trans*-$[Ir(COCH_3)(CO)_2(L)_2]$ (**343**, 79%) suggesting that water-resistant acyl species may be effectively formed during the industrial process. Scheme 36 summarizes this interesting chemistry.

Hydrosoluble iridium alkyl complexes may also be prepared by hydrolysis of alkynes[32,35] and alkenes[35] promoted by water-soluble precursors. The reaction with alkynes follows the well-known mechanism demonstrated by Bianchini *et al.* for ruthenium complexes.[167] A reasonable mechanism, related to that of C≡C hydrolytic breakage, has been proposed by Chin *et al.* to account for the hydrolysis of ethene promoted by $[Cp^*Ir(TPPMS)CI_2]$ **344** in the presence of silver salts in water. Scheme 37 describes the Chin's hydrolysis of alkynes, leading to $[Cp^*Ir(TPPMS)(CO)(CH_2R)]$ (**69**; R = Ph, Bz, Bu^t, *p*-Tol) via the aquo complex $[Cp^*Ir(TPPMS)(OH_2)OTf$ **345**



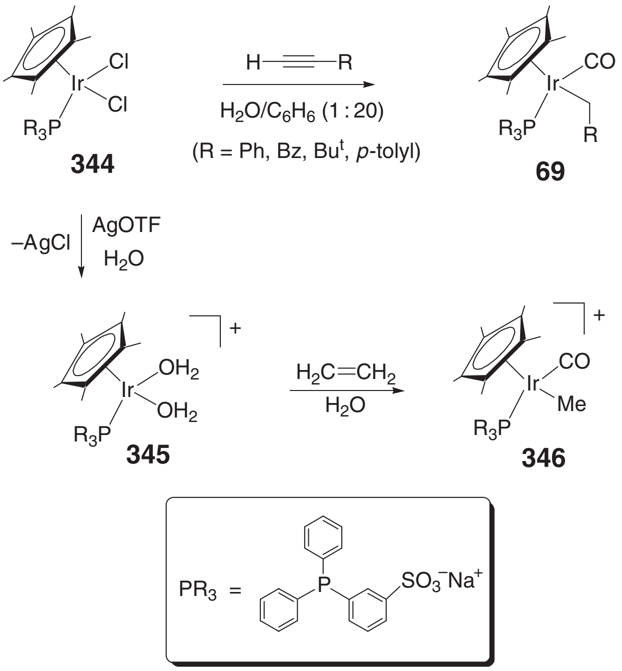
Scheme 35



Scheme 36

and the related hydrolysis of ethene that affords [Cp*Ir(TPPMS)(CO)(CH$_3$)]OTf **346**. Figure 28 shows the molecular structure of [IrCl$_2${η^1-CH$_2$(*p*-Tol)}(CO)(PPh$_3$)$_2$] **61b** obtained by Albertin *et al.* by hydrolysis of *p*-tolylcetylene during the reaction of this alkyne with *fac-* or *mer*-[IrHCl$_2$(PPh$_3$)$_3$] **347** in THF or CH$_2$Cl$_2$.[32]

In Albertin's system, the reaction follows different pathways depending on the nature of both the iridium precursor and the alkyne. Thus, the reaction of **347** with HC≡CC(CH$_3$)$_3$ in the presence of H$_2$O does not promote C–C bond breakage, but results in the formation of the acyl complex [IrCl$_2${η^1-C(O)CH$_2$CBu^t}(PPh$_3$)$_2$] **62**. Thermolysis of **62** in



Scheme 37

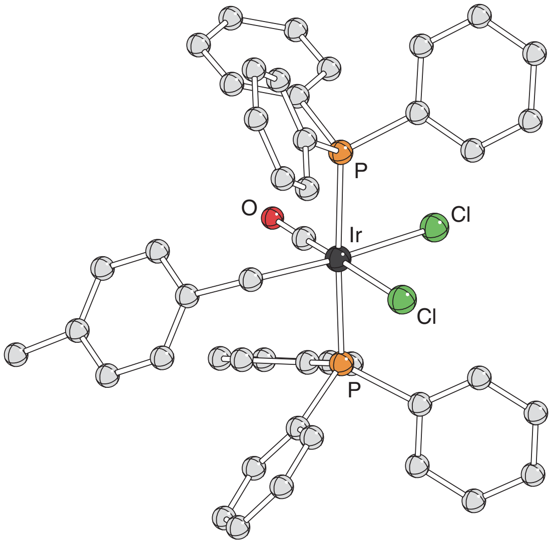
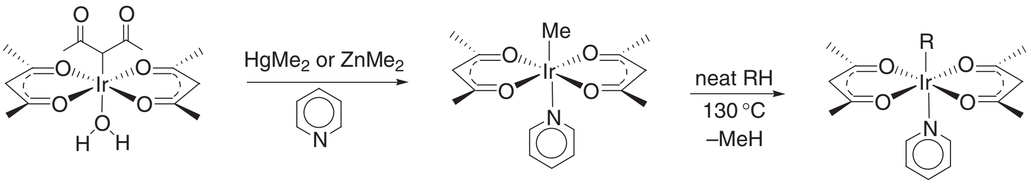


Figure 28 X-ray crystal structure of **61b**.

THF at 60 °C brings about the decarbonylation step yielding the carbonyl(*tert*-butyl) complex $[IrCl_2\{\eta^1\text{-}CH_2CBu^t\}(CO)(PPh_3)_2]$ **348**.

A breakthrough in the field of iridium-promoted C–H bond activation has been recently obtained by Periana and co-workers who described the first example of Ir(III) *O*-ligated complexes capable of bringing about C–H activation of hydrocarbons including alkanes.[168] The air stable methyl derivative, $[IrMe(\kappa^2\text{-}O,O\text{-acac})_2(py)]$ **349**, prepared from $[Ir(\kappa^1\text{-}C_3\text{-acac})(\kappa^2\text{-}O,O\text{-acac})_2(H_2O)]$ **350** by reaction with $ZnMe_2$ or $HgMe_2$ followed by addition of pyridine (Scheme 38), cleanly reacts with a variety of hydrocarbons, including cyclohexane and *n*-octane, to generate the corresponding iridium alkyl derivatives $[IrR(\kappa^2\text{-}O,O\text{-acac})_2(py)]$ **351**. The molecular structure of the cyclohexyl complex $[IrCy(\kappa^2\text{-}O,O\text{-acac})_2(py)]$ (R = Cy **352**) has been determined and a view is given in Figure 29.



350 **349** **351**

RH = C_6H_{12}, *n*-octane, PhH, MesH

Scheme 38

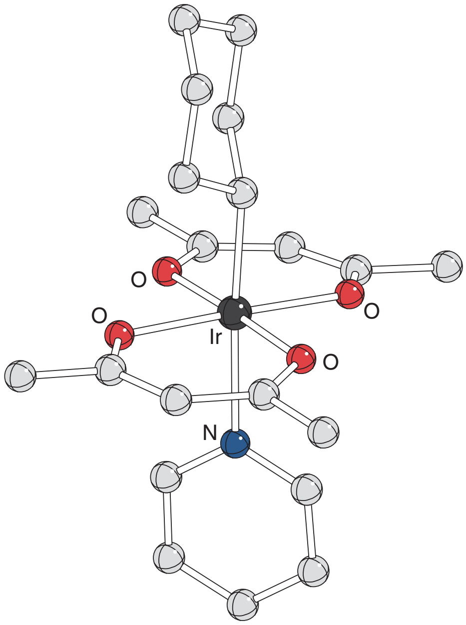
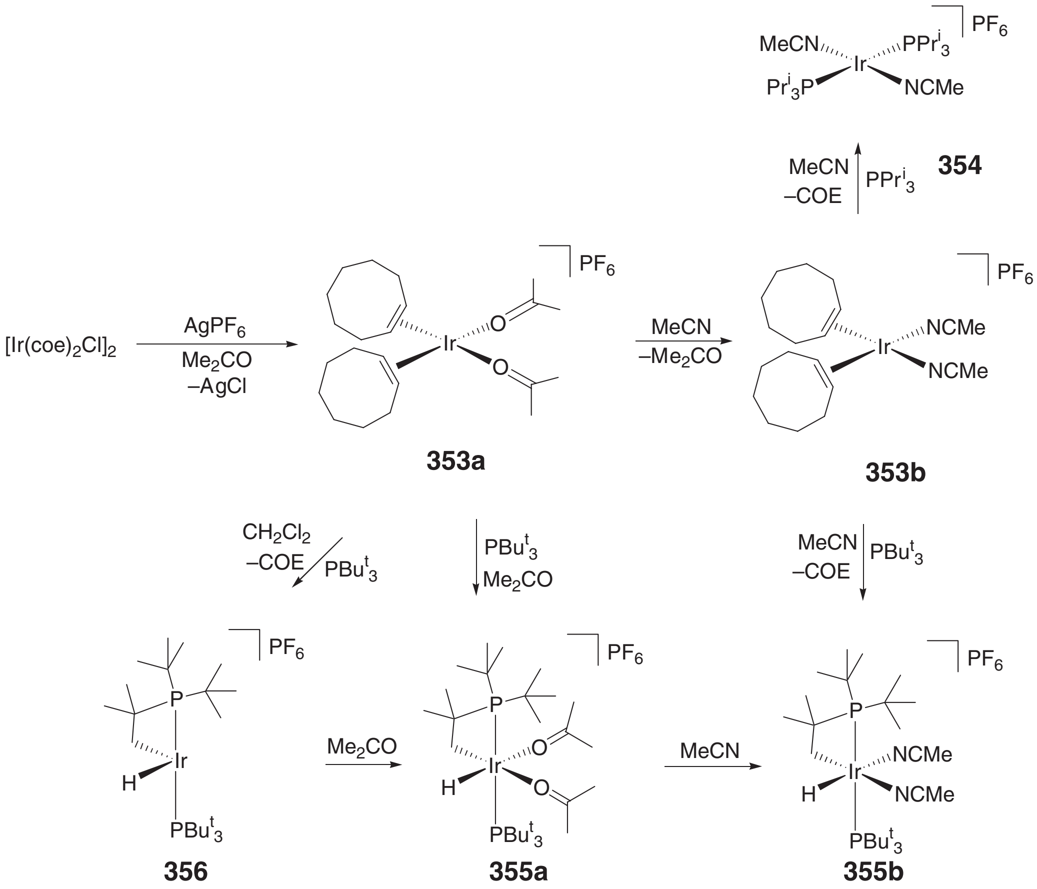


Figure 29 X-ray crystal structure of **352** (R = Cy).

Loss of pyridine from **349** and *trans–cis* isomerization should give an intermediate accounting for the oxidative addition of the hydrocarbon and the H/D isotopic exchange between C_6D_6 and hydrocarbons catalyzed by **349** (for cyclohexane/C_6D_6, measurements yielded TON = 240). The related phenyl derivative [IrPh(κ^2-*O*,*O*-acac)$_2$(py)] **352** catalyzes the anti-Markovnikov hydroarylation of unactivated alkenes.[169,169a–169c] The mechanism of the alkene hydroarylation catalyzed by **352** was theoretically analyzed by DFT methods.[170]

Bis(cyclooctene)–Ir(I) complexes stabilized by acetonitrile or acetone solvent molecules [Ir(coe)$_2$(S)$_2$]PF$_6$ [S = Me$_2$CO **353a**, MeCN **353b** were obtained as hexafluorophosphate salts from the reaction between [Ir(μ-Cl)(coe)$_2$]$_2$ and AgPF$_6$ in the appropriate solvent (Scheme 39).[171] These complexes react with simple alkylphosphines, with selective displacement of the cyclooctene ligand. While PPr$^i_3$ affords the SQP complex [Ir(PPr$^i_3$)$_2$(MeCN)$_2$]PF$_6$ **354**, the bulkier PBu$^t_3$ undergoes facile intramolecular C–H activation, giving cyclometallated, solvent-stabilized bis(phosphine)–Ir(III) species [IrH(PBu$^t_3$){PBu$^t_2$[C(CH$_3$)$_2$(CH$_2$)]}(Solv)$_2$]PF$_6$ [S = Me$_2$CO **355a**, MeCN **355b**]. The lack of cyclometallation with PPr$^i_3$ is puzzling because of the ease of C–H intramolecular activation has been found to follow the order PPr$^i_3$ > PBu$^n_2$Bu^t > PBu$^t_3$ for the reaction of alkylphosphines with [Ir(μ-Cl)(coe)$_2$]$_2$/N-donor ligands.[172] Dissolving **355a** in CH$_2$Cl$_2$ leads to acetone decoordination without coordination of the halocarbon. In contrast, an agostic interaction involving the aliphatic phosphine substituents leads to the first isolated 14-electron alkyl–Ir(III) complex, [IrH(PBu$^t_3$){PBu$^t_2$[C(CH$_3$)$_2$(CH$_2$)]}]PF$_6$ **356**. Agostic interactions in Ir(III) phosphino complexes are well documented and have been carefully studied by both theroretical and experimental methods by Eisenstein and co-workers.[173,173a–173b] A situation similar to **356** was found for the closely related complex [IrH(PBu$^t_2$Ph){PBu$^t_2$(C$_6$H$_4$)}]BPh$_4$ **357** which was characterized by X-ray crystallography (Figure 30).[173]



Scheme 39

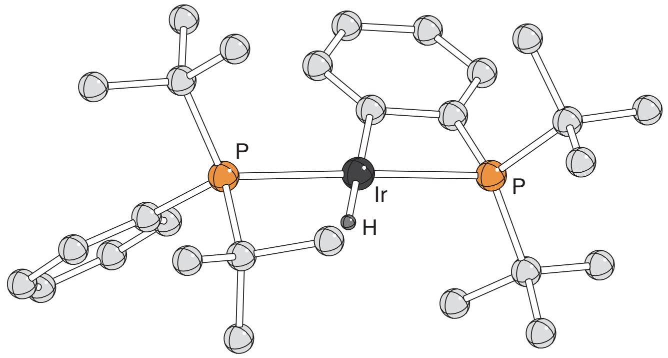


Figure 30 X-ray crystal structure of **357**.

Highly stable diiridium complexes with σ/π-bridging disubstituted aryl ligands have been prepared by Muldoon and Brown via reaction of $[Ir(cod)Cl]_2$ with 0.5 equiv. of Grignard reagents in THF.[174] The compounds, characterized by X-ray diffraction, exhibit a square-planar iridium σ-bonded to the aryl moiety and the second metal π-coordinated to the metallated arene ring. The structure of one of these complexes, $[Ir(\eta^4\text{-cod})(Br)(\mu\text{-}\sigma,\pi\text{-}6\text{-}Me_2C_6H_3)Ir(\eta^4\text{-cod})]$ **358** is shown in Figure 31.

Fluoroalkyl iridium complexes have been thoroughly studied by Hughes and co-workers.[97a,175,175a–175c] Generally these compounds were obtained by oxidative addition of a fluoroalkyl iodide (R_FI) to $[Cp^*Ir(CO)_2]$ to give $[Cp^*Ir(CO)(R_F)I]$, followed by replacement of CO by PMe_3 to afford the desired fluoroalkyl species

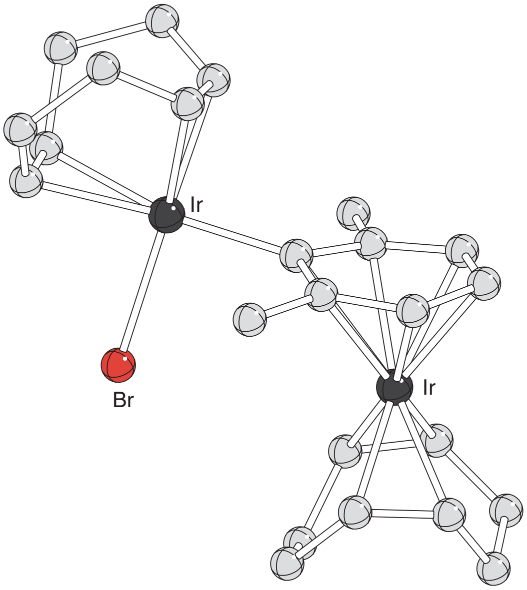


Figure 31 X-ray crystal structure of **358**.

[Cp*Ir(PMe$_3$)(R$_F$)I] **359**. Alkyl(fluoroalkyl) derivatives [Cp*Ir(PMe$_3$)(R$_F$)R] **360** have been prepared by treatment of the triflate derivatives [Cp*Ir(PMe$_3$)(R$_F$)(OTf)] **361** with excess of lithium or zinc alkyls.[175] As an example of this class of compounds, the molecular structure of the methyl(perfluoroisopropyl) complex [Cp*Ir(PMe$_3$){CF(CF$_3$)$_2$}(CH$_3$)] **362** is given below in Figure 32. The solution structure and conformation of such fluoroalkyl iridium derivatives has been determined by ^{19}F{^{1}H} HOESY NMR spectroscopy and correlated for diastereomeric compounds with the X-ray structure of the major diastereomer.[176] Reduction with sodium naphthalenide of [Cp*Ir(PMe$_3$)(C$_4$F$_9$)I] **363**, containing the perfluoro-*sec*-Bu ligand, takes place at the perfluorurated ligand and affords the unique tetrafluorobutatriene complex [Cp*Ir(PMe$_3$)(C$_4$F$_4$)] **364**.[175c]

Related to this topic, the chemistry of the fluorous analog of the Vaska's compound, that is, [Ir(CO)Cl{P(CH$_2$CH$_2$(CF$_2$)$_5$CF$_3$)$_3$}$_2$] **15** has been explored by Horvath and co-workers.[11,12] The oxidative addition of different alkyl iodides including fluoroalkyl species has been reported.

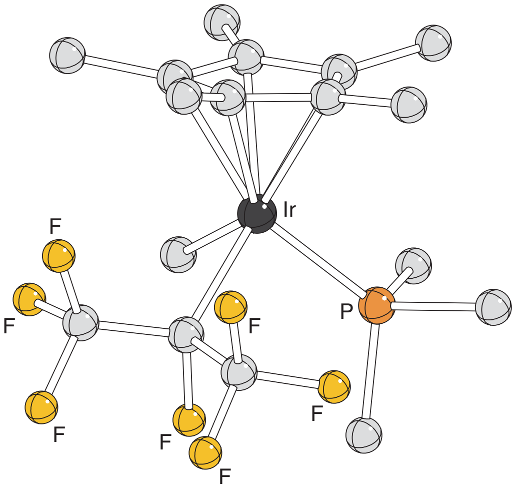


Figure 32 X-ray crystal structure of **362**.

7.04.3.2 Alkenyl Complexes

Common starting materials in the coordination and organometallic chemistry of iridium are the dinuclear COD complexes $[Ir(cod)X]_2$ (X = Cl, Br, I, OMe, $SiMe_3$, etc.).[177,177a] These derivatives are easily prepared and frequently participate, either alone or in combination with additional ligands, in some of the most intriguing iridium-catalyzed processes (*vide infra*, Section 3.5). Usually, in most of these processes, the diene molecule is considered an ideal "innocent" ligand that does not actively participate in the reaction and is readily removable from the coordination sphere of the metal. Although this is frequently the case, the direct participation of diene ligands has been demonstrated in several reactions involving Ir(cod) units. In an elegant study Sola, Oro and their co-workers have shown that this may happen also for a simple system like $[Ir(cod)(MeCN)(PMe_3)]BF_4$ **365**.[178] The relevant role played by COD is witnessed by the reaction with $PhC\equiv CPh$ which affords the alkenyl complex $[Ir(\eta^{3:2}\text{-}C_8H_{11})(Z\text{-}CPh{=}CHPh)(MeCN)(PMe_3)]BF_4$ (**366**, Figure 33) likely via insertion of one diphenylacetylene molecule into an Ir–H bond resulting from the equilibrium Ir(I)-$\eta^{2:2}$-C_8H_{12} $\leftrightarrow$ Ir(III)-$\eta^{3:1}$-$(H)(C_8H_{11})$ via intramolecular C–H oxidative addition of the COD ligand (see Scheme 40). A κ,η^3-cyclooctadiene ligand may be stabilized in the absence of unsaturated substrates just dissolving **365** in acetonitrile. The reaction is straightforward and affords $[Ir(\kappa,\eta^3\text{-}C_8H_{12})(MeCN)_2(PMe_3)]BF_4$ **367** from which $[Ir(\kappa,\eta^3\text{-}C_8H_{12})(PMe_3)_3]BF_4$ **368** is obtained by stepwise replacement of MeCN with PMe_3. Compound **368** is an isomer of the known $[Ir(\eta^{2:2}\text{-}C_8H_{12})(PMe_3)_3]BF_4$ **369a**,[179] but shows different reactivity when heated in dichloroethane. Thus, while **368** is stable at 60 °C for 6 h, **369a** rearranges to a 1 : 1 mixture of two isomers **369b** and **369c**. This nice iridium chemistry highlights the great versatility of the COD ligand which may encompass different coordination modes and bonding hapticities depending on the electronic and steric properties of the iridium fragment.

Isomerization of iridium(I) alkene species to the corresponding Ir(III) hydrido(vinyl) derivatives is often thermodynamically favored for these compounds. Nice examples were provided by Carmona and co-workers who described the transformation of the diethene complexes $[Tp^RIr(C_2H_4)_2]$ (R = Tp, Tp^{Me}, **370**) to the hydrido(vinyl) isomers $[(L)Ir(H)(CH{=}CH_2)C_2H_4)]$ (L = Tp, Tp^{Me}; **371**).[180] The reaction takes place thermally or photochemically and generates a very reactive species capable of reacting with a variety of organic molecules,[181] including nitriles.[182] Similarly, the cationic $[Tpm^{Me}Ir(C_2H_4)_2]PF_6$ **372**, containing the neutral tris(3,5-dimethylpyrazolyl)methane ligand, undergoes alkene C–H bond activation under mild conditions leading to $[Tpm^{Me}IrH(CH{=}CH_2)(C_2H_4)]PF_6$ **373**. Under forcing conditions, **373** rearranges to a hydride-crotyl product via C–C coupling of the hydrocarbon ligands.[183] Also the stibine derivative $[IrCl(coe)(SbPr^i_3)_2]$ **374** rearranges in *n*-hexane at RT to the hydrido(cyclooctenyl) complex *anti,exo*-$[IrHCl(\eta^3\text{-}C_8H_{13})(SbPr^i_3)_2]$ **375**, which in benzene equilibrates with the *anti,endo*-isomer.

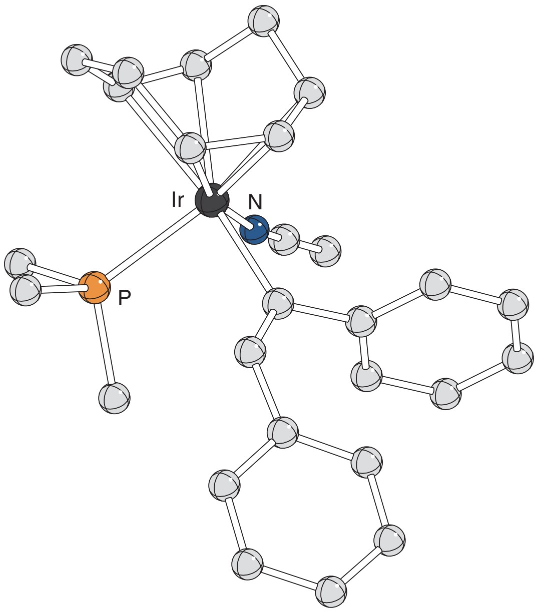
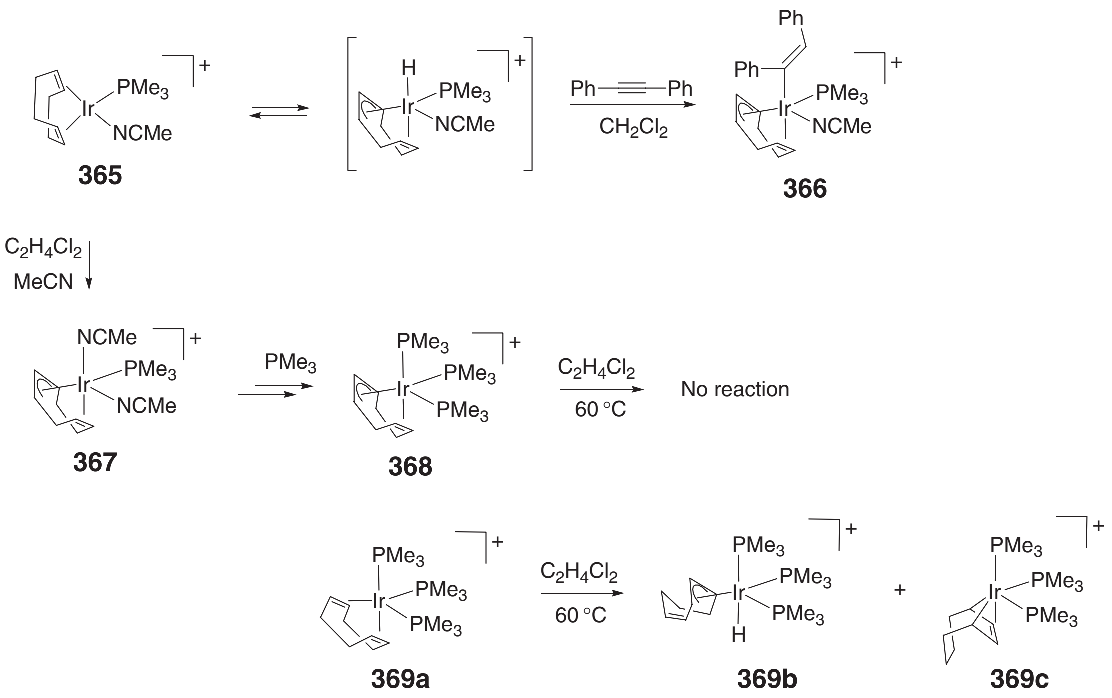


Figure 33 X-ray crystal structure of 366.



Scheme 40

Reaction of **375** with other alkenes such as propene or *n*-hexane affords the corresponding hydrido(alkenyl) species.[184]

An elegant method to form Ir–C σ-alkenyl complexes has been developed by Werner and co-workers based on the CO-induced intramolecular C–C coupling reaction of hydrocarbyl residues and vinylidene units in the precursor *trans*-$[Ir(R^2)\{C{=}C(H)R^1\}(PPr^i_3)_2]$ ($R^1 = Me, Ph, C{\equiv}CPh$; **376**).[185] These reactions and other strictly related, affording compounds *trans*-$[Ir(CO)\{CR^2{=}C(H)R^1\}(PPr^i_3)_2]$($R = Me, Ph, C{\equiv}CPh$; **377**) will be discussed in Section 7.04.4.1, where carbenes and other Ir complexes with multiple carbon bonds are reviewed. Figure 34 shows the

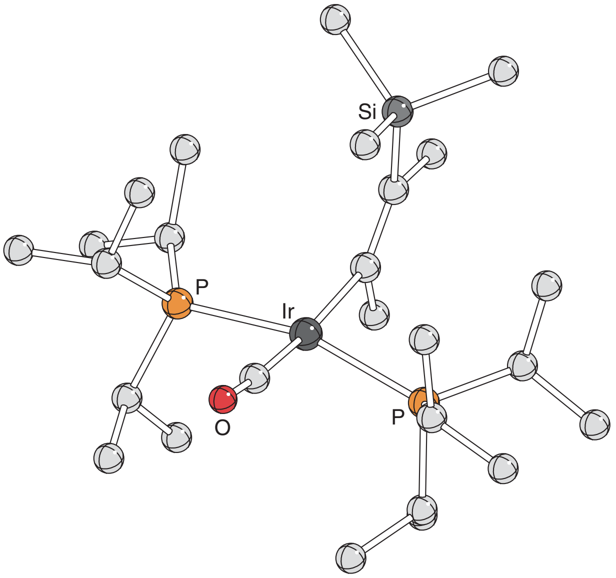
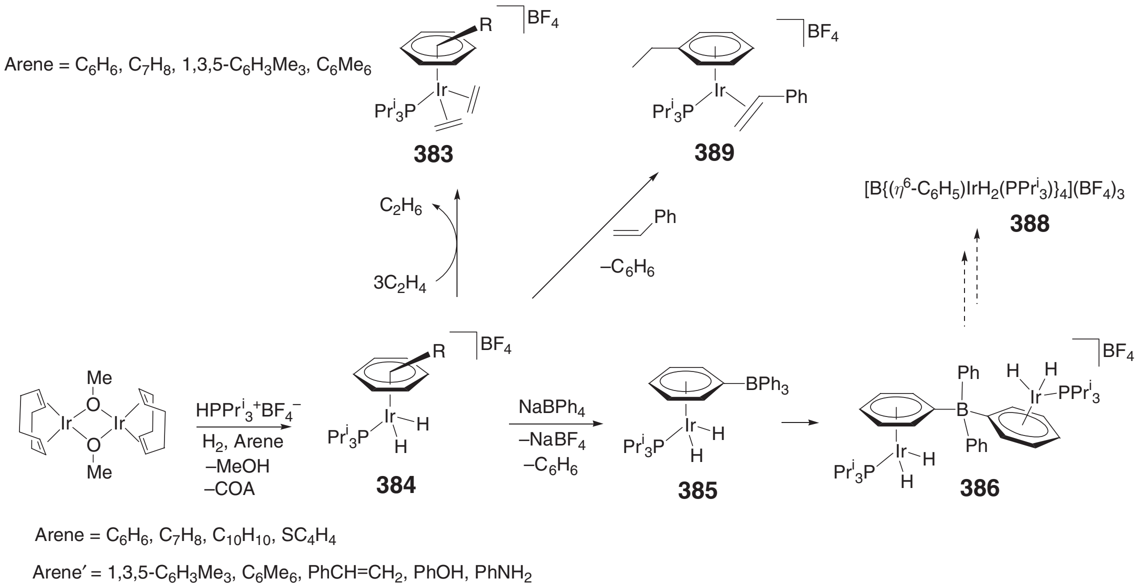


Figure 34 X-ray crystal structure of **378**.



Scheme 41

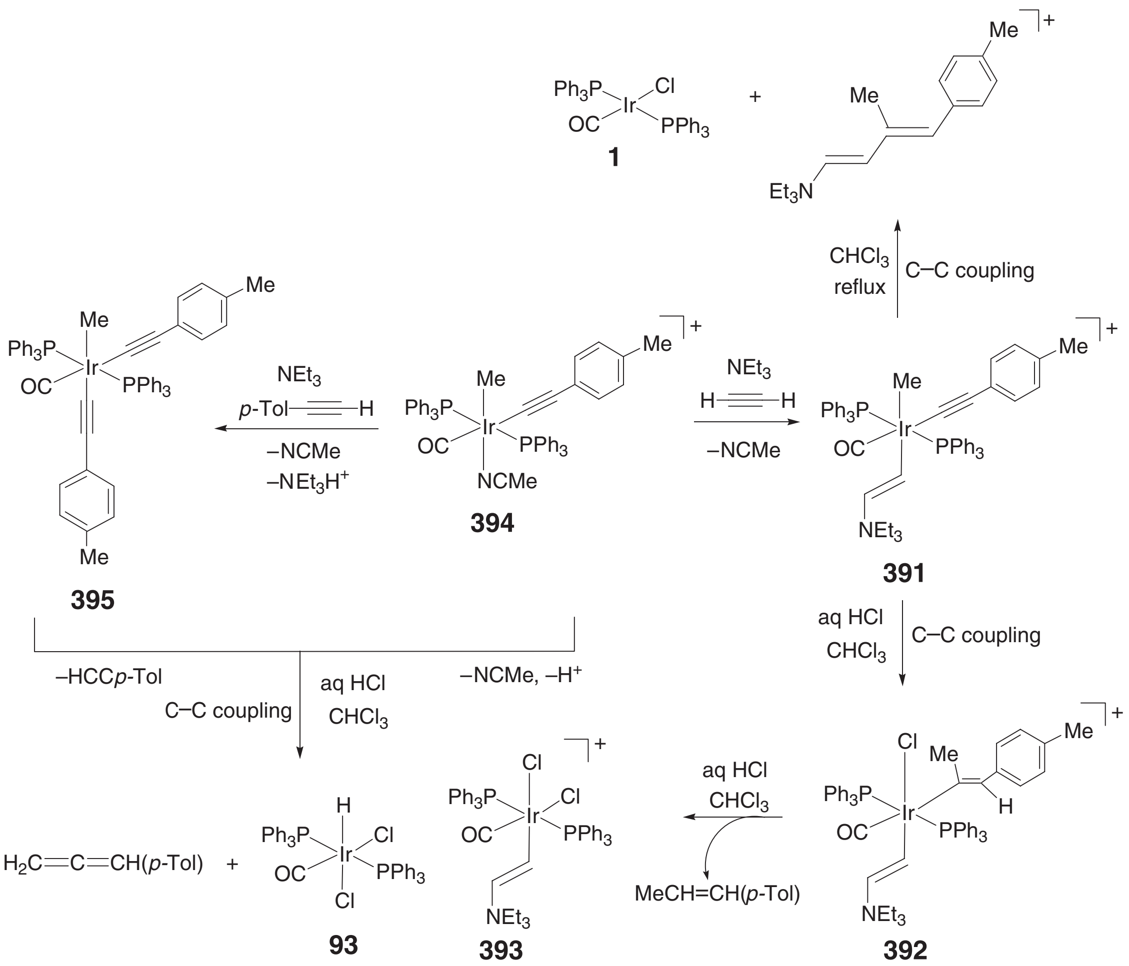
molecular structure of one of these Ir(I) alkenyl complexes, *trans*-[Ir{η^1-(Z)-C(Me)═C(SiMe$_3$)Me}(CO)(PPr$^i_3$)$_2$] **378**, obtained by the reaction of *trans*-[Ir(Me){C═C(Me)SiMe$_3$}(PPr$^i_3$)$_2$] **379** with CO.[185]

The ethene complex [Ir(κ^2-*O,O*-acac)(C$_2$H$_4$)$_2$] **380** reacts with tertiary phosphines to give the corresponding monosubstitution products [Ir(κ^2-*O,O*-acac)(C$_2$H$_4$)(PR$_3$)] (PR$_3$ = PPr$^i_3$, PPh$_3$, PPh$_2$CH$_2$CH$_2$OMe; **381**). Reaction of **381** (R = PPr$^i_3$) with tolane yields the π-alkyne complex [Ir(κ^2-*O,O*-acac)(PhC≡CPh)(PPr$^i_3$)] **382** via alkene displacement.[186] Cationic bis(ethene) complexes [(η^6-arene)Ir(η^2-C$_2$H$_4$)$_2$(PPr$^i_3$)]BF$_4$ (arene = C$_6$H$_6$, C$_7$H$_8$, 1,3,5-C$_6$H$_3$Me$_3$, C$_6$Me$_6$; **383**) were prepared by Oro and co-workers by the reaction of [(η^6-arene)IrH$_2$(PPr$^i_3$)]BF$_4$ **384** with ethene.[187] One equivalent of ethane is generated. Among these arene complexes, the one containing benzene is labile and C$_6$H$_6$ is easily replaced by either substituted arenes and tetraphenylborate anion. Thus, the dihydride **384** (arene = benzene) affords, by reacting with NaBPh$_4$, the remarkable neutral complex [{Ph$_3$B(η^6-C$_6$H$_5$)}IrH$_2$(PPr$^i_3$)] **385** which represents a suitable platform to prepare the polynuclear cations [Ph$_2$B{(η^6-C$_6$H$_5$)IrH$_2$(PPr$^i_3$)}$_2$]BF$_4$ **386**, [PhB{(η^6-C$_6$H$_5$)IrH$_2$(PPr$^i_3$)}$_3$](BF$_4$)$_2$ **387**, and [B{(η^6-C$_6$H$_5$)IrH$_2$(PPr$^i_3$)}$_4$](BF$_4$)$_3$ **388**, in which the BPh$_4^-$ anion is coordinated to four iridium atoms (Scheme 41). The reaction of **384** (arene = benzene) with styrene resulting in the formation of the very unusual ethylbenzene derivative [(η^6-C$_6$H$_5$Et)Ir-(η^2-C$_2$H$_3$Ph)(PPr$^i_3$)]BF$_4$ **389** is also worth mentioning.[187]

A variety of stoichiometric C–C coupling reactions have been described by Chin *et al.* (see also Section 7.04.4.3).[188,188a–188d] These involve Ir(III) precursors with as many as five Ir–C σ-bonds such as in *cis*-[Ir(CO)Me(CH═CHPPh$_3$)$_2$ (C≡CR)(PPh$_3$)]OTf **390**.[188a] Generally, the C–C coupling step takes place via migratory insertion of a methyl ligand promoted by aqueous HCl such as in the (alkyl)(alkenyl)(alkynyl)iridium(III) complex [IrMe(CH═CHNEt$_3$){C≡C (*p*-Tol)}(CO)(PPh$_3$)$_2$]ClO$_4$ **391** (Scheme 42).[188] The resulting bis(alkenyl)chloro iridium(III) complex [Ir{CMe═CH (*p*-Tol)}(CH═CHNEt$_3$)Cl(CO)(PPh$_3$)$_2$]ClO$_4$, **392**, reacts further with aqueous HCl to produce quantitatively the alkenyl dichloro derivative [Ir(CH═CHNEt$_3$)Cl$_2$(CO)(PPh$_3$)$_2$]ClO$_4$ **393** and *cis*-CH$_3$CH═CH(*p*-Tol). Refluxing **392** in chloroform gives Vaska's compound IrCl(CO)(PPh$_3$)$_2$ **1** and the *cis–trans*-1,3-diene [(*p*-Tol)HC═CMeCH═CHNEt$_3$]ClO$_4$, which likely forms via C–C coupling of the two alkenyl ligands.

C–C coupling takes place also by treatment of both the cationic alkyl(alkynyl)[IrMe{C≡C-(*p*-Tol)}(NCMe)(PPh$_3$)$_2$]ClO$_4$ **394** and the neutral alkyl(dialkynyl) [IrMe(CO){C≡C(*p*-Tol)}$_2$(PPh$_3$)$_2$] **395** with HCl. As a result, the *p*-Tol substituted allene CH$_2$═C═CH(*p*-Tol) forms together with the Ir(III) hydrochloride [IrHCl$_2$(CO)(PPh$_3$)$_2$] **93**. The C–C bonding steps have been rationalized by replacing HCl for DCl and studying the distribution of the deuterium label in the final organic compounds.[188]

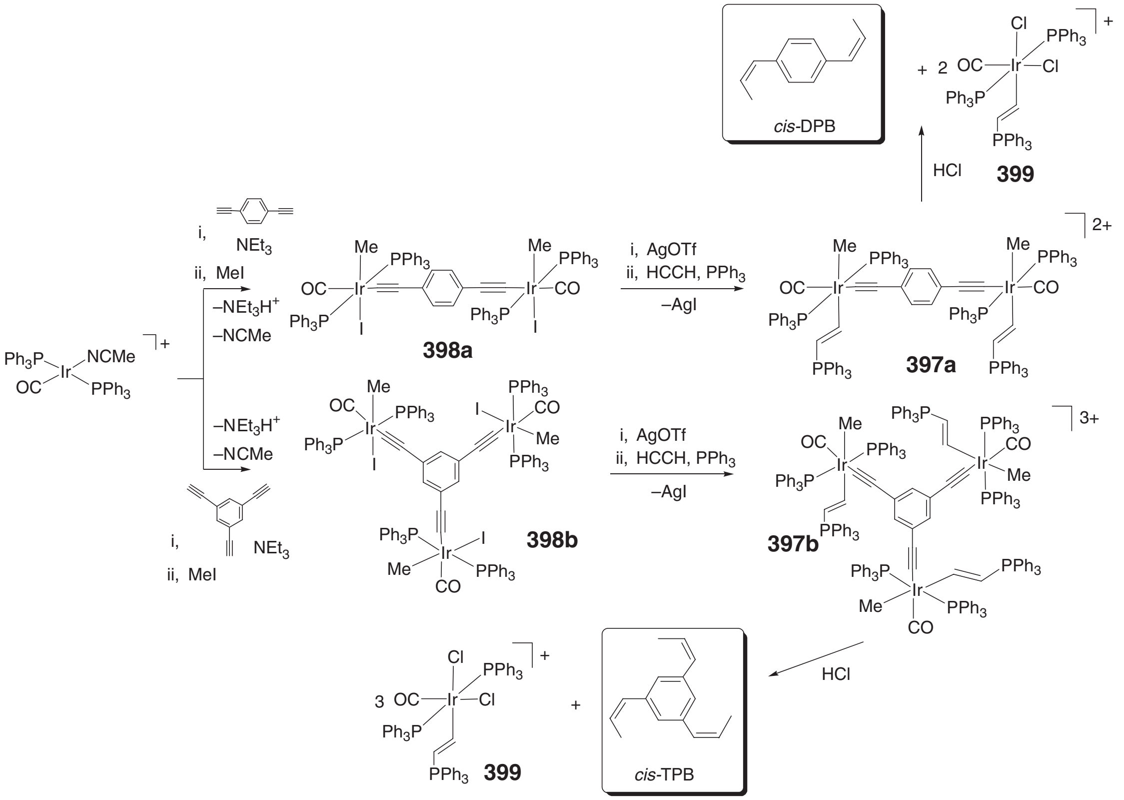
Analysis of deuterium incorporation in the products resulting from the reaction of DCl with the phosphonium ylide complex, [IrR(CH═CHPPh$_3$){C≡C(*p*-Tol)}(CO)(PPh$_3$)$_2$]OTf (R = Me, Bz; **396**), allowed to unravel the mechanism of the diastereocontrolled synthesis of 1,4-and 1,3,5-polyalkenylsubstituted arenes (*cis*-DPB and *cis*-TPB,



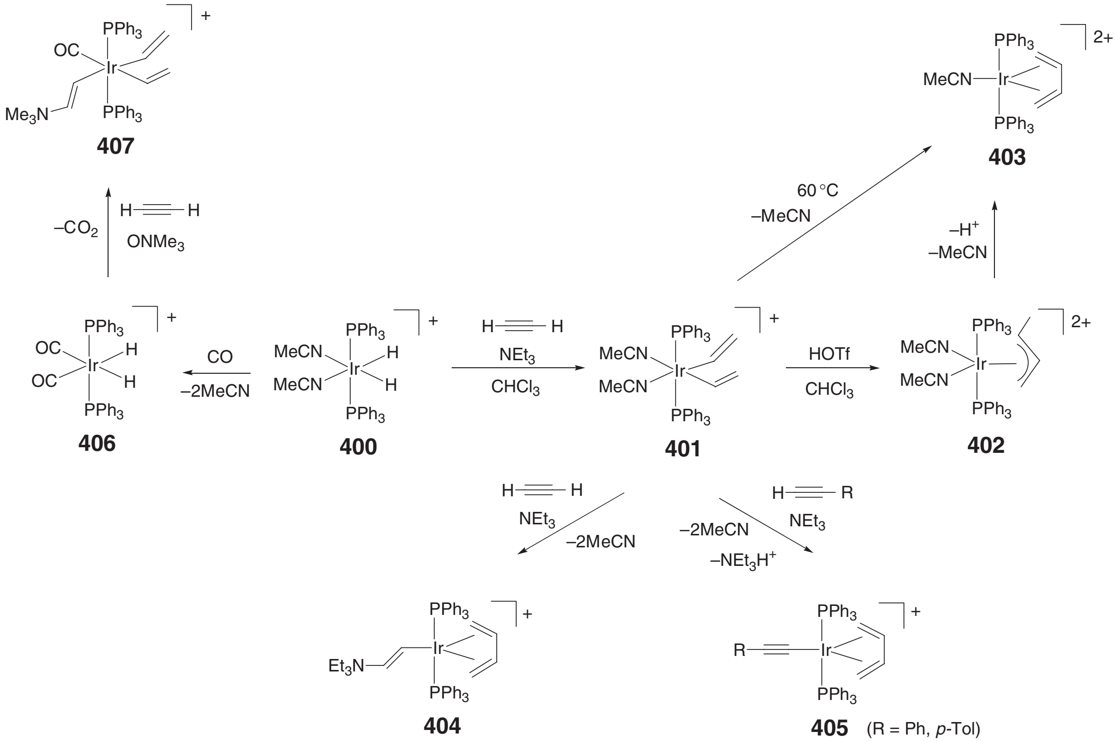
Scheme 42

respectively) promoted by aqueous HCl hydrolysis of di- and trinuclear alkyl(alkenyl)alkynyl Ir(III) precursors (**397a**, and **397b**) (Scheme 43).[188e] These species are prepared as illustrated in Scheme 43 by reacting the corresponding di- and trinuclear complexes [{*trans*-IrMe(I)(CO)$(PPh_3)_2$}$_n$(μ-L)] [$n = 2$, L = 1,4-diethynylbenzene **398a**; $n = 3$, L = 1,3,5-trisethynylbenzene **398b**] with silver salts in the presence of acetylene and triphenylphosphine. Apart from *cis*-DPB and *cis*-TPB, the reaction gives the alkenylphosphonium complex *trans*-[$IrCl_2$(CH=$CHPPh_3$)(CO)$(PPh_3)_2$]Cl **399** as the final iridium compound. The reaction brings about the C–C bond formation between alkyl and alkynyl groups and is proceeding likely via the initial attack of H^+ on the β-carbon of the alkynyl ligands followed by migratory insertion of the alkyl ligand to the α-carbon to produce *cis*-alkenyl complexes.[188d]

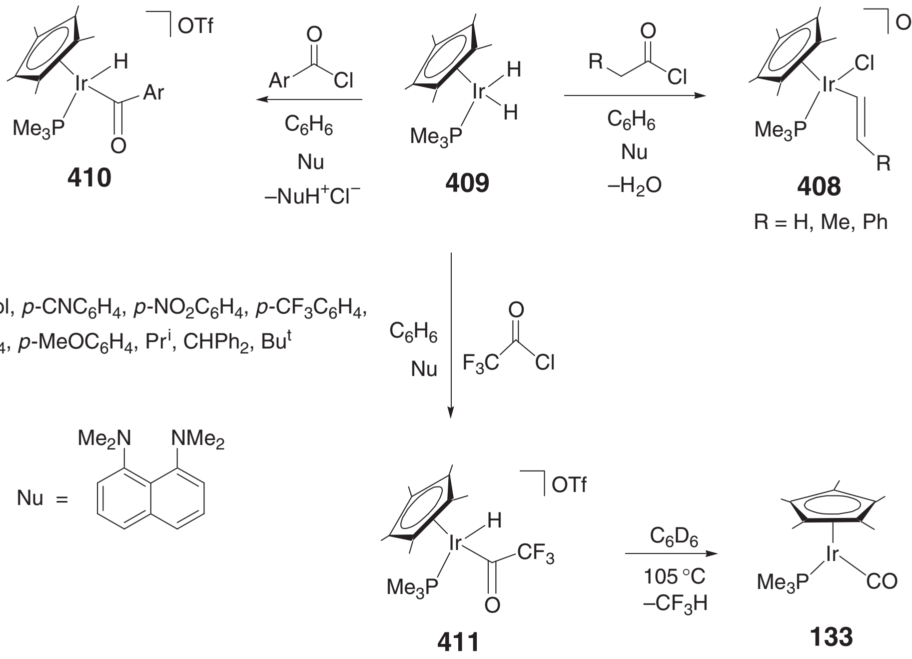
Acetylenes insert across Ir–H bonds to afford Ir(alkenyl) complexes. As an example of this well-known process, Chin reported that 2 equiv. of C_2H_2 insert into the two Ir–H bonds of [$IrH_2(MeCN)_2(PPh_3)_2$] **400** to yield [Ir(CH=$CH_2)_2(MeCN)_2(PPh_3)_2$]PF_6 **401**.[189,189a] Addition of HOTf to **401** in $CHCl_3$ promotes C–C coupling of the two α-carbons giving the η^3-allyl complex [Ir(η^3-$CH_3CHCHCH_2$)$(MeCN)_2(PPh_3)_2$]$(PF_6)_2$ **402**, which slowly undergoes reductive deprotonation leading to the butadiene species [Ir(η^4-CH=CHCH=CH_2)(MeCN)$(PPh_3)_2$]PF_6 **403**.[190] The same compound is also obtained by heating **401** to 60 °C in chloroform. Butadiene complexes, [Ir(η^4-CH=CHCH=CH_2)(L)$(PPh_3)_2$] (L = CH=$CHNEt_3$ **404**, C≡CR (R = Ph, *p*-Tol; **405**)), are also obtained by addition of different acetylenes in the presence of NEt_3. Replacing MeCN with CO in **401** leads to [Ir(CH=$CH_2)_2(CO)_2(PPh_3)_2$]PF_6 **406** which does not undergoes C–C coupling reactions. Reaction of **406** with acetylene in the presence of Me_3NO affords [Ir(CH=$CH_2)_2$(CH=$CHNMe_3)_2$(CO)$(PPh_3)_2$]PF_6 **407**, a rare example of iridium tris(alkenyl) species.[190] Scheme 44 summarizes this chemistry.



Scheme 43



Scheme 44



Scheme 45

Alkenylphosphonium Ir(III) complexes have been also reported by Yamamoto *et al.* from the reaction of $[\{Cp^*IrCl_2\}]_2$ with PhC≡CH and PPh_3. The reaction is proceeding likely via nucleophilic attack of the phosphine to the alkyne π-coordinated to iridium.[191]

Vinyl chloride complexes $[Cp^*Ir(PMe_3)Cl(CH{=}CHR)]$ **408** have been prepared by Bergman *et al.* by the reaction of $[Cp^*Ir(PMe_3)H_2]$ **409** with acetyl chlorides $[RCH_2C(O)Cl$, R = H, Me, Ph] in the presence of *N,N,N′,N′*-tetramethyldiaminonaphthalene as proton scavenger (Scheme 45).[192] The reaction is remarkably different from that occurring with aromatic acyl chlorides which affords hydrido(acyl) derivatives $[Cp^*Ir(PMe_3)(H)\{C(O)R\}]$ **410**. A detailed mechanistic investigation based on studies of kinetics and substituent effects led to the proposal of a common mechanism for the two apparently different reactions. This involves the nucleophilic attack of the electron-rich iridium center at the carbon atom of the acyl chloride, followed by fast chloride loss and subsequent deprotonation of the resulting intermediate by the proton sponge. In the case of acetyl derivatives, the final deprotonation step takes place at the α-acyl carbon and not at the metal hydride. Proton shift in the transient enolate and attack of HCl completes the reaction eventually yielding **408**. Bergman's method to prepare hydrido(acyl) species was successfully extended to fluoroacyl derivatives such as $[Cp^*Ir(PMe_3)(H)\{C(O)CF_3\}]$ **411**. This decomposes when heated in benzene-d_6 at 105 °C to the known iridium(I) carbonyl $[Cp^*Ir(PMe_3)(CO)]$ **133** and trifluoromethane.[67,67a] A mechanism entailing the formation of the carbanion/metal cation ion pair $[Cp^*Ir(PMe_3)I(H)(CO)]^+CF_3^-$ through dissociation of trifluoromethyl anion has been proposed. Further evidence for this mechanism comes from the thermal behavior of the related $[Cp^*Ir(PMe_3)(X)\{C(O)CF_3\}]$ [X = Me **412a**, Cl **412b**] which easily loses a trifluoromethyl anion in CD_3OD to give the an iridium(III) carbonyl cation and CF_3D.[67a]

Using sterically demanding tetrachelating diphosphines, such as [*R,S*-bis(tropp^{Ph})], and the corresponding enantiomers *R,R*-bis(troppPh) and *S,S*-bis(troppPh), Grützmacher and co-workers prepared several rhodium and iridium complexes exhibiting significant strain properties. The Ir(I) cation in the complex [Ir(cod){*R,S*-bis(troppPh)}]OTf **413** exhibits a very strained TBP geometry with both the alkene and the P donor ligand occupying the axial positions of the polyhedron.[193] The molecular structure of the complex cation in **413** is shown in Figure 35.

7.04.3.3 Iridium Alkynyl Complexes

7.04.3.3.1 Mononuclear iridium alkynyl complexes

C–H activation of terminal alkynes is a common reaction in organoiridium chemistry.[179,194] The reaction is thought to proceed via π-coordination of the alkyne and frequently represents a mandatory prerequisite for the tautomerization of

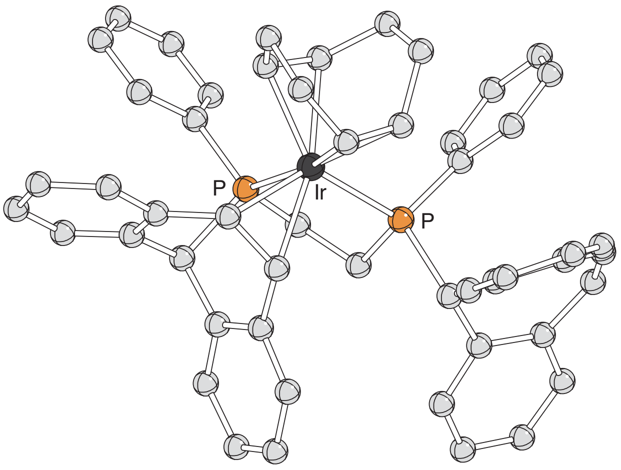
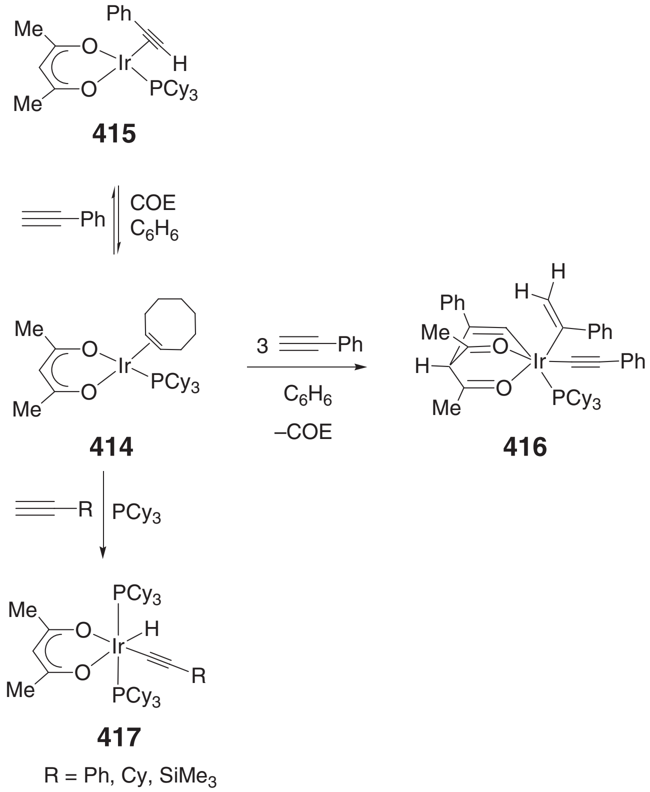


Figure 35 X-ray crystal structure of **413**.

terminal alkynes to vinylidenes.[194,194a–194d] Interesting contributions to this chemistry have been provided by Oro, Esteruelas, Werner, Chin and their coworkers. The reaction of iridium precursors with alkynes is sensible to minor modifications of the system. As an example, the acetylacetonato complex [Ir(acac)(coe)(PCy$_3$)] **414** of Esteruelas reacts reversibly with stoichiometric HC$\equiv$CPh to yield the π-adduct [Ir(acac)(π-HC$\equiv$CPh)(PCy$_3$)] **415**, while using 3 equiv. of alkyne the unusual product [Ir{κ^3-*C,O,O*-CH$=$C(Ph)CH[C(O)CH$_3$]$_2$}(C$_2$Ph)(CPh$=$CH$_2$)(PCy$_3$)] **416** is obtained. Finally, in the presence of PCy$_3$, the C–H activation product, [Ir(acac)H(C$_2$Ph)(PCy$_3$)$_2$] **417**, is generated (Scheme 46).



Scheme 46

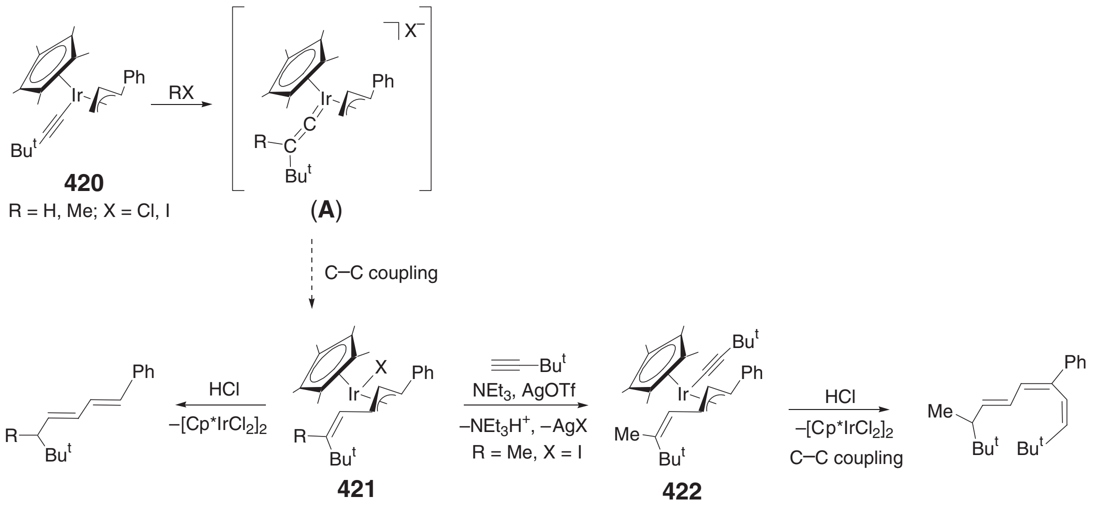
Iridium alkynyl complexes are involved in the catalytic hydrosilylation of alkenes.[179,194,195,195a,195b] Esteruelas *et al.* showed that alkynyl complexes such as $\mathrm{Ir(C{\equiv}CPh)(CO)_2(PCy_3)}$ **418a** and $\mathrm{Ir(C{\equiv}CPh)(TFB)(PCy_3)}$ **418b** catalyze the addition of $\mathrm{HSiEt_3}$ to phenylacetylene to give the products $\mathrm{PhCH{=}CH_2}$, $\mathrm{PhC{\equiv}CSiEt_3}$, resulting from the dehydrogenative silylation of the acetylenic bond and the products, *cis*-$\mathrm{PhCH{=}CH(SiEt_3)}$, *trans*-$\mathrm{PhCH{=}CH(SiEt_3)}$, and $\mathrm{Ph(SiEt_3)C{=}CH_2}$ resulting from *syn*-, *anti*-, and α-addition of silane to $\mathrm{HC{\equiv}CPh}$.[195a] The *anti*-addition of $\mathrm{HSiEt_3}$ to phenylacetylene is also catalyzed by $\mathrm{[Ir(acac)H(SiR_3)(PCy_3)]}$ ($\mathrm{SiR_3 = SiEt_3, SiPh_3, SiHPh_2}$; **419**).[194]

The rich C–C bond formation chemistry studied by Chin and co-workers and related to the use of alkyne and alkynyl ligands has already been mentioned in the preceding section of this chapter where organoalkenyl complexes are summarized.[188,188a–188d] An account on this chemistry is available.[188c] Chin's reactions usually entail coupling between σ-alkynyl and adjacent hydrocarbyl ligands initiated by electrophiles and result in the formation of conjugated alkenes. Worthy of mention in this section are the reactions of the Ir(III) alkynyl complexes with acetylene in the presence of $\mathrm{NEt_3}$ which give the β-ammonium alkenyl derivatives featuring the $\mathrm{Ir\{CH{=}CH(NEt_3)\}}$ moiety.[188,188c,196] Similarly, complexes containing β-phosphonium[196,196a–196c] and β-arsonium[196,196a,196b] alkenyl ligands $\mathrm{Ir\{CR{=}CR(EPh_3)\}}$ (E = P, As) have been prepared. At variance with the analogous ammonium derivatives, the phosphonium alkenyl complexes do not take part in C–C bond-forming reaction between alkyl and alkenyl ligands when an adjacent hydrocarbyl group is available.[196c]

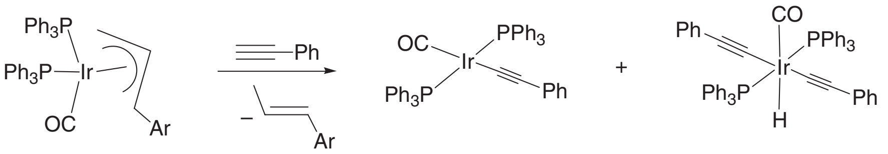
Electrophilic activation mediates the coupling between alkynyl and allyl ligands coordinated to iridium. Thus, $\mathrm{[Cp^*Ir(C{\equiv}CBu^t)\{\eta^3\text{-}CH_2CHCH(Ph)\}]}$ **420**[196a] reacts with RX (HCl or MeI) to yield the η^3-pentadienyl complex $\mathrm{[Cp^*Ir(X)\{\eta^3\text{-}Bu^t(R)C{=}CHCHCHCH(Ph)\}]}$ **421** (Scheme 47). This latter liberates quantitatively *trans*, *trans*-conjugated dienes upon reactions with aqueous HCl.[188b] Electrophilic attack at the alkynyl β-carbon likely provides a transient vinylidene **A** ready to couple with the adjacent allyl ligand favoured by $\eta^3 \rightarrow \eta^1$ slippage of the allyl ligand after $\mathrm{X^-}$ coordination to the metal. Reaction of **421** with further alkyne in the presence of $\mathrm{NEt_3}$ and AgOTf as halide scavenger affords the σ-alkynyl η^3-pentadienyl complex **422** from which after workup the 1,3,5-triene is liberated.[188b]

The 1,3-enyne $\mathrm{H_2C{=}C(CH_2R)C{\equiv}C(\textit{p}\text{-}Tol)}$ was formed together with the iridium complex $\mathrm{(Ph_3P)_2Ir(CO)(Cl)(Br)(H)}$ **423** from the reaction of $\mathrm{[Ir(\eta^1\text{-}CH_2CH{=}CHR)\{C{\equiv}C(\textit{p}\text{-}Tol)\}(CO)(PPh_3)_2]Br}$ **424** with HCl.[197] The proposed mechanism (DCl study) does not involve the expected proton attack on the $\mathrm{C_\beta}$-alkynyl, but on the γ-carbon of the η^1-alkyl group of **424**. On this basis, 1,3-enynes are produced through intramolecolar carbon–carbon coupling between β-carbon of the protonated allyl group and the β-carbon of the alkynyl group.

Iridium acyl(alkoxycarbene) complexes, $\mathrm{[Ir({=}C(OR^1)CH_3)\{(C(O)R)(\eta^2\text{-}O_2CCH_3)(PPh_3)_2]OTf}$ [R = Me, Bz **425**], were prepared by the reaction of $\mathrm{[Ir(R)(\eta^2\text{-}O_2CCH_3)(CO)(PPh_3)_2]OTf}$ [R = Me, Bz **426**] with $\mathrm{HC{\equiv}CH}$ in the presence of alcohols.[198] Acyl cycloalkoxycarbene derivatives were generated using α,ω-alkynols. In the absence of alcohols, acetylene inserts into the Ir–O acetate bond to afford vinylacetate iridacycles containing the $\mathrm{\{\text{-}C({=}CH_2)OC(CH_3)O\text{-}\}}$ ligand.



Scheme 47



427 **428** **429**

Scheme 48

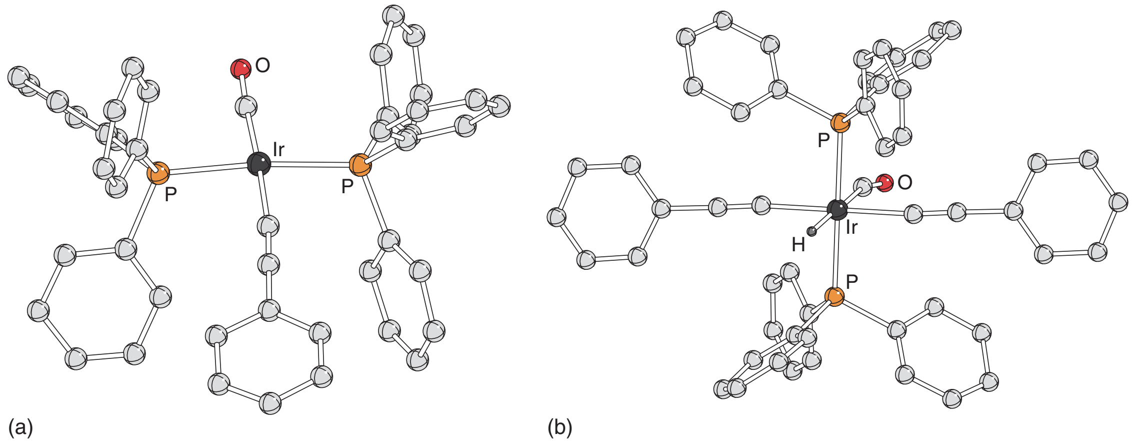


Figure 36 X-ray crystal structures of (a) 428 and (b) 429.

Ir(I) and Ir(III) alkynyls have been prepared by Osakada *et al.* by the reaction of alkynes with π-allyl complexes.[199] The reaction of HC≡CPh with the Ir(I)–π-allyl complex [Ir(CO)(PPh$_3$)$_2$(η^3-CH$_2$CHCH(Ar))] **427** gives a mixture of *trans*-[Ir(C≡CPh)(CO)(PPh$_3$)$_2$] **428** and *trans,trans*-[IrH(CO)(C≡CPh)$_2$(PPh$_3$)$_2$] **429** accompanied by the liberation of 1-Ar-1-propene (Scheme 48). The two alkynyl derivatives were authenticated by X-ray diffraction analyses which confirmed SQP and OCT geometries, respectively (Figure 36).

Half-sandwich iridium complexes of α-amino acids incorporating an alkynyl ligand, [Cp*Ir(AA)(C≡CR)] (AA = Pro, MePro; R = Ph, Bu^t, SiMe$_3$), have been prepared by the reaction of the corresponding chlorides with the alkyne in basic media (KOH).[200] The chiral at iridium complexes epimerize in CHCl$_3$ following a first-order rate law. The molecular structure of both R_{Ir},S_{C},S_{N}-[Cp*Ir(Pro)(C≡CBu^t)] **430**; Figure 37) and S_{Ir},S_{C},S_{N}-[Cp*Ir(MePro)(C≡CBu^t)] **431** have been determined by X-ray crystallography confirming the pseudo-octahedral structure with the amino acidate ligand N,O-chelated.

Coupling of two alkynes at iridium results in the formation of an iridacyclopentadiene ligand which is thought to be an intermediate in the cyclotrimerization of alkynes. As an example, Oro and co-workers described that [Ir(cod)(MeCN)(PMe$_3$)]BF$_4$ **365** easily reacts with phenylacetylene to yield first [IrH(C≡CPh)(cod)-(MeCN)(PMe$_3$)]BF$_4$ **432** and then [Ir(1,4-κ-CH=C(Ph)CH=CPh)(cod)(MeCN)(PMe$_3$)]BF$_4$ **433** which is involved in the poorly selective trimerization of the alkyne.[178] Cyclotrimerization of internal alkynes at iridium has also been reported. For example, the reaction of the butadiene complex [Tp$^{\mathrm{Me}}$Ir{η^4-CH$_2$=C(Me)C(Me)=CH$_2$}] **434**[201] with DMAD produces the iridacycloheptatriene complex [Tp$^{\mathrm{Me}}$Ir(OH$_2$)(CR=CR–CR=CR–CR=CR)] (R = CO$_2$Me **435**) containing an adventitious water molecule completing the coordination around iridium. The H$_2$O ligand is easily replaced by two-electron donors and its mobility allows for selective C-oxidation with Bu^{t}OOH at the distal C=C bond yielding [Tp$^{\mathrm{Me}}$Ir(CR=CR–CR{C(O)R}-CR=CR)] (R = CO$_2$Me **436**) with a pendant ketone functionality coordinated to the metal (Scheme 49).[202]

O'Connor *et al.* reported on the reactivity of the iridacyclopentadiene complexes [L$_2$IrCl(CR=CR–CR=CR)] (L = PPh$_3$, AsPh$_3$; R = CO$_2$Me **436**) and [(triphos)IrCl(CR=CR–CR=CR)] (R = CO$_2$Me **437**) with different alkynes.[203,203a–203d] While **436** does not afford any carbocyclic compounds by reacting with acetylenes,[203,203a,203b] the triphos complex **437** reacts with HC≡CR^1 (R^1 = Ph, Bu^t, CH$_2$CH$_2$OH, CH$_2$CH$_2$CH$_2$OH) and AgBF$_4$ to give the fulvene derivatives [(triphos)Ir{C(H)R^1=CC[C(O)OMe]=CR–CR=CR}]BF$_4$ **438** via a [2 + 2 + 1] cyclotrimerization

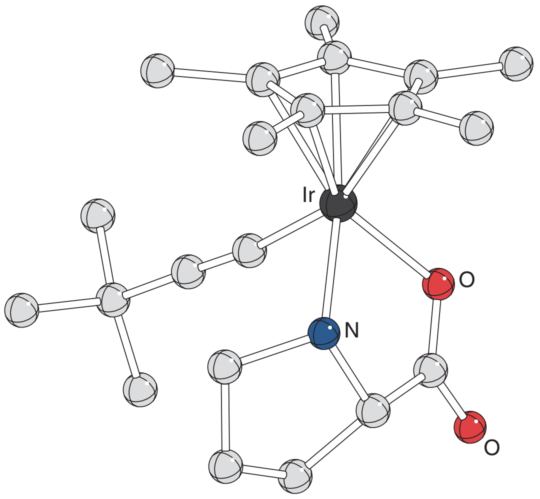
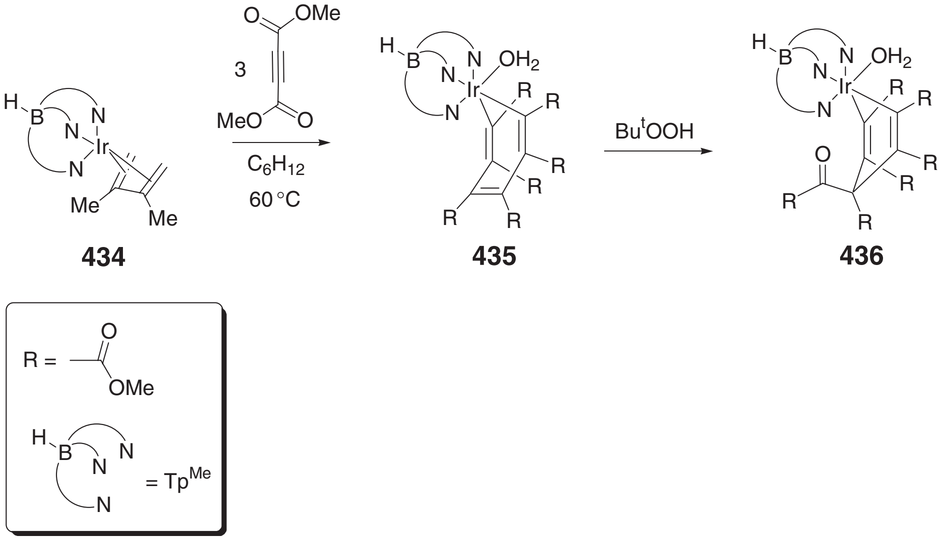


Figure 37 X-ray crystal structure of **430**.

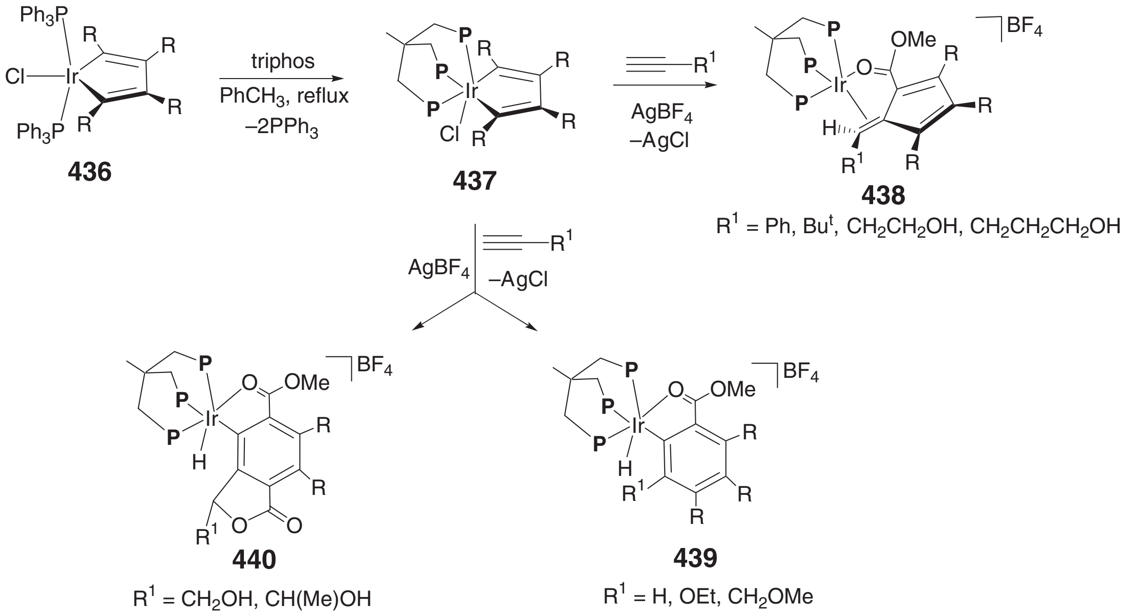


Scheme 49

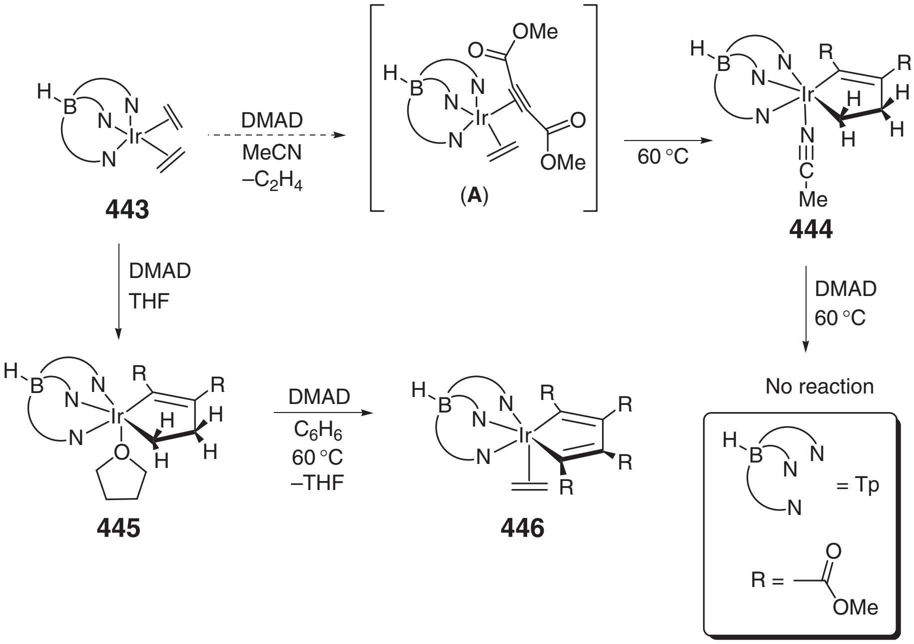
process (Scheme 50).[203c] In contrast, when the identical reaction is carried out with alkynes such as ethyne, ethyl ethynyl ether, methyl propargyl ether, propargyl alcohol, and 3-butyn-2-ol, products resulting from [2 + 2 + 2] cyclization are generated.[203d] The latter are eventually stabilized as aryl(hydrido) complexes of formula [(triphos)IrH{C$_6$R$_4$R^1}]BF$_4$ (R = CO$_2$Me; R^1 = H, OEt, CH$_2$OMe; **439**) or likely as a consequence of chelation of the ester oxygen. Strictly related to **439** are the products obtained with propargyl alcohol and 3-butyn-2-ol where a phthalidyl(hydrido) moiety **440**, resulting from transesterification of the alkynol with one of the methyl ester ring substituents, is found.

A mechanism based on the intermediate formation of an η^4-benzene complex derived from coupling of the alkyne with the iridacyclopentadiene moiety has been proposed on the basis of the isolation of [(triphos)Ir(η^4-C$_6$H$_6$)]PF$_6$ **441** from the reaction of [(triphos)IrCl(CH=CH–CH=CH)] **442** with acetylene in the presence of TIPF$_6$.[204] In O'Connor's system, it is conceivable that the pending ester function in the putative η^4-arene intermediate may drive the reaction toward the C–H activation and the formation of aryl(hydride) species **440** and **441**.[203d]

A slightly different behavior is observed when the bis(ethene) complex [TpIr(C$_2$H$_4$)$_2$] **443** is treated with DMAD in MeCN at 60 °C giving the iridacyclopent-2-ene complex [TpIr(CH$_2$CH$_2$CR=CR)(NCMe)] (R = Co$_2$Me **444**)



Scheme 50



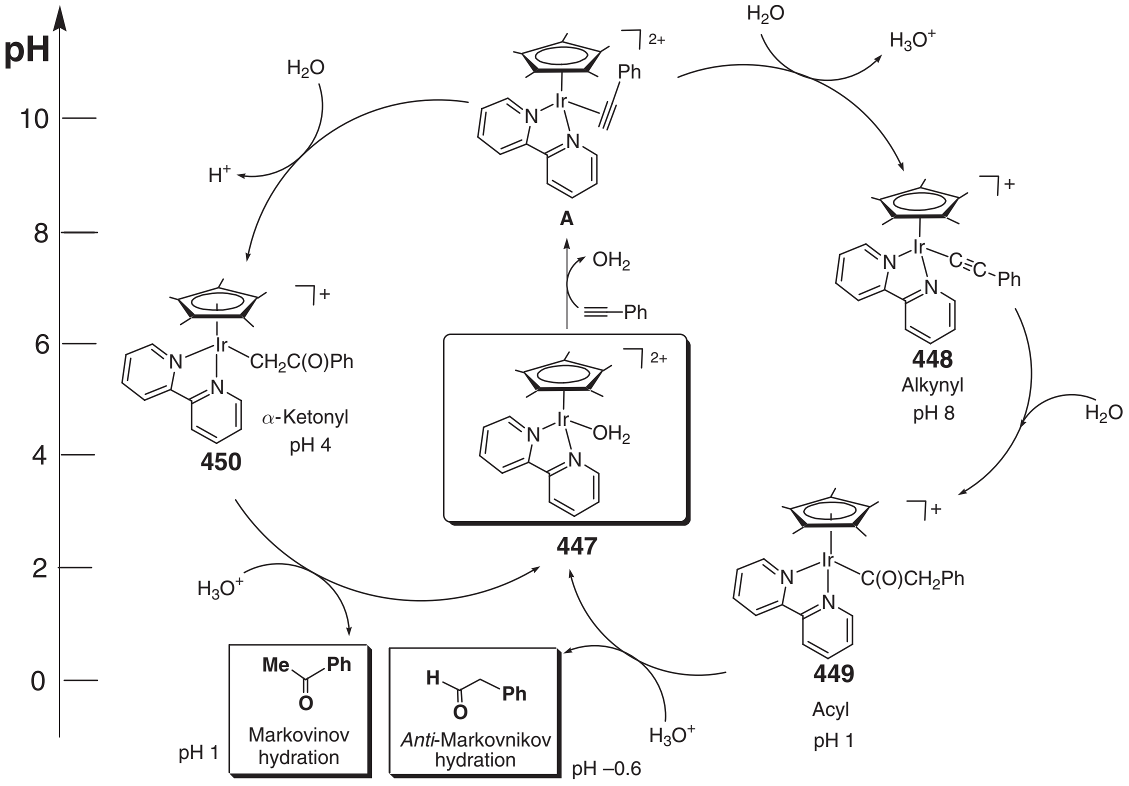
Scheme 51

(Scheme 51).[205] Following the reaction by NMR analysis suggested that **444** forms through an η^2-alkene/η^2-alkyne intermediate **A**. In THF a similar reaction occurs giving the THF-solvated iridacyclopent-2-ene complex [TpIr($CH_2CH_2CR{=}CR$)(THF)] **445**. However, at variance with **444**, heating the THF adduct in benzene to 60 °C promotes a further reaction with DMAD eventually affording the iridacyclopentadiene complex [TpIr{CR=CR–CR=CR}(η^2-$CH_2{=}CH_2$)] **446** in which a formal extrusion of ethene from the possible iridacycloheptadiene intermediate complex may be invoked.[205]

The hydration of alkynes promoted by [Cp*Ir(bpy)(H_2O)]SO_4 **447** has been studied in detail by Ogo *et al.*[206] Following the pathway expected for the anti-Markovnikov hydration, the alkynyl complex [Cp*Ir(bpy)(C≡CPh)]-OTf **448** or the acyl intermediate [Cp*Ir(bpy){C(O)CH_2Ph}]OTf **449** may be isolated from the solution depending on the pH. Structure **448** forms at pH 8.0 by reacting **447** with phenylacetylene. The alkynyl compound adds water and transforms into the hydrosoluble acyl **449** on dissolving in highly acidic solution (pH ca. 1.0). Although acyl complexes may be generated from alkynes via hydrolysis of intermediate vinylidenes,[167] in the present system no evidence for the participation of Ir vinylidenes was found. The acyl complex is chemically robust and reacts further only under extreme acidic conditions (4 M HNO_3/H_2O; pH −0.6) yielding phenylacetaldehyde and regenerating the aquo complex **447**.

Under less acidic conditions, the reaction of **447** with HC≡CPh and the subsequent hydration follows a Markovnikov-type protocol resulting, at pH 4.0, in the α-ketonyl complex [Cp*Ir(bpy)(CH_2COPh)] **450**. Hydrolysis of **450** occurs at pH 1.0 producing acetophenone in quantitative yield without any isomerization to the acyl species.

On these grounds, either Markovnikov or anti-Markovnikov catalytic hydration of phenylacetylene may be active strictly depending on the solution pH and starting from the common water-soluble iridium complex. Thus, under catalytic conditions, **447** reacts at 70 °C with phenylacetylene (100 : 1) at pH 1.0 or pH −0.6 in H_2O to give phenylacetaldehyde (*anti*-Markovnikov) and acetophenone (Markovnikov), respectively. The two possible hydration paths are summarized in Scheme 52.[206] Key points are the formation of the putative complex [Cp*Ir(bpy)(π-HC≡CPh)]$^{2+}$ **A** from which the alkynyl complex **448** forms via deprotonation at about pH 8 (right-hand cycle in the scheme) and the competitive pathway (left-hand cycle) in which nucleophilic attack of OH^- to **A** gives the ketonyl complex **450** in a pH range of about 2–6. At pH 1–2 the anti-Markovnikov path goes ahead with addition of H_2O to **448**, leading to the acyl complex **449**. Protonation of **449** and **450** gives phenylacetaldehyde (anti-Markovnikov hydration) and acetophenone (Markovnikov hydration), respectively.



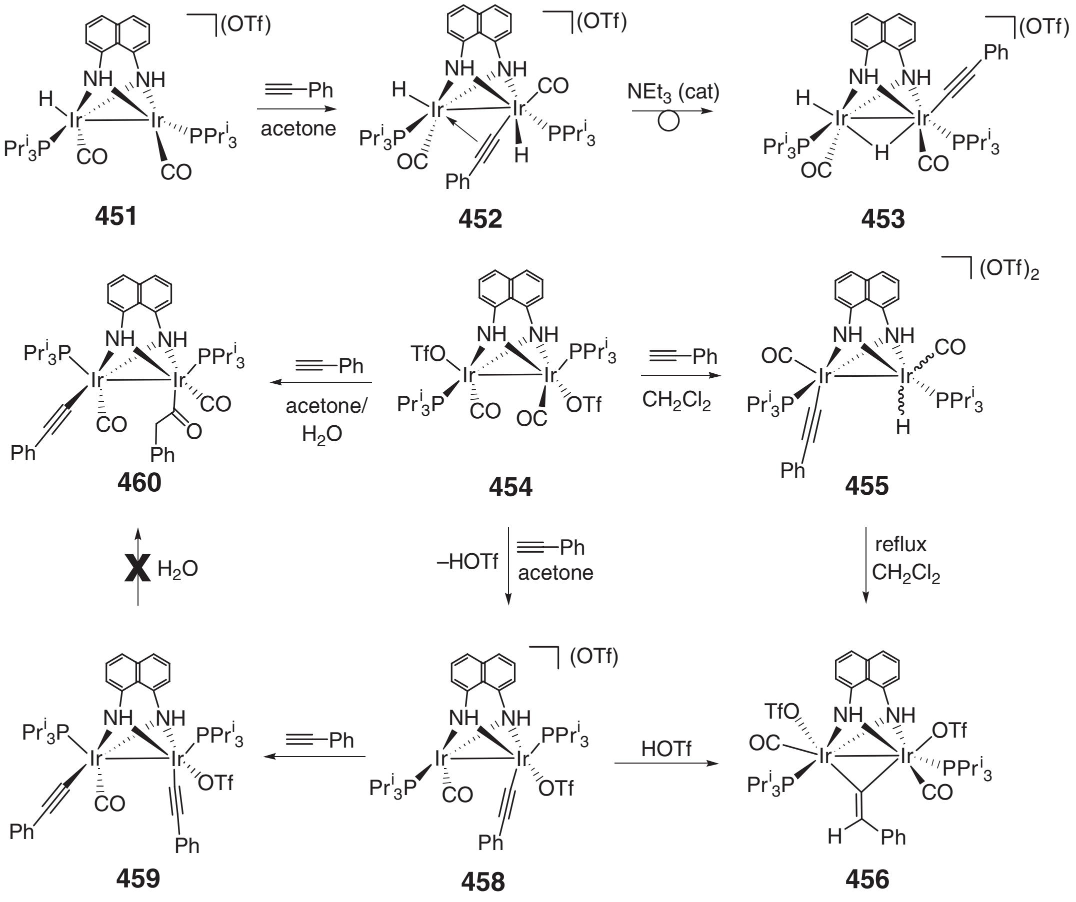
Catalytic hydration of alkynes

Scheme 52

7.04.3.3.2 Dinuclear iridium alkynyl complexes

The oxidative addition of terminal alkynes to diamidonaphthalene-bridged diiridium complexes has been studied by Oro and co-workers.[207] The system investigated shows a complex reactivity where several products may be identified or isolated with a variety of hydrocarbyl ligands such as alkynyl, bisalkynyl, hydrido(alkynyl), vinylidenes, and acyls. In summary, the monohydrido diiridium complex $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2\text{naphth}\}H(CO)_2(PPr^i_3)_2]OTf$ **451** reacts with $HC{\equiv}CPh$ to yield dihydridoalkynyl complex $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2\text{naphth}\}(\mu\text{-}C{\equiv}CPh)H_2(CO)_2(PPr^i_3)_2]OTf$ **452**, in which the alkynyl ligand bridges the two iridium centers in a $\mu,\eta^{1:2}$-coordination mode. Structure **452** is a kinetic product, which on standing in acetone isomerizes to the μ-hydrido complex $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2\text{naphth}\}(\mu\text{-}H)H(C{\equiv}CPh)(CO)_2(PPr^i_3)_2]OTf$ **453** over several days (Scheme 53). Addition of a catalytic amount of NEt_3 completes the transformation of **453** into **454** within 1 h suggesting that the isomerization takes place via an undetected deprotonated intermediate. Addition of phenylacetylene to the bisiridium(II) complex $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2\text{naphth}\}(\eta^1\text{-}O\text{-}OTf)_2(CO)_2(PPr^i_3)_2]$ **454** gives different kinetic products depending on the reaction solvent. In dichloromethane, the diiridium(III) hydrido(alkynyl) complex $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2\text{naphth}\}H(C{\equiv}CPh)(CO)_2(PPr^i_3)_2](OTf)_2$ **455** is first obtained which thermally isomerizes to the neutral vinylidene-bridged complex $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2\text{naphth}\}(\mu\text{-}C{=}CHPh)(\eta^1\text{-}O\text{-}OTf)_2(CO)_2(PPr^i_3)_2]$ **456**. The X-ray determination of **456** shown in Figure 38 features, apart from the bridging phenylvinylidene unit, two coordinated triflate ligands. These are easily replaceable by other σ-donor ligands such as acetonitrile giving the dicationic bridging vinylidene $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2\text{naphth}\}(\mu\text{-}C{=}CHPh)(MeCN)_2(CO)_2(PPr^i_3)_2](OTf)_2$ **457**.[207]

A different reaction occurs by reacting **454** with phenylacetylene in acetone, affording the deprotonated complex $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2\text{naphth}\}(C{\equiv}CPh)(CO)_2(PPr^i_3)_2]OTf$ **458**. The latter can be protonated to give **456**, but can also react with excess of phenylacetylene to give the neutral diiridium(II) compound $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2\text{naphth}\}(C{\equiv}CPh)_2(CO)_2(PPr^i_3)_2]$



Scheme 53

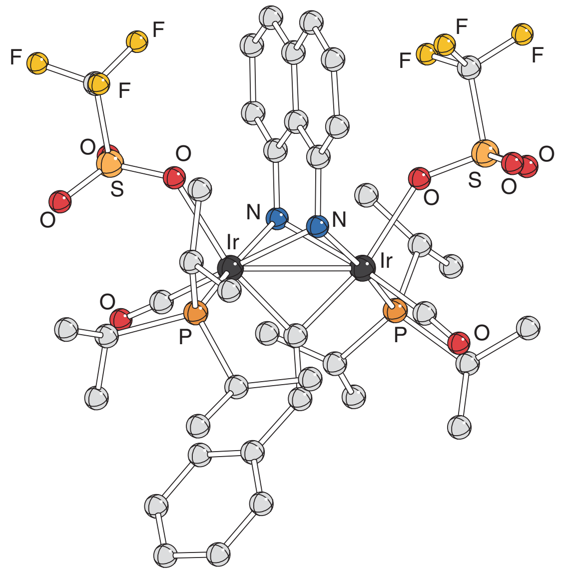


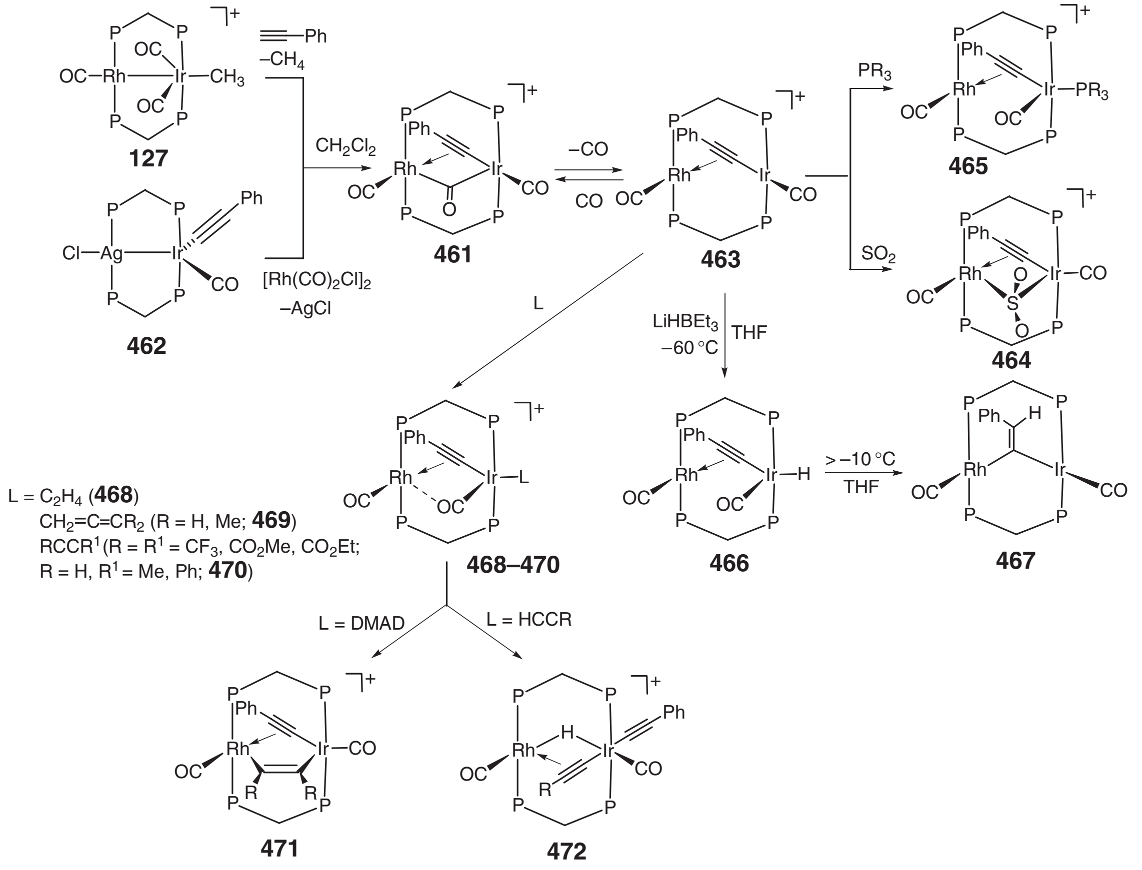
Figure 38 X-ray crystal structure of **456**.

459 which is the thermodynamic product of the reaction in this solvent.[207] Direct alkynylation of **454** with excess of LiC≡CPh in toluene also affords the dialkynyl complex. Finally, partial hydration of the alkyne is observed when the same reaction is performed in wet acetone to yield the dinuclear acyl(alkynyl) diiridium(II) complex $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2naphth\}(C{\equiv}CPh)\{C(O)CH_2Ph\}(CO)_2(PPr^i{}_3)_2]$ **460** as the major reaction product.

Among dinuclear alkynyl iridium complexes is worth mentioning the detailed studies by Cowie and co-workers who investigated the reactivity of the "A-frame" heterodinuclear acetylide compound $[RhIr(CO)_2(\mu\text{-}\eta^{1:2}\text{-}C{\equiv}CPh)(\mu\text{-}CO)(dppm)_2]OTf$ **461**.[208,208a,208b]

Complex **461**, which contains a bridging acetylide group σ-bonded to iridium and π-coordinating to rhodium similar to that described in **452**, was conveniently prepared by transmetallation of the known dimer $[IrAgCl(CO)(C{\equiv}CPh)(dppm)_2]$[209] **462** with either $[Rh(CO)_2Cl]_2$ or $[Rh(cod)Cl]_2$,[208] or directly from the alkyl complex $[RhIrMe(CO)_3(dppm)_2]OTf$ **127**[208a] with phenylacetylene (Scheme 54).[210]

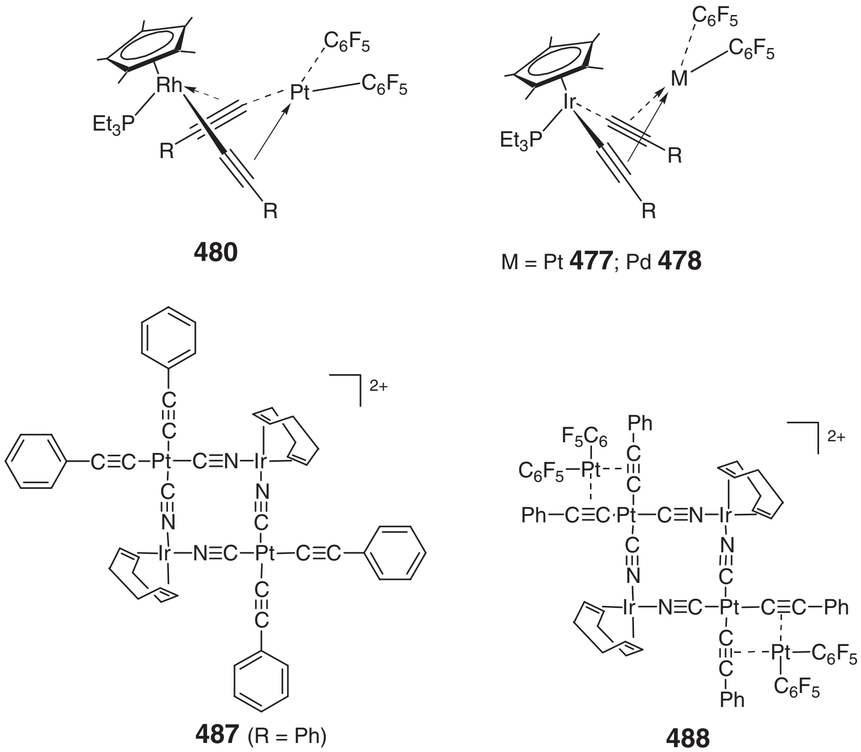
One of the CO ligand is labile and the complex $[RhIr(CO)_2(\mu\text{-}\eta^{1:2}\text{-}C{\equiv}CPh)(dppm)_2]OTf$ **463** is readily generated in refluxing CH_2Cl_2/THF.[208] Apart from CO, restoring **461**, complex **463** easily reacts with SO_2 and tertiary phosphines yielding $[RhIr(CO)_2(\mu\text{-}\eta^{1:2}\text{-}C{\equiv}CPh)(\mu\text{-}SO_2)(dppm)_2]OTf$ **464** and $[RhIr(CO)_2(PR_3)(\mu\text{-}\eta^{1:2}\text{-}C{\equiv}CPh)\text{-}(dppm)_2]OTf$ ($PR_3 = PMe_3$, PMe_2Ph; **465**), respectively. Steric and electronic arguments suggest external attack of the nucleophile to the iridium center and this was proved by reaction with ^{12}CO in enriched ^{13}CO-**462** by LT NMR studies. Hydride attack from $LiBEt_3H$ takes place at iridium (−60 °C) yielding $[RhIr(H)(CO)_2(\mu\text{-}\eta^{1:2}\text{-}C{\equiv}CPh)(dppm)_2]$ **466** which, on warming to RT, rearranges to the bridging vinylidene complex $[RhIr(H)(CO)_2\{\mu\text{-}C{=}C(H)Ph\}(dppm)_2]$ **467**. The rearrangement takes place through isomerization with coordination exchange between H and CO. Allenes, alkenes, and alkynes may also add to **463** yielding simple adducts $[RhIr(L)(CO)_2(\mu\text{-}\eta^{1:2}\text{-}C{\equiv}CPh)(dppm)_2]OTf$ ($L = C_2H_4$ **468**, $CH_2{=}C{=}CR_2$ ($R = H$, Me; **469**), $RC{\equiv}CR$ ($R = CF_3$, CO_2Me, CO_2Et, etc. **470**) which exhibit different stabilities. In a few cases, compounds stable enough to be isolated at room temperature have been obtained. The singular behavior of $[RhIr(DMAD)(CO)_2(\mu\text{-}\eta^{1:2}\text{-}C{\equiv}CPh)(dppm)_2]OTf$ ($R = CO_2Me$ **470**) is worth pointing out, which in solution converts to complex $[RhIr(CO)_2(\mu\text{-}\eta^{1:1}\text{-}DMAD)(\mu\text{-}\eta^{1:2}\text{-}C{\equiv}CPh)(dppm)_2]OTf$ **471**, having the DMAD ligand bridging the two metals in a parallel fashion. H_2 and terminal alkynes add oxidatively to **463** to afford the dihydride $[RhIr(H)(CO)_2(\mu\text{-}\eta^{1:2}\text{-}C{\equiv}CPh)(\mu\text{-}H)(dppm)_2]OTf$ **472** and the dialkynyl complexes $[RhIr(C{\equiv}CR)(CO)_2(\mu\text{-}\eta^{1:2}\text{-}C{\equiv}CPh)(\mu\text{-}H)(dppm)_2]OTf$ ($R = Me$, Ph; **473**). These are produced via unstable π-adducts similar to **470**. In the case of propynyl adduct ($R = Me$), site exchange between terminal and bridging position of the two alkynyl ligands has been observed. The reactivity of **462** with CS_2 and isothiocyanates[208b] has also been reported and a specific paper has been devoted to investigate the chemistry of this intriguing compound with electrophiles.[208a] Remarkably, protic acids HX ($X = BF_4$, OTf) yield the oxidative



Scheme 54

addition products [RhIr(X)(CO)$_2$(μ-H)(μ-C≡Ph)(dppm)$_2$]X **474**. Under CO, displacement of the weakly coordinating triflates and subsequent conversion to the vinylidene-bridged [RhIr(CO)$_4${μ-C=C(H)Ph}(dppm)$_2$]X$_2$ **475** occurs.

Forniés and co-workers reported a rich chemistry centered on polynuclear alkynyl complexes containing iridium. The seminal work on this chemistry deals with the double alkynyl transfer from *cis*-[Pt(C$_6$F$_5$)$_2$(C≡CPh)$_2$] to [Cp*Ir(PEt$_3$)(acetone)$_2$](ClO$_4$)$_2$ **476** yielding the Ir(III)–Pt(II) tweezer complex [Cp*Ir(PEt$_3$)(μ,σ/π-C≡CR)$_2${Pt(C$_6$F$_5$)$_2$}] (R = Ph, Bu^t, SiMe$_3$; **477**) in which the alkynyl groups are σ-bonded to the Ir center and π-bonded to the Pt one (Scheme 55).[211] The analogous palladium derivative [Cp*Ir(PEt$_3$)(μ,σ/π-C≡CR)$_2${Pd(C$_6$F$_5$)$_2$}] **478** was also described.[212] The reaction of the bis(alkynyl) compounds [Cp*Ir(PEt$_3$)(C≡CR)$_2$] **479** with [M(C$_6$F$_5$)$_2$(THF)$_2$] (M = Pd, Pt) yields the same σ/π-dimetallic species. Noticeably, a different bonding arrangement of the alkynyl groups has been found for the analogous rhodium/platinum complex [Cp*Rh(PEt$_3$)(μ,σ/π-C≡CR)$_2${Pt(C$_6$F$_5$)$_2$}] **480** and has been ascribed to the stronger M–C bonds with a third row transition element than for a second row metal (Scheme 55).[212] Heterobimetallic alkynyl(halide)[212] and alkynyl(phosphinite)[213] platinum–iridium complexes have also been reported. The polyalkynylated dinuclear species [Cp*Ir(PEt$_3$)(μ-C≡CR)$_2${Pt(C≡CR)$_2$}] **481** has been prepared via double alkynylation of **476** with the tetrakis(alkynyl)platinate anions [Pt(C≡CR)$_4$]$^{2-}$ **482**. The solid-state structure indicates that the *cis*-Pt(C≡CR)$_2$ moiety is unusually stabilized by η^2-bis(alkyne) interactions originating from the {Cp*Ir(PEt$_3$)(μ-C≡CR)$_2$} moiety.[214] The use of [Ir(cod)Cl]$_2$ as synthon of {Ir(cod)} units allows the synthesis of the complex anion [{(cod)Ir(μ,σ/π—C≡CSiMe$_3$)$_2$}{Pt(C≡CR)$_2$}]$^-$ **483** which may be used as building block for heterotrimetallic compounds via η^2-coordination of the terminal alkynyl ligands to M(C$_6$F$_5$)$_2$ (M = Pd, Pt), Rh(cod), and Pd(allyl) units.[215] Similarly, the reaction of **483** with a stoichiometric amount of AgClO$_4$ yields an unusual hexanuclear trimetallic Ir$_2$Pt$_2$Ag$_2$ complex, [({(cod)Ir(μ,σ/π-C≡CSiMe$_3$)$_2$}{Pt(C≡CR)$_2$})$_2$Ag$_2$] **484**, in which two silver cations hold together two distinct heterobimetallic diynyl anions [(cod)Ir(μ,σ/π-C≡CSiMe$_3$)$_2${Pt(C≡CR)$_2$}]$^-$.[215] The reaction of [Cp*Ir(PEt$_3$)(μ-Cl)$_2${M(C$_6$F$_5$)$_2$}] (M = Pd, Pt; **485**) with polymetallic acetylides as alkynylating agents [M′(C≡CR)]$_n$ (M′ = Cu, Ag) affords tetranuclear IrM′$_2$M compounds where the two bridging coinage-metal cations support a bonding mode similar to



480

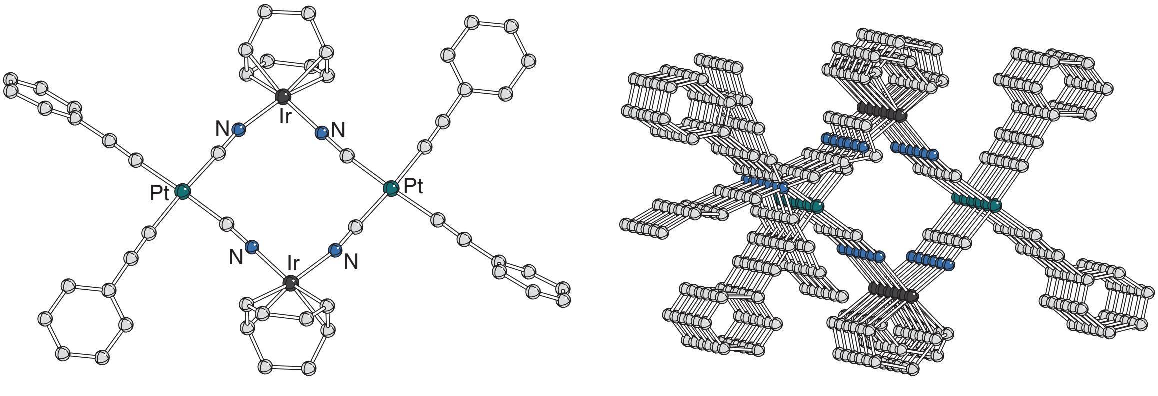
M = Pt **477**; Pd **478**

487 (R = Ph)

488

Scheme 55

that found in **484**.[216] Different anionic supramolecular assemblies have been constructed by replacing **482** with *cis*-$[Pt(CN)_2(C{\equiv}CR)_2]^{2-}$ (R = Ph, Bu^t; **486**).[217] Due to the presence of the cyanide ligands, self-assembling of **486** with $[Ir(cod)(solvate)_2]^+$ affords the heterotetrametallic Ir_2Pt_2 molecular square $(NBu_4)_2$[*cyclo*-{*cis*-Pt(C≡CR)$_2$(μ-CN)$_2$}{Ir(cod)}$_2$] (R = Bu^t, Ph; **487**) containing terminal alkynyl ligands and bridging cyanide units. A nice view of the molecular structure of **487** is shown in Figure 39 showing also the packing diagram with the perfect stacking of the tetrametallic squares. The terminal acetylides may be used to carry out further structural elaborations easily; hexanuclear species $(NBu_4)_2$[{$(C_6F_5)_2$Pt(μ-C≡CPh)$_2$(μ-CN)$_2$}$_2${Ir(cod)}$_2$] **488** were easily formed by simply treating **487** with 2 equiv. of *cis*-[Pt$(C_6F_5)_2$(THF)$_2$] (Scheme 55).



(a)

(b)

Figure 39 (a) Structure of the dianion of **487** and (b) packing diagram of cation with anion showing the stacking arrangement of the tetrametallic core resulting in an infinite channel.

7.04.3.4 Iridium Clusters Involving Alkenyl, Alkynyl, and Related Ligands

The chemistry of homonuclear and heteronuclear iridium cluster compounds has been of enduring interest after the publication of a specific chapter in COMC(1995) highlighting the acetylene chemistry of $Ir_4(CO)_{12}$ **232**.[218] The hydridic anion $[HIr_4(CO)_{11}]^-$ **489** is much more reactive than the homoleptic parent cluster **232** and its reaction with PhC≡CPh affords the end-on alkenyl cluster $[Ir_4(CO)_{11}(CPh{=}CHPh)]^-$ **490** containing an end-on alkenyl ligand via formal insertion of the alkyne across the Ir–H bond.[219] Organometallic clusters derived from the hexanuclear carbonyl $Ir_6(CO)_{16}$ **233** have also been reported. As an example, $[Ir_6(CO)_{15}(CO_2Me)]^-$ **491** and $[Ir_6(CO)_{14}(CO_2Me)_2]^{2-}$ **492** were straightforwardly prepared by treating **489** with NaOMe in MeOH and isolated as PPN salts.[219]

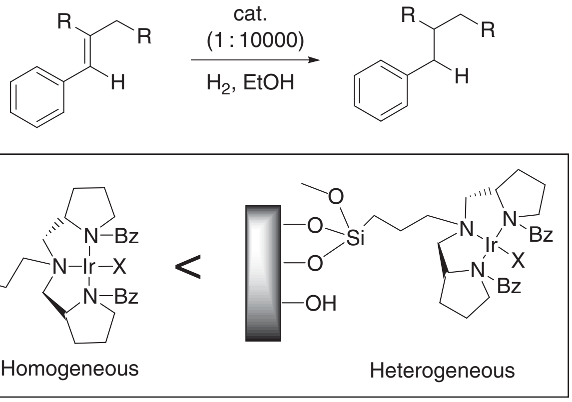
The reaction of W_2Ir_2 and WIr_3 clusters with terminal alkynes affords novel compounds featuring a μ_4-η^2-HCCR unit.[220] The reaction proceeds also by replacing simple alkynes with tungsten acetylide complexes in which an L_nW–C≡CR plays the role of a terminal alkyne.[220] The formation of C_4 units via alkyne coupling or, conversely, the cleavage of the C≡C triple bonds to give μ_x-CR fragments are feasible processes during the thermal reaction of Ir_xM_y clusters ($M = Mo, W$; $x + y = 4$).[221]

The hexametallic complex $[Ir_2Cu_4(C{\equiv}CR)_8(PPh_3)_2]$ **493** has been synthesized and characterized by X-ray diffractometry. The network of relatively short intermetallic Ir···Cu distances suggests that this compound may be better represented as a hexanuclear cluster rather than two separated $[Ir(C{\equiv}CR)_4(PPh_3)_2]^{2-}$ anions held together by four Cu^+ monocations.[222]

Supported metal clusters consisting of four iridium atoms have been proved capable of hydrogenating alkenes with efficiency and selectivity depending on the nature of the oxide support. Hydrocarbon fragments, such as propylidyne, and hydride ligands, deriving from the fragmentation of propene and H_2, have been identified and their relevance in the heterogenized process has been discussed.[223]

7.04.3.5 Iridium Complexes in C–C Bond-forming Catalysis

Organoiridium complexes have a central role in the development of homogeneous catalytic processes. Following the report by Crabtree, which shows that cationic Ir(I) complexes are efficient to catalyze alkene hydrogenation,[224] many advancements have been made in the use of iridium complexes as hydrogenation catalysts,[225,226,226a–226c,227,227a–227d] including their application to the transfer hydrogenation of carbonyl compounds,[228,228a–228d] quinolines,[229] and other substrates.[230,230a–230e] A variety of Cp*Ir complexes have been used as hydrogen transfer catalysts. Apart from isopropanol, the successful use of formic acid and formates as HT agents has been demonstrated.[228a–228c] The catalytic efficiency for alkene hydrogenation by iridium complexes stabilized by chiral triaza ligands has been studied by Corma and co-workers.[231] In this work, a careful comparison between homogeneous and heterogeneous conditions (with the complex heterogenized onto a mesoporous material) has been carried out (Scheme 56). The absence of metal leaching, the easy recovering and reusing as well as the higher general performance make the heterogenized catalyst more efficient than the homogenous ones.[231] Water-soluble iridium complexes, such as *trans*-$[IrCl(CO)(TPPMS)_2]$ **6**, have been prepared by Joó and co-workers and successfully used for the hydrogenation of olefinic double bonds in short-chain unsaturated acids in aqueous solution. The method has been applied to the



Scheme 56

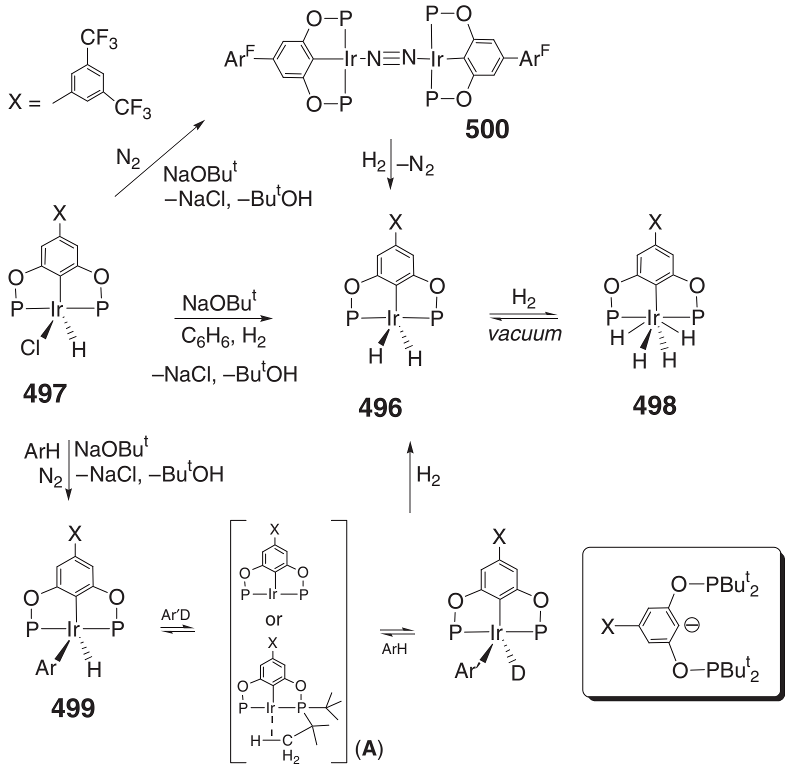
hydrogenation of fatty acids.[5] The tris-aquo complex $[Cp^*Ir(H_2O)_3]^{2+}$ **494** is a catalyst precursor for acidic aqueous hydrogenation of both carbonyl derivatives and alkenes under H_2.[232]

Pincer complexes, such as $(PCP)IrH_2$ **328** [PCP $= \eta^3$-2,6-$(Bu^t{}_2PCH_2)_2C_6H_3$], have been used as efficient and robust catalysts for the dehydrogenation of alkanes,[233,233a–233d] and other substrates such as alkyl arenes,[233c] ethers,[233c] alcohols,[71] secondary[234] and tertiary amines.[234a] η^2-Alkene coordination in pincer-type complexes has been also demonstrated.[235] A chiral version of PCP ligands has been prepared,[236] and its iridium complex *R,R*-$IrH_4\{C_6H_3$-2,6-$(CH_2P^*PhBu^t)_2\}$ **495** used for the transfer dehydrogenation of COA to COE in the presence of TBE. The TONs are however similar to those found with **328**.[233,233a–233d] Bis(phosphinite) pincer-type iridium complexes, (*p*-XPCP)IrH_2 **496**, have been prepared by Brookhart and co-workers via dehydrochlorination of (*p*-XPCP)IrHCl **497** with $NaOBu^t$ in benzene in the presence of hydrogen [X = H, Me, MeO, F, C_6F_5, 3,5-bis(trifluoromethyl)phenyl (Ar^F)] (Scheme 57).[237,237a] The reaction yielded the dihydrides **496** in mixture with the unstable tetrahydrides [(*p*-XPCP)IrH_4] **498**. However, vacuum sublimation at 0 °C and extraction with *n*-pentane left the pure dihydrides, which were active for the catalytic transfer dehydrogenation of COA with TBE.

In the absence of H_2, C–H activation of the aromatic solvent takes place yielding highly fluxional [(*p*-XPCP)Ir(Ar)H] **499** which gives the dihydride after reaction with H_2. The rapid exchange with free arene in **499** follows a zero-order kinetic in arene, implying a dissociative exchange mechanism, which suggests the formation of 14e or agostic intermediate to account for the exchange process **A**. For X = Ar^F the reaction with $NaOBu^t$ in toluene under N_2 affords the catalytically inactive μ-N_2 species [{(*p*-Ar^FPCP)Ir}$_2$(μ-N_2)] **500** which was characterized by X-ray diffraction (Figure 40).[237] Similar compounds with a bridging $\mu,\eta^{1:1}$-N_2 ligand were also obtained for classical PCP systems.[238] Mechanistic studies of the transfer dehydrogenation of COA catalyzed by iridium(*p*-XPCP)Ir complexes were also reported.[239]

Iridium-catalyzed hydrogenation of alkynes,[38] hydrosilylation of alkenes,[195,240] and hydroboration of alkenes[241] and alkynes[242] have also been reported. Iridium complexes have been frequently used as model compounds to get insights into the mechanism of rhodium-catalyzed reactions,[243] but it is not rare that iridium catalysts work better than rhodium ones.[228b,244]

Comparatively less attention has been addressed to the use of Ir complexes as catalysts to bring about C–C bond-forming reactions. Nevertheless, this area has emerged during the last 15 years and nowadays iridium catalysts have



Scheme 57

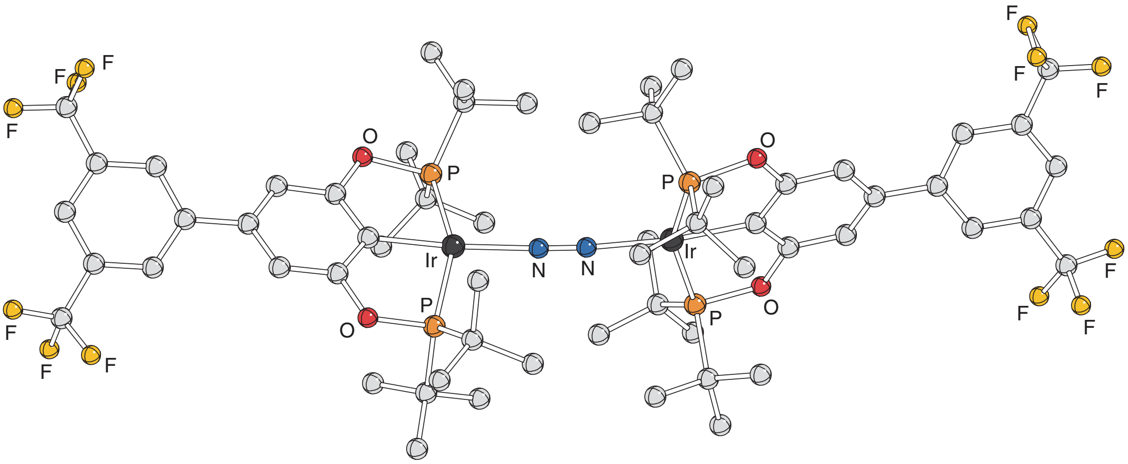


Figure 40 X-ray crystal structure of 500.

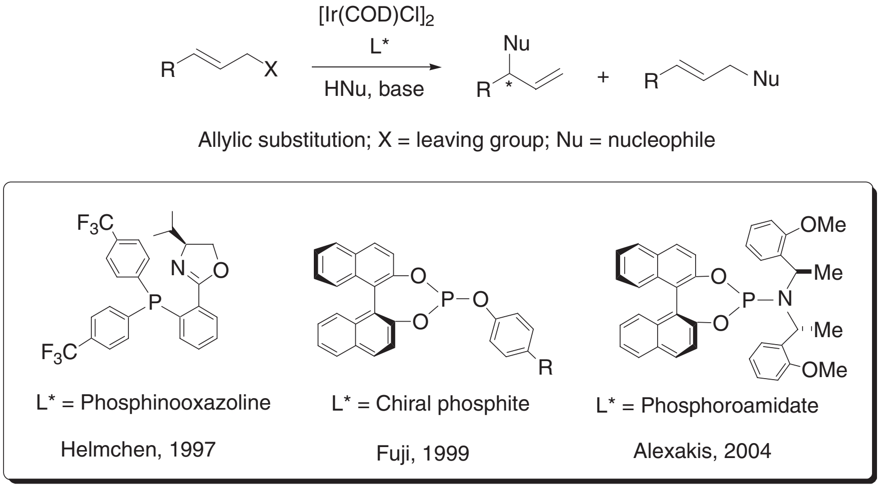
an important role to complement the use of other organometallic catalysts, particularly those of palladium and ruthenium, in promoting efficient catalyzed organic synthesis.

Simple iridium salts and complexes including $[IrCl(coe)_2I]_2$, $[Ir(cod)Cl]_2$, $[Ir(CO)_3Cl]$, $[Ir(acac)Cl]_2$, $[Ir(cod)_2]BF_4$, $[\{Cp^*IrCl_2\}]_2$ and $IrCl_3$, either alone or in the presence of *in situ* added mono- and bidentate phosphines, phosphites, or other mono- or bidentate ligands, have been successfully used to carry out numerous catalytic processes resulting in the formation of C–C bonds. Examples are formation of vinyl ethers via exchange from vinylacetates and alcohols,[245] synthesis of enol and vinyl esters from terminal alkynes and carboxylic acids,[246] alkene hydroarylation,[169] alkene oligomerization and polymerization,[56,58] alkyne dimerization[247] and cyclotrimerization,[248,248a] Heck-type reactions,[249] addition of nitriles to C–C triple bonds,[250] alkylation of ketones with alcohols,[251] Michael coupling[252] and Mukaiyama-type aldol coupling,[253] cyclization of aryl vinyl or divinyl ketones (Nazarov cyclization),[156] oxidative cyclization of alkene–amide substrates,[254] carbonylative [5 + 1] cycloadditions,[255] and catalytic carbonylation of different substrates.[77,256,256a] These include alcohols,[77] N-heterocycles such as isoxazolidines,[256] or allylic esters and phosphates.[256a]

Detailed mechanistic and theoretical analysis of the key mechanistic steps of the Cativa process, for the Cativa process See Ref: 257,257a that is, the iridium-based catalytic carbonylation of methanol to acetic acid, have allowed several groups,[258,258a–258c,72d,e] particularly Haynes and co-workers, to unravel the mechanism of the catalytic process.[259] Ir(I) complexes [Ir(CO)(L–L)I] (LL = dppms, dppe, dppmo) provided important mechanistic information about the influence of stereoelectronic ligand effects on the organometallic reactivity of modified metal centers with MeI.[61] The carbonylation of methanol promoted by iridium and rhodium complexes which is at the basis of both Cativa and Monsanto processes for the synthesis of acetic acid will be described in detail in a different chapter of this volume.

A significant contribution to the use of iridium precursors for allylic alkylations[260] has been provided by Takeuchi and co-workers, who demonstrated how the selectivity achieved by using iridium catalysts complements that obtained with palladium complexes.[261,261a–261f] Fast combinatorial colorimetric screening has been used to individuate Ir(I) catalysts active for the allylic substitution reaction.[262] Fundamental advancements in this field were achieved by Helmchen and co-workers who obtained high regio- and enantioselectivity in asymmetric allylic alkylations of achiral or racemic substrates with chiral phosphinooxazolines[263] and phosphoramidites[264,264a–264c] as ligands (Scheme 58). Further examples of enantioselective allylic substitutions are known.[265,265a] Allylic amination[266,266a–266e] and etherification[267,267a] are promoted by iridium catalysts. High regio- and enantioselectivities (up to 98%) have been obtained by Alexakis and co-workers in the allylic amination of cynnamyl carbonate by using a highly efficient phosphoramidate co-ligand based on a binaphthol unit.[268,268a] Similarly, Hartwig *et al.* obtained branched chiral allylic ethers in high yields and excellent enatioselectivities from inexpensive achiral allylic carbonates and phenoxides using 2% iridium phosphoramidite complex as catalyst generated *in situ*.[267] The iridium-catalyzed asymmetric synthesis of different amino acids has been reported, by using the allylic amination method.[269,269a] Chiral resolution of allylic carbonates (ee up 98%) has been obtained using iridium complexes containing chiral dienes conveniently prepared from readily available and inexpensive (*R*)- or (*S*)-carvone.[267a]

Ir(III)-π-allyl complexes have been postulated as key intermediates in these catalytic processes. Complexes of this type, that is, $[(PHOX)IrX_2(\pi\text{-}CH_2CHCHPh)]$ (X = Cl, Br; **501**), have been independently synthesized and



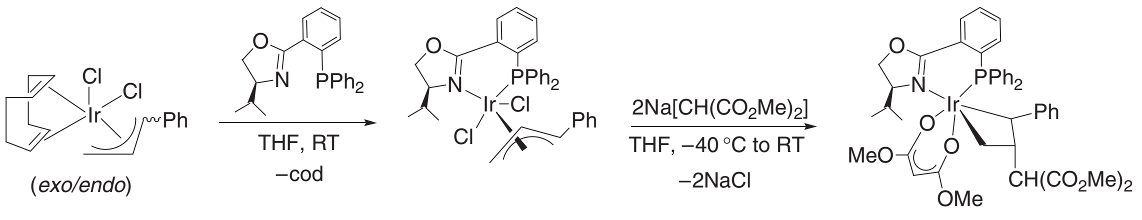
Scheme 58

characterized by Helmchen *et al.* by using a chiral auxiliary bidentate phoshinooxazoline ligand.[270] In contrast to the putative allylic substitution pathway, sodium dimethyl malonate does not react at the terminus of the π-allyl ligand, but at the central carbon yielding an iridacyclobutane species. These reactions are illustrated in Scheme 59 while the X-ray structure of the iridacyclobutane complex $[(PHOX)Ir\{\kappa^2\text{-}O,O\text{-}[CH(CO_2Me)_2]\}\{exo\text{-}CH_2CH[CH(CO_2Me)_2](CHPh)]\}$ **502** is presented in Figure 41.

Propargylic substitution has been reported by Matsuda *et al.* Propargylic-type acetates react at RT with enoxysilanes to give β-alkynyl ketones in high yields.[271] The reaction is catalyzed by $[Ir(cod)\{P(OPh)_3\}_2]OTf$ **503** preliminarily activated with H_2. Substitution at the propargyl carbon proceeds selectively in most types of propargylic esters, but depends on the propargylic substituents. In fact, the reverse selectivity leading to the alternative formation of allenyl products is predominant for esters bearing two aryl groups on the propargyl carbon. Scheme 60 illustrates this intriguing process.

Propargylic amines may be prepared using Ir(I) catalysts. Carreria and Fischer described the use of $[Ir(cod)Cl]_2$ to catalyze the coupling of aldimines and silylalkynes [272,272a] while Ishii and co-workers extended the scope of this reaction showing that coupling of aldehydes, amines, and $Me_3SiC{\equiv}CH$ may yield 1 : 1 : 1 or 1 : 2 : 2 coupling products depending on the amine.[273] The three component coupling using alkylalkynes (l-octyne) was also reported.[274]

Iridium catalysts find many applications in asymmetric catalysis. Apart from enantioselective allylic substitution which has been highlighted above, a variety of enantioselective processes have found advantages by the introduction of chiral iridium catalysts. These include the enantioselective hydroformilation of prochiral alkenes,[275] the asymmetric hydroarylation of norbornene with benzamide catalyzed by electron-rich Ir(I) complexes,[276] the Pauson–Khand-type reactions,[277] the highly enantioselective intramolecular or intermolecular cycloadditions of α,ω-diyines alone [2 + 2 + 2][278,278a–278b] or with carbon monoxide,[279] the intramolecular [4 + 2] cycloaddition of dieneynes,[278] the *ortho*-alkylation of phenol with neat norbornene,[280] the enantioselective hydrogenation of olefins,[275,281,281a–281X,282,282a] ketones,[228a,283,283a–283d] lactams,[284] esters,[281d,283d] enamides,[283d] unsaturated phosphonates,[281c] and imines.[281t,w,285,285a–285k] A review by Valla and Pfaltz describing the scope of iridium-catalyzed asymmetric hydrogenation is available.[286]



(*exo*) **501**

502

Scheme 59

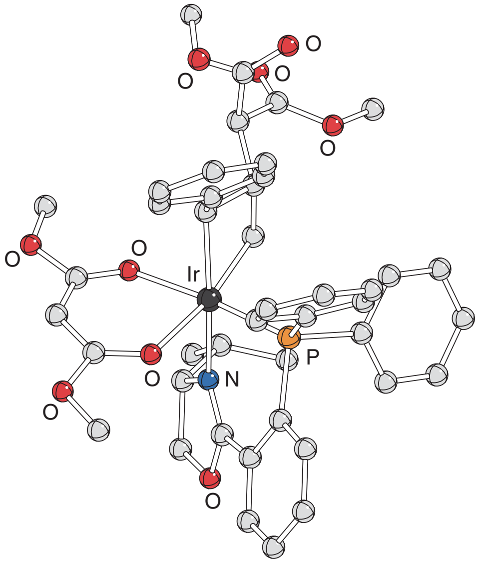
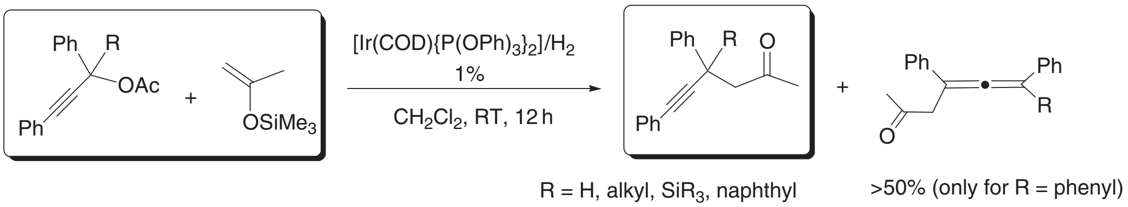


Figure 41 X-ray crystal structure of 502.



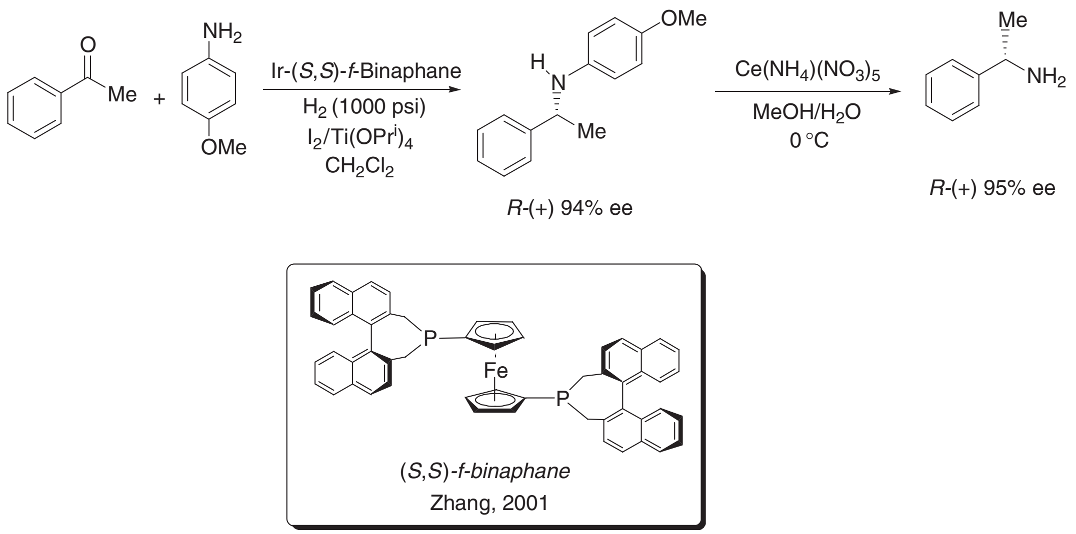
Propargylic substitution with enoxysilanes

Scheme 60

Chiral amines have been conveniently prepared also by asymmetric reductive amination of ketones using iridium catalysts[287] and intriguing results with up to 96% ee have been obtained by Zhang and co-workers employing a catalytic system based on Ir-*f*-binaphane in the presence of $Ti(OPr^i)_4$ and iodine (Scheme 61).[288] Water-soluble aquo complexes $[Cp^*Ir(H_2O)_3](OTf)_2$ **494**, $[Cp^{py}Ir(H_2O)_2](OTf)_2$ **504**, and $[Cp^*Ir(bpy)(H_2O)](OTf)_2$ **505** have been used to catalyze the reductive amination of hydrosoluble aldehydes and ketones as well as the dehalogenation of alkyl halides.[228c] The activity is markedly pH dependent and inactivation of the catalyst takes place reversibly on increasing the solution basicity due to $Ir(H_2O)_x$ deprotonation and formation of mono- or dinuclear hydroxo complexes which are catalytically inactive. The structure of one of these compounds, $[Cp^*Ir(bpy)(OH)]OTf$ **506**, which reversibly forms from **494** around pH 6.6, is presented in Figure 42.

The alkylation of ketones with alcohols is also catalyzed by iridium complexes.[251] The reaction proceeds without any additional solvent and has been carried out by Ishii *et al.* using a mixture of $[Ir(cod)Cl]_2/PPh_3$ and KOH as base. The reaction (Scheme 62) likely proceeds with the formation of an iridium dihydride via hydrogen transfer from the alcohol to iridium followed by aldohol condensation between the produced aldehyde and the excess ketone and eventually hydrogenation of the resulting α,β-unsaturated ketone by the metal dihydride. *N*-Alkylation of primary amines with alcohols catalyzed by $[\{Cp^*IrCl_2\}]_2/K_2CO_3$ produces selectively secondary amines in excellent yield.[289] Although the mechanism of this reaction is not yet clear, the generation of an active Cp^*IrH intermediate has been suggested. Similar catalytic systems[290,290a] or related ones involving NHC[291] have been successfully used in the Oppenauer-type oxidation of alcohols. The H_2O_2 catalytic oxidation of hydroxamic acids to acyl nitroso species has been described. These products are generally trapped as cycloadducts via hetero Diels–Alder reaction with cyclopentadiene.[292] A DFT study of the alkene oxidation of $[(tpa)IrI(C_2H_4)]^+$ and $[(dpa\text{-}R)IrI(cod)]^+$ complexes by H_2O_2 has also been reported.[293]

Reductive alkylation of primary amines to secondary amines has also been carried out using iridium and rhodium complexes supported on solid montmorillonites.[294]



Asymmetric reductive amination of aromatic ketones

Scheme 61

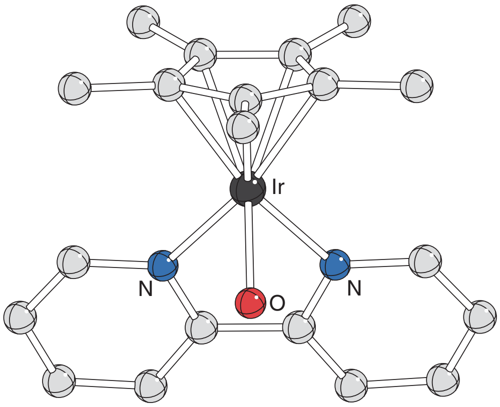
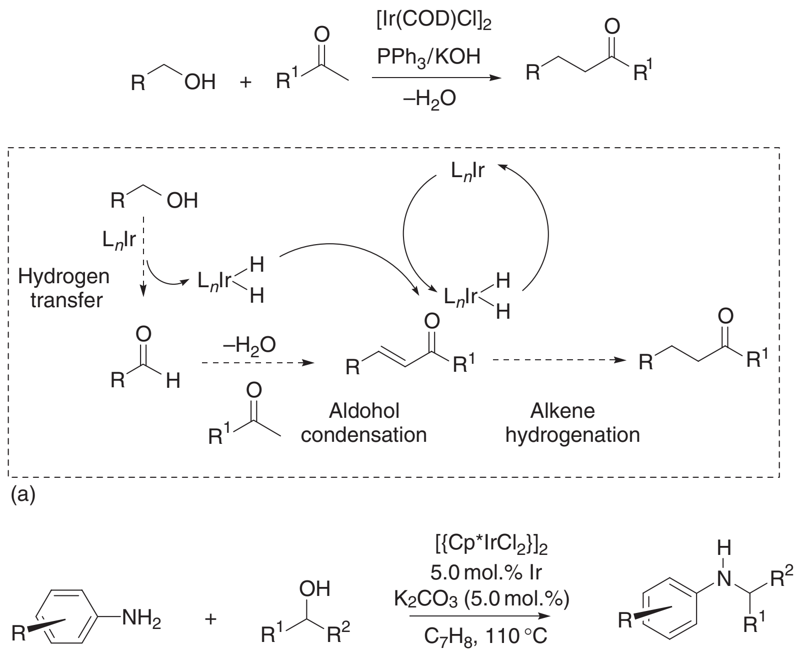


Figure 42 X-ray crystal structure of **506**.

Exciting C–C bond-forming catalytic reactions have been developed by Miura and co-workers who reported on the efficient, iridium-catalyzed ($[Ir(cod)Cl]_2/PR_3$) aromatic homologation using internal alkynes.[295] The process, which is illustrated in Scheme 63, provides an efficient synthetic protocol to prepare polyalkylsubstituted condensed aromatics. Thus, the reaction of benzoyl chloride with 4-octyne in boiling *o*-xylene affords, using bulky PBu^t_3, 1,2,3,4-tetrapropyl naphthalene (99%), while a similar reaction with 2-thenoyl chloride gives the polysubstituted benzothiophene. Naphthalene homologation to anthracene is also possible from 2-naphthoyl chloride with selectivity in anhtracene up to 96% by using PPh_3. A mechanistic hypothesis based on aroyl chloride oxidative addition **A**, 2 decarbonylation of the aroyliridium(III) species **B**, insertion of alkyne into the Ir–C of the aryliridium(III) intermediate **C**, and final elimination of HCl via *ortho*-iridation from the alkenyliridium(III) transient **D** has been suggested (Scheme 64). This final step would afford indeed the five-membered condensed iridacycle **D** from which the polysubstituted naphthalene would be generated via insertion of a second molecule of alkyne and reductive elimination **E**.[295]

The alkynylation of azaheterocycles has been reported by Yamaguchi and co-workers using $[Ir(cod)L_2]$ (L = Cl, OMe, OPh) as catalyst and different quinolines activated by acyl chlorides as substrate.[296]

Apart from the catalytic hydrogenation of unsaturated substrates and the many C–C bond-forming processes discussed above, many other processes catalyzed by iridium complexes have appeared in the literature in the decade

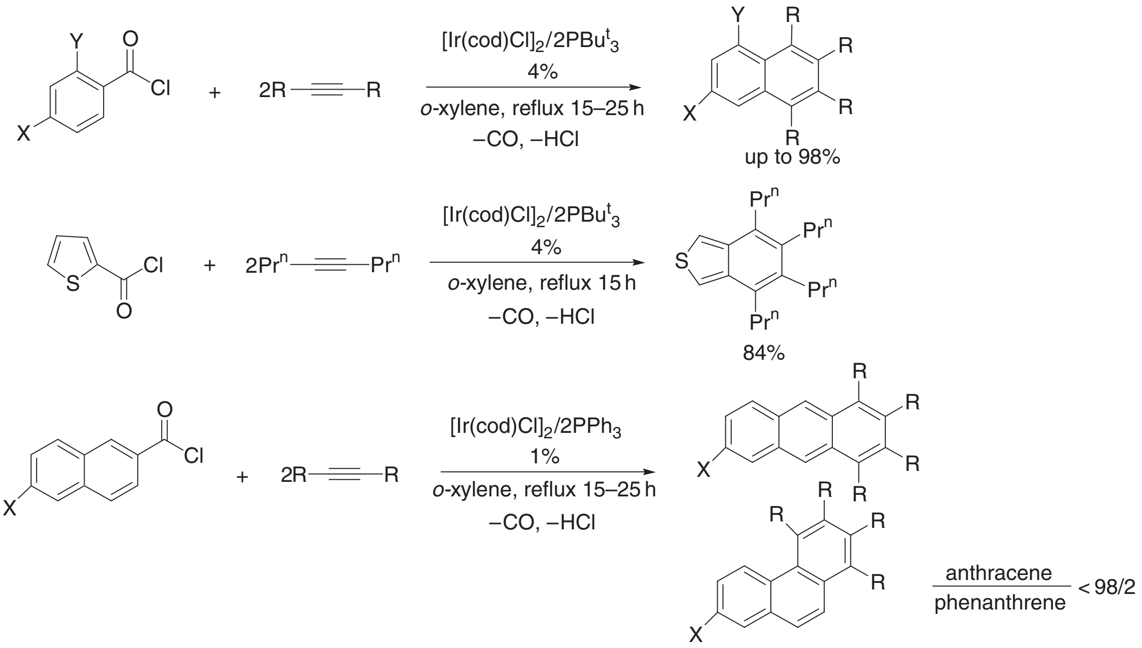


(a) Catalytic alkylation of ketones

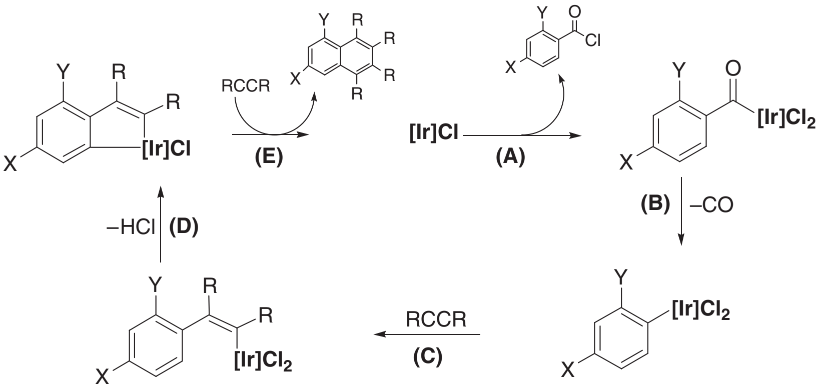
(b) Catalytic *N*-alkylation of amines

Scheme 62

Aromatic homologation with internal alkynes



Scheme 63



[Ir]Cl = Iridium(I) catalyst: $[Ir(cod)Cl]_2/PR_3$

Scheme 64

after the publication of COMC(1995). Classical alkene isomerization,[297,297a–297d] hydrosilylation,[195,240] and hydroborylation[241] of alkenes are typical examples, but many other Ir-catalyzed processes have been reported.

The regioselective addition of thiols to alkynes catalyzed by iridium(I) and rhodium(I) complexes containing N,N-ligands (bim and bpm) and P,N-ligands (PyP) has been reported by Messerle and co-workers.[244] PyP complexes are in most cases more effective in promoting the hydrothiolation of alkynes in comparison with the analogous complexes with N,N-donor ligands with the iridium complexes significantly more effective than their rhodium analogs in promoting the hydrothiolation. The molecular structure of one of these catalysts, namely [(PyP)Ir(CO)Cl] **507**, is shown below in Figure 43. The same complexes have been successfully used as catalysts for the intramolecular hydroamination of aliphatic aminoalkynes. A strong dependence from both the co-ligands and the counter anions on the rate of the hydroamination has been documented.[298]

Ishiyama *et al.* have demonstrated that a simple iridium catalyst generated *in situ* from $[Ir(cod)Cl]_2$ or $[Ir(\mu\text{-}Cl)(coe)_2I]_2$ and bipyridiles are active catalysts for the direct borylation of benzene and other arenes using bis(pinacolate)diboron.[299] Using 4,4′-disubstituted bpy, such as the dtbpy, the reaction may be performed under mild conditions (also at RT). The mechanism of the reaction has been elucidated by isolating key intermediates along the borylation process (Scheme 65). These include the bisboryl complex *cis*-$[Ir(dtbpy)(cod)(Bpin)_2]OTf$ **508** and the catalytically active trisboryl complex $[Ir(dtbpy)(coe)(Bpin)_3]$ **509** which have been isolated and structurally characterized. The molecular structure of **509** is shown below in Figure 44. The same authors also reported that aryl fluorosilanes may be catalytically produced by aromatic C–H silylation using fluorurated disilanes. The reaction is efficiently catalyzed by $[Ir(\mu\text{-}OMe)(cod)]_2$ in the presence of dtbpy.[300]

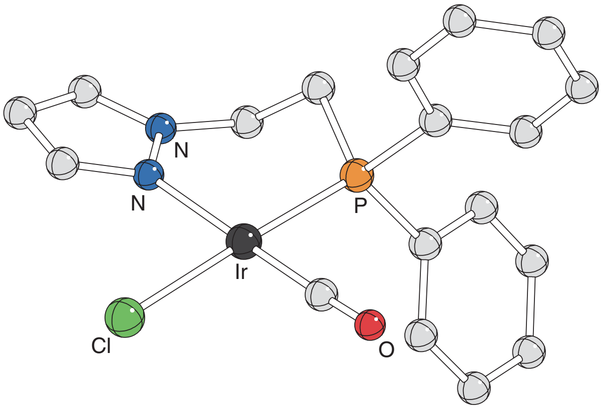
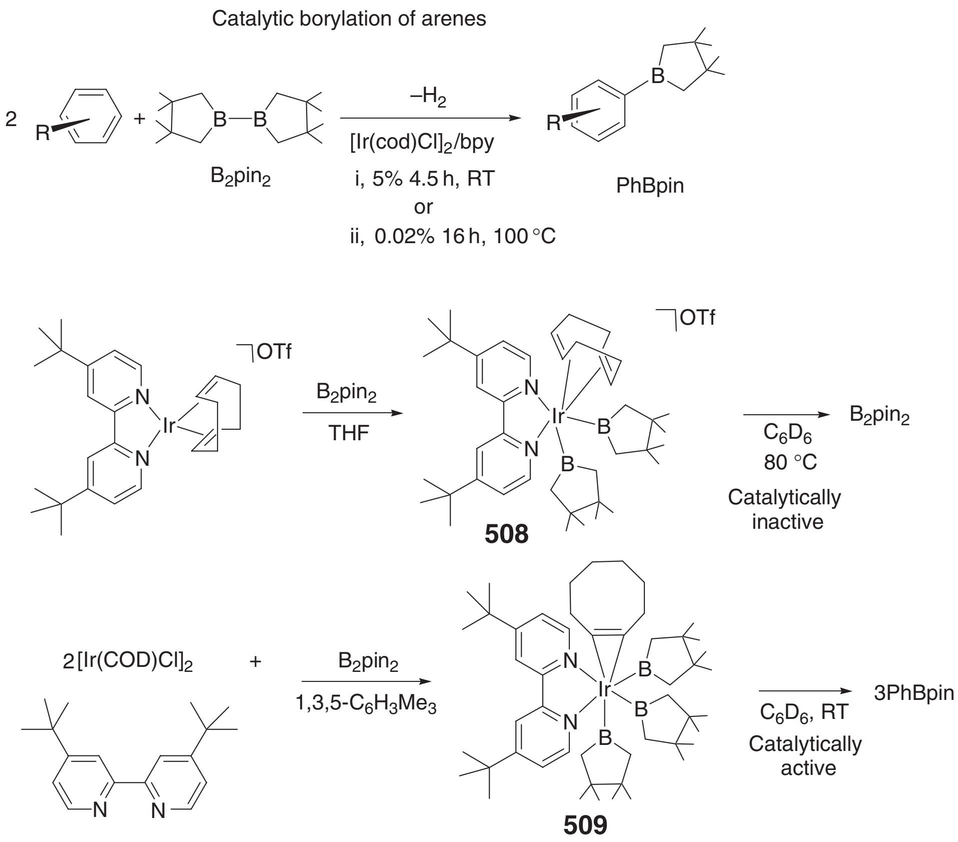


Figure 43 X-ray crystal structure of **507**.



Scheme 65

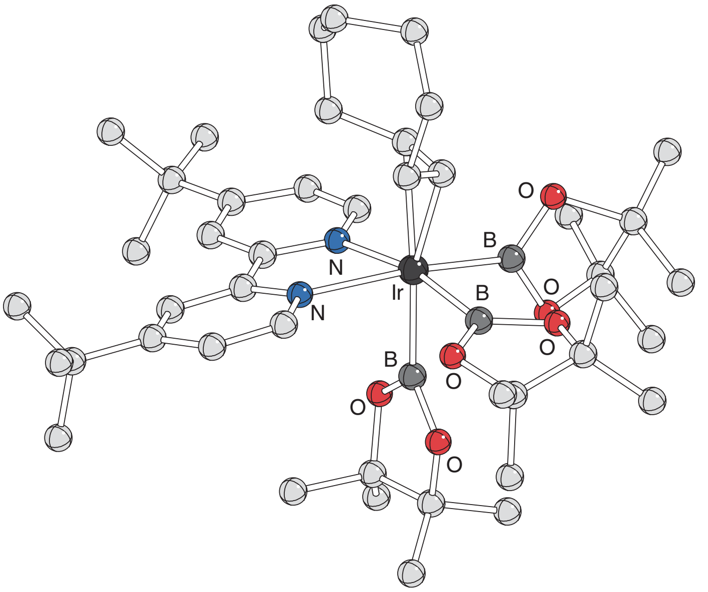


Figure 44 X-ray crystal structure of 509.

Apart from hydrosilylation of alkenes,[195a,240] catalytic transformations involving organosilicon compounds have been extensively studied, mainly by Marciniec and co-workers.[301] Iridium complexes have shown to be active catalysts for these processes: incorporation of CO and silanes into organic substrates has been reported via silylcarbonylation of alkenes[195b,301,302,302a] and vinylsiloxanes,[301] co-dimerization of vinylsilanes with styrene,[301] silylative heterocoupling of styrene with vinylsilanes,[302] and hydroformylation of vinylsiloxanes.[301] The dinuclear iridium–siloxide complex $[\{Ir(cod)(\mu\text{-}OSiMe_3)\}_2]$ **510**, prepared by chloride metathesis from $[Ir(cod)Cl]_2$ with $NaOSiMe_3$ in benzene at RT, is an efficient catalyst for most of the reactions involving organosilicon substrates.[302a]

7.04.4 Iridium–Carbon Multiple Bonds

7.04.4.1 Carbene Complexes, $Ir{=}CRR^1$

After the publication of COMC (1995), the chemistry of iridium carbenes has grown considerably and many intriguing applications of these compounds, particularly in the area of C–C bond-forming reactions and homogeneous catalysis, have been reported.

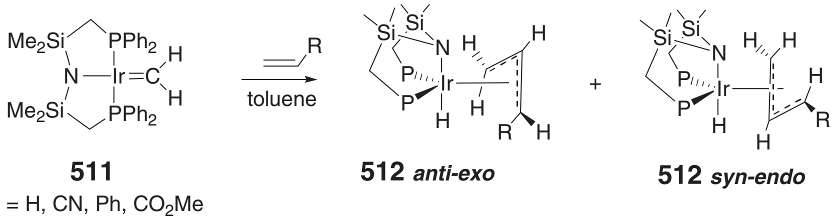
The reactivity of the Fryzuk's methene complex $[\{N(SiMe_2CH_2PPh_2)_2\}Ir({=}CH_2)]$ **511**[303] with electron-deficient alkenes has been reported.[304] C–C bond formation between the methene ligand and the alkene affords Ir(III) allyl hydride complexes (Scheme 66). A mechanism hypothesizing preliminary perpendicular binding of the alkene, formation of a puckered iridacyclobutane intermediate by migratory insertion of the carbene, and β-elimination from the metallacycle to give the hydride allyls $[\{N(SiMe_2CH_2PPh_2)_2\}Ir(\eta^3\text{-}C_3H_4R)]$ (**512**, R = H, CN, Ph, CO_2Me) as a pair of *exo*, *endo*-stereoisomers has been suggested.

SQP Ir(I) carbenes were prepared by Werner and co-workers by the reaction of the mixed phosphine–stibine complex $[IrCl(C_2H_4)(PPr^i_3)(SbPr^i_3)]$ **513** with diaryldiazoalkanes, N_2CAr_2 (Ar = Ph, *p*-Tol).[305,305a,305b] The final product $[IrCl({=}CAr_2)(PPr^i_3)(SbPr^i_3)]$ [R = Ph, 4-C_6H_4Me, C_6H_4Cl **514**] reacts with excess PPr^i_3 to give the bis(phosphino)carbene *trans*-$[IrCl({=}CAr_2)(PPr^i_3)_2)]$ [R = Ph, 4-C_6H_4Me, C_6H_4Cl **515**] (Scheme 67). Reaction of the diphenylcarbene **514** with NaCp affords the cyclopentadienyl carbene complex $[CpIr({=}CPh_2)(PPr^i_3)]$ **516** via displacement of the stibine ligand from the iridium center. The structure of the diphenylcarbene complex **516** was determined by X-ray diffraction (Figure 45).

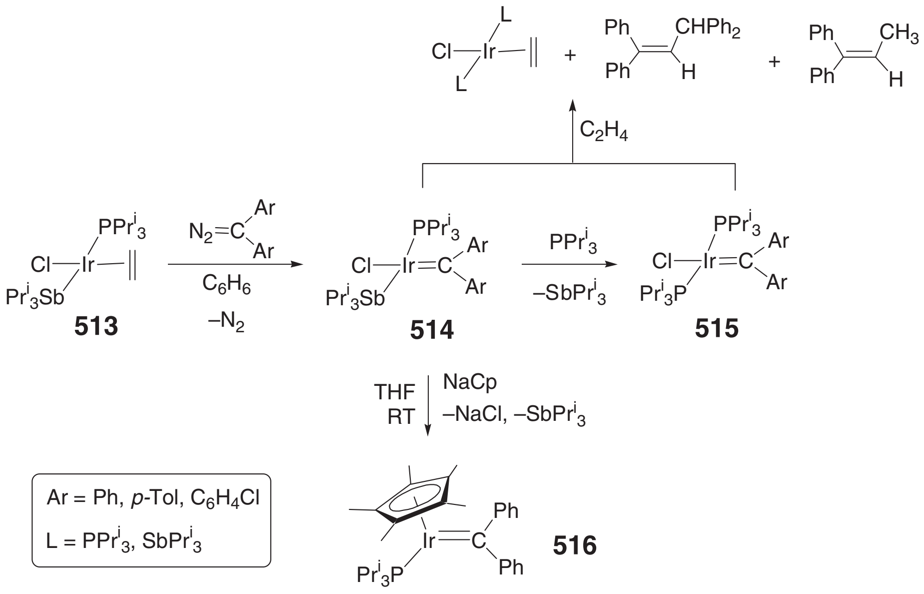
The carbenes **514 and 515** react with ethene to yield, apart from *trans*-$[IrCl(C_2H_4)_2(PPr^i_3)_{2-x}(SbPr^i_3)_x]$ ($x = 0–2$), a mixture of the two alkenes $CH_2{=}CHCHPh_2$ and $CH_3CH{=}CPh_2$, which likely form via C–C coupling from undetected intermediates bearing both carbene and ethene ligands coordinated to iridium.[305b] Similar vinylcarbenes *trans*-$[IrCl\{{=}C(X)\text{–}CH{=}C(Ph)R\}(PPr^i_3)_2]$ **517** (X = $OC(O)CF_3$, OTf; R = Ph, Bu^t) were prepared by treating the allenylidenes $[IrCl\{C{=}C{=}C(R)Ph\}(PPr^i_3)_2]$ [R = Ph **518a**, Bu^t **518b**] with CF_3CO_2H or TfOH.[305a] Addition of the acid across the C(α)–C(β) allenylidene bond accounts for the formation of these species.

Cleavage of η^2-*C,C*-coordinated ketene in $[\{(Me_3C)_2PCH_2P(CMe_3)_2\}IrCl(Ph_2C{=}C{=}O)]$ **519** takes place upon removal of chloride by silver salts in CH_2Cl_2 to give the cationic diphenylalkylidene complex $[\{(Me_3C)_2PCH_2P(CMe_3)_2\}Ir(CO)(C{=}Ph_2)]PF_6$ **520** which was characterized also in the solid state by X-ray diffraction anlysis [$d_{Ir{=}C} = 1.996(8)$ Å] (Figure 46). The reaction is partially reversible and gives back the ketene complex **519** together with the carbonyl $[\{(Me_3C)_2PCH_2P(CMe_3)_2\}IrCl(CO)]$ **521** upon addition of PPNCl (Scheme 68).[306,306a]

Iridium(III) carbenes have also been prepared. $[Tp^{Me}Ir({=}CHMe)(R)(PMe_3)]^+$ **522** was generated by protonation at C(β) of the alkenyl derivatives $[Tp^{Me}Ir(CH{=}CH_2)(R)(PMe_3)]$(R = H, Et).[307] Similarly, the protonation of the iridapyrrole complex $[Tp^{Me}(H)Ir\{C(Me){=}C(Me)C(Me){=}NH\}]$ **523** gave the two possible stereoisomers of the



Scheme 66



Scheme 67

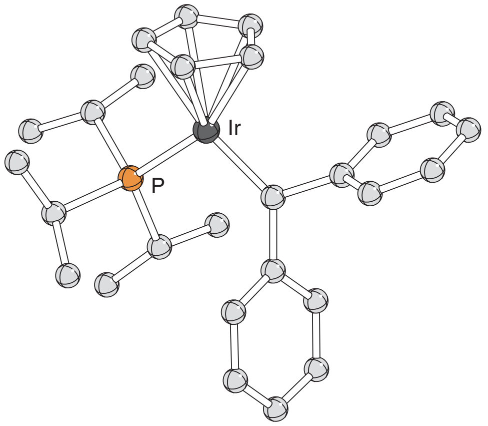


Figure 45 X-ray crystal structure of **516**.

chelating Ir(III) hydrido alkylidene complex $[\mathrm{Tp}^{\mathrm{Me}}(\mathrm{H})\mathrm{Ir}({=}\mathrm{C(Me)CH(Me)C(Me)}{=}\mathrm{NH})]\mathrm{BAr}^{\mathrm{F}}$ **524** (Scheme 69).[308,308a–308d] These compounds undergo thermally and solvent-promoted H migratory insertion reactions onto the electrophilic carbene atom.

Fischer-type carbene iridium complexes have also been described. An excellent account summarizing the work done by Carmona and co-workers in this area has been published.[309] The very unusual Fischer's hydroxycarbene $[\mathrm{Tp}^{\mathrm{Me}}\mathrm{Ir}(\mathrm{CH_2C(Me){=}C(Me)CH_2})\{{=}\mathrm{C(OH)(Ar)}\}]$ **525** was prepared by the reaction of aromatic aldehydes with the dimethylbutadiene complex $[\mathrm{Tp}^{\mathrm{Me}}\mathrm{Ir}\ (\mathrm{CH_2{=}CMeCMe{=}CH_2})]$ **434**.[308a]

The thermal reaction of the trispyrazolylborate complex $[\mathrm{Tp}^{\mathrm{Me}}\mathrm{IrPh_2(N_2)}]$ **526** with 2-ethylphenol produces the hydride alkylidene **527** which exhibits a thermoneutral equilibrium (20 : 1) with the hydride alkene **528** (Scheme 70).[310]

The coordinatively unsaturated fragment $[\mathrm{Tp}^{\mathrm{Me}}\mathrm{IrPh_2}]$, readily generated from $[\mathrm{Tp}^{\mathrm{Me}}\mathrm{IrPh_2(N_2)}]$ **526**, or from $[\mathrm{Tp}^{\mathrm{Me}}\mathrm{Ir(C_2H_4)_2}]$ **370** and C_6H_6 under argon, brings about the regioselective cleavage of two *sp*³ C–H bonds of anisole, phenetole, and *N*,*N*-dimethylaniline, with the formation of a Fischer-type carbene.[311] Related studies in 1,2-DME/benzene mixture have led to the surprising observation that C–C coupling may be promoted after the double

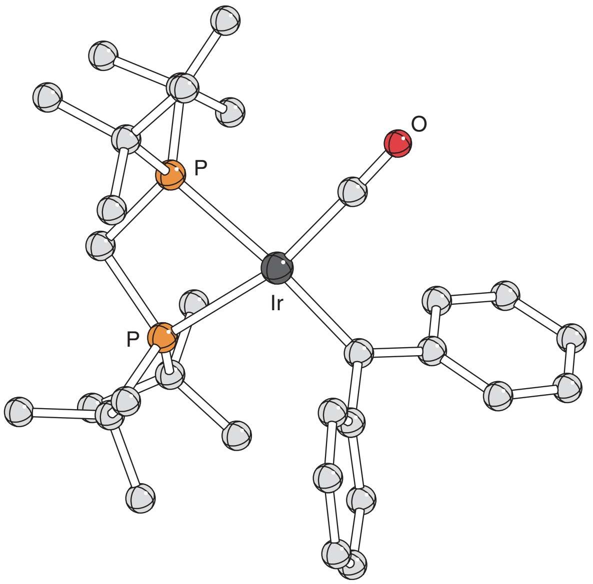
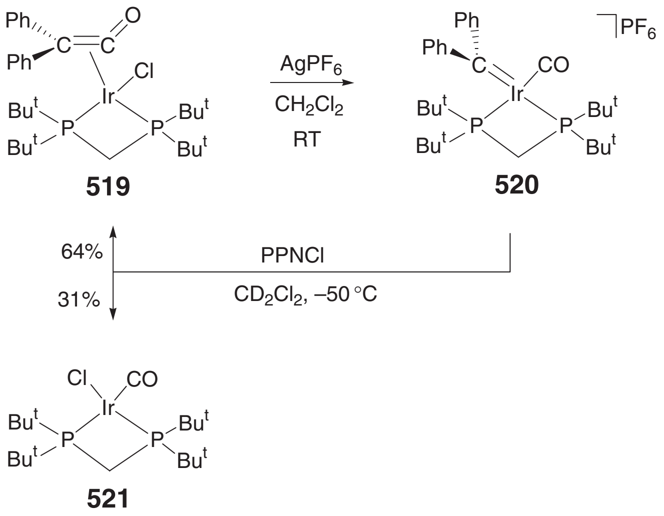


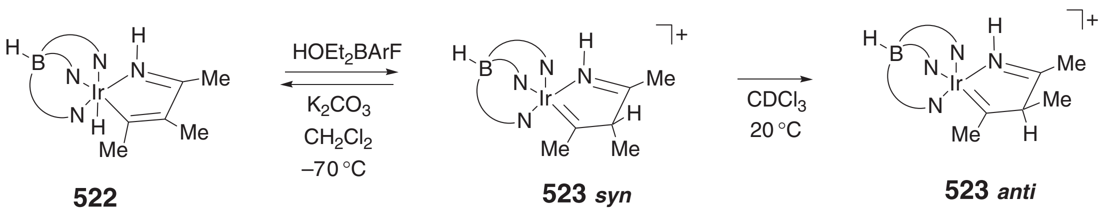
Figure 46 X-ray crystal structure of **520**.



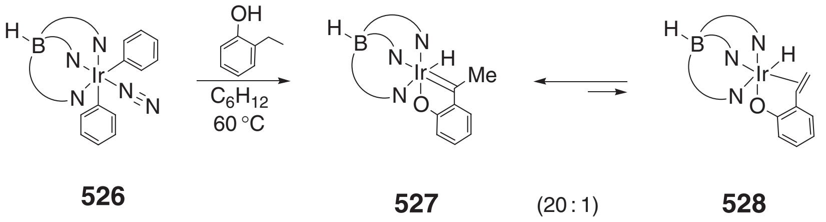
Scheme 68

C–H bond activation step (Scheme 71).[312] A mechanism accounting for the formation of the dihydridocarbene [Tp^{Me}IrH$_2${═C(H)OCH$_2$CH$_2$OMe}] **529** and the aromatic diether PhCH$_2$OCH$_2$CH$_2$OMe has been proposed.

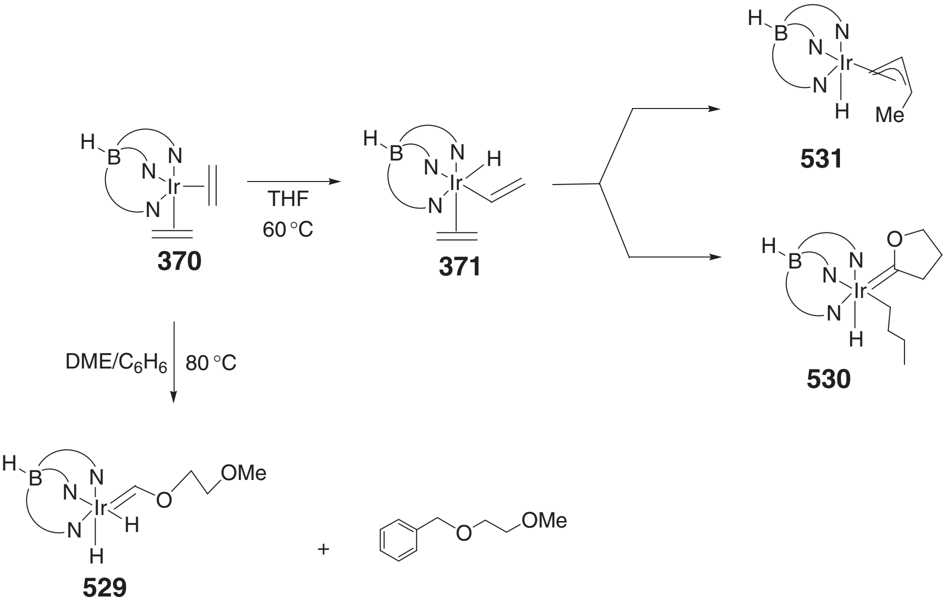
Cyclic carbenes resulting from the regioselective activation of the two α-C–H bonds of the -OCH$_2$- functionality of THF have been also described. The reaction, producing the 2-tetrahydrofuranylidene derivative [Tp^{Me}IrH(Bu)(═C(CH$_2$)$_3$O)] **530**,[313] takes place when the Ir(I) bis(ethene) precursor [Tp^{Me}Ir(C$_2$H$_4$)$_2$] **370** is heated in THF at about 60 °C (see Scheme 71) and affords two independent products following the initial isomerization of **370** to the thermodynamically more stable Ir(III) complex [Tp^{Me}IrH(CH═CH$_2$)(C$_2$H$_4$)] **371**. Indeed, together with the known hydrido(methylallyl) complex [Tp^{Me}IrH(η^3-CH$_2$═CHCHMe)] **531**, the major product is the carbene **530** which forms via double C–H activation at one of the α-carbon atoms of THF. Cyclic ethers other than THF are capable of undergoing this reaction and allow the synthesis of a wide family of Fischer cyclic alkoxycarbenes. *In situ* thermolysis of **370** in THF-d_8 allowed to imagine a possible reaction mechanism involving oxidation of Ir(III) to Ir(V) as the key reaction step. Soon thereafter, the scope of this reaction was broadly extended to a variety of amines and



Scheme 69



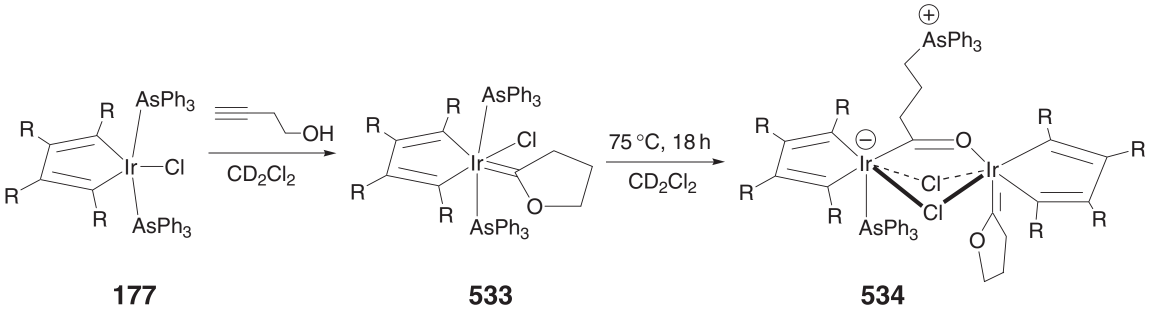
Scheme 70



Scheme 71

ether substrates, including Et$_2$O, by using slightly modified ancillary ligands.[308a–308c] Substrates such as anisole, *N*,*N*-dimethylaniline, THF, PhOEt, and Et$_2$O easily react with [Ir(κ^3-Tp^{Ph})(η^4-isoprene)] **532** to yield heteroatom-substituted carbene complexes.

Cyclization of α,ω-alkynols is a conventional method to prepare cyclooxaalkylidenes. As an example, the reaction of [Ir(CR═CRCR═CR)(AsPh$_3$)$_2$Cl] (R = CO$_2$Me **177**) with 3-butyn-1-ol gives the metallacycle–carbene complex [Ir(CR═CRCR═CR){═C(CH$_2$)$_3$O}(AsPh$_3$)$_2$Cl] **533**, which thermally transforms into the dinuclear acyl compound {[Ir(η^2-C$_4$R$_4$)(AsPh$_3$)](μ-Cl)$_2$[μ-C(O)(CH$_2$)$_3$(AsPh$_3$)][Ir(η^2-C$_4$R$_4$)(═C(CH$_2$)$_3$O)]} **534** via AsPh$_3$-promoted opening of the cyclooxapentylidene ring (Scheme 72).[203a] Cyclic carbenes containing polyphosphines have also been reported.[314]

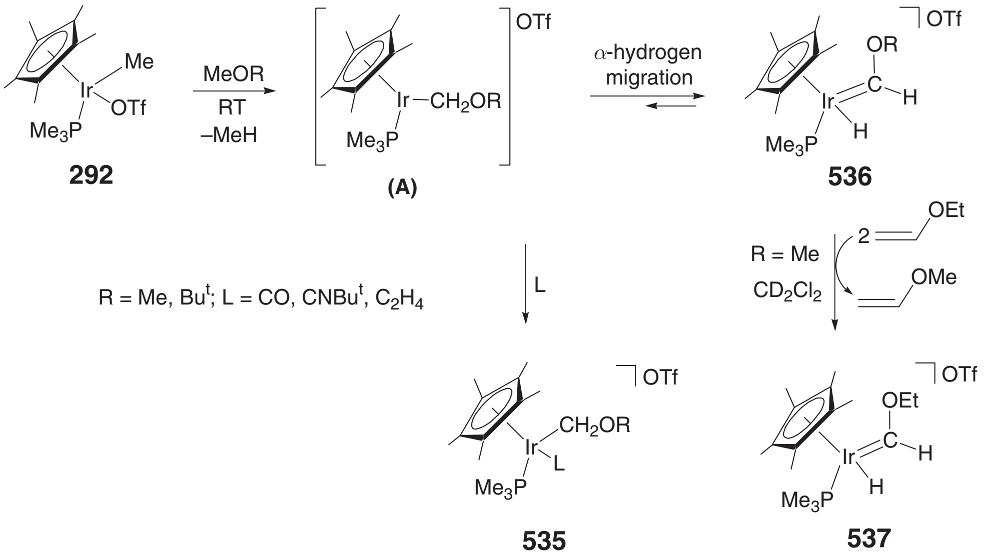


Scheme 72

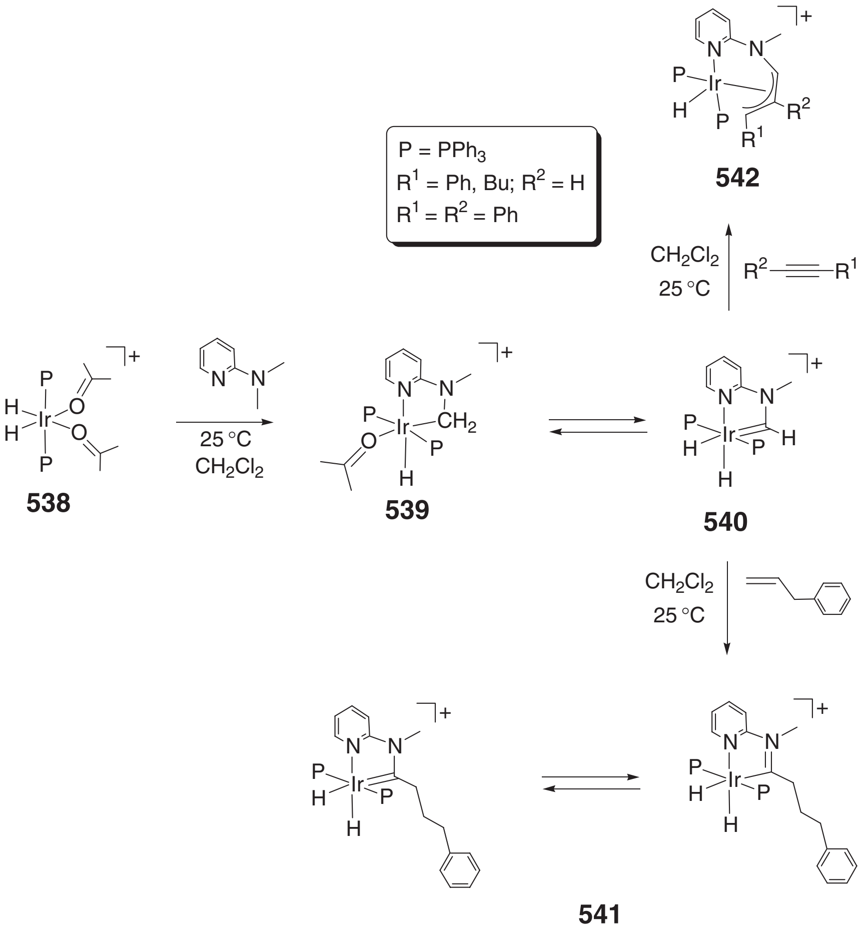
An elegant study by Bergman and co-workers showed that iridium Fischer carbenes may be generated by reversible α-migration.[315] The process, which is summarized in Scheme 73, involves the reaction of $[Cp^*(PMe_3)Ir(Me)(OTf)]$ **292** with methyl ethers (ROMe, R = Me, Bu^t) and goes through initial C–H bond activation and MeH elimination yielding an intermediate cationic alkoxyalkyl complex **A**. This may be trapped with different Lewis bases as $[Cp^*(PMe_3)Ir(L)(CH_2OMe)]$ (L = CO, C_2H_4, CNBu^t **535**) or may spontaneously evolve to give the hydrido Fischer carbene complexes $[Cp^*(PMe_3)IrH({=}CHOR)]$ **536** via α-hydrogen migration. SST NMR experiments have confirmed the proposed mechanism showing fast exchange between the Ir–H and the carbene C–H protons. The reaction has been extended to cyclic ethers including THF. A formal metathesis of the alkoxy group in **536**, leading to the ethoxycarbene $[Cp^*(PMe_3)IrH(CH_2OEt)]$ **537** has been documented by treating the hydridomethoxy carbene $[Cp^*(PMe_3)IrH(CH_2OMe)]$ with 2 equiv. of ethyl vinyl ether and confirmed by ^{17}O NMR studies using ^{17}O-enriched ethers.

During the 1990s, nitrogen heterocyclic carbenes (NHCs) attracted great attention as ligands in homogeneous catalysis due to their similarity to phosphines and the air and moisture stability of the complexes they form.[316,316a–316c] Application of NHCs to iridium has been developed mainly by *Herrmann*, *Crabtree* and their co-workers. The use of Ir(I)–NHCs as catalysts has received increasing attention in several homogeneous processes including alkene hydrogenation,[317,317a–317c] transfer hydrogenation to ketones,[228b,228c,318] aldehydes[319] and imines,[320] hydrosilylation of alkynes[321] and ketones,[322] Oppenauer oxidation of alcohols,[291] and arylation of aldehydes.[323]

A concise review summarizing Crabtree's results is available.[324] The double geminal C–H activation of 2-amino pyridines is worth mentioning here. This unusual pathway has been observed from the reaction of



Scheme 73

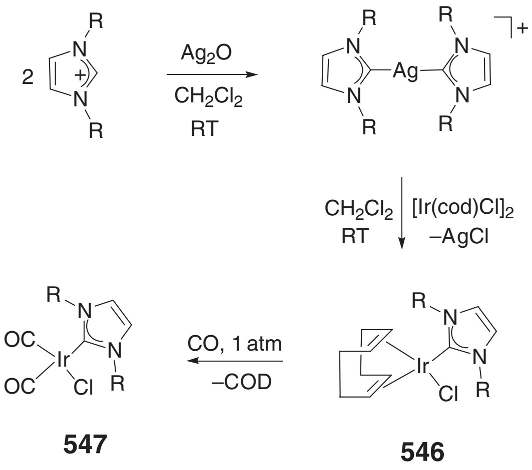


Scheme 74

$[IrH_2(\eta^1\text{-}O\text{-}OCMe_2)_2(PPh_3)_2]BF_4$ **538** with 2-*N*,*N*-dialkylaminopyridines.[325,325a] The process, which has been theoretically modeled, occurs stepwise by way of successive cyclometallation, equilibration between an alkyl hydride **539** and a carbene dihydride **540** via H_2 loss and α-elimination (Schemes 74 and 129). These compounds undergo insertion into alkenes to give the carbene dihydride **541** via a proposed pathway that involves C–C bond formation by a rare C(sp^3)–C(sp^3) reductive elimination followed by double C–H activation step.[326] Insertion of alkynes also occurs yielding η^3-allyl complex **542** via a pathway involving C–C bond formation via C(sp^3)–C(sp^2) reductive elimination step.

The binding modes adopted by *N*,*N*-disubstituted imidazolium salts toward iridium fragments have been studied in detail and combined experimental and theoretical methods have been used to investigate the metallation preference adopted by the cyclometallated carbene ligand.[327,327a–327d] Scheme 137 (see below) illustrates in part this chemistry and points out that metallation does not always take place at the generally presumed more reactive C_2-position of the imidazolyl ring. Bulky mesityl substituents have been used by Nolan and co-workers to prepare the highly stable cationic iridium carbene complex $[Ir(cod)(py)(SIMes)]PF_6$ **543**[317a]. This has been synthesized by the reaction of $[Ir(cod)(py)_2]PF_6$ **544** with SIMes. Complex **543** is an active hydrogenation catalyst capable of hydrogenating simple olefins at RT and atmospheric H_2 pressure.[317b,c] Iridium(I) complexes containing both NHCs and phosphine ligands, $[Ir(cod)](PR_3)(NHC)]$ (NHC = IMe, IMes; R = Cy, Ph, Bu^n **545**), have been prepared and examined as homogeneous hydrogenation catalysts for a variety of alkenes including hindered substrates.[317c]

The average carbonyl stretching frequencies of $[Ir(CO)_2Cl(NHC)]$ complexes have been proposed by Crabtree as a measure of the electron-donor power of NHCs, quantified in terms of Tolman's electronic parameter (TEP).[328] The method was successfully used by Glorius and co-workers to assess the electronic effects in a family of electron-rich, sterically demanding and rigid, N-heterocyclic carbenes derived from bioxazolines (IBiox).[329]



Scheme 75

A simple one-pot synthesis of Ir(I) NHC derivatives was developed by Herrmann and co-workers based on the reaction of $[IrCl(cod)]_2$ in ethanol with the appropriate 1,3-disubstituted imidazolium salt,[330] or with the free NHC ligand.[331] Apart from the conventional synthetic method, based on the *in situ* deprotonation of the respective azolium salts, iridium–NHC complexes have been prepared via the silver transmetallation method involving the reaction of Ag_2O with disubstituted imidazolium salts to generate the silver carbene reagents which transmetallate by treatment with $[IrCl(cod)]_2$ to give [IrCl(cod)(NHC)] **546**.[328] The diene ligand may be easily removed, that is, by flushing with CO to give *cis*-$[IrCl(CO)_2(NHC)]$ **547**, but a second NHC ligand cannot be coordinated by silver abstraction of the residual chloride (Scheme 75).

Cyclopentadienyl iridium(III) NHC derivatives were prepared by Herrmann,[332] Yamaguchi,[291] and their co-workers. Scheme 76 shows the strategy used to prepare these carbenes. The synthesis of $[Cp^*(NHC')IrH]OTf$ **548** (NHC′ = 1-(2-cyclohexenyl)-3-cyclohexylimidazolin-2-ylidene) involves the reaction of $[\{Cp^*IrCl_2\}]_2$ with 1,3-dicyclohexylimidazolin-2-ylidene ligand (NHC) to give $[Cp^*(NHC)IrCl_2]$ **549**, which converts to $[Cp^*(NHC)IrMe_2]$ **550a** by treatment with MeMgCl.[332] Addition of HOTf removes sequentially two molecules of CH_4 and promotes a cyclohexane to cyclohexene transformation at the *N*-heterocyclic carbene ligand based on a CH activation/*β*-hydrogen migration process at the Ir(III) center. Similar methods were used to prepare additional $[Cp^*(NHC)IrCl_2]$ carbenes **549** which may be transformed into the corresponding dihydrides, $[Cp^*(NHC)IrH_2]$ **550b**, and bis(acetonitrile) complexes $[Cp^*(NHC)Ir(N{\equiv}CMe)_2](OTf)_2$ **551** (NHC = 1,3-dialkylylimidazolin-2-ylidene, R = Me, Et, Pr^i).[291]

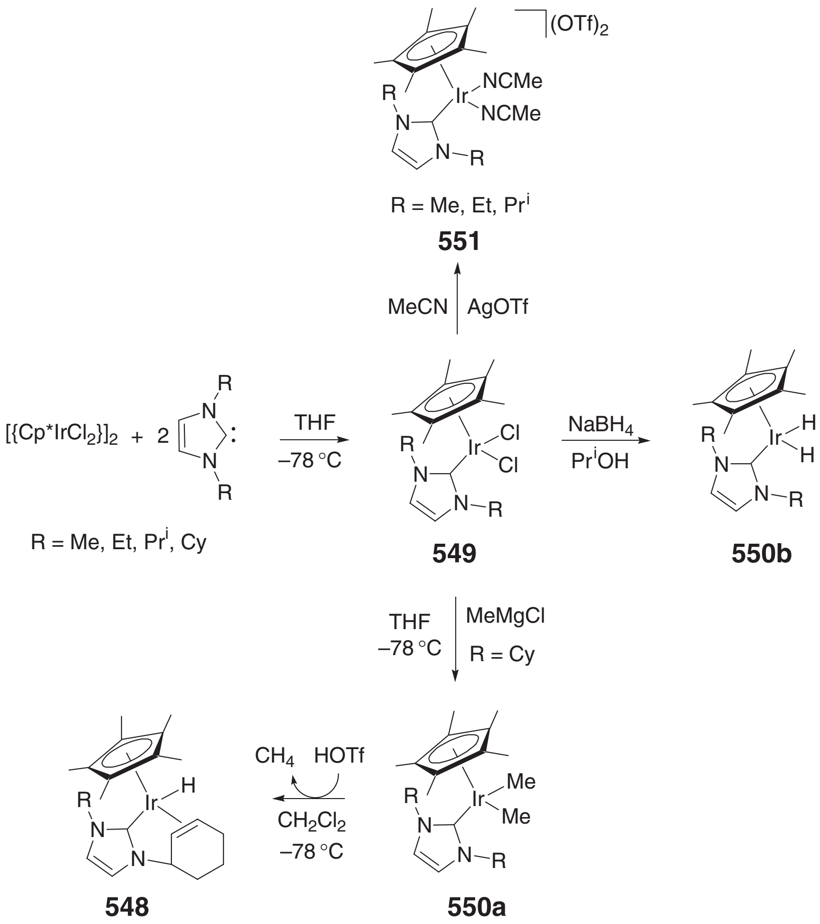
The robust $Cp^*Ir(NHC)$ moiety (NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) has also been used to stabilize $[Cp^*(NHC)Ir{=}PMes]$ complex **552** which contains an unusually stable phosphinidine ligand (Scheme 77).[333]

The water-soluble NHC iridium(I) complex $[Ir(trz)(CO)_2I]OTf$ **553** (trz = 1,2,4-triazol-2-ium-5-ylidene)[334] and a pyridylimidazolylidene species exhibiting a metallacycle structure **554** were also described.[335] The molecular structures of **554** and its precursor containing an agostic Ir···H···C interaction have been reported and the former is presented in Figure 47.

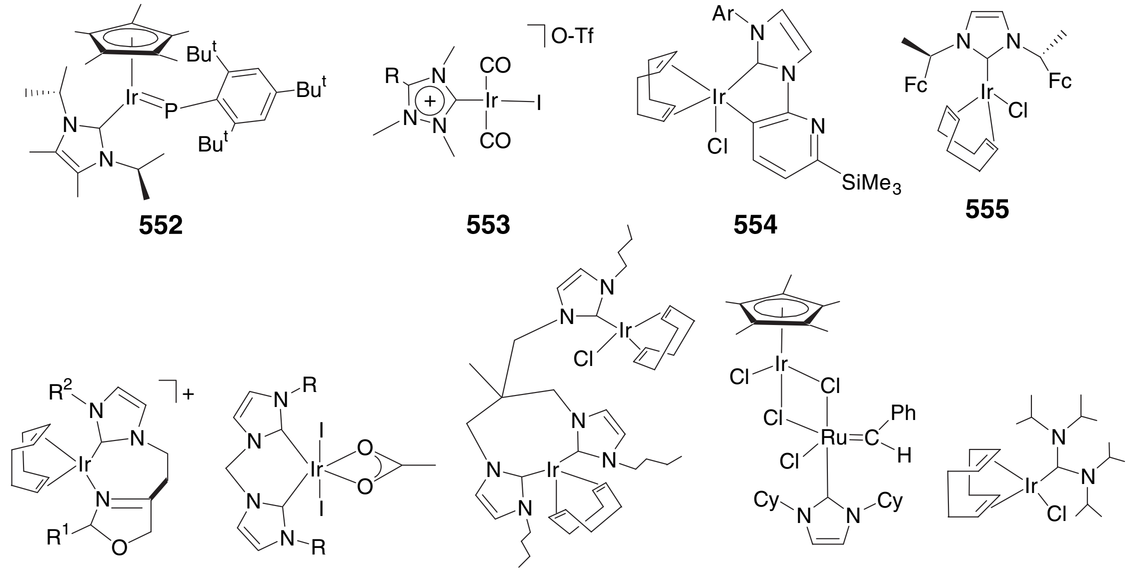
Chiral versions of Ir(I)–NHCs were prepared by Chung *et al.* using optically pure ferrocenyl imidazolium **555** and benzoimidazolium salts, and used for asymmetric hydrogenation of prochiral ketones with ee up to ca. 53% in the hydrogenation of 4-methylacetophenone.[317a] Asymmetric hydrogenation of arylalkenes with high conversions and optimal enantioselectivities (1 bar H_2) was detailed by Burgess and co-workers using optically active Ir(I)–NHC species incorporating an oxazoline moiety **556**.[281L] The same carbene complexes have been successfully used for the asymmetric hydrogenation of dienes.[336]

Ir(I) and Ir(III) complexes containing a chelating bis(NHC) derived from both imidazole **557** and triazole have been prepared and used as efficient catalysts for transfer hydrogenation of ketones,[318] aldehydes,[319] including enolizable ones, and imines.[320] Remarkably, in the case of ketones, a reverse activity (Ir > Rh) was found for these complexes.

Attempts to coordinate iridium by using the tripodal N-heterocyclic carbene ligand [1,1,1-tris(3-butylimidazolium-1-yl)methyl]ethane trichloride ($TIMEH_3^{Bu}$) failed as only monocoordinate $[(COD)Ir(TIMEH^{Bu})](PF_6)_2$ or dicoordinate $[(COD)_2Ir_2(TIME^{Bu})Cl]Cl$ **558** complexes were obtained.[321]



Scheme 76



Scheme 77

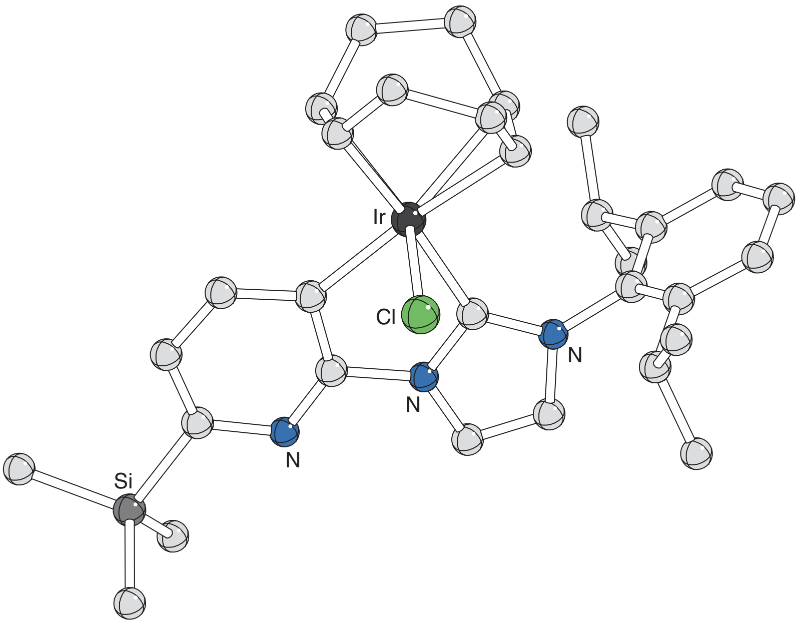


Figure 47 X-ray crystal structure of **554**.

A binuclear Ir/Ru carbene complex, synthesized by the reaction of the ruthenium carbene $[(C_3N_2H_2Cy_2)_2Ru({=}CHPh)]$ with $[\{Cp^*IrCl_2\}]_2$, has been described **559**.[337]

The acyclic version of NHC was successfully used by Hermann and co-workers to prepare $[Ir\{{=}C(NPr^i{}_2)_2\}(cod)Cl]$ **560** by either treatment of $[IrCl(cod)]_2$ with the free bis(diisopropylamino)carbene in THF or *in situ* deprotonation of the formamidinium chloride.[338]

It is also worth recalling that iridium(I)–NHCs linked to organic fragments with biological activity have also been reported. Sparse reports include hypoxanthine-based Ir(I) carbenes[339] and others with imidazolidene ligands based upon the antifungal drugs econazole and miconazole.[340] Tests about their biological activity have not yet been reported.

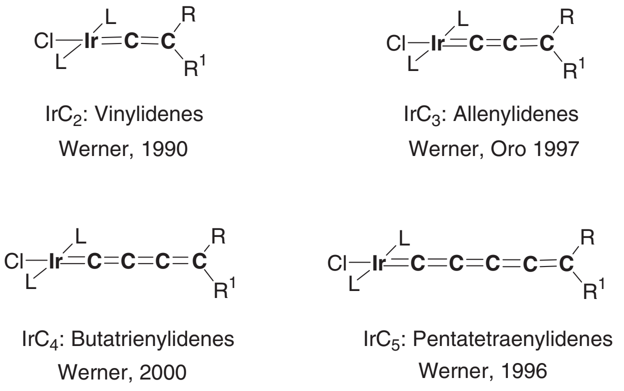
7.04.4.2 Cumulenylidene Complexes, $Ir{=}C{=}(C)_n{=}CRR^1$

Unsaturated iridium carbenes have also had a tremendous expansion thanks mainly to the excellent work by Werner and co-workers who have studied in detail the chemistry of Ir(I) derivatives based on the SQP $[IrX(carbene)(PPr^i{}_3)_2]$ structural unit. A review accounting for the work on iridium-containing cumulenes of formula *trans*-$[IrX\{{=}C({=}C)_nRR^1\}(PPr^i{}_3)_2]$ with $n = 1$, 2, 3, and 4 has been published.[341] Starting from the dihydride $[IrH_2Cl(PPr^i{}_3)_2]$ all the parent compounds with X = Cl and $Ir{=}C{=}C$, $Ir{=}C{=}C{=}C$, $Ir{=}C{=}C{=}C{=}C$, or $Ir{=}C{=}C{=}C{=}C{=}C$ chains have been prepared (Scheme 78). Irrespective of the length of the chain, the iridiacumulenes are highly reactive to both nucleophiles and electrophiles following the general rule which foresee an alternating array of electron-poor and electron-rich carbon atoms along the polyunsaturated carbon chain. Selected examples of the intriguing reactivity shown by some of the Werner iridiacumulenes are presented in the following sections.

7.04.4.2.1 Vinylidene complexes, $Ir{=}C{=}CRR^1$

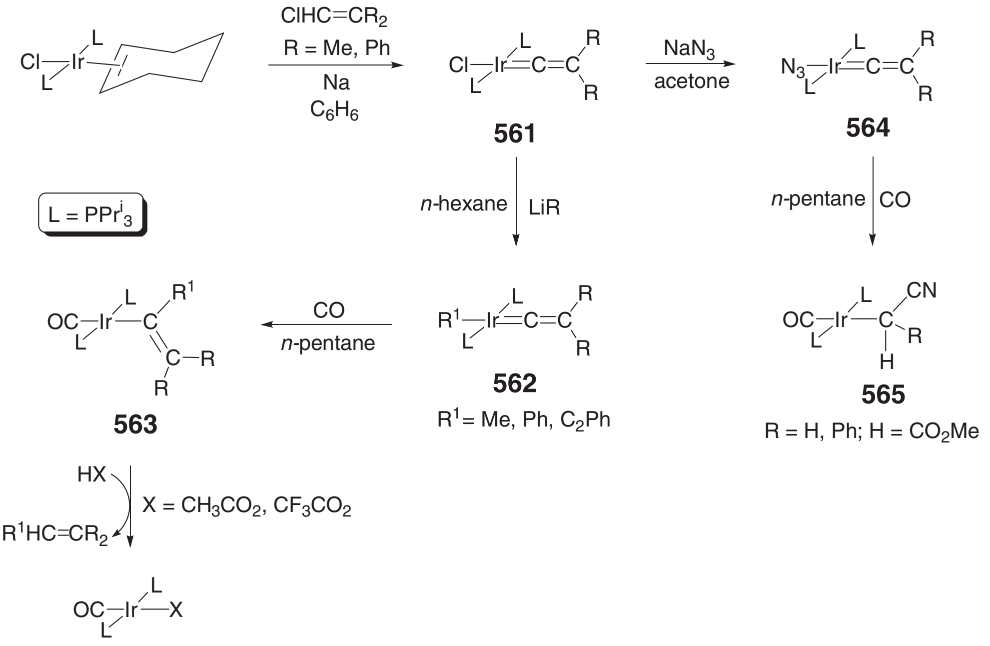
The chemistry and reactivity of iridium vinylidene complexes has progressed during the last decade. Particularly, Werner and co-workers have continued studying unsaturated carbenes of rhodium and iridium and have developed an original route to prepare iridium disubstituted vinylidene complexes, *trans*-$[IrCl(C{=}CRR)(PPr^i{}_3)_2]$ (R = Me, Ph **561**), which are accessible in moderate yield by using vinyl chlorides and sodium (see Scheme 79).[342] Analogous compounds with $SbPr^i{}_3$ were also described.[184,343]

The reactivity of the (vinylidene)iridium(I) complexes *trans*-$[IrCl(C{=}CR^1R^2)(PPr^i{}_3)_2]$ toward both Grignard reagents and organolithium compounds has been investigated.[185] The hydrocarbyl vinylidenes *trans*-$[IrR(C{=}CR^1R^2)(PPr^i{}_3)_2]$ (R = Me, Ph, $C{\equiv}CPh$; **562**), which straightforwardly form upon treatment with the organolithium reagents, react in the



Werner's unsaturated iridium carbenes. L = PPr^i_3

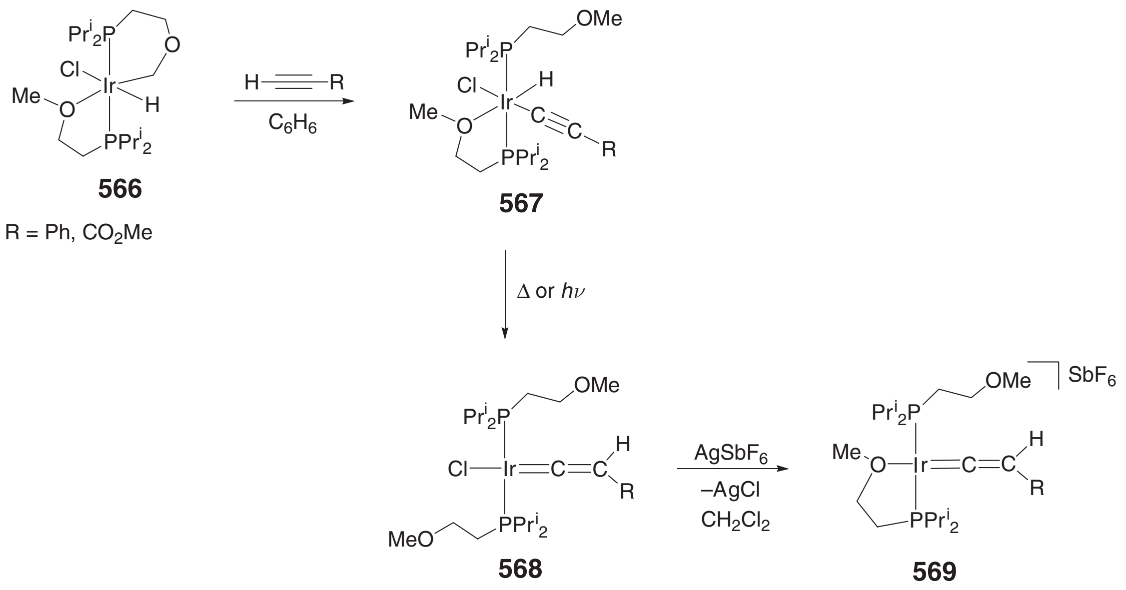
Scheme 78



Scheme 79

presence of CO an intramolecular C–C coupling, affording the *Z*-isomers of the (vinyl)iridium(I) carbonyl complexes *trans*-$[Ir(CO)\{\eta^1\text{-}(Z)\text{-}C(R){=}CR^1R^2\}(PPr^i_3)_2]$ (R = Me, Ph, C≡CPh; **563**). Acid-induced cleavage of the Ir–C σ-bond of these compounds liberates the alkene $CHR{=}CR^1R^2$ forming the SP *trans*-$[IrX(CO)(PPr^i_3)_2]$ (X = CF_3CO_2, CH_3CO_2). The azido compounds *trans*-$[IrN_3(C{=}CHR^1)(PPr^i_3)_2]$ (R^1 = Ph, CO_2Me; **564**), which are prepared by reaction of the chloride **561** with NaN_3, can be used as starting material for the preparation of iridium(I) complexes with an Ir–C σ-bond. The reaction with CO promotes the migratory insertion of the azide to the C(α) carbon of the vinylidene to yield the cyanosubstituted alkyl complexes *trans*-$[Ir(CO)\{C(CN)HR\}(PPr^i_3)_2]$ **565** in excellent yield after elimination of N_2. Migratory insertion of halides was not observed in SP Werner's *trans*-$[IrX(C{=}CR^1R^2)(PPr^i_3)_2]$ vinylidenes, but was invoked by O'Connor *et al.* to account for the formation of halogenated oxametallacycles from the reaction of iridacyclopentadiene halide with methylpropiolate.[203b]

Neutral and cationic square planar (SP) iridium vinylidenes were prepared by the reaction of the octahedral hydridoiridium(III) complex $[IrHCl\{\kappa^2(C,P)\text{-}CH_2OCH_2CH_2PPr^i_2\}\{\kappa^2(P,O)\text{-}Pr^i_2PCH_2CH_2OMe\}]$ **566** with terminal



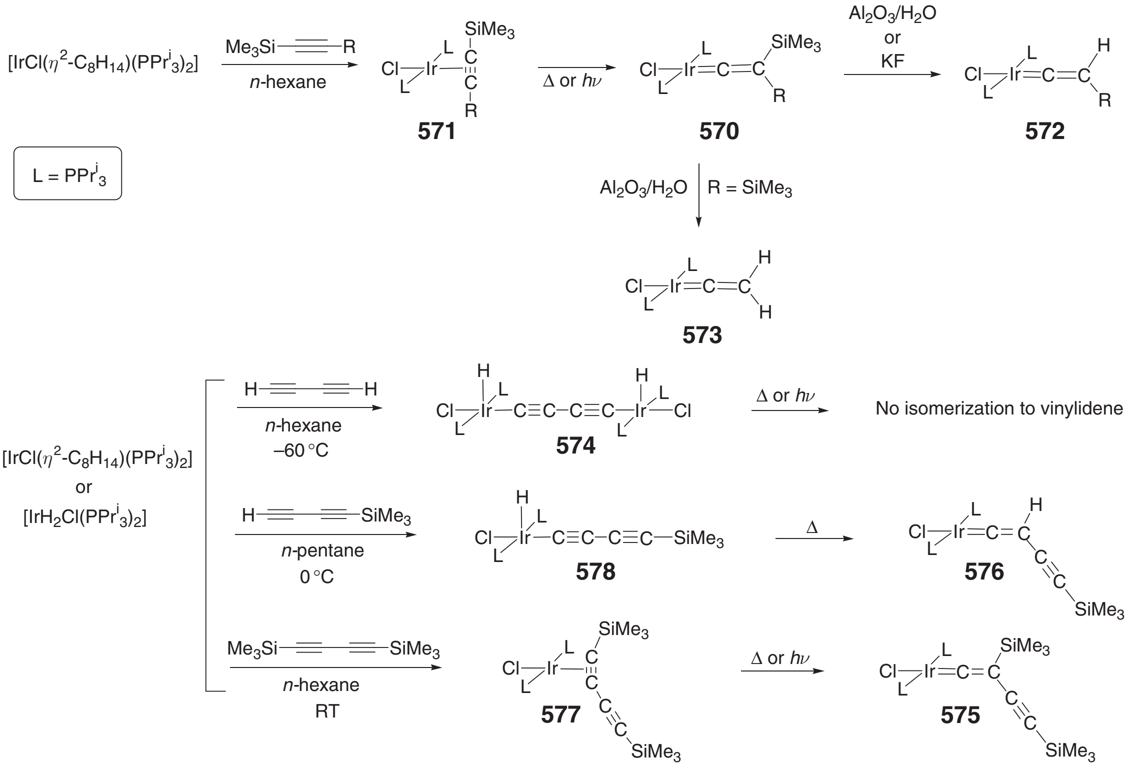
Scheme 80

alkynes.[194b] The reaction goes through the formation of the hydrido(alkynyl) complex $[IrH(Cl)(C{\equiv}CR)\{\kappa(P)\text{-}Pr^i_2PCH_2CH_2OMe\}\{\kappa^2(P,O)\text{-}Pr^i_2PCH_2CH_2OMe\}]$ (R = Ph; R = CO_2Me) **567** from which the vinylidene tautomers $[IrCl\{C{=}C(H)R\}\{\kappa(P)\text{-}Pr^i_2PCH_2CH_2OMe\}\{\kappa^2(P,O)\text{-}Pr^i_2PCH_2CH_2OMe\}]$ (R = Ph; R = CO_2Me) **568** form after thermal or photochemical isomerization. Chloride abstraction with $AgSbF_6$ affords the hexafluoroanimoniate salts of the cationic vinylidenes $[Ir\{C{=}C(H)R\}\{\kappa(P)\text{-}Pr^i_2PCH_2CH_2OMe\}\{\kappa^2(P,O)\text{-}Pr^i_2PCH_2CH_2OMe\}]^+$ **569** (see Scheme 80).

Removal of the labile cyclooctene ligand from $[IrCl(\eta^2\text{-}C_8H_{14})(PPr^i_3)_2]$ by silylalkynes is an excellent method to generate the SP trimethylsilyl substituted vinylidenes *trans*-$[IrCl\{C{=}C(SiMe_3)R\}(PPr^i_3)_2]$ (R = Ph, Me, Bu^n, $SiMe_3$, CH_2OH, CMe_2OSiMe) **570**; these compounds are formed through thermal or photochemical isomerization of the π-alkyne complexes $[IrCl\{\pi\text{-}RC{\equiv}C(SiMe_3)\}(PPr^i_3)_2]$ **571** (Scheme 81).[194c] Cleavage of the C–Si bond of the iridium vinylidenes **570** is easily promoted by protic reagents or fluoride ions. Thus, primary vinylidenes $[IrCl\{C{=}C(H)R\}(PPr^i_3)_2]$ (R = Ph, Me, Bu^n, CH_2OH, CMe_2OSiMe) **572** may be prepared including the quite rare parent vinylidene $[IrCl(C{=}CH_2)(PPr^i_3)_2]$ **573** which forms by hydrolysis of the two C–Si bonds in the bis(silyl)-vinylidene complex $[IrCl\{C{=}C(SiMe_3)_2\}(PPr^i_3)_2]$.

Reactions of $[IrH_2Cl(PPr^i_3)_2]$ or $[IrCl(coe)(PPr^i_3)_2]$ with conjugated dialkynes have also been studied (Scheme 81).[344] Thus, 1,3-butadyine yields the binuclear complex $[\{Ir(H)Cl(PPr^i_3)_2\}(\mu\text{-}C{\equiv}C\text{–}C{\equiv}C)]$ **574** at low temperature, which isomerizes neither upon heating nor upon UV irradiation, to the binuclear compound $[\{Ir(H)Cl(PPr^i_3)_2\}(\mu\text{-}\{C{=}C(H)\text{–}(H)C{=}C\}]$ with a bridging bis(vinylidene) unit. In contrast, the thermal or photochemical reaction of the iridium precursors with $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ or $HC{\equiv}CC{\equiv}CSiMe_3$ affords the (alkynyl)vinylidene complexes $[IrCl\{C{=}C(SiMe_3)C{\equiv}CSiMe_3\}(PPr^i_3)_2]$ **575** and $[IrCl\{C{=}C(H)C{\equiv}CSiMe_3\}(PPr^i_3)_2]$ **576**, respectively. While the former forms via isomerization of an isolable π-bis(alkyne) intermediate $[IrCl\{\pi\text{-}Me_3SiC{\equiv}C\text{–}C{\equiv}CSiMe_3)\}(PPr^i_3)_2]$ **577** and the latter forms via low temperature isomerization of the unstable hydrido(alkynyl) tautomer $[IrH(Cl)\{C{\equiv}C\text{–}C{\equiv}CSiMe_3\}(PPr^i_3)_2]$ **578**, there is no doubt that the two reactions follow the same mechanism involving the π-alkyne/hydrido(alkynyl)/vinylidene sequence with change of the oxidation state of iridium from Ir(I) to Ir(III) and then back to Ir(I) again. This reaction sequence was theoretically modeled for $[IrCl(\pi\text{-}HC{\equiv}CPh)(PH_3)_2]$ by *ab initio* methods which pointed to an energetically favored 1,2-H shift to account for the hydrido(phenylalkynyl) to phenylvinylidene tautomerization.[345]

Stepwise double alkyne to vinylidene tautomerization is the key step responsible for the formation of the η^2-butadienyl iridium(III) complex $[Ir\{\kappa^2\text{-}O,C\text{-}O{=}C(Me)CH{=}CPh\}(\eta^2\text{-}PhCH{=}CHC{=}CHPh)(PPh_3)_2]SbF_6$ **579**.[346] The proposed mechanism, which is illustrated in Scheme 82, involves an alkyne to vinylidene rearrangement (I → II) followed by a hydride insertion (II → III), a second alkyne to vinylidene rearrangement (III → V), and a migratory insertion of the vinyl to the vinylidene (V → VI) resulting in the C–C bond formation.



Scheme 81

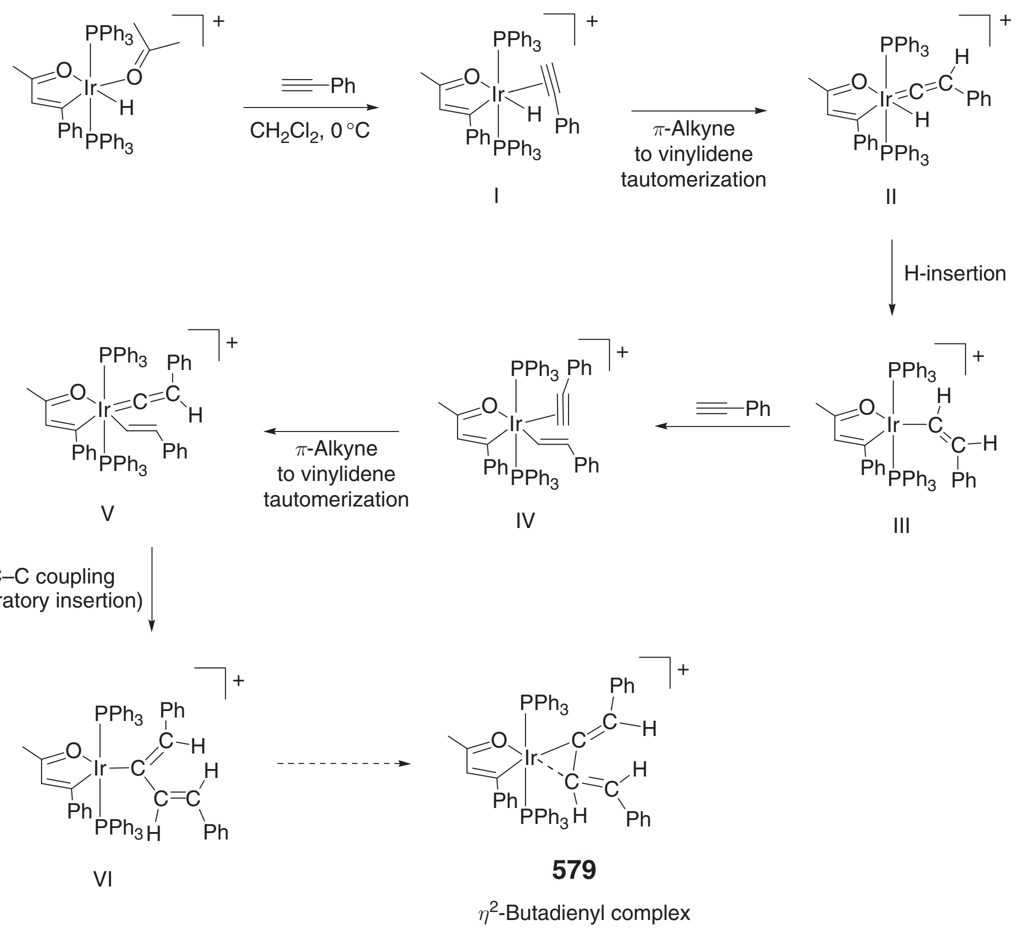
Cowie and co-workers have extensively studied the chemistry of dinuclear cationic A-frame complexes based on two bidentate dppm ligands spanning four coordination positions in a diiridium moiety. It is worth mentioning here that the reaction of $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2]OTf$ **580** with either acetylene or phenylacetylene at −78 °C gives the dinuclear complexes $[Ir_2(CO)(HC{\equiv}CR)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2]OTf$ (R = H, Ph), in which the alkyne is π-bound to one metal.[347] At RT, these alkyne adducts slowly rearrange to the vinylidene-bridged species $[Ir_2(CO)_2(\mu\text{-}I)\{\mu\text{-}C{=}C(H)R\}(dppm)_2]OTf$ **581**. The latter (R = H) reacts with phenylacetylene to afford an unusual unsymmetrical bis(vinylidene) product, $[Ir_2I(CO)_2(C{=}CH_2)\{C{=}C(H)Ph\}(dppm)_2]OTf$ **582**, in which each vinylidene is terminally bound to a different metal. An intriguing terminal to bridging conversion of both vinylidenes yielding $[Ir_2I(L)(CO)_2(\mu\text{-}C{=}CH_2)\{\mu\text{-}C{=}C(H)Ph\}(dppm)_2]OTf$ [L = I **583a**, CO **583b**] is promoted by addition of iodide or by exposing the solution of **582** to CO. The structure of the diiodo derivative **583a** is shown in Figure 48.

The fate of the alkyne addition is strongly dependent on both alkyne and ancillary ligands at the A-frame moiety. Thus, for example, replacing **580** with $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2]OTf$ **122** in the above reaction promotes C–H alkyne activation yielding alkynyl hydrides $[Ir_2H(CH_3)(CO)_2(\mu\text{-}C{\equiv}CR)(dppm)_2]OTf$ [R = Me, Ph **124**].[64] These latter upon warming undergo transfer of the hydride ligand to the β-alkynyl carbon to give the vinylidene-bridged products $[Ir_2(CH_3)(CO)_2\{\mu\text{-}C{=}C(H)R\}(dppm)_2]OTf$ [R = Me, Ph **584**]. At ambient temperature, intramolecular elimination of CH_4 occurs, yielding the alkynyl-bridged "A-frames," $[Ir_2(CO)_2(\mu\text{-}\eta^{2:1}\text{-}C{\equiv}CR)(dppm)_2]OTf$.[64] Bridging vinylidenes similar to **584** have been prepared also by Oro and co-workers via intramolecular rearrangements of μ-H(alkynyl) species.[207] This chemistry is described in Section 7.04.3.3.2.

Mixed metal Rh/Ir bridging vinylidenes supported by A-frame dppm-based scaffolds have also been reported.[208]

7.04.4.2.2 Allenylidene complexes, Ir=C=C=CRR^1

Although less widespread than the rhodium cognate species, iridium allenylidenes are well documented and have been known since 1997 when the first compounds featuring the allenylidene, Ir=C=C=CRR$_1$, moiety were independently obtained by Oro,[348] Werner,[194b,194c] and their co-workers. While not isolated in the solid state or even detected in solution, the existence of an iridium allenylidene was previously invoked by O'Connor *et al.* to



Scheme 82

explain the intriguing formation of the η^1-vinyl(carbonyl) derivative **585** by treatment of the unsaturated Ir(III) iridacyclopentadiene complex [Ir(CR═CRCR═CR)(PPh$_3$)$_2$Cl] (R = CO$_2$Me) **436** with propargyl alcohol in biphasic CH$_2$Cl$_2$/H$_2$O conditions.[203] A mechanism accounting for the formation of **585** has been proposed based on the standard Selegue's protocol,[349] which encompasses the preliminary metal-mediated isomerization of the prop-2-ynyl alcohol to the γ-hydroxyvinylidene **I**, from which the unstable allenylidene [Ir(CR═CRCR═CR)(PPh$_3$)$_2$(C═C═CH$_2$)Cl] **II** may form via intramolecular dehydration. The unusual O'Connor's reaction is then completed by nucleophilic attack of water on C(α) and by keto-enolic retroisomerization of the allenyl intermediate **III** to the unsaturated acyl species **IV**. Decarbonylation of the coordinatively unsaturated acyl eventually affords **585** as indicated in Scheme 83. The intermediate formation of iridium allenylidenes has also been hypothesized by Hidai and co-workers to justify the synthesis of both linear hydroxycarbene and cyclic alkoxycarbene iridium species from the reaction of the dimer [Cp*Ir(μ-Cl)(μ-SPr^i)$_2$IrCp*]OTf with terminal alkynes.[350] EHMO calculations have shown that the Ir═C═C═CRR^1 moiety is much more reactive than analogous ruthenium species toward addition of nucleophiles, including water and alcohols, to α and γ carbons.

Reaction of [Ir(OMe)(PR$_3$)(diene)] (R = Pr$^i_3$, Cy; diene = COD, TFB; **586**) with HC≡CCPh$_2$OH results in the formation of the σ-alkynyl complexes [Ir(C≡CCPh$_2$OH)(PR$_3$)(diene)] **587** which yield the iridium allenylidenes [Ir(C═C═CPh$_2$)(PR$_3$)(diene)] **588** after reaction with HBF·OEt$_2$ (Scheme 84).[348]

Iridium allenylidenes have been prepared and studied mostly by Werner and co-workers.[341] The reaction of the dihydrido complex [IrH$_2$Cl(PPr$^i_3$)$_2$] with 1,1-diphenylpropargylalcohol does not give directly the allenylidene, but produces the hydrido-alkynyl species [IrHCl(C≡CCPh$_2$OH)(PPr$^i_3$)$_2$] **589** which tautomerizes to the vinylidene [IrCl{C═C(H)CPh$_2$OH}(PPr$^i_3$)$_2$] **590** upon irradiation with UV light in *n*-hexane at RT. Addition of catalytic amount of CF$_3$CO$_2$H initiates water elimination transforming **590** into the allenylidene [IrCl(C═C═CPh$_2$)(PPr$^i_3$)$_2$]

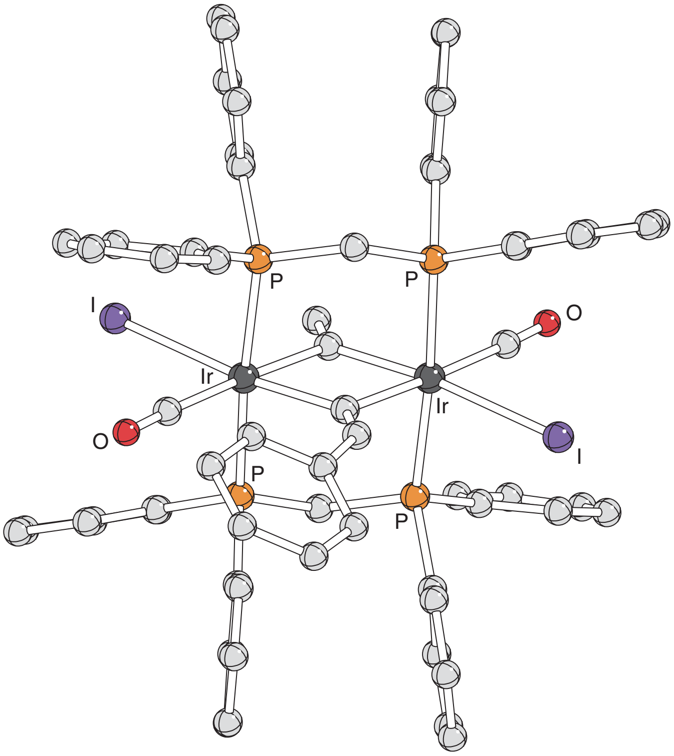
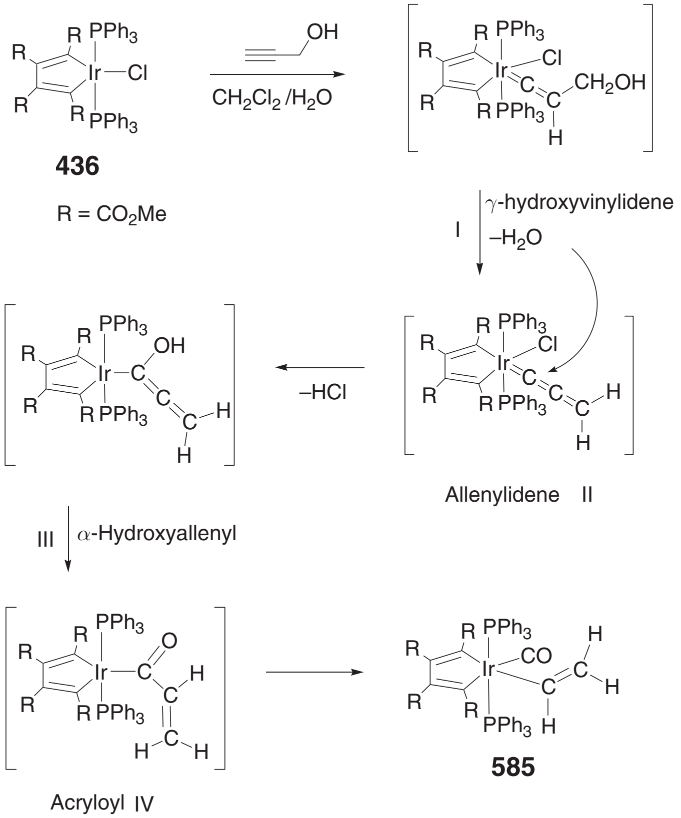
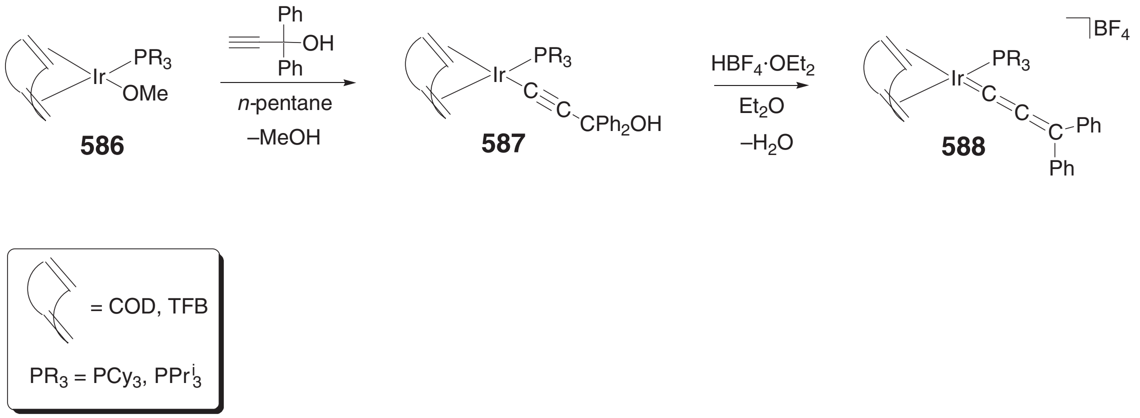


Figure 48 X-ray crystal structure of **583a**.



Scheme 83



Scheme 84

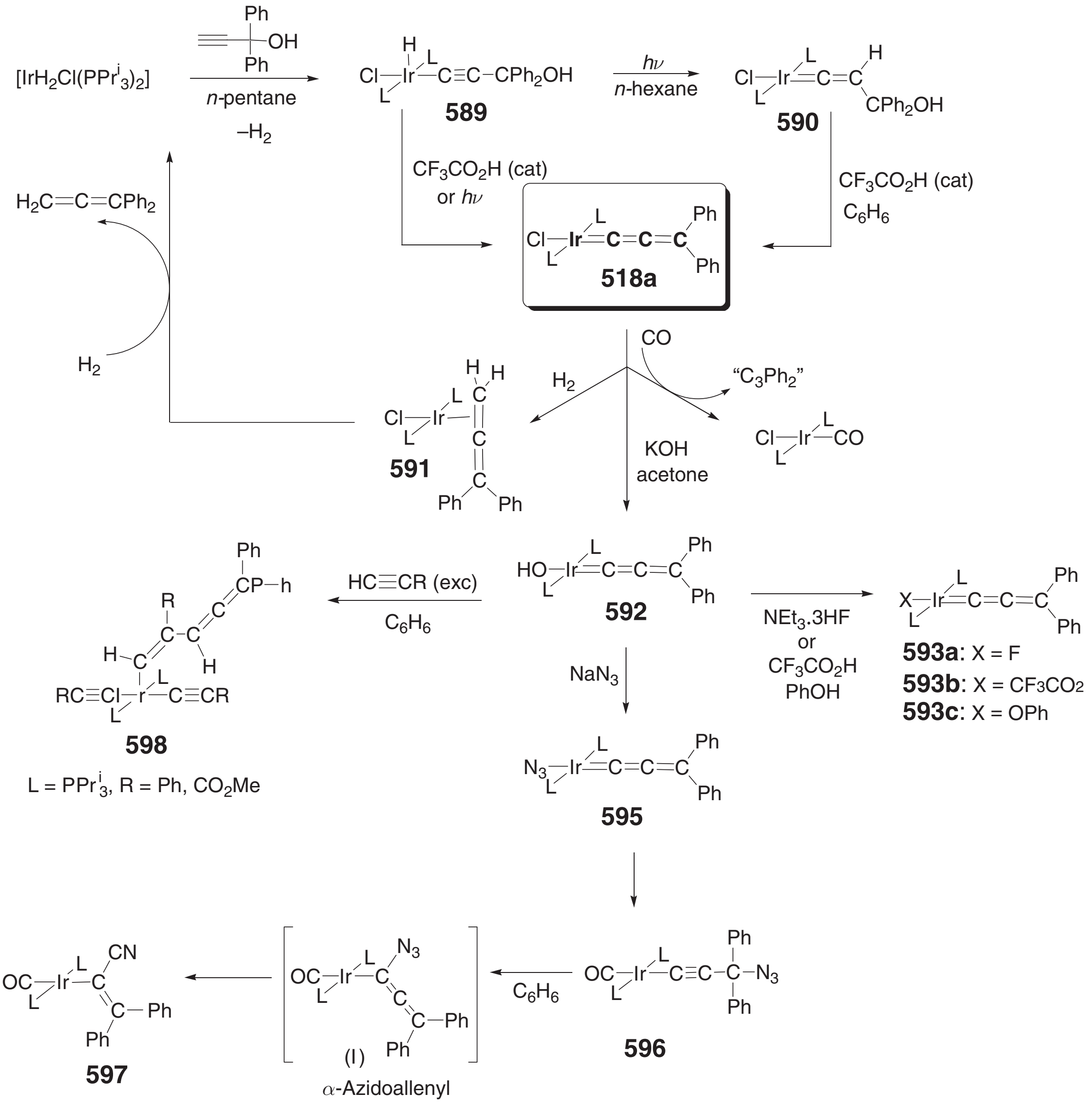
518a.[194b,194c] The reactivity of the Werner allenylidene was briefly investigated. Remarkably, the reaction with CO yields $[IrCl(CO)(PPr^{i}_{3})_{2}]$ via elimination of the C_3Ph_2 unit. The dimer $Ph_2C{=}C{=}C{=}C{=}C{=}CPh_2$ was however not unambiguously detected. Regioselective addition of H_2 to C(α) results in the formation of the 1,1-diphenylallene complex $[IrCl(\eta^{2}\text{-}CH_2{=}C{=}CPh_2)(PPr^{i}_{3})_{2}]$ **591** which upon further exposure to H_2 is released from the coordination sphere giving back the starting dihydride. Treatment with KOH leads to *trans*-$[Ir(OH)(C{=}C{=}CPh_2)(PPr^{i}_{3})_{2}]$ **592**, which reacts with Bronsted acids such as HF, CF_3CO_2H, and PhOH to give the allenylidenes *trans*-$[IrX(C{=}C{=}CPh_2)(PPr^{i}_{3})_{2}]$ [X = F **593a**, κ^{1}-*O*-CF_3CO_2 **593b**, OPh **593c**].[194d] Salt metathesis from *trans*-$[IrCl\{C{=}C{=}C(R)Ph\}(PPr^{i}_{3})_{2}]$ [R = Ph **518a**, Bu^{t} **594**] affords the allenylidenes *trans*-$[IrX\{C{=}C{=}C(R)Ph\}(PPr^{i}_{3})_{2}]$ (X = Br, I, NCO, NCS, OH, N_3).[194d] Migratory insertion of the allenylidene ligand across the Ir–N bond in *trans*-$[IrN_3\{C{=}C{=}C(R)Ph\}(PPr^{i}_{3})_{2}]$ **595** takes place upon reaction with CO to yield the *trans*-alkynyl complex $[Ir(CO)\{C{\equiv}CC(R)Ph(N_3)\}(PPr^{i}_{3})_{2}]$ **596**. This latter, for R = Ph, slowly rearranges in benzene to the metallated acrylonitrile *trans*-$[Ir(CO)\{C(CN){=}CPh_2\}(PPr^{i}_{3})_{2}]$ **597** by elimination of N_2. The intermediate formation of the α-azidoallenyl complex **I** along the decomposition of **596** to **597** has been postulated on the basis of *in situ* IR studies. An unusual C_5-ligand is formed from the reaction of the hydroxo-allenylidene **592** with excess phenylacetylene or methylpropiolate which afford *trans*-$[Ir(C{\equiv}CR)_2\{(E)\text{-}C(H){=}C(R)C(H){=}C{=}CPh_2\}(PPr^{i}_{3})_{2}]$ **598**.[194d,351] A part of this interesting chemistry is summarized in Scheme 85.

The reaction of the parent allenylidene **518a** and its iodo analog with electrophiles has also been investigated.[305c] With MeI, the η^{2}-butatriene species *trans*-$[IrX(\eta^{2}\text{-}CH_2{=}C{=}C{=}CPh_2)(PPr^{i}_{3})_{2}]$ **599** are produced via C–C coupling and HI elimination. Depending on both the reaction conditions and the nature of the electrophile, oxidative addition or formation of iridium carbenes may result from the attack of different HX electrophiles (see, e.g., **600** and **601** in Scheme 86). Ir=C (carbene) to Ir≡C (carbyne) transformation leading to *trans*-$[IrCl({\equiv}C\text{-}CH{=}CPh_2)(PPr^{i}_{3})_{2}]CF_3CO_2$ **602** has also been demonstrated and has been associated to the tendency of the HX anion to behave as a good leaving group.[305c] Some of these intriguing transformations are illustrated in Scheme 86.

7.04.4.3 Higher Cumulenylidene Complexes, $Ir{=}C{=}(C)_{n}{=}CRR^{1}$ ($n>1$)

The challenging search for iridiacumulenes higher than IrC_3 (see Scheme 78) was successfully accomplished by Werner and Ilg in the last decade. Remarkably, the synthesis of IrC_4, iridiapentabutaene, species[352,33] was much more tricky than that of the higher homolog, iridiahexapentaene, IrC_5 and was reported in 2000—four years after the synthesis of IrC_5 was.[353]

The pentatetraenylidene complex $[IrCl(C{=}C{=}C{=}C{=}CPh_2)(PPr^{i}_{3})_{2}]$ **603** was indeed prepared by dehydration of $[Ir(H)Cl\{C{\equiv}C\text{–}C{\equiv}C\text{–}C(OH)Ph_2\}(PPr^{i}_{3})_{2}]$ **604** with triflic anhydride in the presence of NEt_3.[353] The alkynyl(hydride) precursor **604** was in turn obtained via reaction of the dihydrido complex $[IrH_2Cl(PPr^{i}_{3})_{2}]$ with the unsaturated alcohol $HC{\equiv}C\text{–}C{\equiv}C\text{–}C(OH)Ph_2$. Thermal or photochemical activation of **604** does not afford the pentatetraenylidene, but favors the isomerization to the (alkynyl)vinylidene $[IrCl\{C{=}C(H)C{\equiv}C\text{–}C(OH)Ph_2\}(PPr^{i}_{3})_{2}]$ **605** from which **603** cannot be obtained by dehydration methods (Scheme 87).

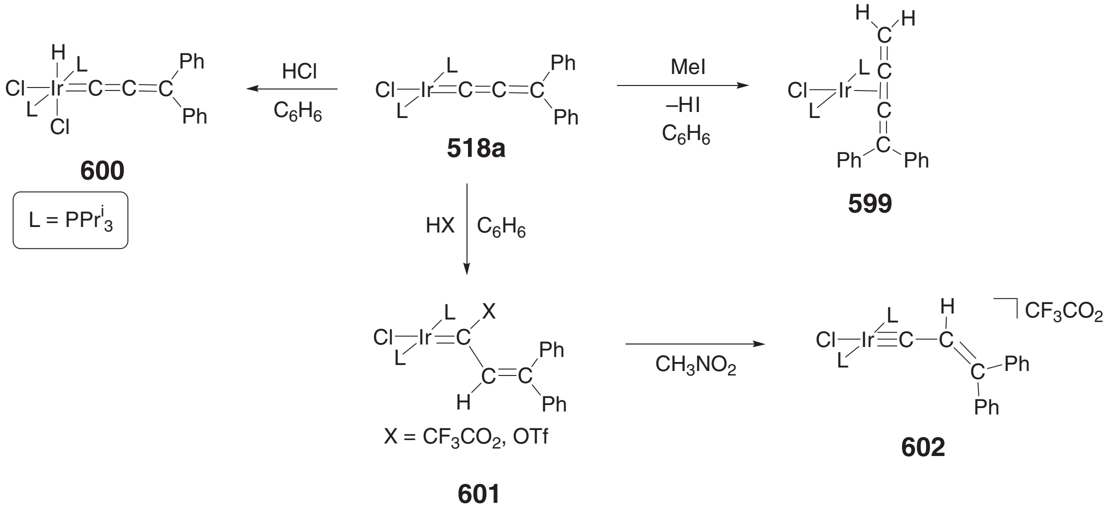


Scheme 85

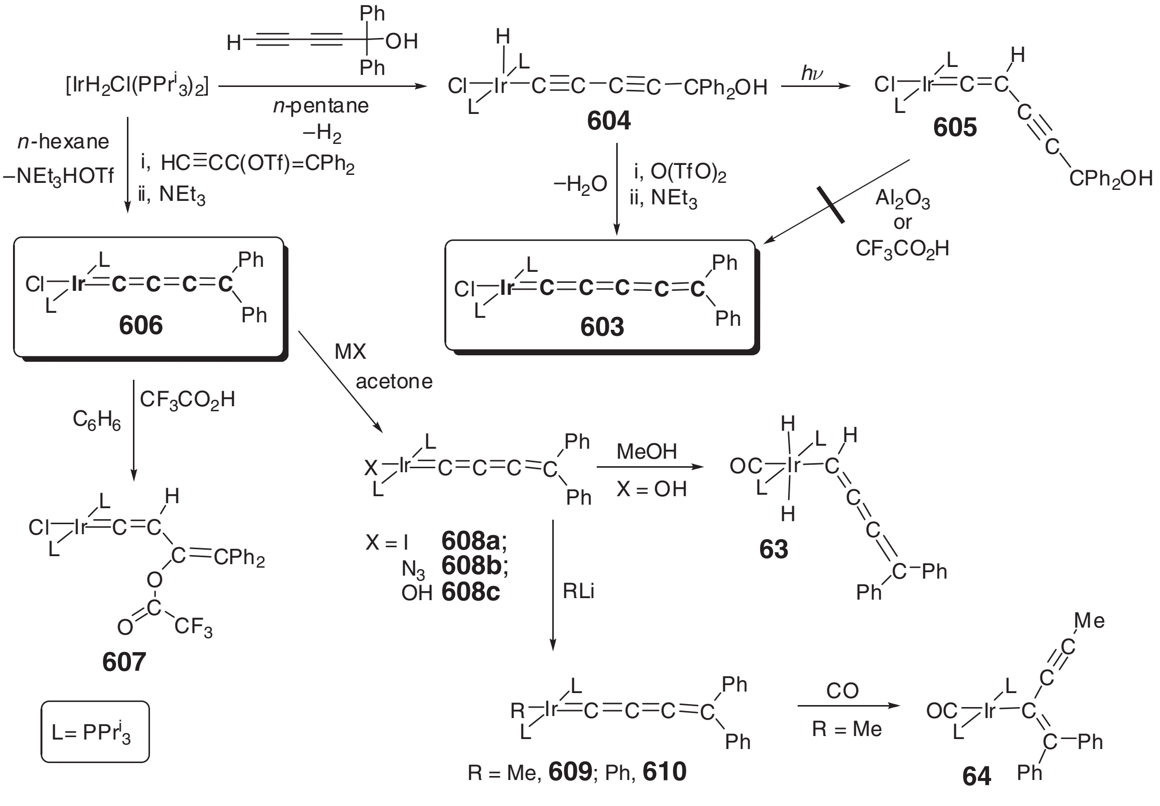
The use of the enol triflate $HC{\equiv}C–C(OTf){=}CPh_2$ that contains an excellent leaving group at the C(γ) carbon was the key to the successful synthesis of the more elusive butatrienylidene derivative, $[IrCl(C{=}C{=}C{=}CPh_2)(PPr^i{}_3)_2]$ 606, which was reported by Ilg and Werner in 2000.[352]

Compounds 603 and 606 were characterized by X-ray crystallography (Figure 49) confirming that the unsaturated C_4- and C_5-chains are nearly linear and deviate only weakly at C_1 from the ideal value of 180 °.

The two iridacumulenes share most of their chemical properties with the simpler allenylidene 518a. The reactivity of the butatrienylidene has been explored in more detail (see Scheme 87).[33] Thus, CF_3CO_2H adds across C(β)–C(γ) of the IrC_4 moiety to yield the vinylvinylidene $[IrCl\{C{=}C(H)–C(OC(O)CF3){=}CPh_2\}(PPr^i{}_3)_2]$ 607 similarly to 518a, while chloride metathesis takes place with a variety of alkaline salts to yield $[IrX(C{=}C{=}C{=}CPh_2)(PPr^i{}_3)_2]$ (X = I 608a, N_3 608b, OH 608c). As found for the allenylidene derivative, the hydroxo iridiacumulene behaves as Broensted base toward PhOH and promotes the decarbonylation of MeOH. This latter reaction results in the astonishing formation of the butatrienyl complex $[IrH_2(CO)\{C(H){=}C{=}C{=}CPh_2\}(PPr^i{}_3)_2]$ 63. The reaction with



Scheme 86



Scheme 87

MeLi or PhLi, which gives the organyl species $[IrR(C{=}C{=}C{=}CPh_2)(PPr^i_3)_2]$ (R = Me **609**, Ph **610**), is also worth mentioning. Exposure of a pentane solution of **610a** to CO brings about the migratory insertion of the C_4-chain to the $Ir–CH_3$ bond yielding the alkynyl-substituted vinyl species $[Ir(CO)\{C(C{\equiv}CCH_3){=}CPh_2\}(PPr^i_3)_2]$ **64** rather than the expected α-methyl butatrienyl complex.

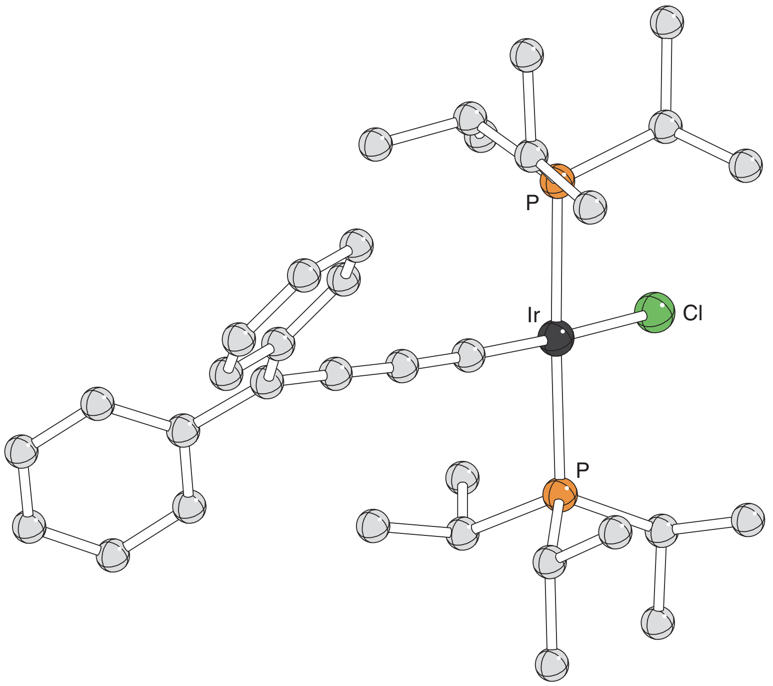
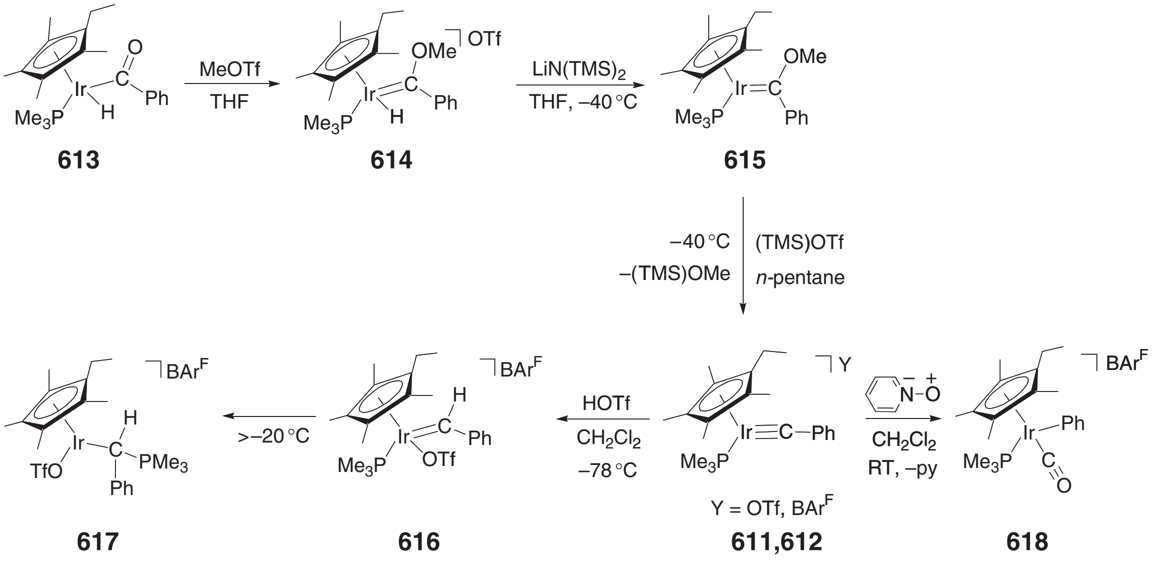


Figure 49 X-ray crystal structure of 606.

7.04.4.4 Carbyne Complexes, Ir≡CR

At variance with carbene, iridium carbynes are very rare and are limited to a handful of cationic compounds. These include the Bergman carbyne $[(C_5Me_4Et)(PMe_3)Ir{\equiv}CPh]Y$ (Y = OTf; 611, BAr^F; 612)[354] and the Werner carbynes *trans*-$[IrCl\{{\equiv}CCH{=}C(Ph)R\}(PPr^i_3)_2]Y$ (Y = CF_3CO_2, BPh_4; R = Ph, Bu^t; 602) (*vide supra* Scheme 86).[305c] Scheme 88 illustrates the synthesis of the Bergman carbyne involving: (i) methylation of the (hydrido)benzoyl complex $[(C_5Me_4Et)Ir(PMe_3)(H)\{C(O)Ph\}]$ 613, (ii) deprotonation of the hydrido alkoxycarbene 614, and



Scheme 88

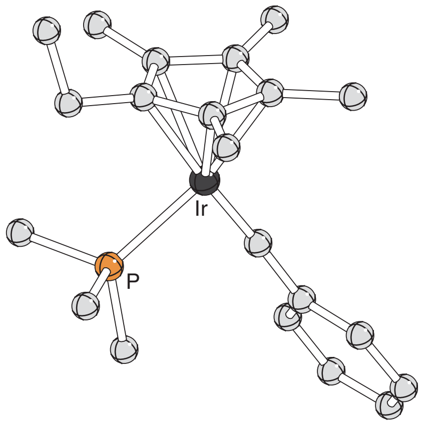


Figure 50 X-ray crystal structure of cations in **611** and **612**.

(iii) demethoxylation of the resulting Fischer carbene **615** by (TMS)OTf at low temperature. The exceptional stability of the benzylidyne complexes **611** and **612** allowed to explore its basic reactivity.[354] Noticeably, treatment with HOTf at −78 °C gave the carbene $[(C_5Me_4Et)Ir(PMe_3)(OTf)\{{=}C(H)Ph\}]BAr^F$ **616**, which is stable below −20 °C when it isomerizes to the phosphonium ylide $[(C_5Me_4Et)Ir(OTf)\{C(PMe_3)(H)Ph\}]BAr^F$ **617** via phosphine migration from the metal to the nucleophilic carbene carbon. Reaction with pyridine *N*-oxide gives a cationic phenyl(carbonyl) complex $[(C_5Me_4Et)Ir(PMe_3)(Ph)(CO)]BAr^F$ **618** likely through an intermediate cationic acyl derivative. The structure of the benzylidyne derivative has been determined which showed a short Ir–C separation [(1.734(6) Å)] and a linear Ir–C–C array [(175.7(4)°] (see Figure 50).

Mixed tetranuclear Mn_2Ir_2 clusters incorporating either μ- or μ_3-benzylydine ligands have been reported from the reaction of $(PPN)Ir(CO)_4$ and the manganese carbyne complex $[Cp(CO)_2Mn({\equiv}CC_6H_5)]BBr$.[355]

7.04.5 Iridium Complexes with Extended π-system Ligands

7.04.5.1 Cyclopentadienyl Complexes

7.04.5.1.1 General reactivity studies

The effects of cyclopentadienyl and phosphine ligands on the basicities and nucleophilicities of $[Cp^RIr(CO)(PR_3)]$ complexes were studied by Wang and Angelici. The basicities of the series of complexes $[CpIr(CO)(PR_3)]$ **619** [$PR_3 = P(p\text{-}C_6H_4CF_3)_3$ **619a**, $P(p\text{-}C_6H_4F)_3$ **619b**, $P(p\text{-}C_6H_4Cl)_3$ **619c**, PPh_3 **619d**, $P(p\text{-Tol})_3$ **619e**, $P(p\text{-}C_6H_4OCH_3)_3$ **619f**, PPh_2Me **619g**, $PPhMe_2$ **619h**, PMe_3 **619i**, PEt_3 **619j**, PCy_3 **619k**] have been measured by the heat evolved (ΔHHM) when the complex is protonated by CF_3SO_3H in dichloroethane (DCE) at 25 °C. The ΔHHM values range from 28.0 kcal mol^{-1} for **619a** (33.8 for Cp^*) to 33.2 kcal mol^{-1} for **619i** (38.0 for Cp^*) and are directly related to the basicities of the PR_3 ligands in the complexes. It was observed that the steric size of the Cp^* ligand reduces the nucleophilicities of the $[Cp^*Ir(CO)(PR_3)]$ complexes.[356]

The mechanisms of silicon–hydrogen activation by $[Cp^*Ir(PMe_3)(Me)(OTf)]$ **292** and rearrangements of the resulting silyliridium complexes were investigated. Silylene complexes of the type $[Cp^*Ir(PMe_3)(H)(SiR_2)]X$ (X = OTf, R = Mes **297a**; $X = B(C_6F_5)_4$, R = Ph **297b**) were isolated, and their involvement in the process discussed. The kinetics of the isomerization of the cyclometallated iridium(V) complex $[Cp^*Ir(PMe_3)(H)\{\kappa^2\text{-}Si,C\text{-}SiH(Mes)(C_6H_2Me_2CH_2)\}]OTf$ **296** to the iridium silylene were examined by NMR. The primary kinetic isotope effect measured implied a rate-limiting hydride migration from silicon to iridium.[357]

Bergman and co-workers showed the exceptionally low temperature carbon–hydrogen/carbon–deuterium exchange reaction catalyzed by $[Cp^*Ir(PMe_3)(H)(CH_2Cl_2)]^+$ **620**. The catalytic activity of **620** in alkane C–H activation at an unexpectedly high rate and surprisingly low temperature was studied, likely involving a dihydridoalkyl intermediate that undergoes reductive elimination of only alkane and not H_2.[358]

A comparative study on a series of chelate complexes $[Cp^*Ir(TsNCH_2CH_2NTs)]$ **621**, $[Cp^*Ir(TsNCH_2CO_2)]$ **622**, $[Cp^*Ir(CO_2CO_2)]$ **623** was performed to clarify the roles of carboxylato and sulfonamido ligands. Complexes **621** and **622** were found to be monomeric in solution and in the solid state, while **623** appears to exist as an oligomer or polymer, broken up by reaction with a ligand L such as a phosphine, CO, or 2-methoxypyridine to form [Cp*Ir(L)(CO$_2$CO$_2$)] **624**. Enthalpies for the reactions of THF-solvated monomers **621** and **622** with PMe$_3$ were determined to be −28.7 and −28.5 kcal mol^{-1}.[359]

The DNA binding of cationic complexes [Cp*Ir(AA)(dppz)](OTf)$_n$ (dppz = dipyrido[3,2-a:2′,3′-c]phenazine; *n* = 1, AA = AccysOH **625a**; *n* = 2, AA = AcmetOMe **625b**, H$_2$cysOMe **625c**; *n* = 3, AA = H$_2$metOMe **625d** containing S-coordinated amino acids (HmetOH = methionine, HcysOH = cysteine) was studied by UV–visible titration, 2D-NOESY and gel electrophoresis. The observed steady decrease in absorbance on UV–visible titration with DNA and the bathochromic shifts are consistent with stable intercalative DNA binding for these complexes. X-ray structural analyses are reported for [Cp*IrCl(dppz)]OTf **626** and [Cp*Ir(9-Etgua)(phen)](OTf)$_2$ **627** (9-Etgua = 9-ethylguanine).[360]

7.04.5.1.2 Ligand substitution in cyclopentadienyl complexes

Functionally substituted (η^5-cyclopentadienyl)dicarbonyl iridium compounds were prepared from reactions of the corresponding substituted cyclopentadienyl–Na, –Li, or –Tl reagents with chlorodicarbonyl(pyridine)iridium. Ring-substituted compounds include chloro, benzyl, acetyl, carbomethoxy, methyl, benzoyl, trimethylsilyl, cyano, dimethylamino, tetra-Ph, dimethylaminoethyl, (tetramethyl)dimethylaminoethyl, methoxyethyl, pentabenzyl, and pentamethyl. The symmmetric and antisymmetric carbonyl stretching frequencies as well as the ^{13}C NMR chemical shifts of the carbonyl substituents were correlated with various Hammett substituent parameters.[95a]

The new unsymmetrical ligand, Ph$_2$PNHC$_6$H$_4$PPh$_2$, obtained by deprotonation of (2-diphenylphosphino)benzeneamine with BuLi followed by reaction with ClPPh$_2$ in THF was used as a monodentate ligand to coordinate [{Cp*IrCl$_2$}]$_2$ through the NPPh$_2$–phosphorus to yield [Cp*IrCl$_2${κ^1-*PN*-Ph$_2$PNHC$_6$H$_4$PPh$_2$}] **627**.[361]

A wide range of transition metal complexes bearing aniline- and alkylphosphine-substituted cyclopentadienyl ligands have been synthesized, including [Cp^{x}IrI$_2$] **307**, [Cp^{x}IrH$_2$] **308**, [Cp^{x}IrMeI] where I stands for iodide **309**, [Cp^{x}IrMe$_2$] **310**, [Cp^{x}Ir(H)(SnPh$_3$)] **628**, [Cp^{x}Ir(H)(Li)] **629**, [Cp^{N}Ir(OTf)$_2$] **311**, [Cp^N(PMe$_3$)IrI$_2$] **312**, [Cp^{N}Ir(C$_2$H$_4$)$_2$ **313**, [Cp^N(PMe$_3$)IrH$_2$] **630** (see also Scheme 29). The planar-chiral Cp^P and Cp^N ligands influence dramatically the reactivity at the metal center compared to Cp* complexes. Lithium salts **629** were obtained by deprotonation of dihydride **308** with *tert*-butyllithium showing diastereoselectivity in their reactions with Ph$_3$SnCl to form **628**.[153]

Optically active iridium complexes with cyclopentadienyl–phosphine ligands were obtained by reacting the dimer [Ir(μ-Cl)(coe)$_2$]$_2$ with the ligands (*S*)-(C$_5$H$_4$CH$_2$CH(Ph)PPh$_2$)Li and (*R*)-(C$_5$H$_4$CH(Cy)CH$_2$PPh$_2$)Li to give (*S*)-[Ir(η^5-C$_5$H$_4$CH$_2$CH(Ph)PPh$_2$-κP)(coe)] **631a** and (*R*)-[Ir(η^5-C$_5$H$_4$CH(Cy)CH$_2$PPh$_2$-κP)(coe)] **631b**, which upon treatment with CH$_3$I at room temperature afford the cationic iridium(III) compounds (*S*,*S*$_{\text{Ir}}$)-[Ir(η^5-C$_5$H$_4$CH$_2$CH(Ph)PPh$_2$-κP)(CH$_3$)(coe)]I **632a** as a single diastereomer and (*R*)-[Ir(η^5-C$_5$H$_4$CH(Cy)CH$_2$PPh$_2$-κP)(CH$_3$)(coe)][I] **632b** as a 9 : 1 mixture of two diastereomers. Carbonyl homologs were obtained by reacting [IrCl(CO)(PPh$_3$)$_2$] with the chiral ligands to afford (*S*)-[Ir(η^5-C$_5$H$_4$CH$_2$CH(Ph)PPh$_2$-κP)(CO)] **633a** and (*R*)-[Ir(η^5-C$_5$H$_4$CH(Cy)CH$_2$PPh$_2$-κP)(CO)] **633b**, which upon reaction with CH$_3$I yielded the cationic iodides (*S*)-[Ir(η^5-C$_5$H$_4$CH$_2$CH(Ph)PPh$_2$-κP)(CH$_3$)(CO)]I **634** and (*R*)-[Ir(η^5-C$_5$H$_4$CH(Cy)CH$_2$PPh$_2$-κP)(CH$_3$)(CO)]I **635** as mixtures of diastereomers. No migratory insertion of the Me group into the carbonyl–metal bond has been observed even after prolonged heating.[362]

Chiral-at-metal iridium(III) half-sandwich complexes were synthesized by Brunner *et al.*[363] [Cp*Ir(beapy)Cl] **636** was synthesized by the reaction of [{Cp*IrCl$_2$}]$_2$ and the deprotonated ligand Hbeapy, the condensation product of benzylamine and 2-pyrrolcarbaldehyde (Figure 51). Two enantiomers (S_M) and (R_M) arise, differing only in the metal chirality. Similarly, the optically active bidentate Schiff base ligands (+)-2-N-[(*S*)-1-phenylethyl]pyrrolcarbaldimine, NN*H, and (+)-N-[(*S*)-1-phenylethyl]salicylaldimine, ON*H, react with [{Cp*IrCl$_2$}]$_2$ to give the half-sandwich complexes [Cp*Ir(NN*)Cl] and [Cp*Ir(ON*)Cl]. In both cases, two diastereomers (R_M,S_C) and (S_M,S_C) arise, differing only in the metal configuration.[364]

Half-sandwich optically active amino acidate alkynyl complexes [Cp*Ir(AA)(C≡CR)] (AA = Pro; R = CMe$_3$ **430a**, SiMe$_3$ **430b**: AA = N-methyl-L-prolinate (MePro); R = CMe$_3$ **431a**, SiMe$_3$ **431b** were obtained by Oro and co-workers.[200] The crystal structures of (R_{Ir},S_{C},S_{N}) **430a** and (S_{Ir},S_{C},S_{N}) **431a** were determined by X-ray analysis, with the metals η^5-bonded to the Cp* group, linked in a chelate fashion through the aminic N and one of the carboxylate oxygens to the amino acidate, and bonded to a terminal almost linear *t*-butylethynyl ligand (see Figure 37).

The synthesis of Ir(III) cyanide compounds and organometallic cyanide cages starting from tricyanometallate building blocks was described by Rauchfuss and co-workers,[365] who also studied the coordination solids derived from [Cp*Ir(CN)$_3$]$^-$. Et$_4$N[Cp*Ir(CN)$_3$] **637** was found to react reversibly in MeCN with Rh$_2$(OAc)$_4$ to afford crystals of the one-dimensional coordination solid [Et$_4$N][{Cp*Ir(CN)$_3$}{Rh$_2$(OAc)$_4$}] **638**.[366] The structure of the polymer

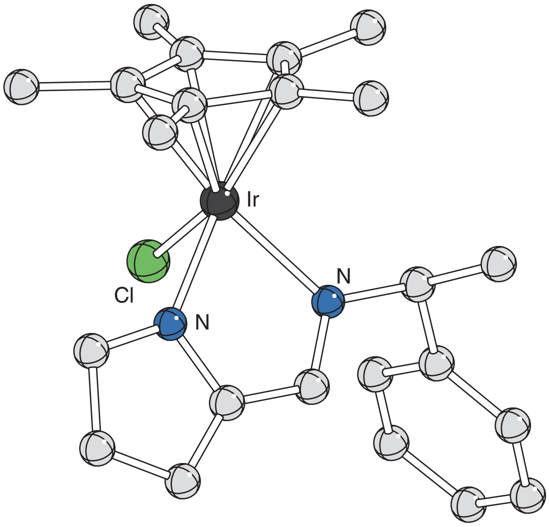


Figure 51 X-ray crystal structure of **636**.

consists of helical anionic chains containing $Rh_2(OAc)_4$ units linked via two of the three CN ligands of $Cp^*Ir(CN)_3^-$ (Figure 52).

The highly insoluble purple $[Et_4N][\{Cp^*Ir(CN)_3\}\{Rh_2(O_2CCF_3)_4\}]$ **639** was obtained using the more Lewis-acidic $Rh_2(O_2CCF_3)_4$ in place of $Rh_2(OAc)_4$. Aqueous solutions of $Et_4N[Cp^*Ir(CN)_3]$ and $AgNO_3$ afforded the colorless solid $Ag[Cp^*Ir(CN)_3]$ **640** which by recrystallization in pyridine gave the hemipyridine adduct $[Ag\{Ag(py)\}\{Cp^*Ir(CN)_3\}_2]$ **641**. The solid-state structure of **641** reveals a three-dimensional coordination polymer consisting of chains of $Cp^*Ir(CN)_3^-$ units linked to alternating Ag^+ and $Ag(py)^+$ units.

Acetonitrile ligands can be activated in the cationic complex $[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)(NCMe)]OTf$ **642**. Reactions with protic amines, alcohols, and H_2O produce amidine complexes $[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)\{NH{=}C(NR^1R^2)Me\}]OTf$ **643** (R^1, $R^2 = Me_2$; Me, H; Pr^i, H; $CH_2(CH_2)_3CH_2$), imino-ether complexes $[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)\{NH{=}C(OR^1)Me\}]OTf$ **644** ($R^1 = Me$, Et, Pr^i), and amido complex $[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)\{NH(CO)Me\}]$ **645**, respectively.[367] Tautomerization of **645** gives the enol form $[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)\{N{=}C(OH)Me\}]$ **646** in polar solvents. Tertiary amines (NMe_3, NEt_3) react with **642** in chlorinated solvents to

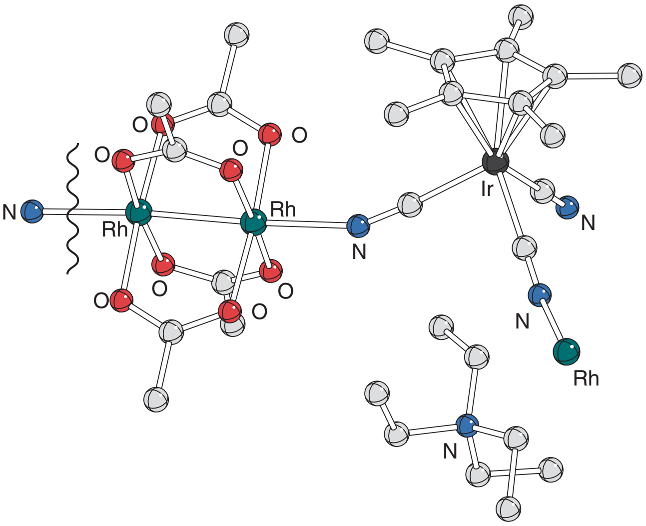


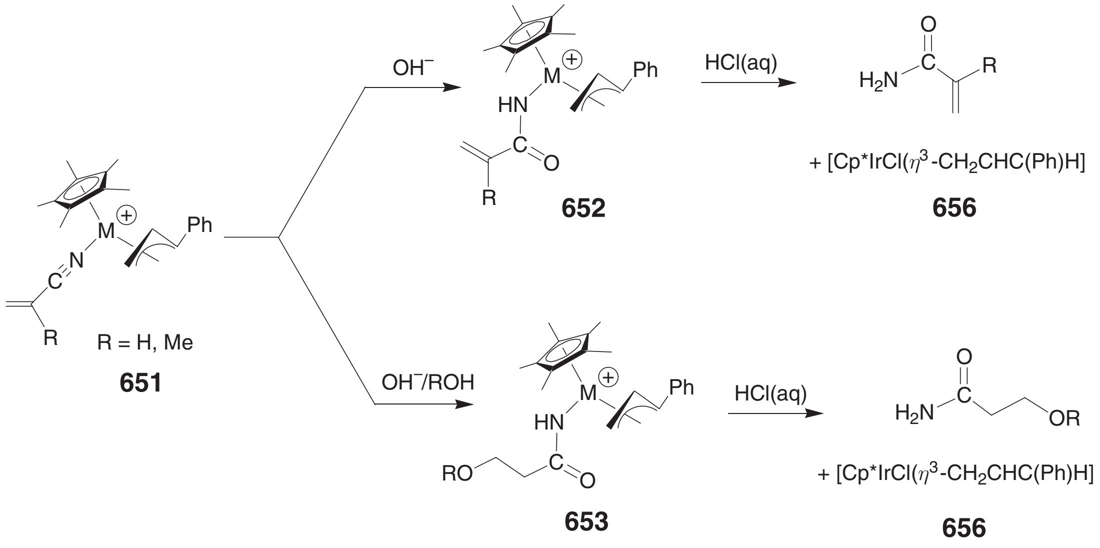
Figure 52 X-ray crystal structure of **638**.

give the chloro complex $[\mathrm{Cp^*IrCl}(\eta^3\text{-}\mathrm{CH_2CHCHPh})]$ **647** and quaternary ammonium salts. Free amidines $\mathrm{NH{=}C(NR_2)Me}$ and imino-ethers $\mathrm{NH{=}C(OR^1)Me}$ are obtained together with $[\mathrm{Cp^*Ir}(\eta^3\text{-}\mathrm{CH_2CHCHPh})\text{-}(\mathrm{PPh_3})]\mathrm{OTf}$ **648** by reaction of **643** and **644** with $\mathrm{PPh_3}$. Catalytic applications of **621** and $[\mathrm{Cp^*Ir}(\eta^3\text{-}\mathrm{CH_2CHCHPh})(\mathrm{NCCH{=}CHMe})]\mathrm{OTf}$ **649** include the hydration of the nitriles in the presence of $\mathrm{Na_2CO_3}$ to produce amides.

η^3-Allyliridium(III) complexes $[\mathrm{Cp^*Ir(C{\equiv}CBu^t)}\{\eta^3\text{-}\mathrm{CH_2CHCH(Ph)}\}]$ **420**, $[\mathrm{Cp^*Ir(X)}\{\eta^3\text{-}\mathrm{Bu^t(R)C{=}CHCHCHCH\text{-}(Ph)}\}]$ (**421**; R = H, X = Cl; R = Me, X = I), $[\mathrm{Cp^*Ir}\{\eta^3\text{-}\mathrm{CH(Ph)CHCHCH{=}C(Bu^t)Me}\}(\mathrm{NCMe})]^+$ **650**, and $[\mathrm{Cp^*Ir(C{\equiv}CBu^t)}\{\eta^3\text{-}\mathrm{CH(Ph)CHCHCH{=}C(Bu^t)Me}\}]$ **422** were prepared from the reactions of **642** with $\mathrm{HC{\equiv}CBu^t}$ in the presence of $\mathrm{NEt_3}$, HCl, and MeI (see also Scheme 47). The crystal structures of **420** and **422** have been determined by X-ray diffraction data analyses. C–C bond-forming reactions were carried out by the reactions of **421** and **422** with HCl, to yield *trans,trans*-1,3-pentadienes, $\mathrm{PhCH{=}CHCH{=}CHCH_2(Bu^t)}$ and $\mathrm{PhCH{=}CHCH{=}CHCHMe(Bu^t)}$, and *cis,trans,trans*-1,3,5-heptatriene, $\mathrm{(Bu^t)CH{=}CHC(Ph){=}CHCH{=}CHCH\text{-}Me(Bu^t)}$, respectively.[188b] Similarly, hydroxide ions and alcohols or amines are added regioselectively to the nitrile and vinyl groups of $\mathrm{CH_2{=}CHCN}$ in $[\mathrm{Cp^*Ir}\{\eta^3\text{-}\mathrm{CH_2CHCH(Ph)}\}(\mathrm{NCCH{=}CH_2})]^+$ **651**. The unsaturated amido complex $[\mathrm{Cp^*Ir}\{\eta^3\text{-}\mathrm{CH_2CHCH(Ph)}\}\{\mathrm{NHC(O)CH{=}CH_2}\}]$ **652**, alkoxo amido complexes $[\mathrm{Cp^*Ir}\{\eta^3\text{-}\mathrm{CH_2CHCH(Ph)}\}\{\mathrm{NHC(O)CH_2CH_2OR}\}]$ (R = Me, Et, **653**), amino amido complexes $[\mathrm{Cp^*Ir}\{\eta^3\text{-}\mathrm{CH_2CHCH(Ph)}\}\{\mathrm{NHC(O)CH_2CH_2NR^1R^2}\}]$ ($\mathrm{R^1}$, $\mathrm{R^2}$ = Me; Me, H; **654**), and an amino imino-ether complex $[\mathrm{Cp^*Ir}\{\eta^3\text{-}\mathrm{CH_2CHCH(Ph)}\}\{\mathrm{NH{=}C(OMe)CH_2CH_2NMe_2}\}]^+$ **655** were prepared from the reactions of **651** with $\mathrm{OH^-}$, $\mathrm{OH^-/ROH}$ (R = Me, Et), $\mathrm{OH^-/HNR^1R^2}$ ($\mathrm{R^1}$, $\mathrm{R^2}$ = Me; Me, H), and $\mathrm{MeOH/NHMe_2}$. Subsequent addition of aqueous HCl to **652**–**655** yields $[\mathrm{Cp^*IrCl}\{\eta^3\text{-}\mathrm{CH_2CHCH(Ph)}\}]$ **656** and quantitative amounts of $\mathrm{H_2NCOCH{=}CH_2}$, $\mathrm{H_2NCOCH_2CH_2OR}$, $\mathrm{H_2NCOCH_2CH_2NR^1R^2}$, and $\mathrm{MeOCOCH_2CH_2NMe_2}$, respectively (Scheme 89).[368]

Mechanistic investigations on the “water substitution” in $[\mathrm{Cp^*Ir(H_2O)_3}]^{2+}$ **494** by $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$, py, $\mathrm{SCN^-}$, 4-CNpy, nicotinamide, TU, and DMS were studied by stopped-flow spectroscopy by Merbach and co-workers.[369] Spectrophotometric titrations allowed the measurement of the proton dissociation constants of **494** ($\mathrm{p}K_\mathrm{a} = 3.86$). The equilibrium constants $\mathrm{K_1}$ for the formation of the monosubstituted complexes $[\mathrm{Cp^*Ir(H_2O)_2L}]^{2+}$ (L = neutral ligand) or $[\mathrm{Cp^*Ir(H_2O)_2L}]^{+}$ (L = anionic ligand) lie in the range 10^2–10^5 $\mathrm{M^{-1}}$ and follow the sequences $\mathrm{K_{(Cl-)} < K_{(Br-)} < K_{(I-)}}$ and $\mathrm{K_{(4-CNpy)} < K_{(nicotinamide)} < K_{(py)} < K_{(TU,\ DMS)}}$. Similar investigations have also been extended to a series of half-sandwich Ir(III) aqua cations $[\mathrm{Cp^*Ir(A\text{–}B)(H_2O)}]^{2+/+}$ with a variety of different bidentate N,N or N,O ligands.[370]

Solvent exchange on the half-sandwich organic solvates $[\mathrm{Cp^*Ir(Solv)_3}]^{2+}$ [Solv = MeCN **657a** or DMSO **657b**] was studied as a function of temperature, pressure, and concentration of free solvent by ^{1}H NMR line-broadening techniques in $\mathrm{CD_3CN}$ and/or $\mathrm{CD_3NO_2}$.[371]



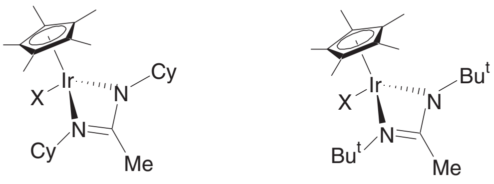
Scheme 89

The iridium(III) dimethyl derivatives [Cp*Ir(L)Me$_2$] (L = PPh$_3$ **300a**, PMePh$_2$ **300b**, PMe$_2$Ph **300c**, and PMe$_3$ **300d** react with NOBF$_4$ in CH$_2$Cl$_2$ to give the iridium(III) cationic alkylnitrosyl derivatives [Cp*IrMe$_2$(NO)]BF$_4$ **303** and [Cp*Ir(L)Me(NO)](BF$_4$)$_2$ (**304**, L = PMePh$_2$ **304b**, PMe$_2$Ph **304c**, PMe$_3$ **304d**) (see Scheme 27). EPR spectroscopy suggests that the reaction proceeds through the iridium(IV) intermediates (**658a–d**)$^+$. Treatment of **658d** with NOBF$_4$ in acetonitrile gives, in addition to **304d**, the acetonitrile substitution products [Cp*Ir(PMe$_3$)Me(MeCN)]BF$_4$ **659** and [Cp*Ir(PMe$_3$)(MeCN)$_2$](BF$_4$)$_2$ **660**.[149a]

(Pentamethylcyclopentadienyl)iridium amidinate complexes were synthesized and structurally characterised by Simpson and Marshall[372] Reaction of [{Cp*IrCl$_2$}]$_2$ with lithium amidinates provides a series of amidinato iridium complexes [Cp*Ir(X){RN═C(Me)NR}] **661** with R = Bu^t, Cy; X = Cl, Br. Alkyl or hydride derivatives are formed by addition of Grignard reagents or sodium isopropoxide to the starting complex. Cationic complexes may be obtained by the interaction with AgSbF$_6$ in the presence of an appropriate ligand. In all of these compounds, the amidinate ligand adopts a symmetrical bidentate coordination geometry (see Scheme 90).

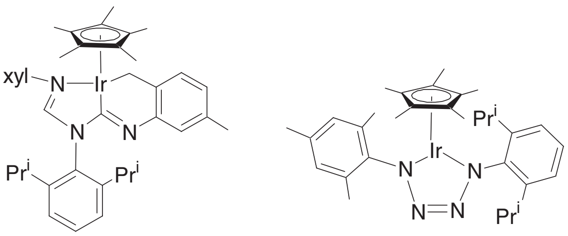
Reactions of [Cp*Ir(NR)] R = Bu^t **662a** or 2,6-Pr$^i_2$C$_6$H$_3$ **662b** with 2,6-xylyl isocyanide [(Xyl)NC], mesityl isocyanate, and mesityl azide were studied by Danopoulos *et al.*[373] The bridged dimers [Cp*Ir(μ-NC$_5$H$_9$)]$_2$ (C$_5$H$_9$ = cyclopentyl **663** and [Ir$_2$Cp$^*_2$(η-NC$_6$H$_{11}$)(μ-NHC$_6$H$_{11}$)]Cl **664** were synthesized. The crystal structures of compounds **663**, **664**, [Cp*Ir(η^2-Bu^{t}NCNBu^t)(CNBu^t)] **665**, [Cp*Ir{N(xyl)CHN(2,6-Pr$^i_2$C$_6$H$_3$)CNC$_6$H$_3$(Me)CH$_2$}] **666**, [Cp*Ir{N(2,6-Pr$^i_2$C$_6$H$_3$)C(O)N(Mes)}] **667**, and [Cp*Ir{N(2,6-Pr$^i_2$C$_6$H$_3$)N$_3$(Mes)}] **668** were determined (Scheme 91).

A general and unprecedented synthetic procedure to isolate and fully characterize a series of η^4-*o*-quinone methide complexes **I** (R^1 = H, R^2 = H, Me; R^1 = Me, R^2 = H, Pr^i) including *o*-quinone methide has been described.[374] Coordination of 2-alkylphenols to [Cp*Ir(acetone)$_3$](BF$_4$)$_2$ and subsequent deprotonation with NEt$_3$ affords [Cp*Ir{η^5-(2-alkyl)oxodienyl}]BF$_4$ complexes **669** in 85–90% yield. Deprotonation of **669** with KOBu^t gives 81–96% yields of neutral *o*-quinone methide complexes [Cp*Ir{η^4-C$_6$H$_3$R^1[═C(R^2)$_2$]O}] [**670**, shown in Scheme 92; R^1 = R^2 = H **670a**; R^1 = Me, R^2 = H **670b**; R^1 = H, R^2 = Me **670c**; R^1 = Pr^i, R^2 = Me **670d**, in which the {Cp*Ir} fragment is coordinated in η^4-fashion to the two C–C double bonds of the six-membered ring. Although stable under argon at RT, Cp*Ir-*o*-quinone methide complexes **670a** exhibit unusual reactivity toward acids or electrophiles. Then, treatment of **670a** with 1 equiv. of HBF$_4$·Et$_2$O or I$_2$ leads to the oxodienyl complexes [Cp*Ir(η^5-C$_7$H$_7$O)]BF$_4$ **669a** or [Cp*Ir(η^5-C$_7$H$_6$IO)]I **671**; reaction with HC≡CC(O)OMe afforded a new *o*-quinone methide complex **672** from coupling between the electrophilic alkyne and the exocyclic C(═CH2) of complex **670a**. Finally, treatment of **670a** with N-methylmaleimide gave the tricyclic Ir complex **673** as a result of an unprecedented [2 + 3] cycloaddition with part of the *o*-quinone methide complex **670a**.



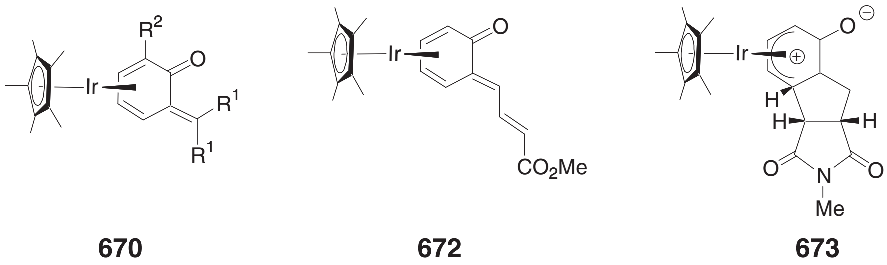
X = Cl, Br **661**

Scheme 90



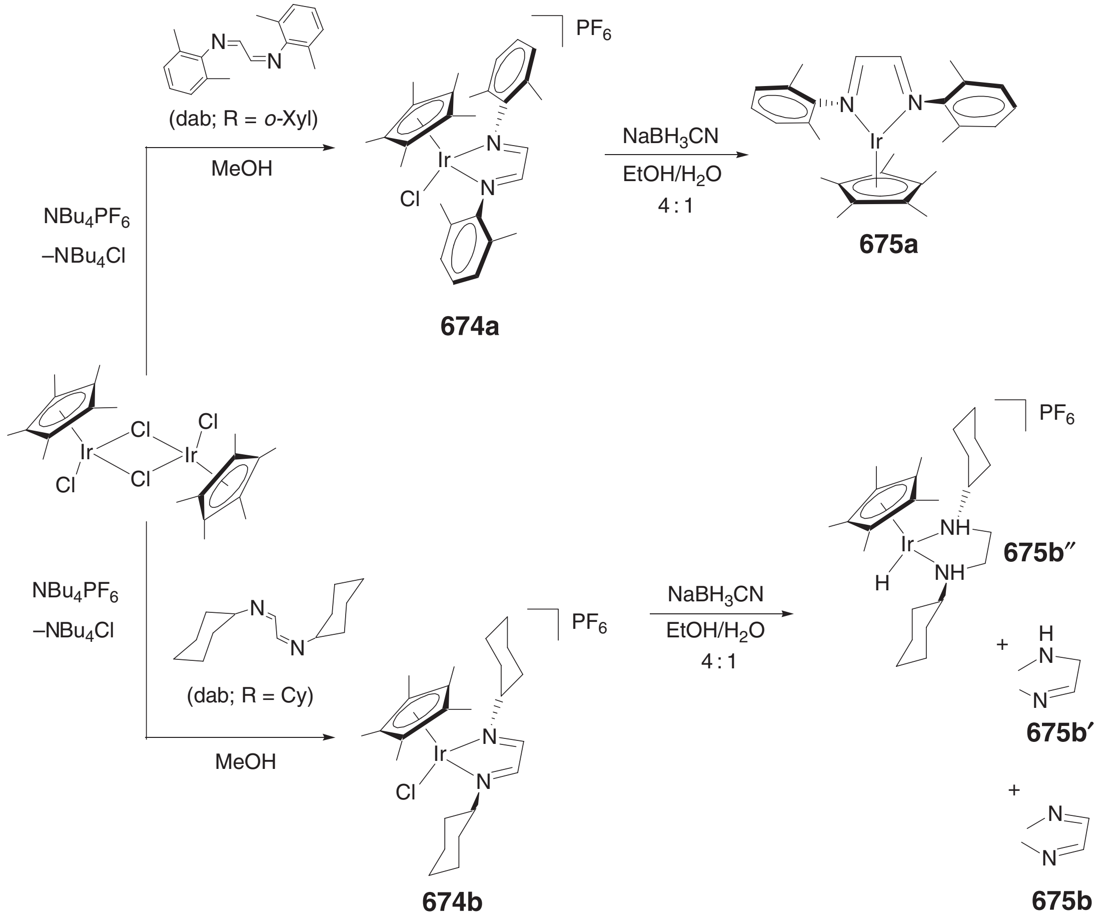
666 **668**

Scheme 91



Scheme 92

The reaction of $[\{Cp^*IrCl_2\}]_2$ in the presence of the good π-accepting α-diimine ligands 1,4-disubstituted-1,4-diaza-1,3-butadiene (dab) (R = *m*-Xyl, 2,6-$Pr^i_2C_6H_3$, *o*-Tol, Cy) has been investigated by Kaim and co-workers.[375,376] In methanol the iridium precursor forms the iridium(III) complex $[Cp^*IrCl(dab)]PF_6$ [R = *m*-Xyl **674a**, Cy **674b** which, for R = *m*-Xyl, by reaction with $Na(BH_3CN)$, does not form an iridium(III) hydride but, unexpectedly, the coordinatively unsaturated Ir(I) complex $[Cp^*Ir(dab)]$ **675a** (Scheme 93). Analysis of the metrical parameters and *ab initio* theoretical calculations indicate that the reduction has occurred primarily at dab ligand to form an ene-1,2-diamido/Ir(III) moiety (Ir^{3+}/dab^{2-} structure) or, alternatively, a metallaligand six-π-electron delocalized iridahetero-aromatic system. When the α-diimine substituents are axially shielding groups, such as 2,6-dialkylphenyl, this behavior occurs even in protic media ($EtOH/H_2O$). However, in protic media the complex with R = cyclohexyl



Scheme 93

undergoes Cl/H exchange with total or partial hydrogenation of the α-diimine ligand resulting in the formation of a mixture of Ir(III) hydride species $[\mathrm{Cp^*IrH\{RN{=}CHCH{=}NR\}}]\mathrm{PF_6}$ **675b**, $[\mathrm{Cp^*IrH\{RHNCH_2CH{=}NR\}}]\mathrm{PF_6}$ **675b′**, and $[\mathrm{Cp^*IrH\{RHNCH_2CH_2NHR\}}]\mathrm{PF_6}$ **675b″**.

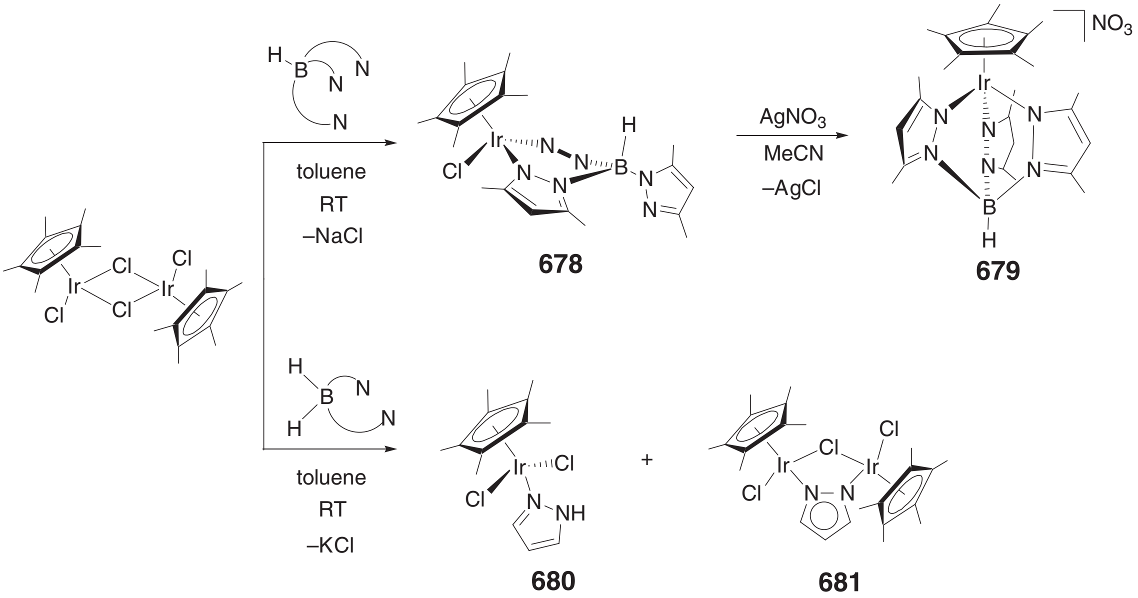
The mononuclear Ir(III) complexes of formulas $[\mathrm{Cp^RIrCl_{(3-n)}(R_2pzH)_n}]^{(n-1)+}$ (**676**, $n=1$, 2) were obtained by Stobart and co-workers through reactions of pyrazole (pzH, i.e., R = H) or substituted pyrazoles (R = Me, $\mathrm{Bu^t}$) with iridium Cp or Cp* precursors. Dinuclear complexes of formulas $[\mathrm{Cp^RIrCl(\mu\text{-}pz)}]_2$ (R = H, Me **677**) containing pyrazolyl bridges can be isolated through further reaction of the mononuclear compounds, or directly from the chloro-bridged dimers $[\{\mathrm{Cp^RIrCl}\}]_2$ by treatment with pyrazole in the presence of $\mathrm{NEt_3}$, although the dipyrazole iridium cation $[\mathrm{Cp^*IrCl(pzH)_2}]^+$ does not undergo this type of dimerization.[377]

Mixed sandwich complexes of iridium(III) $[\mathrm{Cp^*Ir(Tp^R)Cl}]$ ($\mathrm{Tp^R}$ = Tp or $\mathrm{Tp^{Me}}$ **678**) have been synthesized by Pettinari *et al.*[378] by reaction of $[\{\mathrm{Cp^*IrCl_2}\}]_2$ with $\mathrm{KTp^R}$. While the Cp* ligand exhibits the expected η^5-hapticity, the potentially tridentate $\mathrm{Tp^R}$ ligands behave as κ^2-ligands. Reaction between $[\mathrm{Cp^*Ir(Tp)Cl}]$ and $\mathrm{AgNO_3}$ in acetonitrile yields ionic $[\mathrm{Cp^*Ir(Tp^R)}]\mathrm{NO_3}$ complexes **679** with tridentate κ^3-coordination of the trispyrazolylborate. B–N hydrolysis takes place easily when $\mathrm{Tp^R}$ is replaced with bis(pyrazolylborate) ligands. Two different compounds have been obtained from the reaction of KBp and $[\{\mathrm{Cp^*IrCl_2}\}]_2$, namely the monomeric $[\mathrm{Cp^*IrCl_2(pzH)}]$ **680** and the binuclear $[\{\mathrm{Cp^*IrCl}\}_2(\mu\text{-Cl})(\mu\text{-pz})]$ **681**. Scheme 94 summarizes this chemistry.

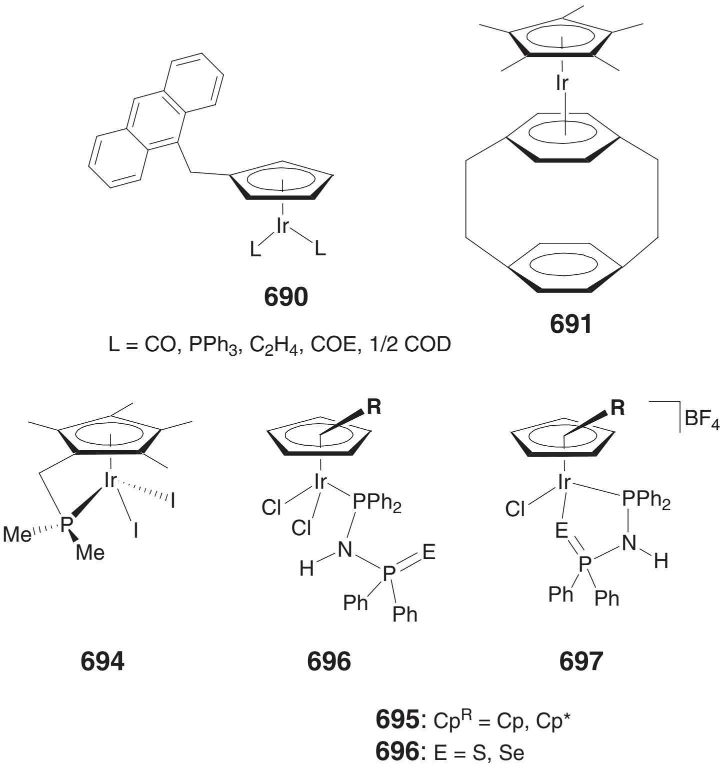
Ligand activation in the complex $[\mathrm{Cp^*Ir(MDMPP\text{-}P,O)Cl}]$ **682** (see also Scheme 8) was achieved by reaction with tetracyanoethene (TCNE) in the presence of $\mathrm{KPF_6}$ affording $[\mathrm{Cp^*IrCl(PPh_2\{2\text{-}O\text{-}3\text{-}((NC)_2CHC(CN)_2)\text{-}6\text{-}MeOC_6H_2\})}]$ **683**, $[\mathrm{Cp^*Ir(PPh_2\{2\text{-}O\text{-}3\text{-}((NC)_2C{=}C(CN))\text{-}6\text{-}MeOC_6H_2\}_2(CN)}]\mathrm{PF_6}$ **684**, $[\{\mathrm{Cp^*Ir(PPh_2\{2\text{-}O\text{-}3\text{-}((NC)_2C{=}C(CN))\text{-}6\text{-}MeOC_6H_2\}\}(CN)\{Cp^*Ir(MDMPP\text{-}P,O)\}}]\mathrm{PF_6}$, **685** and $[\{\mathrm{Cp^*Ir(MDMPP\text{-}P,O)}\}_2(\mathrm{CN})]\mathrm{PF_6}$ **686**, depending on the reaction conditions. Reaction of **683** with $\mathrm{KPF_6}$ or AgOTf in the absence and presence of xylyl isocyanide (XylNC) gave **684** or $[\mathrm{Cp^*MCl\{PPh_2(2\text{-}O\text{-}3\text{-}((NC)_2CHC(CN)_2)\text{-}6\text{-}MeOC_6H_2)\}(XylNC)}]\mathrm{OTf}$ **687**.[379]

Reaction of the Ir dimer $[\{\mathrm{Cp^*IrCl_2}\}]_2$ in $\mathrm{CH_2Cl_2}$ or $\mathrm{Me_2CO}$ with $\mathrm{AgBF_4}$ (1 : 2 molar ratio) and the tris(diphenylthiophosphinoyl)methanide tripod ligand $(\mathrm{SPPh_2})_3\mathrm{CH}$ leads to the cationic compound $[\mathrm{Cp^*IrCl\{\kappa^2\text{-}\mathit{S,S'}\text{-}(SPPh_2)_2CH(SPPh_2)\}}]\mathrm{BF_4}$ **688** which may be deprotonated by Tl(I) pyrazolate affording $[\mathrm{Cp^*Ir\{\kappa^3\text{-}\mathit{S,S',S''}\text{-}(SPPh_2)_3C\}}]\mathrm{BF_4}$ **689**. The redox properties of the complexes were studied by cyclic voltammetry.[380]

9-Anthrylmethyl-functionalized cyclopentadienyl derivatives of iridium(I) were synthesized by Cicogna *et al.* and their luminescence properties were studied.[381] The ligand was prepared by reacting 9-bromomethylanthracene with CpNa and transformed into its thallium(I) derivative by reaction with thallium ethoxide. The 9-anthrylmethylcyclopentadienyl ($\mathrm{AnCH_2C_5H_4}$) derivatives of iridium(I) of formula $[(\eta^5\text{-}\mathrm{AnCH_2C_5H_4})\mathrm{IrL_2}]$ (**690**, L = $\mathrm{C_2H_4}$, CO, $\mathrm{PPh_3}$,



Scheme 94



Scheme 95

COE; $L_2 = C_7H_8$, 1,5-COD) were obtained in good yields by reaction with the corresponding iridium(I) chloride precursors (Scheme 95). Intramolecular charge-transfer process between the photoexcited 9-anthracenyl group and the cyclopentadienyl metal unit was invoked to explain the observed anthracenic fluorescence quenching and was studied by detailed EPR characterization of the corresponding cation radicals.[382]

Mononuclear [2.2]paracyclophane dicationic complexes $[Cp^*Ir(\eta^6\text{-pcp})](BF_4)_2$ (**691**, pcp = [2.2]paracyclophane) were crystallized and their structures obtained (Figure 53). The metal atom is bonded to the benzene ring on one side of the pcp ligand in the η^6-coordination mode and supported by the Cp* ligand to afford a triple-decker sandwich structure.[383]

Ir(I) complexes with triseleno- and telluro-ether tripodal ligands were prepared by the reaction of $[IrCl(cod)]_2$ with two molar equivalents of L_3 ($L_3 = MeC(CH_2ER)_3$; E = Se; R = Me; E = Te, R = Me or Ph) and two molar equivalents of NH_4PF_6 at RT in CH_2Cl_2 affording $[Ir(cod)(L_3)]PF_6$ **692**. The crystal structures of $[Ir(cod)\{MeC(CH_2SeMe)_3\}]PF_6$ and $[Ir(cod)\{MeC(CH_2TePh)_3\}]PF_6$ reveal distorted square-pyramidal geometries. The Ir(III) complex $[Cp^*IrM(L_3)](PF_6)_2$ **693** was prepared instead via the reaction of $[\{Cp^*IrCl_2\}]_2$ with 2 equiv. of L_3 and double the amount of $TlPF_6$ in refluxing MeOH.[384]

The diiodo complexes $[Ir(\eta^5,\kappa^1\text{-P–L})I_2]$ **694** derived from the dimethylphosphino-substituted cyclopentadienyl precursor $[M(C_5Me_4CH_2PMe_2)]$, where M = Li, Na, or K(**a**), was prepared by Green and co-workers by the reaction of $[IrCl(cod)]_2$ with the salt of functionalized cyclopentadiene in THF at 0 °C. Structure **694** is only moderately stable (Scheme 95).[385]

The uncoordinated P-atom of the bis(diphenylphosphine)amine (dppa) ligand in $[Cp^RIrCl_2(\eta^1\text{-}PPh_2NHPPh_2)]$ (Cp^R = Cp, Cp* **695**) reacts with S or Se to form $[Cp^RIrCl_2(\eta^1\text{-}PPh_2NHP(E)Ph_2)]$ (E = S, Se **696**) containing the P-coordinated monosulfide or monoselenide ligands. The Se derivatives also were directly prepared from the corresponding $[\{Cp^*IrCl_2\}]_2$ dimer and dppaSe. Chloride abstraction from **696** yields cationic complexes $[Cp^*IrCl(\kappa^2\text{-}P,E\text{-}PPh_2NHP(E)Ph_2)]^+$, where the monochalcogenide ligand behaves as a chelated *P*,*E*-ligand **697** (Scheme 95).[386]

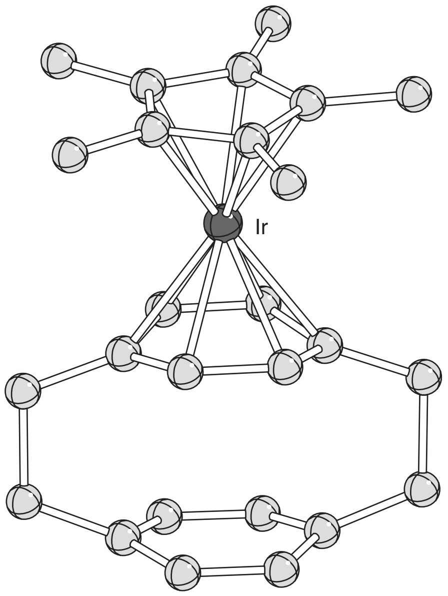
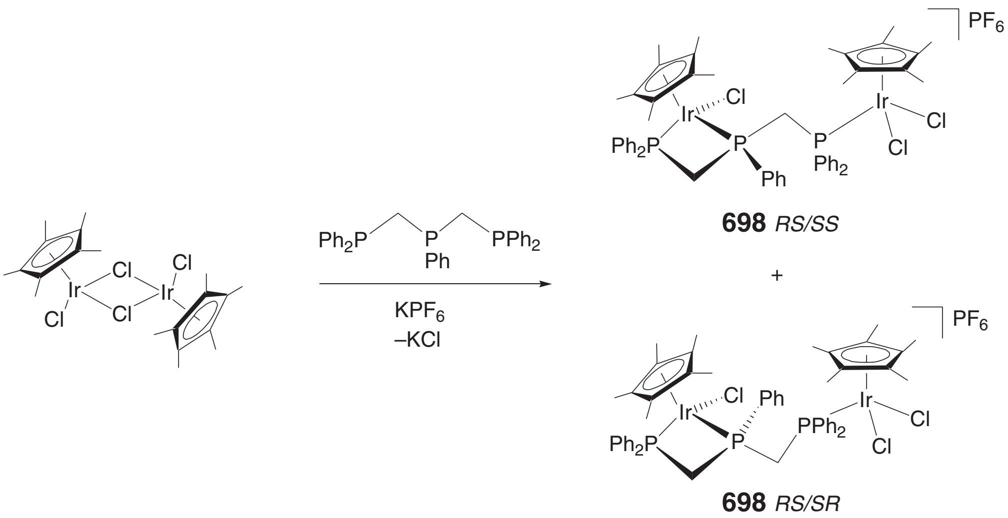


Figure 53 X-ray crystal structure of **691**.

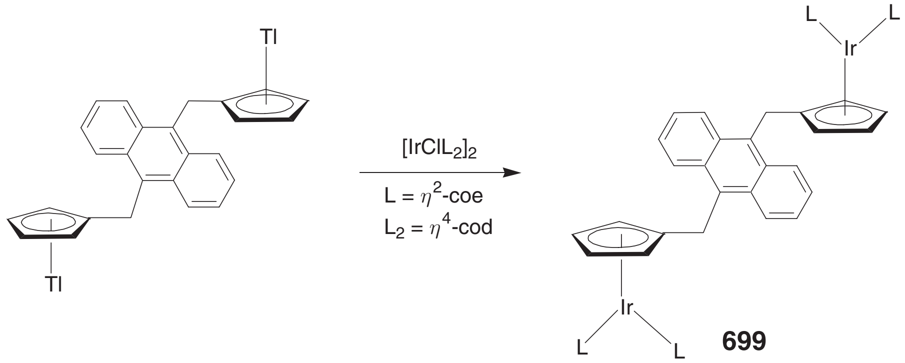
7.04.5.1.3 Polymetallic cyclopentadienyl complexes and clusters

Reaction of $[\{Cp^*IrCl_2\}]_2$ with the triphosphine bis(diphenylphosphinomethyl)phenylphosphine (dpmp) in the presence of KPF_6 gives only the dinuclear monocationic complex $[Cp^*IrCl_2(dpmp)IrClCp^*]PF_6$ **698** showing two chiral centers (Scheme 96). The diastereomers, produced in about 1 : 1.1 ratio, do not isomerize after prolonged standing at 120 °C but could be separated and characterized by mass spectrometry and X-ray analyses.[387]

Homobimetallic anthracene-bridged η^5-cyclopentadienyl derivatives of iridium(I) were synthesized by Diversi and co-workers by the reaction of 9,10-bis[(cyclopentadienylmethyl)thallium(I)]anthracene, obtained from 9,10-bis-(cyclopentadienylmethyl)anthracene, with $[IrClL_2]_2$ (L = coe, L_2 = cod); the corresponding bimetallic iridium(I) complexes $[L_2Ir\{C_5H_4CH_2(9,10\text{-anthrylene})CH_2C_5H_4\}IrL_2]$ **699** were obtained (Scheme 97). Electrochemical and fluorescence data were explained by intramolecular charge-transfer process between the photoexcited 9,10-anthrylene group and the $CpML_2$.[388]



Scheme 96



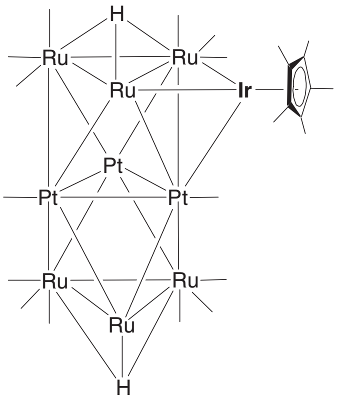
699

Scheme 97

The reaction of the dianion $[Pt_3Ru_6(CO)_{21}(\mu\text{-}H)_2]^{2-}$, generated *in situ* by the deprotonation of $[Pt_3Ru_6(CO)_{21}(\mu\text{-}H)_3(\mu_3\text{-}H)]$, with $[Cp^*Ir(NCMe)_3]^{2+}$ yields the higher nuclearity cluster complex $[Pt_3Ru_6(CO)_{21}(\mu_3\text{-}IrCp^*)(\mu_3\text{-}H)_2]$ **700**. The iridium atom occupies a triply bridging position across one of the Ru_2Pt triangles. The hydride ligands have adopted triply bridging positions on the two Ru_3 triangles (Scheme 98).[389]

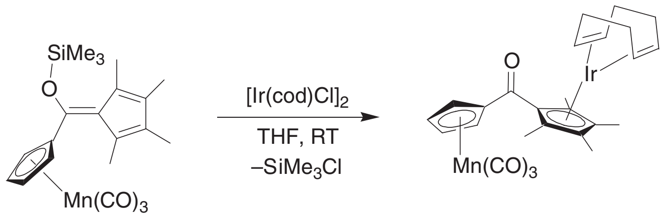
A series of tetrahedral clusters involving ligand and core metal variations, including 60-electron tetrahedral clusters $[MIr_3(CO)_{11-x}(PMe_3)_x(Cp^R)]$ **701** and $[M_2Ir_2(CO)_{10-x}(PMe_3)_x(Cp^R)]$ **702** [M = Mo, $x = 0$, $Cp^R = C_5H_4Me$ **702a**, C_5HMe_4 **702b**, C_5Me_5 **702c**; M = W, $Cp^R = C_5H_4Me$, $x = 1$ **702d**, $x = 2$ **702e**] have been carefully studied by a variety of chemico-physical methods including crystallography, Raman spectroscopy, cyclic voltammetry, UV–vis–NIR and Ir spectroelectrochemistry and modeled by theoretical methods (DFT). These methodical analyses have allowed the authors to assess cluster rearrangement to accommodate steric crowding, the utility of metal–metal stretching vibrations in mixed metal cluster characterization, the tuning of electronic structure by systematic modifications of the tetranuclear cluster core, and to identify how the different cluster species interconvert upon electrochemical oxidation or reduction.[390]

Heterodinuclear complexes with a bis(cyclopentadienyl) bridging ligand were synthesized by Heck and Kornich.[391] The reaction of $\{M\}[\eta^5\text{-}C_5H_4CO_2Me]$ (($\{M\} = W(CO)_3Me$ **703a**), $Mn(CO)_3$ **703b**) with tetramethylcyclopentadienyllithium and Me_3SiCl affords $\{M\}[\eta^5\text{-}C_5H_4C(OTMS)(C_5Me_4)]$ **704** in high yields. Hydrolysis of **704** results in the quantitative formation of $\{M\}[\eta^5\text{-}C_5H_4C(O)(C_5Me_4H)]$ **705**. Complexes **704** and **705** are versatile precursors for the synthesis of homo- and heterodinuclear complexes containing a bis(cyclopentadienyl) ketone ligand. Deprotonation of **703b** and further reaction with $[Ir(cod)Cl]_2$ yields the tetrametallic compound $[\{Mn(CO)_3\}[(\eta^5\text{-}C_5H_4)C(O)(\eta^5\text{-}C_5Me_4)]\{Ir(cod)\}]$ **706** (Scheme 99).



700

Scheme 98



703b **706**

Scheme 99

A beautiful homometallic cyclic hexamer with a cubic cavity was obtained by a self-assembly reaction between $[Cp^*Ir(H_2O)_3]$,$^{2+}$ generated *in situ* from treating $[\{Cp^*IrCl_2\}]_2$ with AgOTf in water, and 6-purinethione riboside (Hputrb), yielding $[\{Cp^*Ir(putrb)\}_6](OTf)_6$. **707** The X-ray crystal structure of the Rh analog was obtained.[392] Similarly, quasi-octahedral iridium macrocycles bearing a Cp* were obtained by the reactions of $[\{Cp^*IrCl_2\}]_2$ with bidentate ligands L (L = pyrazine, 1,4-$(CN)_2C_6Me_4$, 1,4-$(CN)_2$-2,5-$Me_2C_6H_2$) giving $[Cp^*_2Ir_2Cl_4(\mu\text{-}L)]$ **708**, which were converted into tetranuclear complexes $[Cp^*_2M_2Cl_2(L)(L')]_2(OTf)_4$ **709** containing different ligands on treatment with AgOTf. Complex **709** was characterized by X-ray crystallographic methods (Figure 54).[393]

Two rare examples of heterobimetallic trihydride complexes, $[Cp^*Ru(\mu\text{-}H)_3IrCp^*]$ **710** and $[Cp^{Et}Ru(\mu\text{-}H)_3IrCp^*]$ **711**, containing Ru and Ir with substituted cyclopentadienyl rings as ancillary ligands, were synthesized by Shima and Suzuki from the reaction of $[Cp^RRu(CH_3CN)_3]BF_4$ and $Li[CpIrH_3]$ in THF at RT (Scheme 100). Replacing the ruthenium precursor with the cubane $[\{Cp^RRuCl\}]_4$ yields the same dinuclear hydrides. The structure of **711** was determined by X-ray crystallography showing an Ru–Ir distance of only 2.4858(2) Å. H/D scrambling occurs at both hydride sites and Cp^R substituents. η^2-Coordination of benzene to give a transient $[Cp^RRu(\mu\text{-}H_3)(\eta^2\text{-}C_6D_6)IrCp^*]$ followed by C–D oxidative addition/C–H reductive elimination at iridium have been hypothesized to account for the

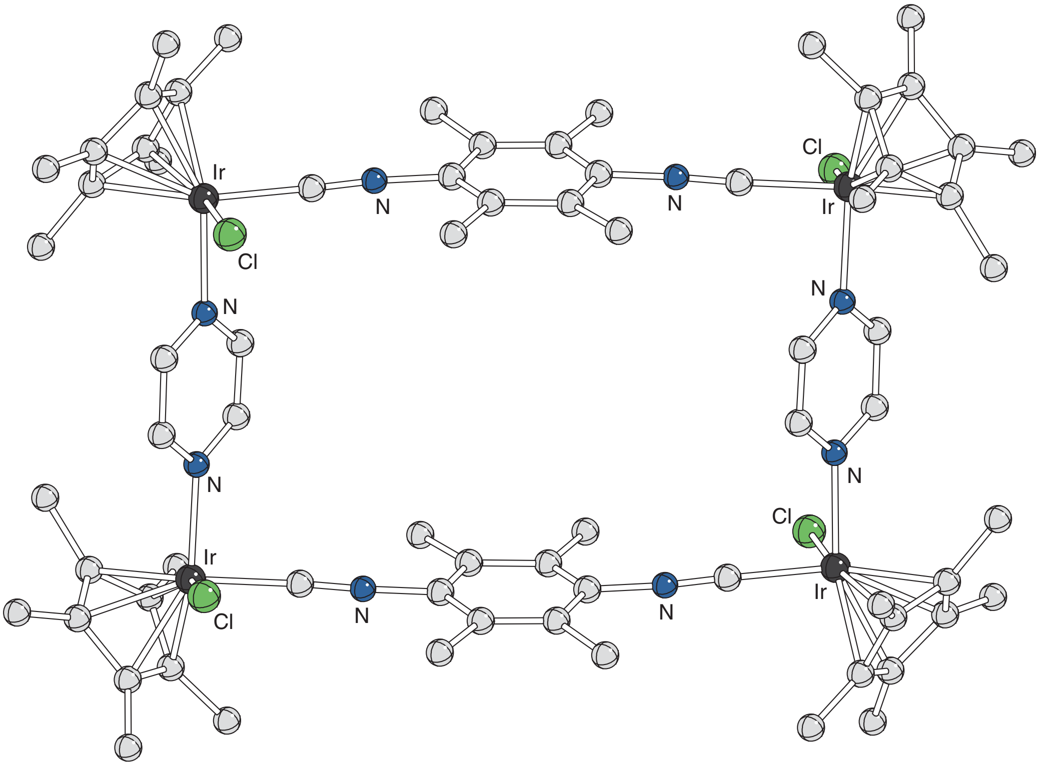
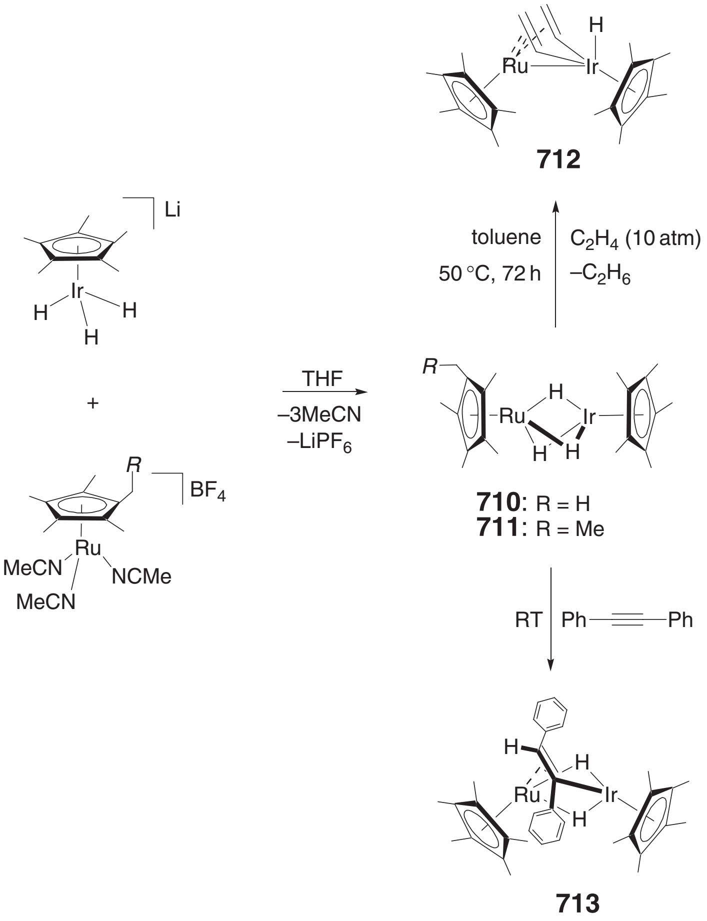


Figure 54 X-ray crystal structure of **708**.

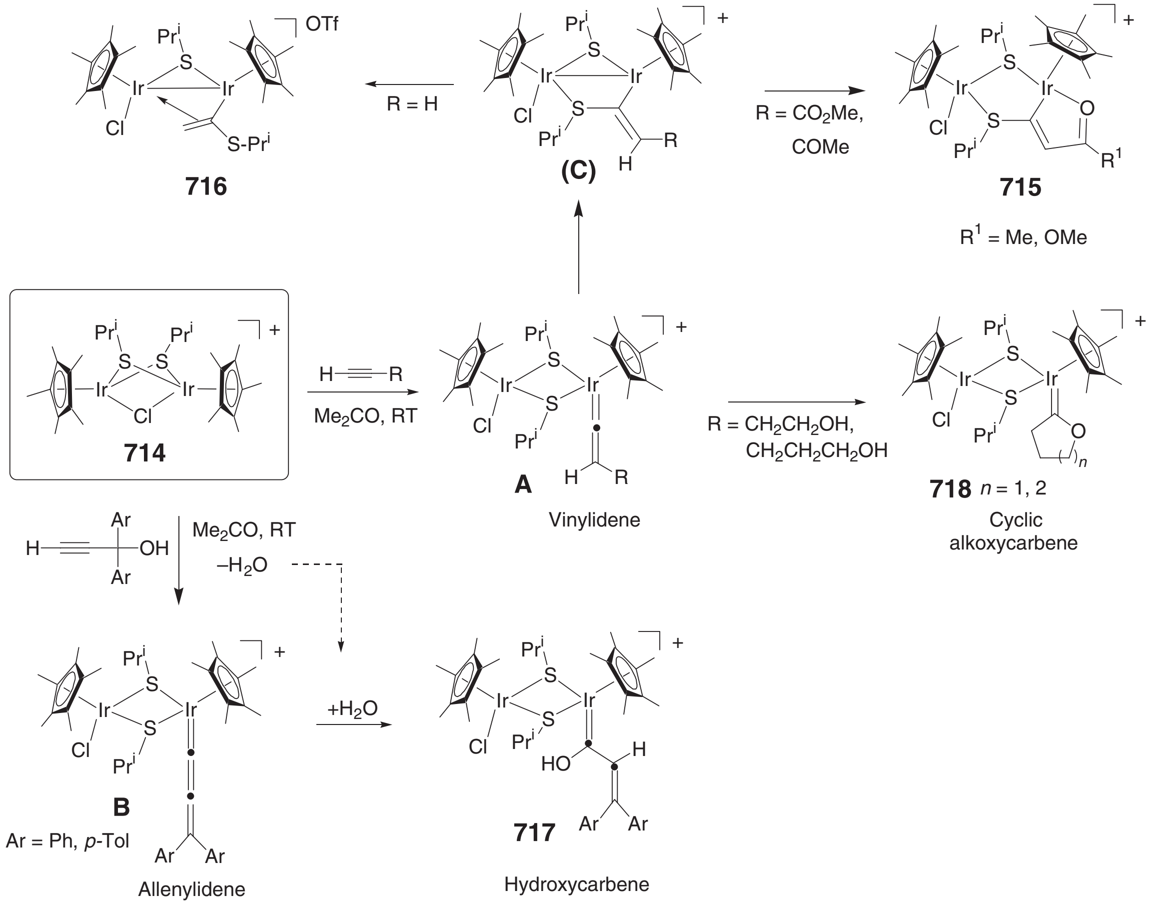


Scheme 100

scrambling process. The reactions of **710** with ethene at 50 °C selectively gave [Cp*IrH(μ,$\eta^{1:2}$-CH═CH$_2$)$_2$RuCp*] **712** and ethane showing complete site selectivity at which alkene C–H activation occurs. Similar site selectivity was observed for the reaction with PhC≡CPh yielding [Cp*Ir(μ-σ,π-(*Z*)-CPh═CHPh)(μ-H)$_2$RuCp*] **713** with complete incorporation of the three hydrides of **710**.[394]

7.04.5.1.3.(i) Sulfur-bridged complexes

Reactions of the cationic diiridium complex [Cp*Ir(μ-Cl)(μ-SPr^i)$_2$IrCp*]OTf **714** with terminal alkynes were investigated by Ishii *et al.* and are summarized below in Scheme 101.[350] Treatment of **714** with methylpropiolate in acetone at RT afforded the cationic complexes [Cp*IrCl(μ-SPr^i){μ-S(Pr^i)C═CHCOOMe}IrCp*]OTf **715**, in which the substituted vinyl ligand forms an Ir(1)–C–S–Ir(2) bridge and is further coordinated to the Ir(1) center at the carbonyl oxygen. On the other hand, [Cp*IrCl(μ-SPr^i){μ-C(SPr^i)═CH$_2$}IrCp*]OTf **716** was obtained by the reaction of **714** with acetylene gas. Complex **714** reacted with different propargylic alcohols such as 1,1-diphenyl- or 1,1-di (*p*-Tol)-2-propyn-1-ol to afford the hydroxycarbene complexes [Cp*IrCl(μ-SPr^i)$_2$Ir{═C(OH)CH═CAr$_2$}Cp*]OTf (Ar = Ph **717a**, *p*-Tol **717b**), while the reactions of **714** with 3-butyn-1-ol and 4-pentyn-1-ol produced cyclic alkoxycarbene derivatives [Cp*IrCl(μ-SPr^i)$_2$Ir{═C(CH$_2$)$_{n+2}$O}Cp*]OTf (**718**; $n = 1$, 2). All of the products are considered to be formed via the initial formation of a dinuclear vinylidene **A** or allenylidene **B** complex followed by the intramolecular nucleophilic attack of an SPr^i ligand **C**, H$_2$O, or the ω-OH group at the C$_\alpha$-atom of the vinylidene-type ligand. The molecular structures of complexes **714** and **716** were determined by X-ray diffraction studies.



Scheme 101

The reaction of $[\{Cp^*IrCl_2\}]_2$ with excess H_2S gas for 5 min afforded the doubly bridged hydrosulfido complexes $[Cp^*IrCl(\mu\text{-}SH)_2IrCp^*Cl]$ **719** which were further transformed into the triply bridged cationic hydrosulfido complexes $[Cp^*Ir(\mu\text{-}SH)_3IrCp^*]Cl$ **720** by continuous stirring under H_2S.[395] The molecular structures of **719** and **720**·BPh_4 were determined by X-ray analyses (Figure 55). The SH ligands in complex **719** take *anti*-configuration in the solid state, as mixtures of the *syn*- and *anti*-isomers in solution. Strong H bonds between the Cl anion and two of the SH ligands were found in **720**·Cl, and were maintained in $CDCl_3$ solution. When complex **719** was treated with NEt_3 at RT, the cubane-type sulfido clusters $[(Cp^*Ir)_4(\mu_3\text{-}S)_4]$ **721** were produced in high yields.

Reaction of **719** with $[RhCl(cod)]_2$ or $[Pd(PPh_3)_4]$ afforded the cationic triangular sulfido clusters $[(Cp^*Ir)_2Rh(\mu_3\text{-}S)_2(cod)]^+$ **722** or $[Cp^*Ir)_2Pd(\mu_3\text{-}S)_2Cl(PPh_3)]^+$ **723**, respectively. The crystal structures of **719**, $[(Cp^*Ir)_2Rh(\mu_3\text{-}S)_2(cod)][RhCl_2(cod)]$, and $[(Cp^*Ir)_2Pd(\mu_3\text{-}S)_2Cl(PPh_3)]Cl$ were determined by X-ray crystallography.[396] Treatment of $[Rh(\mu\text{-}Cl)(cod)]_2$ with the hydrido-hydrogen sulfido complex $[Cp^*Ir(PMe_3)H(SH)]$ in the presence of NEt_3 afforded the hydrido-mono(sulfido) derivative $[Cp^*Ir(PMe_3)(\mu\text{-}H)(\mu_3\text{-}S)\{Rh(cod)\}\{RhCl(cod)\}]$ **724**, whereas the corresponding reaction with the bis(hydrogen sulfido) complex $[Cp^*Ir(SH)_2(PMe_3)]$ gave the bis(sulfido) complex $[Cp^*Ir(\mu_3\text{-}S)_2\{Rh(cod)\}_2]$**725** with the liberation of trimethylphosphine (Figure 56).[397,398]

Treatment of $[Cp^*Ir(\mu\text{-}SH)_3IrCp^*]Cl$ **720** with acrylonitrile and NEt_3 in MeCN or DCE gave $[Cp^*Ir(\mu\text{-}SCH_2CH_2CN)_3IrCp^*]^+$ **726**, $[Cp^*Ir(\mu\text{-}S)(\mu\text{-}SCH_2CH_2CN)_2IrCp^*]$ **727**, or $[Cp^*Ir(\mu\text{-}SCH_2CH_2CN)_2(\mu\text{-}SCH_2CH_2Cl)IrCp^*]^+$ **728**, depending upon the conditions employed. From the reaction of **727** with $[(Cp^*Ru)_4(\mu\text{-}Cl)_4]$, a sulfido-thiolato cluster $[Cp^*_3RuIr_2(\mu_3\text{-}S)(\mu\text{-}SCH_2CH_2CN)_2Cl]$ **729** was obtained.[399] Treatment of the hydrosulfido- or hydroselenido-bridged dinuclear complexes $[Cp^*IrCl(\mu\text{-}EH)_2IrCp^*Cl]$ (E = S, **719**–S; Se, **719**–Se) with $M'Cl_3$ (M' = Sb, Bi) in THF at room temperature afforded the clusters $[Cp^*IrCl(\mu\text{-}EM'Cl_2)_2IrCp^*Cl]$ (M' = Sb, **730**–Sb; Bi, **730**–Bi).[400] The X-ray structures consist of the cubane-type $M_2M'_2E_2Cl_2$ cores with weak $MCl\cdots M'$ bonding interactions besides the normal M–E, M–Cl, and M′–E bonds.

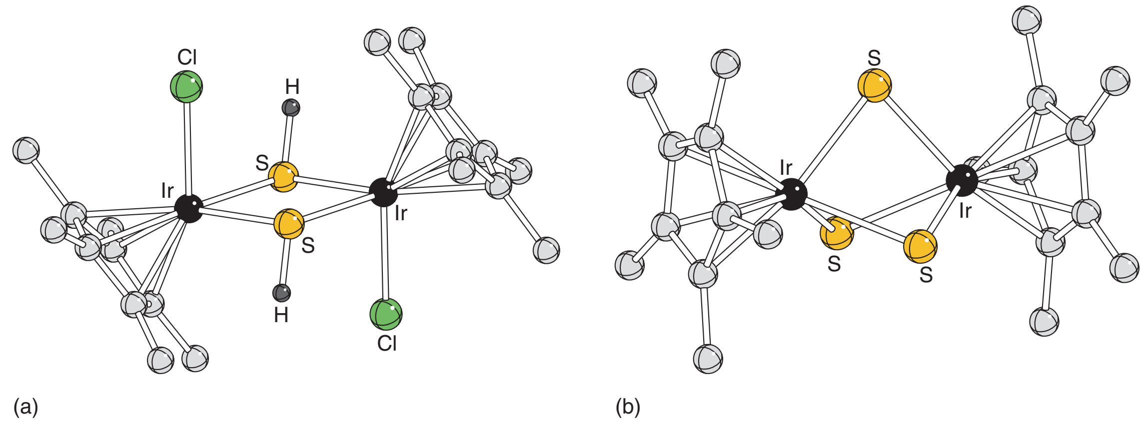


Figure 55 X-ray crystal structures of (a) **719** and (b) **720**. Hydrogen atoms (apart from those of the two hydrosulfido ligands in **719**) are omitted for the sake of clarity.

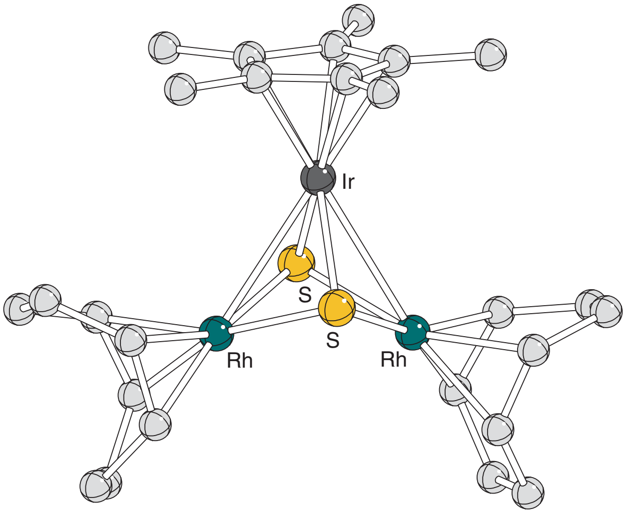


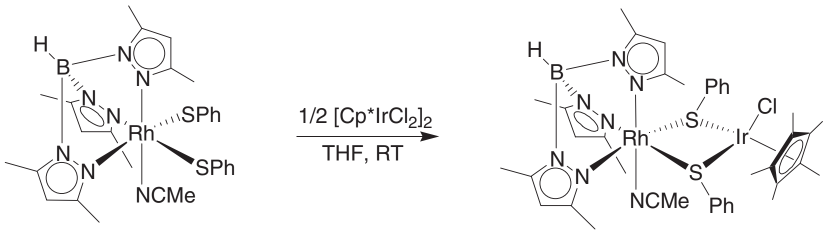
Figure 56 X-ray crystal structure of **725**.

Mixed metal sulfido cluster [(PdCl$_2$)(Cp*Ir)$_2$(μ_3-S)$_2$] **731** dissolved in CH$_2$Cl$_2$ reacted with 2 equiv. of L (L = nicotinamide, isonicotinamide, or N-methylnicotinamide) in the presence of AgBF$_4$ to give the cationic clusters [(PdL$_2$)(Cp*Ir)$_2$(μ_3-S)$_2$](BF$_4$)$_2$ **732**. In the solid state, the PdIr$_2$S$_2$ cores are self-assembled into one-dimensional chains via intermolecular H-bonding between the amide groups for L = nicotinamide or two-dimensional sheets via the H-bonding between the amide groups and the BF$_4$ anions for L = isonicotinamide, whereas no organization of the cluster cores is observed for L = N-methylnicotinamide.[401]

Reactions of [{Mo(=O)(DMF)$_3$}$_2$(μ-S)$_2$]I$_2$ **733** with [(Cp*IrCl)$_2$(μ-SH)$_2$] and excess [Me$_4$N]Cl in DMF at room temperature afforded cubane-type clusters with a terminal oxo ligand, [{Mo(=O)Cl$_2$}{MoCl$_2$(DMF)}(Cp*Ir)$_2$(μ_3-S)$_4$] **734**. Cluster **734** reacted with MePhNNH$_2$ in DMF at room temperature, yielding the methylphenylhydrazido^{2-} cluster [{Mo(NNMePh)Cl$_2$}{MoCl$_2$(DMF)}(Cp*Ir)$_2$(μ_3-S)$_4$] **735**. The mixed chalcogenido analog [{Mo(=O)Cl$_2$}-{MoCl$_2$(DMF)}(Cp*Ir)$_2$(μ_3-S)$_2$(μ_3-Se)$_2$] **736** was also synthesized.[402]

Complex [Tp^{Me}Rh(SPh)$_2$(MeCN)], obtained from the reaction of [Tp^{Me}Rh(coe)(MeCN)] with 1 equiv. of the organic disulfide PhSSPh, was treated further with [{Cp*IrCl$_2$}$_2$] in THF at RT and yielded the thiolato-bridged dinuclear complexes [Tp^{Me}RhCl(μ-SPh)$_2$IrCp*Cl] **737** (Scheme 102).[403]

Reactions of [{Cp*IrCl$_2$}$_2$] with the ligand (MeS)$_2$CH$_2$ in CH$_2$Cl$_2$ solution led to the neutral dinuclear complexes [{Cp*IrCl$_2$}$_2${μ-(MeS)$_2$CH$_2$}] **738**. Compound **738** reacts with AgBF$_4$ in the same solvent to give the mononuclear



737

Scheme 102

cationic complex $[Cp^*IrCl\{\eta^2\text{-}(MeS)_2CH_2\}]BF_4$ **739**. Reactions of the starting complexes $[\{Cp^*IrCl_2\}_2]$ with the bulkier ligand $(PhS)_2CH_2$ afforded the mononuclear neutral derivative $[Cp^*IrCl_2(\eta^1\text{-}(PhS)_2CH_2)]$ **740**.[404]

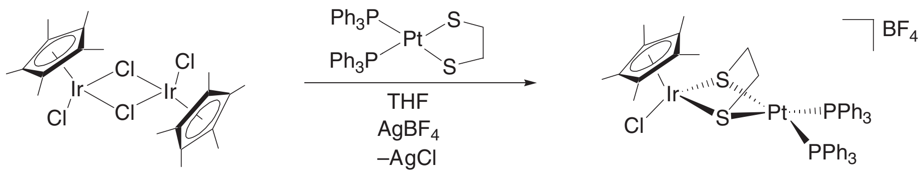
The reaction of $[Cp^*M(MeCN)_3](PF_6)_2$ (M = Rh, Ir) with $[Cp^*_2Ru_2S_4]$ gives the cluster compounds $[Cp^*_3MRu_2S_4(MeCN)](PF_6)_2$, **741**–Rh (M = Rh) and **741**–Ir (M = Ir). Crystallographic studies of **741**–Rh show that the dication consists of an asymmetric $RhRu_2S_4$ core containing an isosceles triangle of metal atoms with an Ru–Ru bond of 2.88 Å. The three metal atoms are joined by two $\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}S_2$ units, each persulfide being monodentate toward Rh.[405]

Iridium carbonyl half-sandwich compounds, $[Cp^*Ir(CO)(EPh)_2]$ (E = S, **204**–S; Se, **206**–Se), were prepared by the photo-induced reaction of $[Cp^*Ir(CO)_2]$ with the diphenyl dichalcogenides, E_2Ph_2, and used as neutral bridging ligands in carbonyl metal complexes such as $[Cp^*Ir(CO)(\mu\text{-}EPh)_2\{M(CO)_x\}]$ ($x = 4$; M = Cr, Mo; x = 3; M = Fe). A trimethylphosphine analog, $[Cp^*Ir(PMe_3)(\mu\text{-}SeMe)_2\{Cr(CO)_4\}]$ **742**, was also obtained. The new heterobimetallic complexes were characterized by IR and NMR spectroscopy, and the structure of the iridium/molybdenum complex $[Cp^*Ir(CO)(\mu\text{-}SePh)_2\{Mo(CO)_4\}]$ **743** was determined by a single crystal X-ray structure analysis.[100]

The cationic heterobimetallic dithiolato-bridged complex $[(PPh_3)_2Pt(\mu\text{-}edt)IrClCp^*]BF_4$ (edt = $S(CH_2)_2S$ **744**) was prepared by the reaction of $[Pt(edt)(PPh_3)_2]$ and $[\{Cp^*IrCl\}_2]$ in THF in the presence of a double proportion of $AgBF_4$ (Scheme 103).[406]

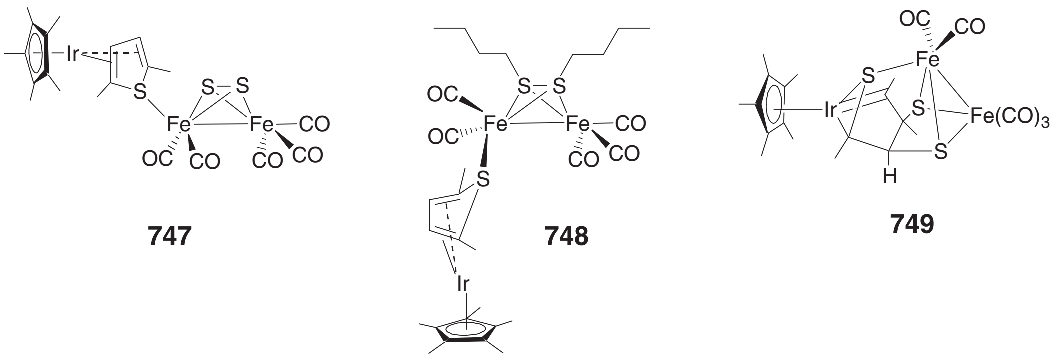
The reactions of $[Cp^*Ir(\eta^5\text{-}DMT)]^{2+}$ **745** with different transition metal carbonyls were described by Angelici and co-workers.[407,408] The reaction of **745** with $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ and $[(\mu\text{-}CO)(\mu\text{-}Bu^nS)Fe_2(CO)_6]^-$ yields products that contain the reduced $[Cp^*Ir(\eta^4\text{-}DMT)]$ **746** moiety.[407] X-ray diffraction studies of the products $[Cp^*Ir\{\eta^4\text{-}DMT\text{-}kS\text{-}Fe_2(CO)_5(\mu\text{-}S_2)\}]$ **747** and $[Cp^*Ir\{\eta^4\text{-}DMT\text{-}kS\text{-}Fe_2(CO)_5(\mu\text{-}S^nBu)_2\}]$ **748** show that the $[Cp^*Ir(\eta^4\text{-}DMT)]$ unit is coordinated through its S atom to an Fe atom of the $Fe_2(\mu\text{-}S)_2(CO)_5$ dimer core. Reaction of **746** with $[Fe_2(\mu\text{-}S_2)(CO)_6]$ leads to a completely different product **749** in which the two bridging S atoms of the $[Fe_2(\mu\text{-}S)_2(CO)_5]$ core are bonded at two carbons of a rearranged DMT ligand (Scheme 104).

The reactions of $[Cp^*Ir(\eta^4\text{-}DMT)]$ **746** and $[Cp^*Ir(C,S\text{-}DMT)]$ **750** with $Ru_3(CO)_{12}$, $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$, and $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ resulted in a variety of products encompassing different bridging coordination modes of the DMT moiety.[407] With the ruthenium carbonyl both **746** and **750** give the CO-substituted product $[Cp^*Ir\{\eta^{4:1}\text{-}DMT\cdot Ru_3(CO)_{11}\}]$ **751**, in which the DMT group is η^4-coordinated to the Ir and S-coordinated to an Ru in the plane of the triangular $Ru_3(CO)_{11}$ cluster. With $Re_2(CO)_{10}$, **746** reacts to give the similar CO-substituted product $[Cp^*Ir\{\eta^{4:1}\text{-}DMT\cdot Re_2(CO)_9\}]$ **752**, with the thiophene ligand S-coordinated in an equatorial position of the metal–metal dimer $Re_2(CO)_9$. However, the reaction is not selective and **752** is accompanied by the formation of $[Cp^*Ir\{\eta^{4:1}\text{-}SC_3H_2MeC(O)Me\}\{Re_2(CO)_9\}]$ **753**, in which the DMT ligand was converted to a ring-opened acylthiolate unit that is S-coordinated to $Re_2(CO)_9$. The same kind of DMT activation and the same coordination mode was also

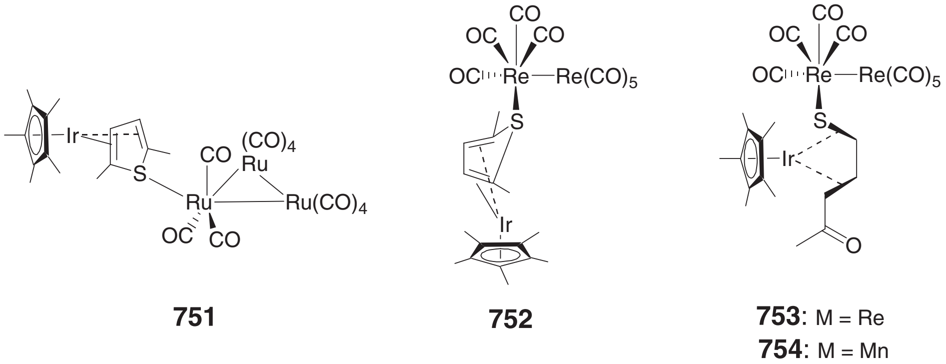


744

Scheme 103



Scheme 104



Scheme 105

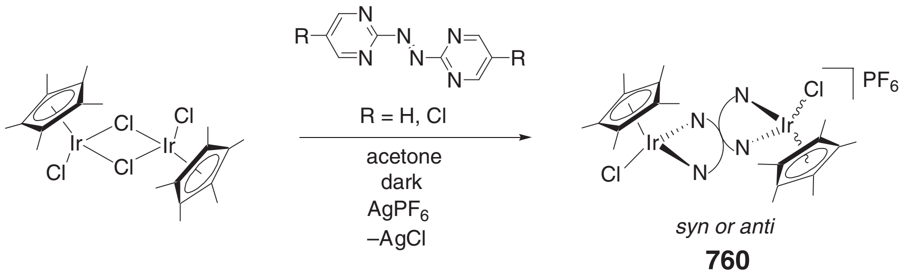
determined from the reaction of **750** with $Mn_2(CO)_{10}$ which gives $[Cp^*Ir\{\eta^{4:1}\text{-}SC_3H_2MeC(O)Me\}\{Mn_2(CO)_9\}]$ **754** (Scheme 105). Finally, the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with **746** gives the product $[Cp^*Ir\{\eta^{4:1}\text{-DMT}\cdot Ru(\eta^6\text{-}C_6H_6)Cl_2\}]$ **755**.

7.04.5.1.3.(ii) Nitrogen-bridged complexes

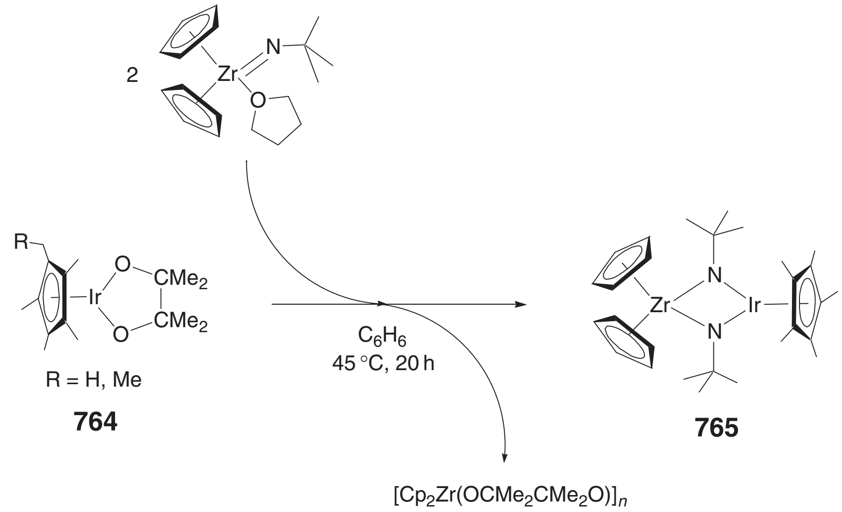
Novel amido-bridged dinuclear Ir(III) and Ir(II) complexes $[Cp^*Ir(\mu\text{-}NHC_6H_4R)_3IrCp^*]Cl$ (R = Me, H, Cl, CF_3 **756**), $[Cp^*Ir\{\mu\text{-}1,8\text{-}(NH)_2\text{naphth}\}(\mu\text{-}X)IrCp^*]X$ (X = Cl, Br **757**, $[Cp^*Ir\{\mu\text{-}1,8\text{-}(NH)_2\text{naphth}\}IrCp^*]$ **758**, and $[Cp^*Ir\{\mu\text{-}1,8\text{-}(NH)_2\text{naphth}\}(\mu\text{-}H)IrCp^*]O_2CCF_3$ **759** were prepared from $[\{Cp^*IrX\}]_2$ (X = Cl, Br) and the corresponding LiNHR species. The molecular structures of **756**$\cdot ClO_4$ and **758** were determined by X-ray crystallographic methods.[409]

The dinuclear complex cations $[(\mu\text{-}L)\{Cp^*IrCl\}_2]^{2+}$ (L = abpy or abcp **760**) could be isolated as diamagnetic bishexafluorophosphates from the reaction of $[\{Cp^*IrCl\}_2]_2$ with azopyridyl acceptors in the presence of $AgPF_6$ (Scheme 106).[410] A careful electrochemical analysis shows that apart from the reversible one-electron process there exist also two reductive chloride-releasing steps separated by unusually large potential differences ΔE_{EC} which confirms the capability of azopyridyl bridges for mediating efficient metal–metal communication beyond mere electron transfer. The complexes $[\{Cp^*Ir\}(\mu\text{-}L)\{Cp^*IrCl\}]^+$ **761a** and $[Cp^*Ir(\mu\text{-}L)]_2$ **761b** were spectroelectrochemically characterized. The neutral complex $[Cp^*Ir(\mu\text{-}L)]_2$ **761** is distinguished by a series of intense absorption bands in the near IR, the lowest absorption energies being displayed by the Ir_2/abcp combination.

Reaction of $[Cp^RIr(thf)_3](OTf)_2$ [$Cp^R = Cp^*$ **762a**, Cp^{Et} **762b**] with the zirconium nitrene derivative $[Cp_2Zr(NBu^t)(thf)]$ gives cyclopentadienyl transfer from Zr to Ir forming, respectively, the ionic pair products **763a** and **763b**, of which $[\{Cp^{Et}IrCp\}\{[CpZr(NHBu^t)(OTf)_3(thf)\}]$ **763b** was crystallographically characterized. The reaction of the pinacolate complex $[Cp^*Ir(OCMe_2CMe_2O)]$ **764** with $[Cp_2Zr(NBu^t)(thf)]$ gives the heterobinuclear bis(imido) complex $[Cp^*Ir(\mu\text{-}NBu^t)_2ZrCp_2]$ **765** with complete transfer of an imido group from zirconium to iridium (Scheme 107).[411]

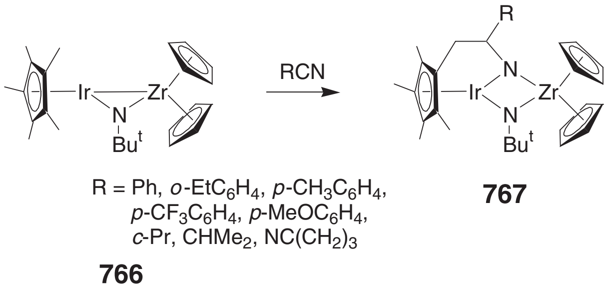


Scheme 106



Scheme 107

A mechanistic study was carried out on the insertion of nitriles into a zirconium–iridium heterobimetallic complex. The reaction of [$Cp_2Zr(\mu\text{-}NBu^t)IrCp^*$] **766** with nitriles (Scheme 108) yields the cyclometallated species [$Cp_2Zr(\mu\text{-}NBu^t)(\mu\text{-}NC(H)(R)CH_2\text{-}\eta^5\text{-}C_5Me_4)Ir$] (R = Ph **767a**, *o*-$EtC_6H_4$ **767b**, *p*-$CH_3C_6H_4$ **767c**, *p*-$CF_3C_6H_4$ **767d**, *p*-$MeOC_6H_4$ **767e**, *c*-Pr **767f**, $CHMe_2$ **767g**, $NC(CH_2)_3$ **767h**) (see Scheme 108).[412] An intermediate observed in the reaction of **766** with *c*-PrCN was characterized by NMR spectroscopy as a tetramethylfulvene complex with a bridging alkylidene-amido moiety, [$Cp_2Zr(\mu\text{-}NBu^t)\{\mu\text{-}NC(c\text{-}Pr)H\}(\eta^5\text{-}C_5Me_4CH_2)Ir$] **768**. The reaction of **766** with 2-arylacetonitriles yields two non-interconvertible complexes: a cyclometallated species analogous to **767**, and the new olefinic species [$Cp_2Zr(\mu\text{-}NBu^t)(\mu\text{-}NCH{=}CHR)IrCp^*$][R = Ph **769a**, *p*-$CF_3C_6H_4$ **769b**, *p*-$MeOC_6H_4$ **769c**].



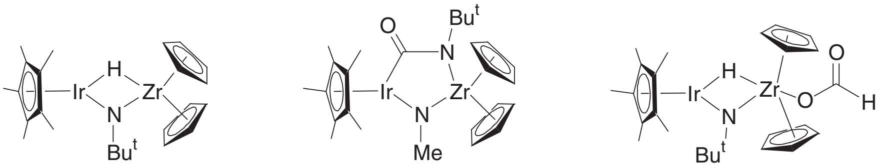
Scheme 108

Direct addition of CO_2 across a Zr–Ir bond leading to stoichiometric reduction of carbon dioxide to formate was shown by Bergman and co-workers.[413] $[Cp_2Zr(\mu\text{-}NBu^t)IrCp^*]$ **766** reacts rapidly with CO_2 and heterocumulenes. Insertion of CO_2 into an M–H bond, leading to a unique heterobimetallic formato complex and stoichiometric conversion of the formato complex to **766** and Li formate by addition of base, was also demonstrated. Different reactions gave the products listed in Scheme 109 and a possible mechanism for their formation was suggested.

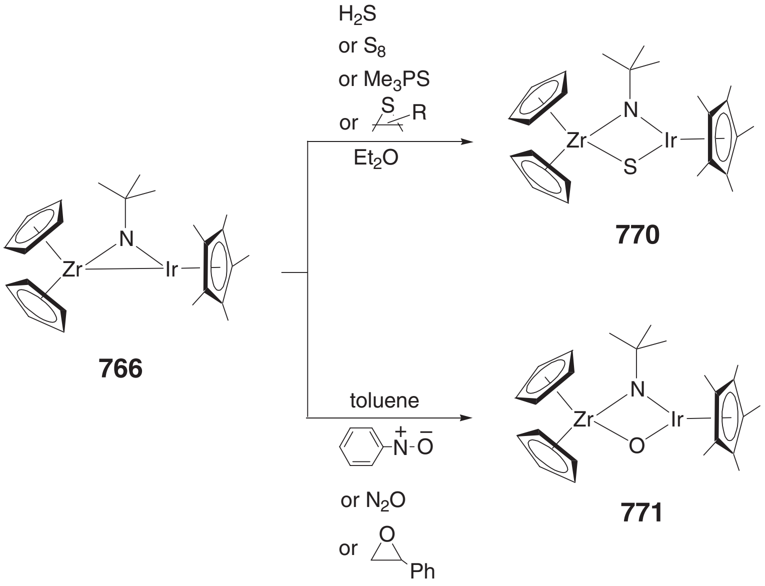
Evidence for an unusually rapid sulfur atom abstraction using this class of compounds was also shown by the same authors.[414] Imido complex **766** reacts with $Me_3P{=}S$, S_8, H_2S, and thiiranes to form the bridging sulfido complex $[Cp_2Zr(\mu\text{-}NBu^t)(\mu\text{-}S)IrCp^*]$ **770** with the removal of the metal–metal bond. Thiiranes react with the imido complex **766** with similar sulfur transfer resulting in the formation of **770** and alkene. The addition of *cis*-2-butene sulfide to **766** gave only *cis*-2-butene. Similarly, the addition of *trans*-2-butene sulfide resulted only in the formation of *trans*-2-butene, showing no involvement of ring-opened intermediates. Abstraction of an oxygen atom is also feasible; then, the imido complex **766** reacts with pyridine N-oxide, N_2O, and styrene oxide to form the bridging oxo complex $[Cp_2Zr(\mu\text{-}NBu^t)(\mu\text{-}O)IrCp^*]$ **771** (Scheme 110).

The stepwise formation of quasi-octahedral macrocyclic complexes of iridium(III) was observed for the reactions of $[\{Cp^*IrCl_2\}_2]$ with bidentate ligands (L) such as 1,4-diisocyano-2,5-dimethylbenzene **a**, 1,4-diisocyano-2,3,5,6-tetramethylbenzene **b**, pyrazine **c**, or 4,4′-dipyridyl **d** which gave the corresponding dinuclear complexes $[Ir_2Cl_2(Cp^*)_2(L)]$ **772**, which were converted into tetranuclear complexes $[(\{Cp^*Ir(\mu\text{-}Cl)\}_2)_2(L)_2](OTf)_4$ **773** on treatment with Ag(OTf).[415]

Diiridium complexes with mono- and dibridging aryldiazenido ligands were obtained by Sutton *et al.*[416] $[Cp^*Ir(C_2H_4)(p\text{-}N_2C_6H_4OMe)]BF_4$ **774** was synthesized by reacting the diazonium salt $[p\text{-}N_2C_6H_4OMe]BF_4$ with $[Cp^*Ir(C_2H_4)_2]$ at low temperature. Complex **774** reacts with iodide or bromide to give neutral complexes of formula $[\{Cp^*IrX\}_2(\mu\text{-}\eta^2\text{-}p\text{-}N_2C_6H_4OMe)(\mu\text{-}\eta^1\text{-}p\text{-}N_2C_6H_4OMe)]$ (X = I **775a**, Br **775b**).[417] When **774** is reacted with



Scheme 109



770

766

771

Scheme 110

$[\mathrm{Cp^*Ir(CO)_2}]$ in EtOH at reflux, the monobridging aryldiazenido complex $[\{\mathrm{Cp^*Ir(CO)}\}_2(\mu\text{-}\eta^2\text{-}p\text{-}\mathrm{N_2C_6H_4OMe})]\mathrm{BF_4}$ **776** is obtained. Compound **774** reacts also with phosphines such as $\mathrm{PMe_3}$, $\mathrm{PPh_3}$, $\mathrm{P(}p\text{-tol)_3}$ to give $[\mathrm{Cp^*Ir(PR_3)_2}(p\text{-}\mathrm{N_2C_6H_4OMe})]\mathrm{BF_4}$ **777a–c**, which were shown by both X-ray structure determination and by ^{15}N NMR spectroscopy to have the aryldiazenido ligand bound with doubly bent geometry. Complexes **777b** and **777c** react further with $\mathrm{PMe_3}$ to give $[\mathrm{Cp^*Ir(PPh_3)(PMe_3)}(p\text{-}\mathrm{N_2C_6H_4OMe})]\mathrm{BF_4}$ **778b** and $[\mathrm{Cp^*Ir\{P(}p\text{-tol)_3\}(PMe_3)}(p\text{-}\mathrm{N_2C_6H_4OMe})]\mathrm{BF_4}$ **778c**. In addition, **777b** reacts with CO or $\mathrm{CN^-}$ to give $[\mathrm{Cp^*Ir(CO)(PPh_3)}(p\text{-}\mathrm{N_2C_6H_4OMe})]\mathrm{BF_4}$ **779** or $\mathrm{Cp^*Ir(CN)(PPh_3)}(p\text{-}\mathrm{N_2C_6H_4OMe})$ **780**.[418]

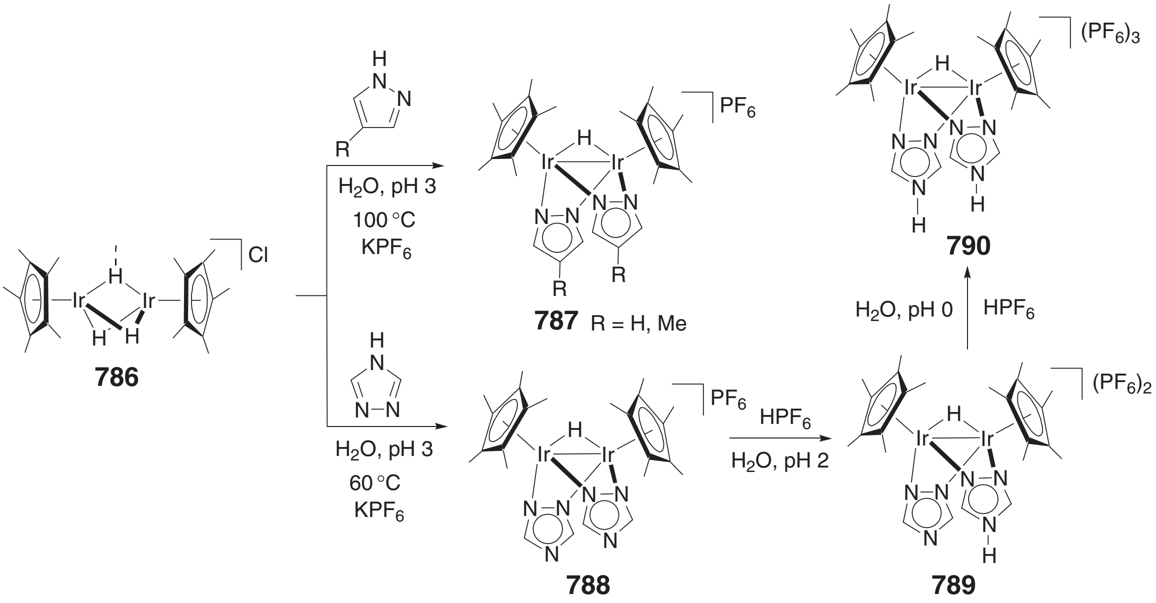
The synthesis and characterization of heterodinuclear IrPt complexes containing pyrazolate (pz) bridging ligands was obtained by Oro and co-workers.[419] The reaction of the Ir derivative $[\mathrm{Cp^*Ir(pz)_2(Hpz)}]$ **781** with $[\{\mathrm{PtIMe_3}\}_4]$ gives $[\mathrm{Cp^*Ir}(\mu\text{-pz})_2(\mu\text{-I})\mathrm{PtMe_3}]$ **782**. In the presence of NaOH, the trispyrazolate dimer $[\mathrm{Cp^*Ir}(\mu\text{-pz})_3\mathrm{PtMe_3}]$ **783** is obtained. Complex **783** was characterized by X-ray diffraction. The reaction of **781** with $[\mathrm{PtBr_2Me_2S}_x]$ gives $[\mathrm{Cp^*Ir}(\mu\text{-pz})_2(\mu\text{-Br})\mathrm{PtBrMe_2}]$ **784** as the only product.

Electrochemical reduction of the dinuclear pyrazine $[\mathrm{Cp^*IrCl}(\mu\text{-L})\mathrm{IrClCp^*}]^{2+}$ ions [L = bpip and bxip **785**] proceeds via the paramagnetic intermediates $[\mathrm{Cp^*IrCl}(\mu\text{-L})\mathrm{IrClCp^*}]^{+}$ (L = bpip) or $[\mathrm{Cp^*Ir}(\mu\text{-L})\mathrm{IrClCp^*}]^{2+}$ (L = bxip) and $[\mathrm{Cp^*Irl}(\mu\text{-L})\mathrm{IrCp^*}]^{+}$. The main difference between bpip and bxip systems is the destabilization of the chloride complexes through the bxip ligand for reasons of steric interference.[420]

The dinuclear cation $[\mathrm{Cp^*_2Ir_2}(\mu\text{-H})_3]^+$ with three bridging hydrides 786 react in aqueous acidic solution with pyrazole and 4-methylpyrazole to give the bispyrazolato complexes $[\{\mathrm{Cp^*Ir}\}_2(\mu\text{-H})(\mu\text{-}\eta^{1:1}\text{-}\mathrm{N_2C_3H_2R})_2]^+$ (R = H **787a**, R = Me **787b**) (Scheme 111). The reactions of complexes 786 with 1,2,3-triazole and 1,2,4-triazole were also investigated. With 1,2,4-triazole the bistriazolato complex $[\{\mathrm{Cp^*Ir}\}_2(\mu\text{-H})(\mu\text{-}\eta^{1:1}\text{-}\mathrm{N_3C_2H_2})_2]^+$ 788 was obtained. Successive protonation of the triazolato ligands in 788 leads to $[\{\mathrm{Cp^*Ir}\}_2(\mu\text{-H})(\mu\text{-}\eta^{1:1}\text{-}\mathrm{N_3C_2H_2})(\mu\text{-}\eta^{1:1}\text{-}\mathrm{N_3C_2H_3})]^{2+}$ 789 and $[\{\mathrm{Cp^*Ir}\}_2(\mu\text{-H})(\mu\text{-}\eta^{1:1}\text{-}\mathrm{N_3C_2H_3})_2]^{3+}$ 790.[421]

7.04.5.1.4 Carborane cyclopentadienyl derivatives

Most cyclopentadienylmetallaboranes containing the vertex units $\mathrm{Cp^RM}$ (M = Co, Rh, Ir; $\mathrm{Cp^R}$ = Cp, Cp*) and $\mathrm{Cp^RRu}$ donating two and one skeletal electrons, respectively, have structures closely related to binary boranes or borane anions. Smaller clusters of this type, such as metallaborane analogs of *arachno*-$\mathrm{B_4H_{10}}$ (e.g., $[\mathrm{(CpIr)_2B_2H_8}]$), *arachno*-$\mathrm{B_5H_{11}}$ (e.g., $[\mathrm{CpIrB_4H_{10}}]$), *nido*-$\mathrm{B_6H_{10}}$ (e.g., $[\mathrm{CpIrB_5H_9}]$), and *arachno*-$\mathrm{B_6H_{12}}$ (e.g., $[\mathrm{(CpIr)_2B_4H_{10}}]$), have the same skeletal electron counts as those of the corresponding boranes. In the metallaborane structures closely related to metal-free boranes, the favored degrees of BH and CpM vertexes appear to be 5 and 6, respectively.[422]



Scheme 111

Transition metals such as Ir were used to control polyborane formation.[423] Metal-assisted borane condensation is demonstrated by the formation of [*arachno*-2,5-$\{Cp^*IrH\}_2B_4H_8$] **791** by the reaction of two BH_3·THF moieties with the metal centers of [$\{Cp^*IrH\}_2(\mu\text{-}H)B_2H_5$] **792**. Mild thermolysis of **791**, which contains separated B_2H_4 fragments, results in H_2 elimination and the formation of the [*nido*-1,2-$\{Cp^*Ir\}_2(\mu\text{-}H)B_4H_7$] **793**.

The treatment of [$Cp^*IrB_4H_{10}$] **794** and [$Cp^*IrB_3H_9$] **795** with Lewis bases afforded the substituted iridatetra- and iridatriboranes [$Cp^*IrB_3H_7(L)$] (L = PMe_3 **796a**, PMe_2Ph **796b**, $PMePh_2$ **796c**, PPh_3 **796d**, py **796e**, NEt_3 **796f** and [$Cp^*IrB_2H_6(L)$] (L = PMe_3 **797a**, PMe_2Ph **797b**, $PMePh_2$ **797c**, PPh_3 **797d**, py **797e**, NEt_3 **797f**), plus the adduct BH_3·L as co-product.[424] With PPh_3, py, and NEt_3, the formation of the iridapentaborane [1-Cp*-*nido*-1-IrB_4H_8] **798** was also observed. In contrast to reaction with nucleophiles, treatment of **794** with Br_2 and *N*-bromosuccinimide gave the dibromo- and monobromo derivatives [1-Cp*-1-H-2,5-Br_2-*arachno*-1-IrB_4H_7] **799** and [1-Cp*-1-H-2-Br-*arachno*-1-IrB_4H_8] **800**, respectively.

Novel iridaboranes were obtained by Fehlner and co-workers by the reaction of either [$\{Cp^*IrCl_2\}_2$] or [$Cp^*_2Ir_2HCl_3$] with $LiBH_4$. The dihydrido borallyl complex [$Cp^*Ir(H)_2B_3H_7$] **801** was isolated in parallel with Cp^*IrH_4. In contrast, reaction of [$Cp^*_2Ir_2H_2Cl_2$] with $LiBH_4$ leads exclusively to [$Cp^*_2Ir_2(H)_3B_2H_5$] **802**, which is isolobal with **801** (Scheme 112).[425]

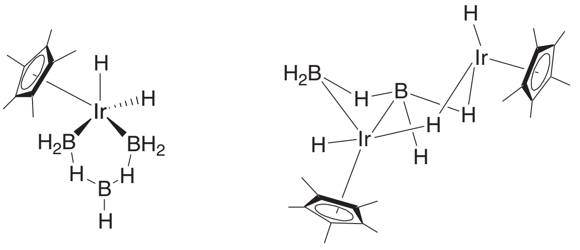
The reaction of [$\{Cp^*IrCl_2\}_2$] with $Li_2Se_2C_2B_{10}H_{10}$, that is, the dilithium salt of 1,2-*ortho*-carborane-1,2-diselenolate, leads to the green 16-electron diselenolene complex [$Cp^*Ir\{Se_2C_2(B_{10}H_{10})\}$] **803** which easily adds 2-electron ligands such as PMe_3 to give the 18-electron diselenolate complex [$Cp^*Ir(PMe_3)\{Se_2C_2(B_{10}H_{10})\}$] **804**.[426]

Complexation of the unprecedented silaborate ligand [$MeSiB_{10}H_{10}$]$^{3-}$ to yield the sandwich anion [$Cp^*Ir(MeSiB_{10}H_{10})$]$^-$ **805** was accomplished by reaction of the monodeprotonated silaborate with the respective pentamethylcyclopentadienyl transition metal chloride.[427]

The macropolyhedral metallaborane *syn*-[$Cp^*IrB_{18}H_{20}$] **806** was prepared by Shea *et al.*[428] The molecule consists of two *nido*-subclusters featuring ten $\{B_{10}\}$ and twelve $\{IrB_{11}\}$ vertices fused together through a joint formed by three boron atoms. The chemistry of this borane has been investigated.[428a] In particular, the addition of PMe_2Ph to the fused-iridacarborane cluster **806** gave [$Cp^*Ir(H)B_{18}H_{19}(PMe_2Ph)$] **807** providing a decrease in the degree of intimacy of the intercluster fusion, which is now held up by two boron atoms only, and a *nido* → *arachno* conversion of the character of either of the subclusters, namely a *nido*-11-vertex $\{IrB_{10}\}$ and a *nido*-10-vertex $\{B_{10}\}$.[428b] Reaction with MeNC gives the intriguing boro-carbene complex [$Cp^*Ir(H)B_{18}H_{19}\{C(NHMe)_2\}$] **808** which has a structure similar to **807**, but with the ligand coordinated to boron now being the carbene $\{:C(NHMe)_2\}$. This results from an unusual reductive combination of two acetonitrile residues and the loss of a C atom. The fused double-cluster [$Cp^*IrB_{18}H_{18}(PH_2Ph)$] **809**, obtained by the reaction of *syn*-[$Cp^*IrB_{18}H_{20}$] **806** and PH_2Ph, retains the three-atoms-in-common cluster fusion intimacy of **806**, in contrast to [$Cp^*Ir(H)B_{18}H_{19}(PHPh_2)$] **810**, which exhibits an opening to a two-atoms-in-common cluster fusion intimacy. Compound **809** forms via spontaneous dihydrogen loss from its precursor [$Cp^*Ir(H)B_{18}H_{19}(PH_2Ph)$] **811**.[429]

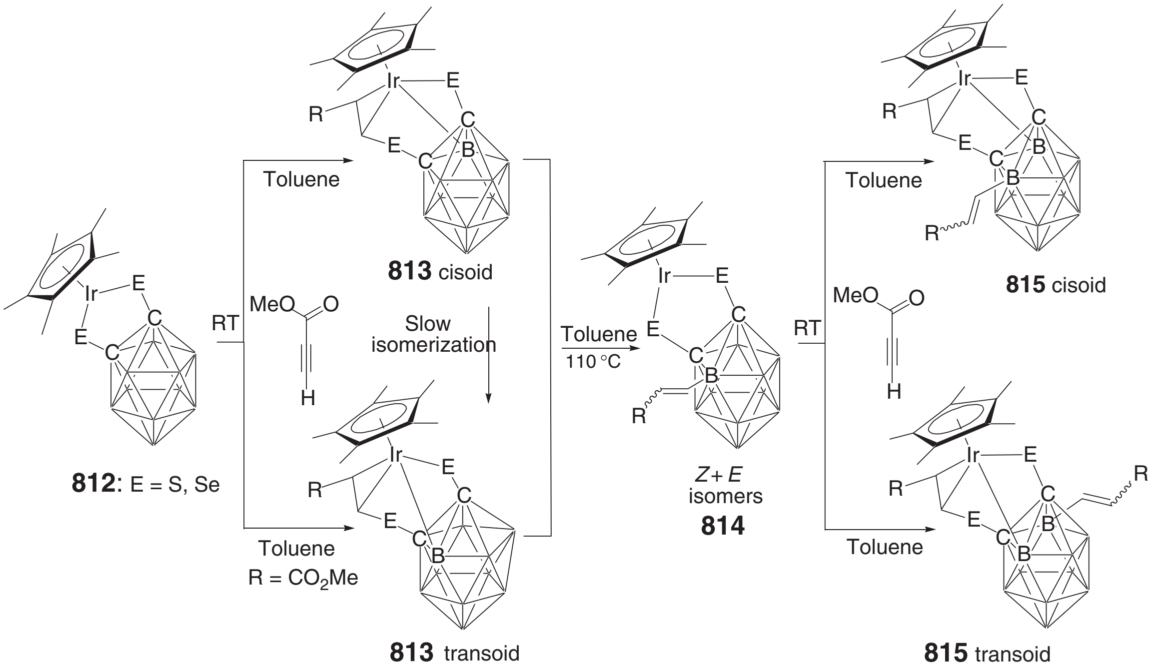
An important aspect of the chemistry of iridaboranes studied by Herberhold *et al.* is the metal-induced B–H activation observed by addition of terminal alkynes to Cp*Ir complexes containing a chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolato ligand [$E_2C_2(B_{10}H_{10})$]$^{2-}$. The reaction of the 16e half-sandwich complexes [$Cp^*Ir\{E_2C_2(B_{10}H_{10})\}$] (E = S, Se **812**) with acetylene, propyne, or 3-methoxypropyne leads to 18e complexes with an iridium–boron bond in each case. These reactions start with an insertion of the alkyne into one of the metal–chalcogen bonds, followed by B–H activation, metal-mediated transfer of one H atom from the carborane to the terminal C of the alkyne and finally *ortho*-metallation of the carborane. Scheme 113 shows these reactions and related processes.[430]

[$\{Cp^*Ir\}\{E_2C_2(B_{10}H_{10})\}$] **812** reacts with methyl acetylenecarboxylate, $MeO_2CC{\equiv}CH$, at RT to give the complexes [E = S **813a** or Se **813b**] as mixtures of isomers, in which the alkyne was inserted into one of the Ir–chalcogen



801 **802**

Scheme 112



Scheme 113

bonds.[431] The reaction results in an Ir-induced B–H activation, and, after transfer of a proton from carborane to the alkyne, an Ir–B bond was eventually formed. Heating of these mixtures at 110 °C in toluene gives mixtures of isomers [E = S **814a** or Se **814b**]; the latter, in turn, add further alkyne to provide **815** [E = S **815a** or Se **815b**] as a mixture disteroisomers (cisoid + transoid), which differ in the configuration of the olefinic substituent at the B(3) boron atom and could be separated by chromatography.

The reactions of the 16e half-sandwich complexes [Cp*Ir{$S_2C_2(B_{10}H_{10})$}] **812a** and [η^6-(4-Pr^{i}toluene)M{S_2C_2-($B_{10}H_{10}$)}] [M = Ru **816**, Os **817**] with both HC≡CCO$_2$Me and DMAD were also studied by Herberhold *et al.* to obtain more evidence for B–H activation, orthometallation, and B(3,6)-substitution of the carborane cluster. The reactions of **812a** with methylacetylenemonocarboxylate gave two geometrical isomers, in which the alkyne is inserted into one of the Ir–S bonds, followed by H transfer from the carborane via the metal to the former alkyne and formation of an Ir–B bond. The reaction of **812a** with DMAD takes place at room temperature to give complexes formed by addition of the C≡C triple bond to the metal center and insertion into one of the metal-S bonds.[432,432a]

The syntheses and characterizations of [1,2-Ph$_2$-3-(Cp*)-3,1,2-*pseudocloso*-Ir$C_2B_9H_9$] **818** were reported from the reaction between Tl$_2$[7,8-Ph$_2$-*nido*-7,8-$C_2B_9H_9$] and [{Cp*IrCl$_2$}]$_2$.[433]

7.04.5.1.5 Ligand activation and related catalytic applications

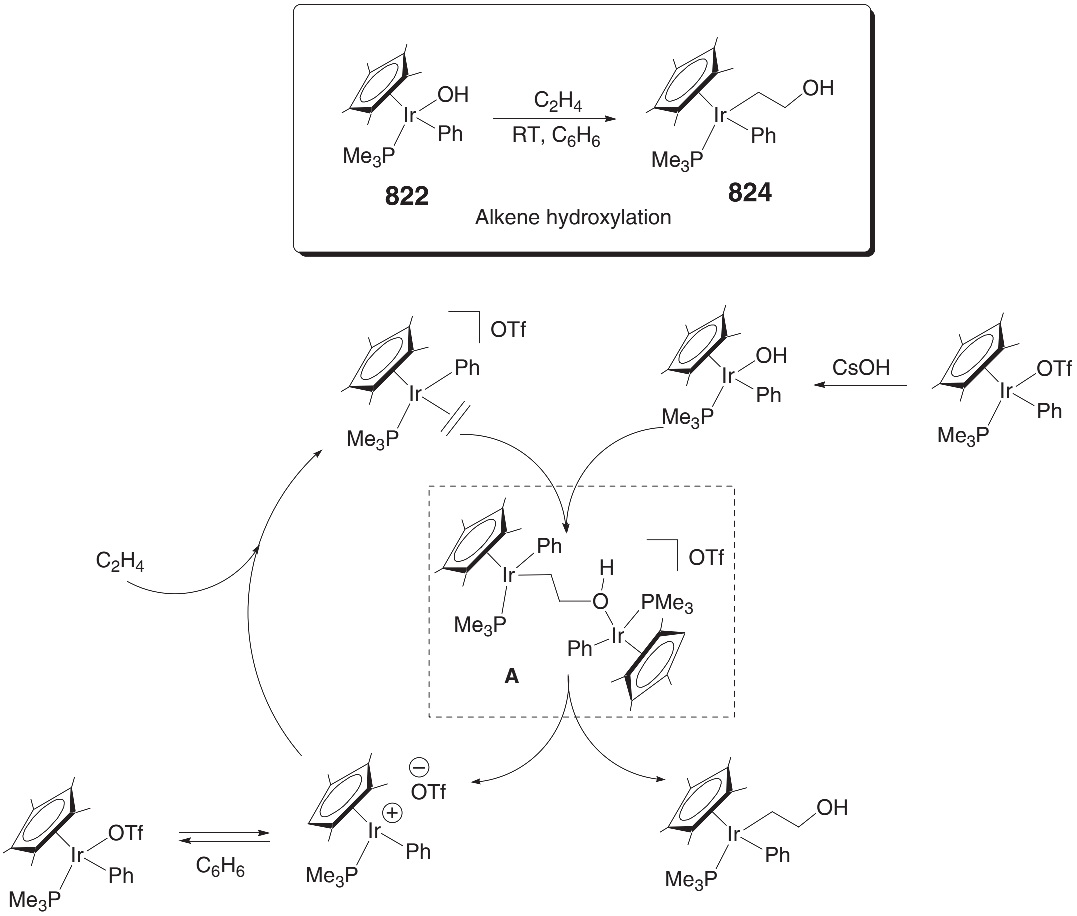
The major application of Ir cyclopentadienyl complexes in catalysis regards C–H and C–E bond activation and will be discussed elsewhere in this chapter and in other sections of COMC-III. Other few examples of remarkable ligand-activation reactions relevant to homogeneous catalysis mediated by cyclopentadienyl Ir complexes are summarized below. The Ir(III) dimethyl complexes [Cp*Ir(PR$_3$)Me$_2$] (PR$_3$ = PPh$_3$ **300a**, PMePh$_2$ **300b**, PMe$_2$Ph **300c**, PMe$_3$ **300d** catalyze the dehydrogenative coupling of dimethylphenylsilane in the presence of one-electron oxidants to yield Me$_2$PhSi–SiPhMe$_2$. The dimethylphosphine complexes **300** react with triphenylsilane in the presence of oxidants such as [Cp$_2$Fe]PF$_6$ to give methane and [Cp*Ir(Ph)(SiFPh$_2$)(PR$_3$)] (PR$_3$ = PPh$_3$ **819a**, PMePh$_2$ **819b**, PMe$_2$Ph **819c**, PMe$_3$ **819d**). Complex **819d** was structurally characterized by single crystal X-ray diffraction.[150]

The pH-dependent transfer hydrogenation of water-soluble carbonyl compounds with [Cp*Ir(H$_2$O)$_3$]$^{2+}$ complexes **494** as catalyst precursors in the presence of HCOONa as terminal reductive agent was studied by Watanabe *et al.*[230b] The active catalyst, a dinuclear μ-hydride/μ-formate/μ-hydroxo complex, [(Cp*Ir)$_2$(μ-H)(μ-OH)(μ-HCOO)]$^+$ **820**, was isolated and characterized by ^{1}H NMR, IR, and ESI-MS. The rate of this transfer hydrogenation is maximum at pH 3.2 because **820** is generated from the reaction of **494** with HCOONa at pH 3.2 in the highest yield. The study was extended to precursors $[Cp^{Py}Ir(H_2O)_2]^{2+}$ **504**, and $[Cp^*Ir(bpy)(H_2O)]^{2+}$ **505** for transfer hydrogenation, reductive amination, and dehalogenation of water-soluble carbonyl compounds and alkyl halides in the presence of HCOONa and $HCOONH_4$ as hydrogen donors. The hydride complex $[Cp^*Ir(bpy)(H)]^+$ **821** was identified as an active catalytic species.[228b]

Iridium alkoxides were conveniently synthesized and their catalytic decomposition by Ir cations studied, resulting in a new pathway for coordinatively saturated metal alkoxides via β-hydride elimination.[434] Reaction of $NaOCH_2R$ (R = Me, CMe_3, CH_2CMe_3) with $[Cp^*Ir(PMe_3)(Ph)(OH)]$ 822 in pentane gave $[Cp^*Ir(PMe_3)(Ph)(OCH_2R)]$ (R = Me, CMe_3 **823**). The crystal structure of **823** was determined.

The mechanism of addition of an Ir–OH bond to ethene involving catalytic tandem activation by two $[Cp^*Ir(PMe_3)(Ph)]^+$ cationic species was described by Ritter and Bergman.[435] The reaction of the hydroxoiridium complex 822 with ethene at 25 °C to give $[Cp^*Ir(PMe_3)(Ph)(CH_2CH_2OH)]$ 824 was studied as a homogeneous model for the alkene hydroxylation. A detailed mechanistic study provides evidence that this process is catalyzed by $[Cp^*Ir(PMe_3)(Ph)]^+$ cations according to the mechanism shown in Scheme 114 requiring the cooperative participation of two iridium centers. In fact, in this reaction, both ethene and OH^- are brought together by two $[Cp^*Ir(PMe_3)(Ph)]^+$ fragments. A dinuclear cation **A** resulting from the intermolecular attack of the hydroxy ligand in 822 to the coordinated ethene molecule in $[Cp^*Ir(PMe_3)(Ph)(C_2H_4)]^+$ was proposed as key intermediate and to be rate-limiting for the reaction.

In a second catalytic cycle, $[Cp^*Ir(PMe_3)(Ph)]^+$ cations catalyze the turnover of $[Cp^*Ir(PMe_3)(Ph)(CH_2CH_2OH)]$ and 822 to give $[Cp^*Ir(PMe_3)(Ph)(CH_2CHO)]$ **825**, $[Cp^*Ir(PMe_3)(Ph)H]$ **826**, and H_2O. This transformation



Scheme 114

involves the Meerwein–Ponndorf–Verley-type reaction of an alkoxide intermediate with $[Cp^*Ir(Ph)(PMe_3)]^+$ cations, a new mechanism for β-hydride elimination of coordinatively saturated alkoxides.

A key intermediate for the nucleophilic phenol-functionalization reaction was observed by Le Bras *et al.*[436] Treatment of $[Cp^*Ir(\eta^5\text{-}C_6H_5O)]BF_4$ ($C_6H_5O = $6-oxo-2,4-cyclohexadien-1-yl **827** with an excess of tertiary phosphine ($PR_3 = PMe_3$, PEt_3, and PMe_2Ph) affords the η^4-phenol tautomer $[Cp^*Ir\{\eta^4\text{-exo-2-}(PR_3)C_6H_5O\}]BF_4$ [$PR_3 = PMe_3$ **828a**, PEt_3 **828b**, and PMe_2Ph **828c**] in which the phosphine has been nucleophilically added at C2 with complete regioselectivity. The X-ray molecular structure tautomer for **828a** is described in Figure 57. Oxidation of the η^4-dienone complexes **828** by I_2 affords the related phosphonium salts $[(C_6H_4OH)PR_3]BF_4$, and the starting Ir complex is recycled as $[\{Cp^*IrI_2\}]_2{\cdot}I_2$ **829**, the X-ray crystal structure of which can be viewed as an infinite chain of dimeric $[Cp^*Ir(\mu\text{-}I)I]_2$ bridged by I_2 units.

This chemistry was further developed by Amouri and co-workers (Scheme 115). Thus, alkylated phenols (3,5-dimethylphenol and 3,4-dimethylphenol) react with $[Cp^*Ir(Solv)_3](BF_4)_2$ **657** prepared *in situ* from $[\{Cp^*IrCl_2\}]_2$ and $AgBF_4$ in acetone. Subsequent treatment with NEt_3 produced the (oxo-η^5-cyclohexadienyl)iridium complexes $[Cp^*Ir(\eta^5\text{-}C_6H_3R_2O)BF_4$ [R = H **830a**, Me **830b**]. The X-ray molecular structure of **830b** was determined. These (oxo-η^5-cyclohexadienyl)iridium derivatives react with NaOMe in MeOH to give the novel Ir cyclohexadienone complexes $[Cp^*Ir\{\eta^4\text{-}C_6H_3R_2O(OMe)\}]$ [R = H **831a**, Me **831b**] in 75–90% yield with nucleophilic attack occurring exclusively at the *ortho*-position relative to the C═O function. Addition of $HBF_4{\cdot}OMe_2$ to **831** in CD_3CN affords the starting material **830** with MeOH. Further exposure to $HBF_4{\cdot}OMe_2$ produces the corresponding phenolic compounds $[Cp^*Ir(\eta^6\text{-}C_6H_3R_2OH)](BF_4)_2$ **832**. The Ir cyclohexadienone complexes **831** can be easily oxidized by I_2 to produce the free cyclohexadienones which rearomatize to generate the free *ortho*-substituted phenols in yields of more than 80%. $[\{Cp^*IrI_2\}]_2$ is also produced during the phenol decomplexation.[437]

An efficient procedure for the synthesis of 2-methoxyestradiol was found by the same authors, based on Cp*Ir moiety.[438] 5,6,7,8-Tetrahydro-2-naphthol and β-estradiol gave η^6-arene complexes with $[Cp^*Ir(Solv)_3](BF_4)_2$ as described above. In the case of the complexed hormone, the Cp*Ir moiety coordinates the A-ring either α (metal down) or β (metal up) relative to the Me group at C(13). The novel iridium cyclohexadienone compound of the complexed steroid was then oxidized by iodine to produce 2-methoxyestradiol, an anticancer agent which possesses important antitumor effects *in vivo*, in 60% overall yield from β-estradiol.[439]

Dissociation of carbanions from acyl iridium compounds was studied both experimentally and computationally.[67] Instead of reductive elimination of aldehyde, or decarbonylation to give a trifluoroalkyl hydride, heating

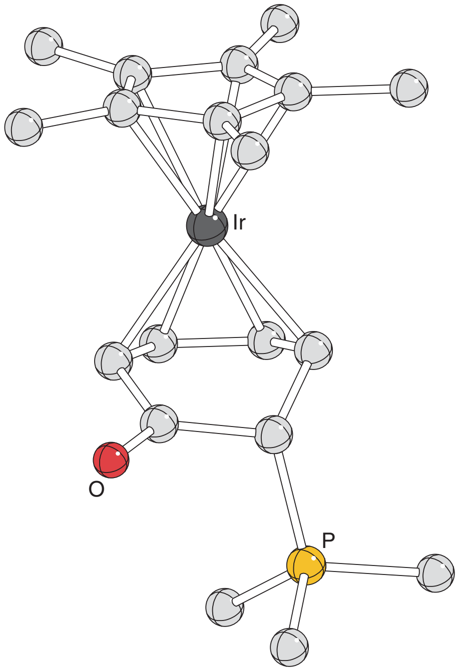
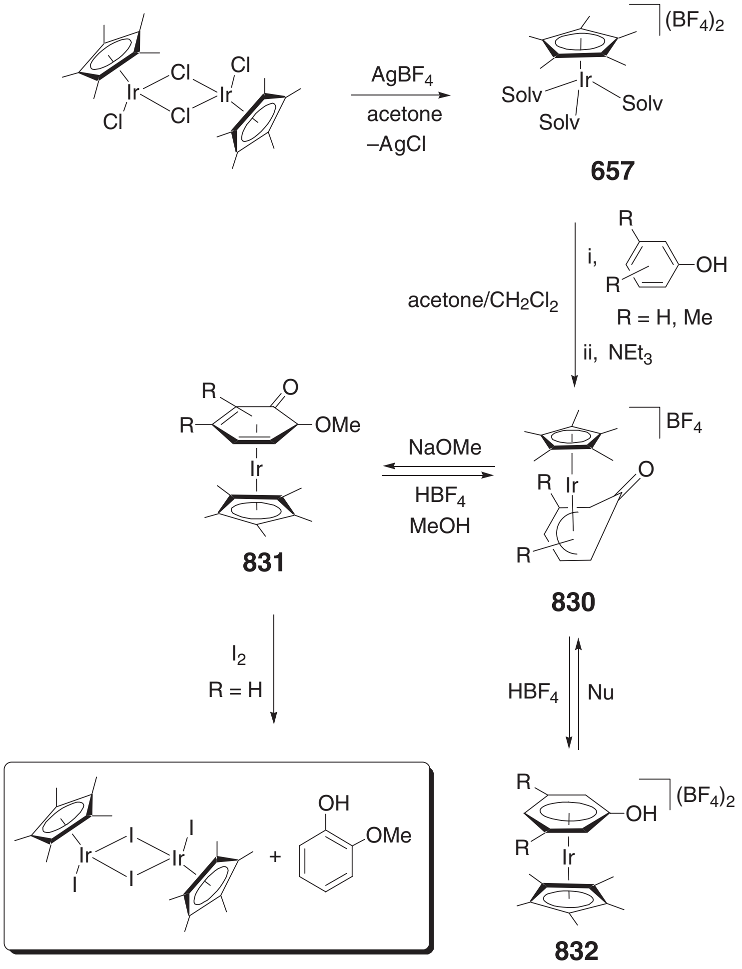


Figure 57 X-ray crystal structure of **828a**.



Scheme 115

[Cp*Ir(PMe$_3$)(H){C(O)CF$_3$}] **411** leads to the quantitative formation of [Cp*Ir(PMe$_3$)(CO)] **133** and CF$_3$H (see Scheme 45). Three other fluoroacyl hydrides, [Cp*(PMe$_3$)Ir(H)(C(O)R$_F$)] ($R_F = CF_2CF_3$, $CF_2CF_2CF_3$, or $CF_2(CF_2)_6CF_3$), undergo R$_F$–H elimination to give **1** at a faster rate than CF$_3$H elimination from **411**.

Tilset and co-workers showed that the electrochemical and chemical oxidation of [Cp*Ir(dmso)Me$_2$] **833** in DMSO forms methane and traces of ethene (20 : 1) as well as [Cp*Ir(dmso)$_2$Me]$^+$ **834**. Labeling studies indicate that three of the methane H atoms arise from the Ir-bonded Me, while the fourth appears to arise from adventitious H$_2$O. By contrast, oxidation of the Rh analog [Cp*Rh(dmso)Me$_2$] gave only ethane and [Cp*Rh(dmso)$_2$Me]$^+$. New syntheses of [Cp*Ir(dmso)Me$_2$] and [Cp*Rh(dmso)Me$_2$] are also described.[440]

A computational study of ethene C–H bond activation by [Cp*Ir(PR$_3$)] has been carried out by Poli *et al.*[441] to study by DFT methods the Bergman thermal reaction of [Cp*Ir(PPh$_3$)(H)(Cy)] **835** with C$_2$H$_4$.[442] Indeed, it was previously demonstrated that both [Cp*Ir(PMe$_3$)(H)(CH═CH$_2$)] **836** and [Cp*Ir(PMe$_3$)(H$_2$C═CH$_2$)] **837** are formed (2 : 1) when [Cp*Ir(PMe$_3$)] is thermolytically generated in the presence of ethene. The ethene adduct is the thermodynamic product of the reaction and, at high temperature (170 °C in C$_6$H$_6$), the vinyl hydride converts to the η^2-ethene adduct. An explanation for the observed kinetic isotope effects has been proposed.

7.04.5.2 Indenyl Compounds

One of the main applications of indenyl (Ind) ligands to Ir is the synthesis of the [Ir(cod)(Ind)] catalyst for the selective borylation of arenes to give *meta*-substituted areneboronic acid pinacolates, as recently reviewed.[443,443a]

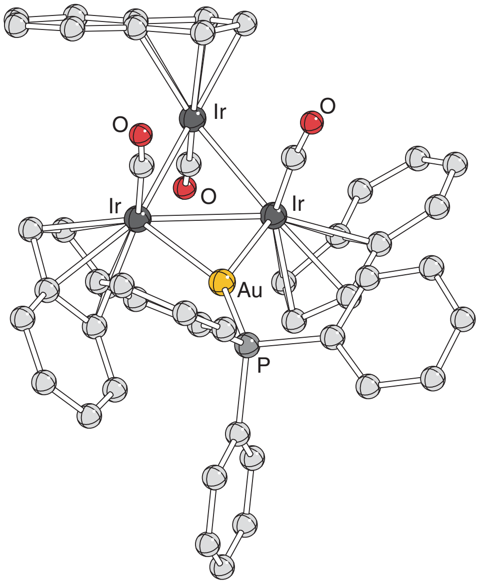


Figure 58 X-ray crystal structure of **282c**.

Arenes are borylated selectively in the presence of chloro, fluoro, bromo, and iodo groups without the formation of Suzuki coupling products. The catalyst has been successfully used together with a palladium catalyst, to obtain tandem borylation and Suzuki coupling to give biaryl coupling products and a polyphenylene polymer. The iridium borylation catalyst allows access to a wide variety of starting materials for Suzuki coupling reactions.

The reactions of $[(\eta^5\text{-}C_9H_7)_3Ir_3(\mu\text{-}CO)_3]$ **281** with various metal electrophiles have already been discussed in Section 1.4 describing iridium carbonyl clusters.[132] Tetranuclear clusters of formula, $[Ir_3\{M(PPh_3)\}(CO)_3(\eta^5\text{-}C_9H_7)_3]PF_6$ [M = Cu **282a**, Ag **282b**, Au **282c**], $[Ir_3Tl(\mu\text{-}CO)_3(\eta^5\text{-}C_9H_7)_3]PF_6$ **283**, and $[Ir_3(HgR)(CO)_3(\eta^5\text{-}C_9H_7)_3]PF_6$ [R = Ph **284a**, CpW(CO)$_3$ **284b**] were prepared and properly characterized also by X-ray diffraction methods. The structure of the Ir_3Au derivative is shown in Figure 58.

The cluster $[Ir_3(CO)_3(\eta^5\text{-}C_9H_7)_3]$ **281** reacts with $HBF_4\cdot OEt_2$ to form $[Ir_3(\mu\text{-}H)(CO)_3(\eta^5\text{-}C_9H_7)_3]BF_4$ **838**. Deprotonation of **838** with NEt_3 generates $[C_s\text{-}Ir_3(CO)_3(\eta^5\text{-}C_9H_7)_3]$, which rapidly gives an equilibrium mixture containing $[C_{3v}\text{-}Ir_3(\mu\text{-}CO)_3(\eta^5\text{-}C_9H_7)_3]$ as the major isomer.[444]

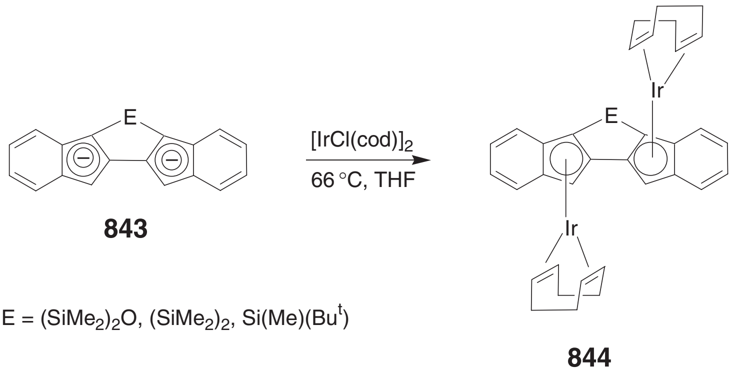
The 1-(ferrocenyl)indenyl ligand has been used to stabilize heterobimetallic derivatives such as $[\{\eta^5\text{-}1\text{-}(ferrocenyl)indenyl\}Ir(cod)]$ **839** and $[\{\eta^5\text{-}1\text{-}(ferrocenyl)indenyl\}Ir(coe)_2]$ **840**, and the bis(carbonyl) $[\{\eta^5\text{-}1\text{-}(ferrocenyl)indenyl\}Ir(CO)_2]$ **200**. These complexes have already been discussed in Section 7.04.2.2.[98]

The reaction of $[IrH_5(PPr^i_3)_2]$ and indene at 60 °C leads to the formation of $[(\eta^3\text{-}C_9H_7)IrH_2(PPr^i_3)_2]$ **841** and $[(\eta^5\text{-}C_9H_7)IrH_2(PPr^i_3)]$ **842**. The molecular structures of these products have been determined by single crystal X-ray diffraction studies.[445]

The first unsymmetrical monosilanylene-bridged 2,2′-bis(indenyl) system, 1,1′-$(2,2'\text{-}C_9H_6)_2Si(Me)(Bu^t)$ **843**, was synthesized and its coordination chemistry methodically explored with a variety of transition metal ions. Diiridium complexes with these double-bridged ligands were prepared using appropriate Ir precursors. The complexes $[1,1'\text{-}\{(2,2'\text{-}\eta^5\text{-}C_9H_5)Ir(cod)\}_2(SiMe_2)_2O]$ **844a**, $[1,1'\text{-}\{(2,2'\text{-}\eta^5\text{-}C_9H_5)Ir(cod)\}_2(SiMe_2)_2]$ **844b**, and $[1,1'\text{-}\{(2,2'\text{-}\eta^5\text{-}C_9H_5)Ir(cod)\}_2Si(Me)(Bu^t)]$ **844c** were reported exclusively in the form of antifacial isomers (Scheme 116).[446]

Indenyl iridium(I) complexes $[(\eta^5\text{-}C_9H_7)Ir(diphos)]$ **845** [diphos = 2 PPh_3, dppe, *rac*-cypenphos, (*S*,*S*)-chiraphos, (*R*)-prophos, (*R*,*R*)-renorphos and (*R*)-phenphos] have been synthesized by reacting $[(\eta^5\text{-}C_9H_7)Ir(C_2H_4)_2]$ with the appropriate diphosphine.[447]

Iridium catalysts $[Ind^RIr(cod)]$ containing trifluoromethyl-substituted indenyl ligands [**846**, $Ind^R = C_9H_7$, $(1\text{-}CF_3)C_9H_6$, $(2\text{-}CF_3)C_9H_6$, $(1,3\text{-}CF_3)_2C_9H_5$] have been developed for the hydroboration of 4-(benzyloxy)cyclohexene to *cis*-3-(benzyloxy)cyclohexanol. Compared to unsubstituted complexes, trifluoromethyl substitution yields a 3–10% increase in selectivity which has been attributed to the strong electron-withdrawing effect of the trifluoromethyl group. Iridium complexes give high levels of selectivity (93–98%).[448]



843

E = (SiMe$_2$)$_2$O, (SiMe$_2$)$_2$, Si(Me)(Bu^t)

844

Scheme 116

Polymetallic Ir–M$_x$ indenyl compounds are also known. The reaction of [Re$_2$(μ-H)$_2$(CO)$_8$] with [Ir(CO)(η^2-coe)(η^5-C$_9$H$_7$)] provides [IrRe$_2$(μ-H)$_2$(CO)$_9$(η^5-C$_9$H$_7$)] **847** in 80% yield. The molecular structure of **847** consists of an IrRe$_2$ triangle incorporating one Ir(CO)(η^5-C$_9$H$_7$) and two Re(CO)$_4$ fragments (Figure 59).

Cluster **847** is readily deprotonated with KOH/EtOH, and the resulting anion was isolated as the PPN salt, [PPN][IrRe$_2$(μ-H)(CO)$_9$(η^5-C$_9$H$_7$)] **848**. The reaction of **847** with PPh$_3$ leads to [IrRe$_2$(μ-H)$_2$(CO)$_8$(PPh$_3$)(η^5-C$_9$H$_7$)] **849**, which contains the phosphine coordinated to one rhenium atom.[449] The reaction of [Ir(CO)(η^2-coe)(η^5-C$_9$H$_7$)] with excess internal alkyne C$_2$R$_2$ (R = Ph, Tol) leading to mononuclear and dinuclear iridium complexes [Ir(CO)(η^2-C$_2$R$_2$)(η^5-C$_9$H$_7$)] [R = Ph **138a**, *p*-Tol **138b**], [Ir$_2$(CO)$_2$(μ-C$_2$R$_2$)(η^5-C$_9$H$_7$)$_2$] [R = Ph **139a**, *p*-Tol **139b**], and to the η^4-butadiene complex [Ir(η^4-HRC=CRCR=CRR^1)(η^5-C$_9$H$_7$)] [R = Ph, R^1 = Ph **850a**, R = *p*-Tol, R^1 = Ph **850b**) has been mentioned in Section 7.04.1 Compound **850b** contains a 1-phenyl-1,2,3,4-(tetrakis)tolyl-1,3-butadiene ligand formed through both alkyne coupling and CH bond activation of benzene.[70]

The chemistry of the *anti*-[Cr(CO)$_3$-μ,$\eta^{1:1}$-indenyl-Ir(cod)] complex has already been described in Section 7.04.2.3.[110]

Optically active Ir complexes containing chiral, menthyl-substituted indenyl ligand (−)-2-menthylindene and (−)-2-menthyl-4,7-dimethylindene have been described by Schumann *et al.*[450,450a] Metathetic reaction of the chiral lithium salts of these indenyl systems with standard iridium(I) precursors gave [Ir(cod){L}] [L = (−)-(2-menthylindenyl), [Ir(C$_2$H$_4$)$_2${L} **851**], [L = (−)-(2-menthylindenyl) **852a**, (−)-(2-menthyl-4,7-dimethylindenyl) **852b**], and [Ir(coe)$_2${L}] [L = (−)-(2-menthyl-4,7-dimethylindenyl) **853**]. All compounds were formed stereomerically pure and

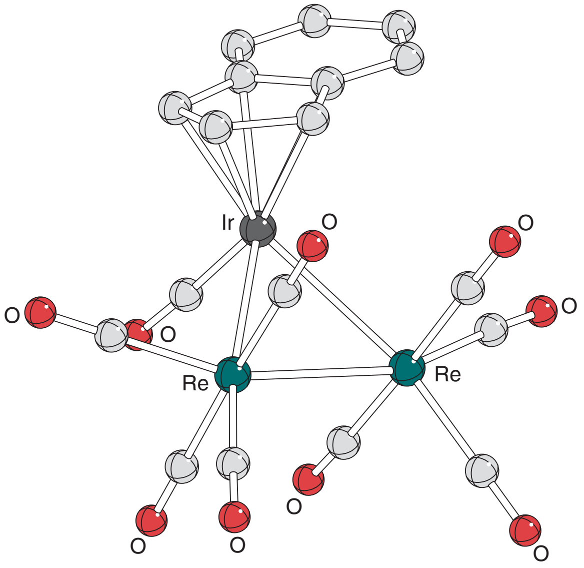


Figure 59 X-ray crystal structure of **847**.

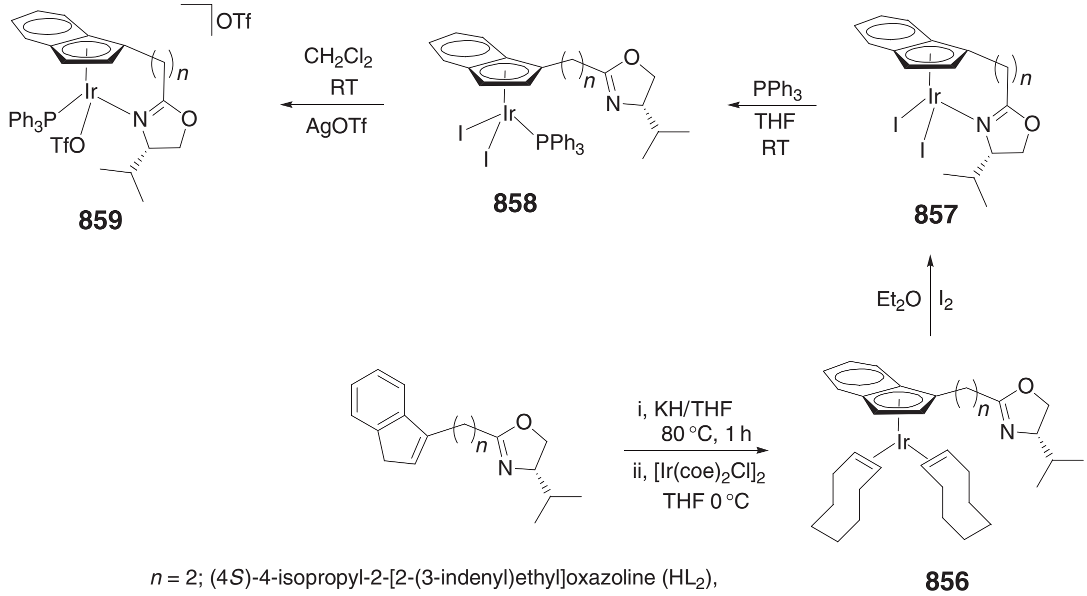
could be isolated in pure form after chromatography on dried alumina under nitrogen. The structure of **851** was determined by single crystal X-ray diffractometry.

Highly diastereoselective oxidative addition of alkyl halides to $[\{\eta^{5:1}\text{-Ind(CH}_2)_4\text{PR}_2\}\text{Ir(CO)}]$ (R = Ph, Cy **854** with MeI gave a diastereomeric mixture of $[\{\eta^{5:1}\text{-Ind(CH}_2)_4\text{PR}_2\}\text{Ir(Me)(CO)}]\text{I}$ (R = Ph, **314**, R = Cy = **855** in a 92 : 8 ratio, which did not afford the corresponding acetyl complex upon heating under reflux in CH_2Cl_2.[154]

Iridium diastereomeric planar-chiral complexes with ancillary chiral alkyloxazoline-substituted η^5-indenyl ligands (4*S*)-4-isopropyl-2-[2-(3-indenyl)ethyl]oxazoline **a**, HL^2), (4S)-4-isopropyl-2-[3-(3-indenyl)propyl]oxazoline **b**, HL^3), and 2-[3-(3-indenyl)propyl]oxazoline **c**, HL) were prepared and structurally characterized (see Scheme 117 below).[155] Deprotonation of the oxazoline ligand HL^n followed by complexation with $[IrCl(coe)_2]_2$ gave the corresponding planar-chiral indenyl complexes $[(\eta^5\text{-L}^n)\text{Ir(coe)}_2]$ ($n = 1$ **856a**, $n = 2$ **856b**) as an equimolar mixture of diastereomers. Iodination of **856** gave the corresponding diiodo complexes, $[(\eta^{5:1}\text{-L}^n\text{-}\kappa\text{–}N)\text{IrI}_2]$ ($n = 1$ **857a**, $n = 2$ **857b**), where the oxazoline is now *N*-coordinated. The Ir–N bond in **857** may be displaced by PPh_3, giving $[(\eta^5\text{-L}^n)\text{IrI}_2(\text{PPh}_3)]$ ($n = 1$ **858a**, $n = 2$ **852b**). Removal of the iodide ligands in **858** with AgOTf brings back the *N*-coordination of oxazoline and creates a new chiral center at metal, affording $[(\eta^{5:1}\text{-L}^n\text{-}\kappa\text{–}N)\text{Ir(PPh}_3)(\text{OTf})]\text{OTf}$ ($n = 1$ **859a**, $n = 2$ **859b**) as a mixture of only two diastereomers of the four possible. The corresponding iridium(III) complex bearing the non-chiral ligand L, $[(\eta^{5:1}\text{-L-}\kappa\text{–}N)\text{Ir(PPh}_3)(\text{OTf})]\text{OTf}$ **860**, has also been prepared. The coordinated triflate ligand of **860** is slowly replaced by water in $CDCl_3$ to afford the monoaquo dication, $(S^*_{\mathrm{Pl}},R^*_{\mathrm{Ir}})\text{-}[(\eta^{5:1}\text{-L})\text{Ir(PPh}_3)(\text{H}_2\text{O})](\text{OTf})_2$ **861**.

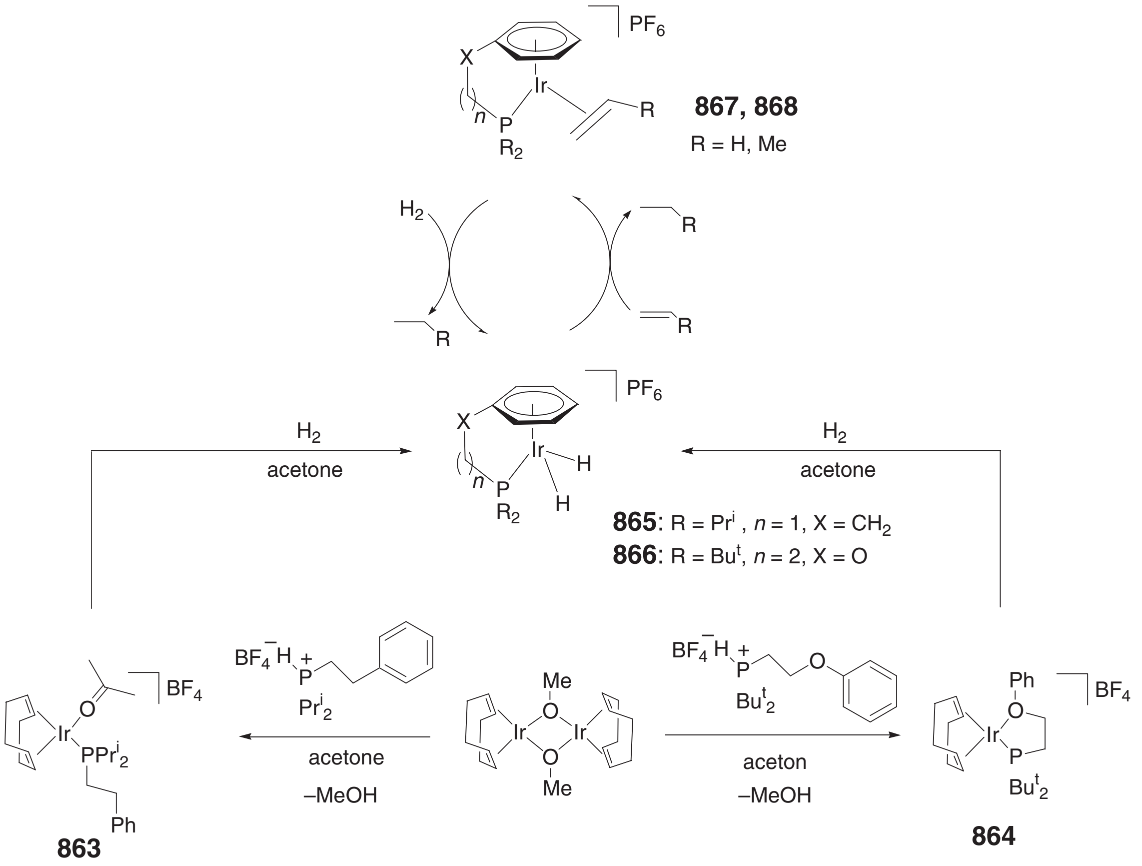
7.04.5.3 Arene Compounds

A few examples of (η^6-arene)Ir complexes have been reported. The dimer $[IrCl(coe)_2]_2$ reacts with $AgPF_6$ in acetone to give *cis*-$[\text{Ir(acetone)}_2(\text{coe})_2]\text{PF}_6$, which upon treatment with $^i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{C}_6\text{H}_5$ (L_1) affords the half-sandwich-type complex $[(\eta^6\text{-L}_1\text{-}\kappa - P)\text{Ir(cod)}]\text{PF}_6$ **862** (Scheme 118).[451] The methoxy-bridged dimer $[\text{Ir}(\mu\text{-OMe})(\text{coe})]_2$ gives upon treatment with the phosphonium salt $L_1{\cdot}HBF_4$ the complex $[\text{Ir(cod)(acetone)}(\text{L}_1\text{-}\kappa\text{-}P)]\text{BF}_4$ **863**, whereas with $L_2{\cdot}HBF_4$ ($L_2 = {}^t\text{Bu}_2\text{PCH}_2\text{CH}_2\text{OPh}$) a bis(chelate) complex $[\text{Ir(cod)}(\text{L}_2\text{-}\kappa^2\text{-}O,P)]\text{BF}_4$ **864** is generated. Both **863** and **864** react with H_2 in acetone to yield the dihydridoiridium(III) derivatives $[(\eta^6\text{-L}_2\text{-}\kappa\text{–}P)\text{IrH}_2]\text{BF}_4$ **865** and $[(\eta^6\text{-L}_2\text{-}\kappa\text{–}P)\text{IrH}_2]\text{BF}_4$ **866**, respectively. Compounds **865** and **866** react with excess ethene or propene giving the Ir(I) alkene complexes $[(\eta^6\text{-L}_1\text{-}\kappa\text{–}P)\text{Ir(CH}_2{=}\text{CHR)}]\text{BF}_4$ [R = H **867a**, Me **867b**] and $[(\eta^6\text{-L}_2\text{-}\kappa\text{–}P)\text{Ir(CH}_2{=}\text{CHR)}]\text{BF}_4$ R = H **868a**, Me **868b**], which in the presence of H_2 regenerate the dihydrido precursors.



n = 2; (4*S*)-4-isopropyl-2-[2-(3-indenyl)ethyl]oxazoline (HL_2),
n = 3; (4*S*)-4-isopropyl-2-[3-(3-indenyl)propyl]oxazoline (HL_3)

Scheme 117



Scheme 118

The reaction of **865** with 2 equiv. of PhC≡CPh affords the π-alkyne complex $[(\eta^6\text{-L}_1\text{-}\kappa\text{–}P)\text{Ir(PhC}{\equiv}\text{CPh)}]\text{BF}_4$ **869**. The latter forms via the stilbene derivative $[(\eta^6\text{-L}_1\text{-}\kappa\text{–}P)\text{Ir}(Z\text{-PhCH}{=}\text{CHPh})]\text{BF}_4$ **870** as an intermediate, which was isolated by reacting **867b** with *Z*-stilbene and was characterized crystallographically (Figure 60).

The reactivity of fluorinated benzynes coordinated to Ir was investigated by Hughes *et al.* (Scheme 119).[452] Treatment of the tetrafluorobenzyne complex $[\text{Cp}^*\text{Ir(PMe}_3)(\eta^2\text{-C}_6\text{F}_4)]$ **871** with acetic acid affords the

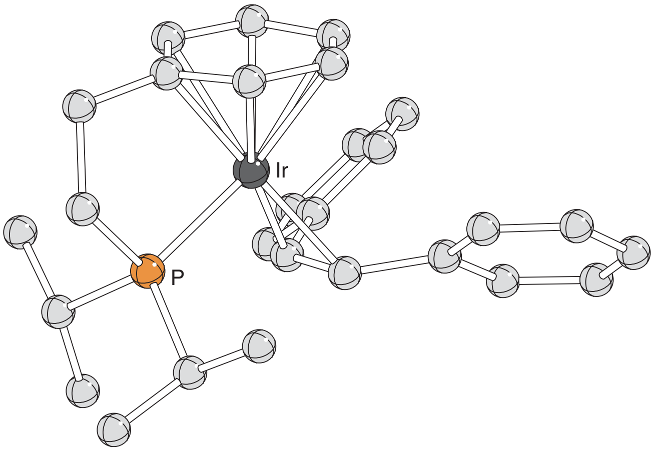
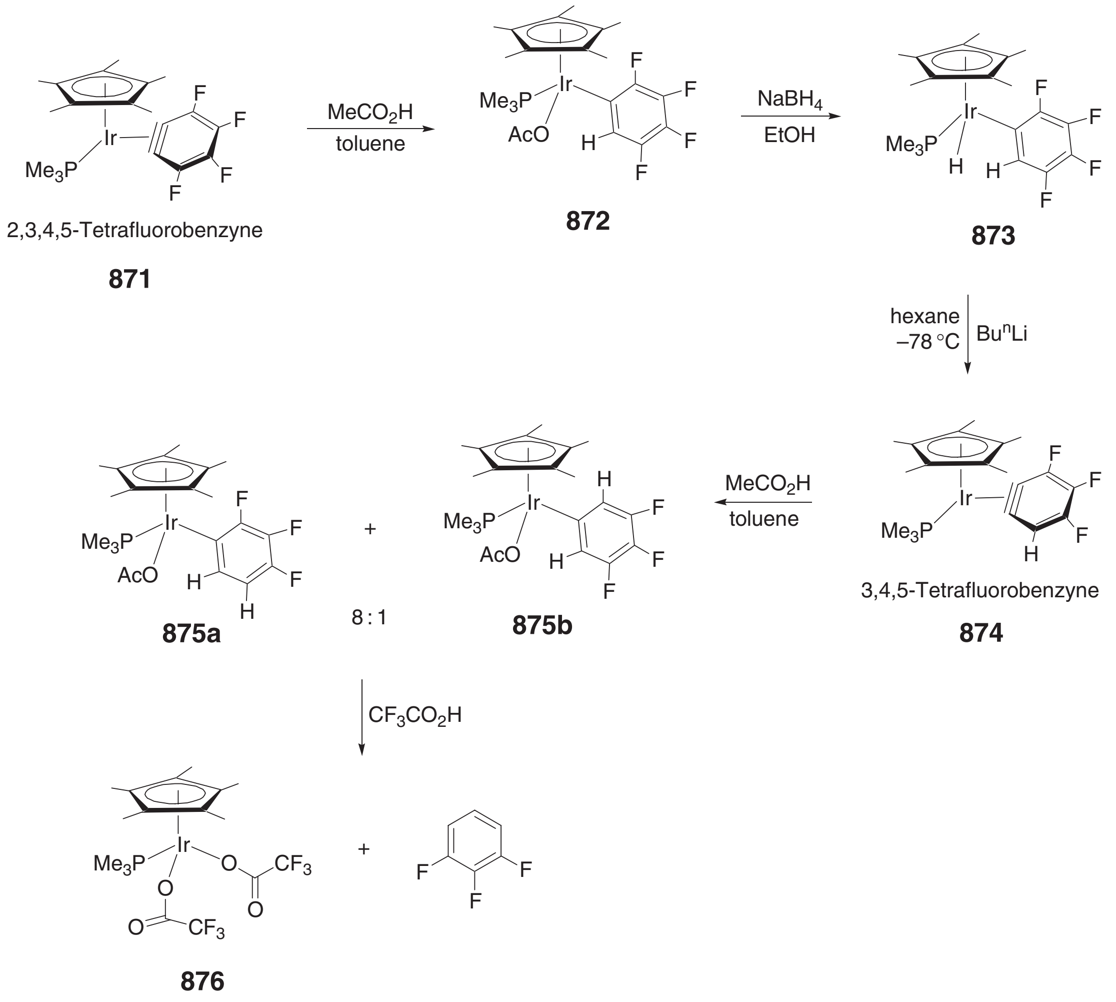


Figure 60 X-ray structure of **870**.



Scheme 119

tetrafluorophenyl complex [Cp*Ir(PMe$_3$)(2,3,4,5,-C$_6$F$_4$H)(O$_2$CMe)] **872**, which, on treatment with NaBH$_4$, yields the hydride complex [Cp*Ir(PMe$_3$)(2,3,4,5,-C$_6$F$_4$H)H] **873**. Treatment of **873** with Bu^{n}Li affords the trifluorobenzyne complex [Cp*Ir(PMe$_3$)(3,4,5,-C$_6$F$_3$H)] **874** which, with MeCO$_2$H, gives a mixture of two protonation products [Cp*Ir(2,3,4-C$_6$F$_3$H$_2$)(PMe$_3$)(O$_2$CMe)] **875a** and [Cp*Ir(PMe$_3$)(3,4,5-C$_6$F$_3$H$_2$)(O$_2$CMe)] **875b** in an 8 : 1 ratio. Upon further reaction of the mixture with CF$_3$CO$_2$H, 1,2,3-C$_6$F$_3$H$_3$ and [Cp*Ir(PMe$_3$)(O$_2$CCF$_3$)$_2$] **876** are obtained with **875a** reacting faster than **875b**. Treatment of **871** with Br$_2$, I$_2$, or MeI gives the oxidative addition products [Cp*Ir(PMe$_3$)(2-C$_6$BrF$_4$)Br] **877**, [Cp*Ir(PMe$_3$)(2-C$_6$IF$_4$)I] **878**, or [Cp*Ir(PMe$_3$)(2-C$_6$MeF$_4$)I] **879**, respectively. X-ray crystal structures of complexes **873–875**, **877, 878** have been determined.

Iridium derivatives of general formula [(η^6-arene)IrH$_2$(PR$_3$)]BF$_4$ [384; arene = benzene: R = Pr^i, Cy; R = Pr^i: arene = toluene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, hexamethylbenzene, 1-methylstyrene, phenol, aniline] and [(η^6-arene)Ir(η^2-C$_2$H$_4$)(PPr$^i_3$)]BF$_4$ [383; arene = benzene, toluene, 1,3,5-trimethylbenzene, hexamethylbenzene] have been reported by Oro and co-workers and have been described in Section 7.04.2.2 (see also Scheme 41).[187] Just to report an example of this chemistry, the dihydride [(η^6-C$_6$H$_6$)IrH$_2$(PPr$^i_3$)]BF$_4$ **880** prepared from [Ir(μ-OMe)(cod)]$_2$ and [HPPr$^i_3$]BF$_4$ in acetone/benzene solution under H$_2$ easily undergoes benzene replacement when treated with an excess of arenes, for example, C$_6$H$_5$Me, C$_6$H$_3$Me$_3$, C$_6$Me$_6$, C$_6$H$_5$NH$_2$ other than benzene, to afford products of arene substitution, that is, [(η^6-C$_6$H$_{6-n}$R$_n$)IrH$_2$(PPr$^i_3$)]BF$_4$ **881**. Complex [(η^6-1,3,5-C$_6$H$_3$Me$_3$)IrH$_2$(PPr$^i_3$)]BF$_4$ **882** was characterized by X-ray crystallography (Figure 61).[453]

Olefinic- and cyclopropyl-substituted arenes (C$_6$H$_5$R^1) were reacted with [Cp*Ir(acetone)$_3$]Y$_2$ (Y = ClO$_4$, OTf) to give η^6-arene complexes [Cp*Ir(η^6-C$_6$H$_5$R^1)]Y$_2$ [R^1 = CH=CH$_2$, CH=CHCH$_3$, CMe=CH$_2$, *c*-Pr]. Complexes

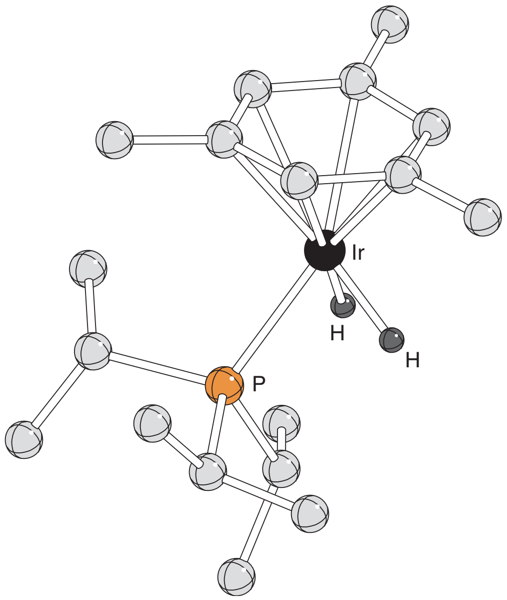
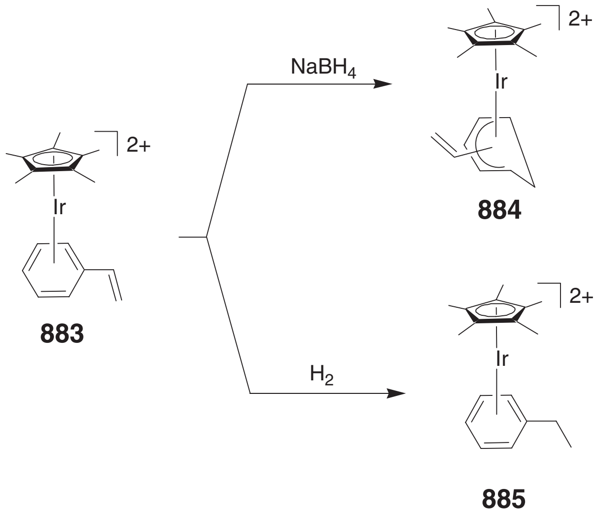


Figure 61 X-ray crystal structure of **882**. Hydrogen atoms (except for Ir–H) have been omitted for clarity.



Scheme 120

$[Cp^*Ir(\eta^6\text{-}C_6H_5R^1)](OTf)_2$ are readily converted into η^3-allyl complexes, $[Cp^*Ir\{\eta^3\text{-}CH(Ph)CHCH_2\}(MeCN)]^+$ and $[Cp^*Ir\{\eta^3\text{-}CH_2C(Ph)CH_2\}(MeCN)]^+$, in the presence of Na_2CO_3 in MeCN. The η^6-styrene complex, $[Cp^*Ir(\eta^6\text{-}C_6H_5CH{=}CH_2)](ClO_4)_2$ 883, reacts with $NaBH_4$ to give η^5-cyclohexadienyl complexes 884 while with H_2 the η^6-ethylbenzene complex $[Cp^*Ir(\eta^6\text{-}C_6H_5CH_2H_3)](ClO_4)_2$ 885 is readily generated (Scheme 120).[454]

7.04.6 Iridium Fullerene Complexes

Since the publication of COMC (1995) (Vol 7, Chapter 3.3.1.1), the coordination chemistry of fullerene and its derivatives has continued to be investigated mainly by Balch and Olmstead. A review summarizing the research in this field has been published in 1998.[455] Iridium has continued to be central in developing this chemistry and several new iridium complexes have been described involving either fullerene or some of its derivatives.

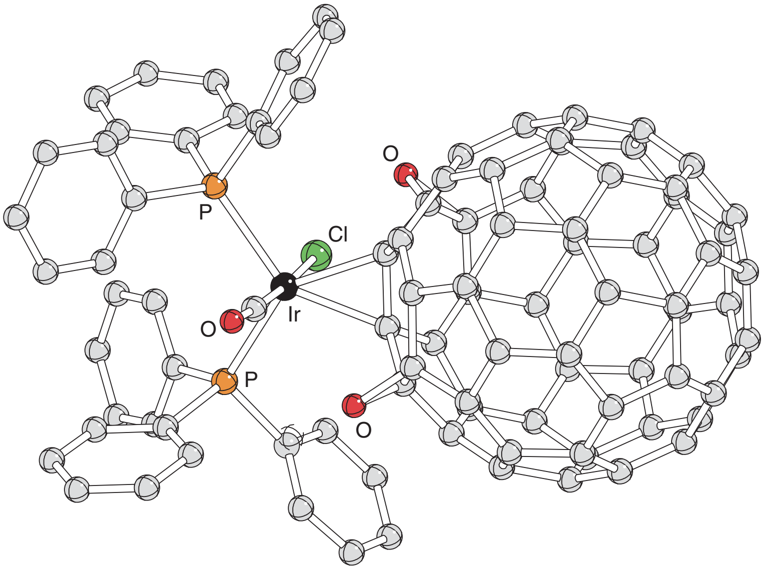


Figure 62 X-ray crystal structure of **886**.

The diepoxide, $C_{60}O_2$, obtained by *m*-chloroperbenzoic acid oxidation of C_{60} in toluene reacts with the Vaska's complex $[IrCl(CO)(PPh_3)_2]$ **1** to give black-colored crystals of $[(\eta^2\text{-}C_{60}O_2)Ir(CO)Cl(PPh_3)_2]\cdot 5C_6H_6$ **886** which was authenticated by X-ray methods (Figure 62).[456] The crystals, isostructural with those of $[(\eta^2\text{-}C_{60})Ir(CO)Cl(PPh_3)_2]$[457] $[(\eta^2\text{-}C_{60}O)Ir(CO)Cl(EPh_3)_2]$ (E = P,[458] As[459]), show the expected η^2-coordination of the fullerene dioxide with the two epoxidic oxygens disordered on different sites onto the fullerene globe. A similar coordination mode was found by X-ray analysis in $[(\eta^2\text{-}C_{70}O)Ir(CO)Cl(PPh_3)_2]$ **887** which exhibits a disordered position of the epoxidic oxygen over two different sites.[460]

The use of $[Ir_2(CO)_2Cl_2\{Ph_2P(CH_2)_nPPh_2\}_2]$ ($n = 5$ or 7), which is a bifunctional version of the Vaska's compound, has allowed for the isolation of dinuclear iridium-fullerene complexes with either C_{60} and C_{70} precursors.[461] The molecular structure of the complex $[(\eta^2\text{-}C_{60})_2Ir_2(CO)_2Cl_2\{\mu\text{-}Ph_2P(CH_2)_7PPh_2\}_2]$ **888** features a dumbbell shape diiridium geometry with remarkable short contacts between fullerenes in adjacent molecules (3.27 Å) (Figure 63).

Dendrimers containing phosphines have been used to prepare the Vaska's-type complexes *trans*-$[Ir(CO)Cl\{PPh_2(G\text{-}I)\}_2]$ and *trans*-$[Ir(CO)Cl\{PPh_2(G\text{-}2)\}_2]$. These reversibly coordinate fullerenes in PhCl.[462] Fullerene derivatives of iridium hydrides have been described by Usatov *et al.*[463,464,465,466] The reaction of both C_{60} and C_{70} with the iridium hydrides $[IrH(CO)(PPh_3)_3]$ and $[IrH(cod)(PPh_3)_2]$ led to η^2-derivatives $[(\eta^2\text{-}C_n)IrH(CO)(PPh_3)_2]$ [$n = 60$ **889** or 70 **890**] and $[(\eta^2\text{-}C_{60})IrH(cod)(PPh_3)]$ **891**, respectively (Scheme 121). Coordination of a second equivalent of $[MH(CO)(PPh_3)_2]$ (M = Rh, Ir) to the monoadducts 889 and 890 gave

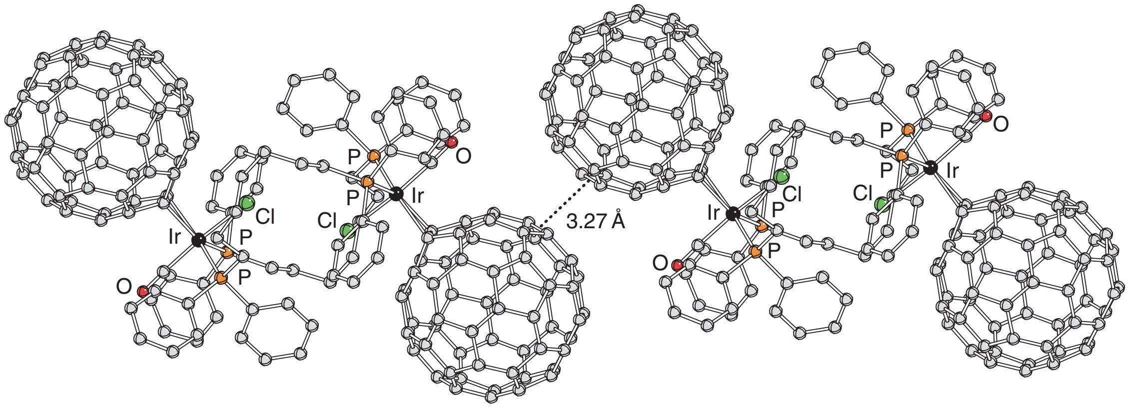
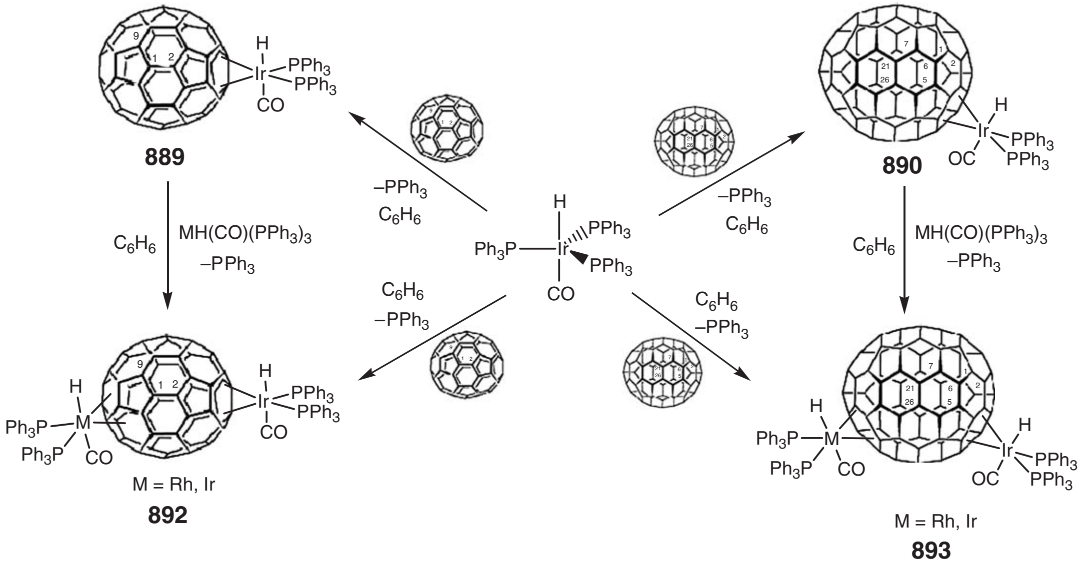


Figure 63 X-ray crystal structure of **888** showing the short fullerene–fullerene intermolecular contacts.



Scheme 121

homo- or heterodinuclear fullerene complexes $[(\eta^2\text{-C}_n)\{\text{Ir}_{2-x}\text{Rh}_x\text{H(CO)(PPh}_3)_2\}]$ ($n = 60$ **892**, 70 **893**; $x = 0$, 1).[464] The addition of organic radicals to **889** was demonstrated.[467,468]

Incorporation of two different polyhedral clusters, namely, a fullerene and a phosphacarborane, as ligands in the coordination sphere of an iridium atom was accomplished in the complex $[(\eta^2\text{-C}_{60})\text{Ir}(o\text{-HCB}_{10}\text{H}_9\text{CCH}_2\text{PPh}_2\text{-}B,P)(\text{Bu}^t\text{NC})_2]$ **894**. This was synthesized by refluxing a toluene solution of C_{60} with the carboranyliridium dihydride complex $[\text{IrH}_2(o\text{-HCB}_{10}\text{H}_9\text{CCH}_2\text{PPh}_2\text{-}B,P)(\text{PPh}_3)(\text{L})]$ (L = CO or PPh_3 **895**) in the presence of $\text{Bu}^t\text{N}{\equiv}\text{C}$.[469] The carboranyl derivative undergoes oxidation in CHCl_3 to yield $[(\eta^2\text{-C}_{60}\text{O}_2\text{-}O,C)\text{Ir}(o\text{-HCB}_{10}\text{H}_9\text{CCH}_2\text{PPh}_2\text{-}B,P)(\text{Bu}^t\text{NC})_2]$ **896** containing an iridaperoxide unit with the fullerene σ-bonded to the metal.[470]

Reaction of C_{60} in a 1:1 molecular ratio at RT with the alkoxyiridium dimer, $[\text{Ir}(\mu\text{-OR})(\text{cod})]_2$ (R = Me, Et, Pr^n, Ph), in toluene yielded fullerene complexes of formula $[(\eta^{2:2}\text{-C}_{60})\{\text{Ir}(\text{cod})(\mu\text{-OR})\}_2]$ **897** with two adjacent 6:6 ring fusions of the buckminsterfullerene molecule linked to the metals.[471] The structure of the mixed methoxide/phenoxide species $[(\eta^{2:2}\text{-C}_{60})\{\text{Ir}_2(\text{cod})_2(\mu\text{-OMe})(\mu\text{-OPh})\}]$ **898** was determined by X-ray crystallography (Figure 64).

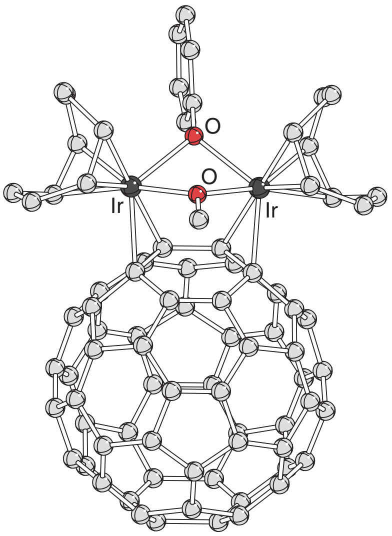


Figure 64 X-ray crystal structure of **898**.

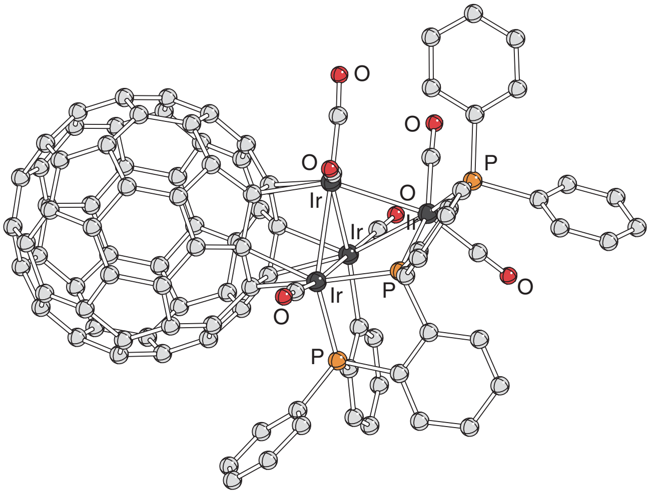


Figure 65 X-ray crystal structure of **900**.

The chemistry of hexahedral metal fullerenes has been expanded to include polymetallic clusters by Park and co-workers, who recently described some spectacular examples of multimetallic functionalization of the C_{60} molecule.[472] Prolonged boiling of the cluster $[Ir_4(CO)_9(PPh_3)_3]$ **899** with C_{60} in PhCl gave the tetrairidium derivative $[Ir_4(CO)_6\{\mu_3\text{-}PPh_2(o\text{-}C_6H_4)P(o\text{-}C_6H_4)PPh(\eta^1\text{-}o\text{-}C_6H_4)\}(\mu_3\text{-}\eta^{2:2:2}\text{-}C_{60})]$ **900** in moderate yield (36%).[473] The X-ray structure of **900** (Figure 65) shows an intriguing array of three iridium atoms face-capping the C_{60} molecule in an $\eta^{2:2:2}$-bonding mode with alternating long and short C–C bonds as well as the fullerene-promoted formation of a unique triphosphane ligand deriving from *o*-phosphination and *o*-metallation of the three PPh_3 on the Ir_4 assembly.

The reaction of $[Ir_4(CO)_8(PMe_3)_4]$ with excess C_{60} in refluxing 1,2-dichlorobenzene, followed by treatment by $C\equiv NBz$ at 70 °C, gave the bisfullerene–metal complex $[Ir_4(CO)_3(\mu_4\text{-}CH)(PMe_3)_2(\mu\text{-}PMe_2)(CNBz)(\mu\text{-}\eta^{2:2}\text{-}C_{60})(\mu_4\text{-}\eta^{1:1:2:2}\text{-}C_{60})]$ **901**, which features two metal atoms bridging two C_{60} molecules, one of them exhibiting an unprecedented $\mu_4\text{-}\eta^{1:1:2:2}\text{-}C_{60}$ bonding mode. Cyclic voltammetry (CV) electrochemistry indicated an enhanced electronic communication between the wide channels separating the two activated C_{60} units.[474]

Electroreduction of C_{60} in the presence of $[IrCl(CO)_2(p\text{-toluidine})]$ produces an electroactive film of possible composition $C_{60}\{Ir(CO)_2\}_n$ **902** coating the electrode.[475] Laser ablation of this electrodeposited film indicates that a family of irida-fullerene anionic cages C_xIr^- ($x = 59-57$)[476,477] are generated. The structures of these heterofullerenes were optimized by DFT methods.[476,477,478] The theoretical analysis suggests that the metal atom is replacing the C_2-unit at a 6 : 6 ring junction of the fullerene and is part of the polycarbon skeleton protruding outward in the fullerene surface. Laser ablation studies in the presence of 2-butene suggest the iridium atom in these heterofullerenes is still endowed with additional bonding capability as compounds such as $[C_{59}Ir(2\text{-butene})]^-$, $[C_{58}Ir(2\text{-butene})]^-$, $[C_{57}Ir(2\text{-butene})]^-$, and $[C_{56}Ir(2\text{-butene})]^-$ have been observed by mass spectroscopy.[478] The related higher-nuclearity substitutionally doped fullerene $C_{69}Ir^-$ was also studied by theoretical methods[479] and investigated by photofragmentation mass spectroscopy.[480]

^{193}Ir Mössbauer spectra of several iridium fullerene derivatives have been recorded and used in combination with theoretical methods to assess the donor–acceptor properties of the polycarbon molecules.[481,482,483]

7.04.7 Iridium Hydride Complexes

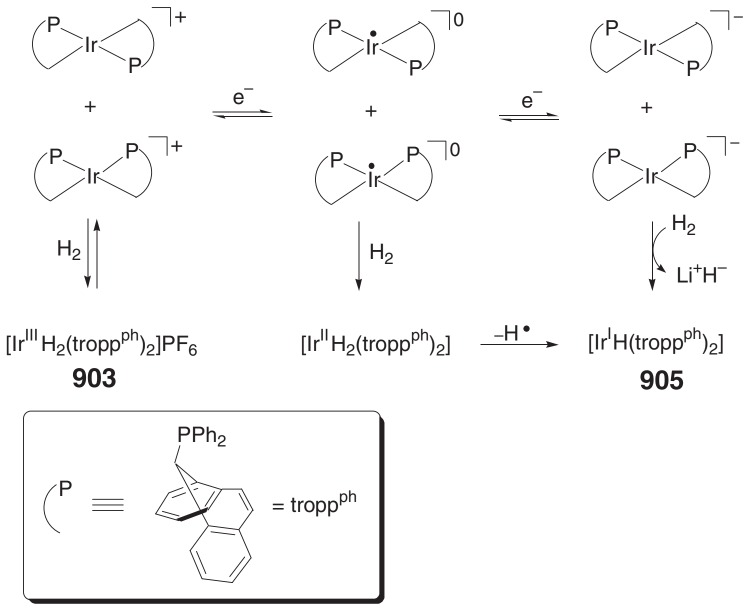
The chemistry of iridium hydrides has been largely expanded after the publication of COMC (1995) (see COMC (1995), Vol 7, Chapters 3.6 and 3.11) and several new iridium hydrides have been described with a hydride content ranging between one and five. Both terminal and bridging classical iridium hydrides and non-classical hydrides (*i.e.* molecular hydrogen complexes) have been reported as being iridium hydrides among the most studied compounds of this sort due to the high thermodynamic stability of the Ir–H bond. This fact, coupled to the kinetic inertness of organoiridium species, when compared to related rhodium derivatives, makes iridium hydrides quite amenable for fundamental M–H structural and bonding studies and useful model compounds for mechanistic investigations in both catalytic and stoichiometric processes.

7.04.7.1 Monohydride Complexes

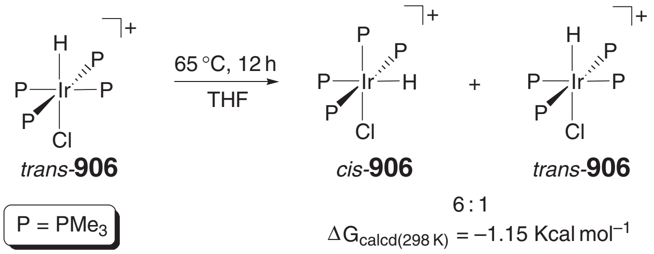
Iridium monohydrides may be prepared by the reaction of suitable iridium precursors with dihydrogen via heterolytic splitting mediated intra- or intermolecularly by an external base or by oxidative addition of hydrogenated substrates (HX) to a low-valent iridium complex. Nucleophilic attack by hydride anion and β-elimination from coordinated ligand may also result in the formation of Ir–H bonds.

Worth to be mentioned are the studies by Grützmacher *et al.*[484,485] on the tetracoordinated Ir complexes $[Ir(tropp^{ph})_2]^n$ ($n = 1, 0, -1$) with the metal spanning different formal oxidation states from +1 to −1. Depending on the oxidation state of the metal, reaction with dihydrogen led to the Ir(III) dihydride $[IrH_2(tropp^{ph})_2]PF_6$ **903** or to Ir(I) monohydrides via heterolytic activation of H_2. Interestingly, the hydrogenation of the Ir(−I) complex $[Li(THF)_x][Ir(tropp^{ph})_2]$ **904** yielded, apart from the expected monohydride $[IrH(tropp^{ph})_2]$ **905**, lithium hydride via H_2 heterolytic splitting (Scheme 122).[484]

Compounds $[IrH(X)(PMe_3)_4]Y$ (X = halide) undergo an unexpected *trans*- to *cis*-isomerization.[486] The process, which is thought to be general for this kind of derivatives, was experimentally proved on the hydrochloride complexes $[IrH(Cl)(PMe_3)_4]Y$ (Y = PF_6, Ts **906**) and $[IrH(Cl)(dmpe)_2][OOCCH(CN)_2]$ **907** (Scheme 123). Quantum



Scheme 122



Scheme 123

mechanical calculations using PH_3 and $PH_2CH_2CH_2PH_2$ models suggest that the two structures are nearly isoenergetic, so that the *cis* ⇔ *trans* equilibrium is controlled by the higher entropy of the lower symmetry *cis*-structure.

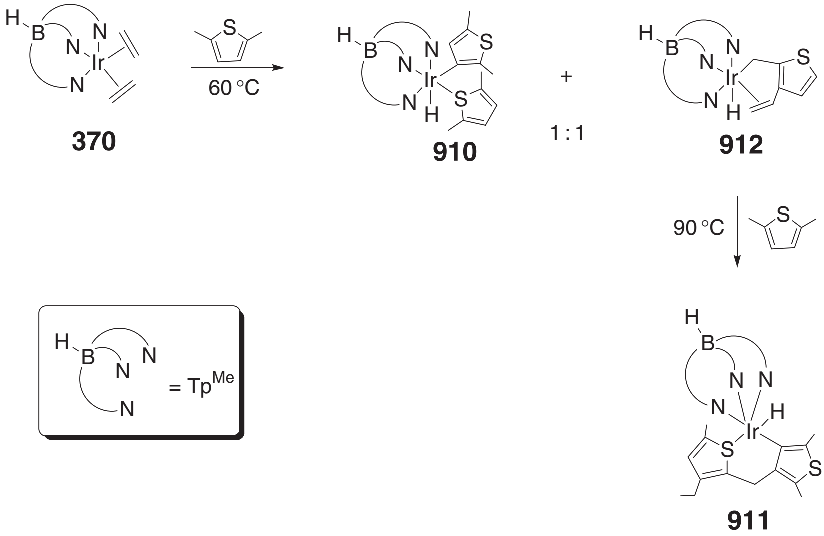
The reactivity of $[IrH(CO)(PPh_3)_2]$ **908** with both C_{60} and C_{70} fullerenes has been studied by Usatov *et al.*[463,464,487,488,488a] The resulting exohedral monohydrido complexes were formed with complete stereo- and regioselectivity with the fullerene molecules η^2-coordinated via the 1,2-bond to form only one isomer in both cases. Double metallation of fullerene was also observed yielding more than one isomer.

Carmona and co-workers studied in detail the chemistry of trispyrazolylborato iridium complexes giving particular attention to the 3,5-dimethyl substituted ligand Tp^{Me}, hydrotris(3,5-dimethyl-1-pyrazolyl)borate. These complexes were found to be able to promote the C–H bond activation in different organic molecules affording a variety of hydride compounds.

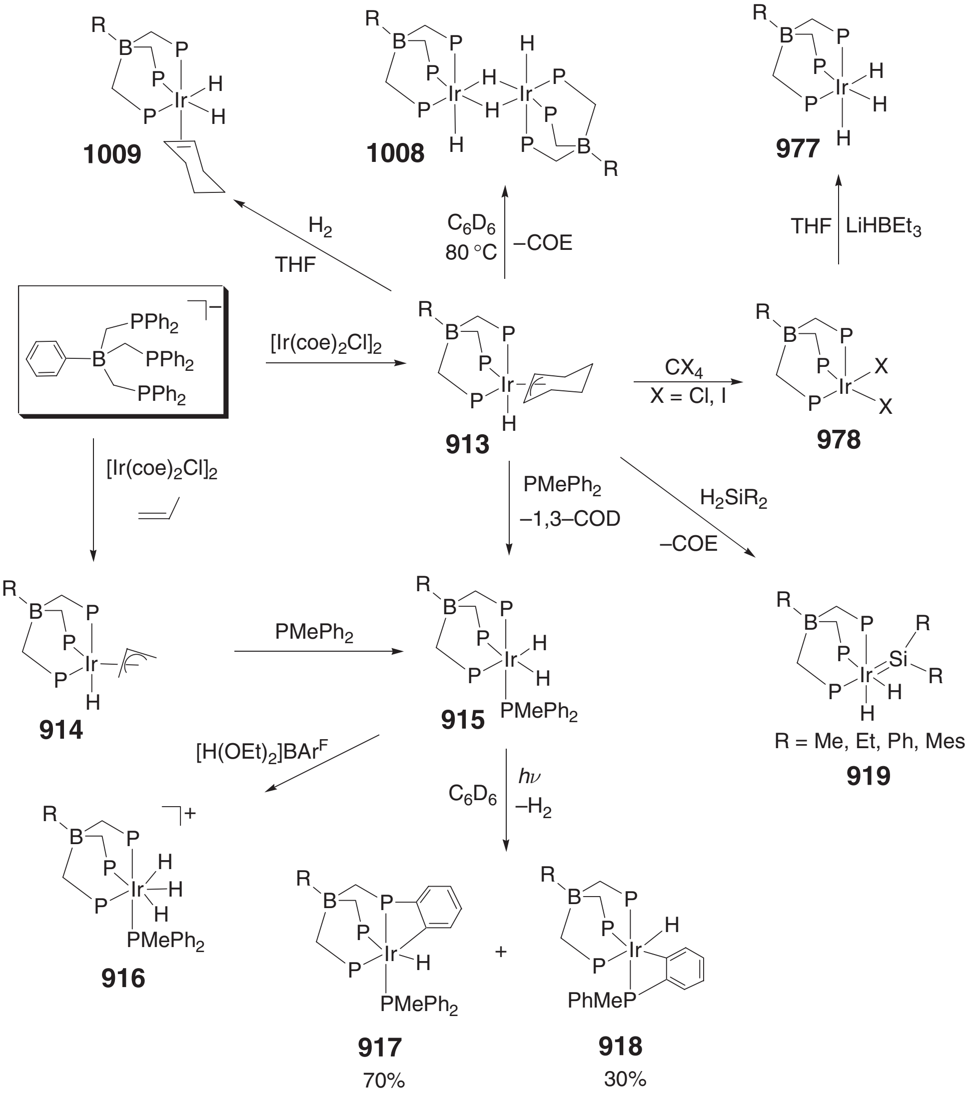
The diene complexes $[Tp^{Me}Ir(\eta^4\text{-}2,3\text{-}RR^1C_4H_4)]$ [R, $R^1 = H$; $R = Me$, $R^1 = H$; R, $R^1 = Me$] were chosen for comparative studies on photochemical C–H bond activation reactions which take place only at the C–R and C–R^1 moieties. The C–H activation was found to depend on the nature of the R and R^1 substituents. Relevant to this section, the dimethyl substituted diene ligand was readily activated at one of the methyl groups, yielding the hydrido-allyl complex $[Tp^{Me}Ir(H)(\eta^3\text{-}CH_2C\{C(Me){=}CH_2\}CH_2\}]$ **909**.[201]

C–H bond activation is likely responsible for the formation of the the two iridacycle monohydrides **910 and 911** resulting from the reaction of $[Tp^{Me}Ir(C_2H_4)_2]$ **370** with neat 2,5-Me_2T at 90 °C (Scheme 124). The reaction is thermally controlled. At 60 °C, the C–H activation product $[Tp^{Me}Ir(H)(2,5\text{-}Me_2\text{thienyl})(\eta^1\text{-}S\text{-}2,5\text{-}Me_2T)]$ **912** together with the iridacycle **910** are formed. Further heating to 90 °C results in the coupling of the thiophenic fragment in **910** with a second molecule of 2,5-Me_2T to yield the complex ligand featuring **911**. A mechanism accounting for the formation of the two iridacycles, which entails a series of C–H activation and C–C bond-coupling steps, has been proposed.[489]

Iridium mono- and dihydrides of the tripodal anionic phosphine ligand $[PhB(CH_2PPh_2)_3]^-$ ($PhBP_3$) were studied by Tilley and co-workers and their chemical properties compared with those of the related Cp^* and Tp^{Me} iridium complexes.[490,491] Of particular relevance to provide high-yield entry to the chemistry of $(PhBP_3)Ir$ are the two allyl hydrides $[(PhBP_3)Ir(H)(\eta^3\text{-}C_8H_{13})]$ **913** and $[(PhBP_3)Ir(H)(\eta^3\text{-}C_3H_5)]$ **914** which were synthesized from the reaction of $[Li(TMEDA)](PhBP_3)$ with the corresponding $[IrCl(alkene)_2]_2$ complex (Scheme 125). The reaction of **913** with $PMePh_2$ gave the dihydride $[(PhBP_3)Ir(PMePh_2)H_2]$ **915** which, upon protonation with $[H(OEt_2)]BAr^F$, transformed into the classical trihydride $[(PhBP_3)Ir(PMePh_2)H_3]BAr^F$ **916**. Photolysis of **915** provided the cyclometallated products $[\{PhB[(CH_2PPh_2)_2(CH_2PPhC_6H_4\text{-}C,P)]\}Ir(H)(PMePh_2)$ **917** and $[(PhBP_3)Ir(H)(PMePhC_6H_4\text{-}C,P)]$ **918**. The use of these hydrides as well as of some of their derivatives in promoting either Si–H or C–H bond activation was also demonstrated. Extrusion of silylenes from secondary silanes R_2SiH_2 has been reported to give the silylene dihydrides $[(PhBP_3)Ir(H)_2({=}SiR_2)]$ **919**. Similar reactions take place with related germane derivatives R_2GeH_2.[492]



Scheme 124

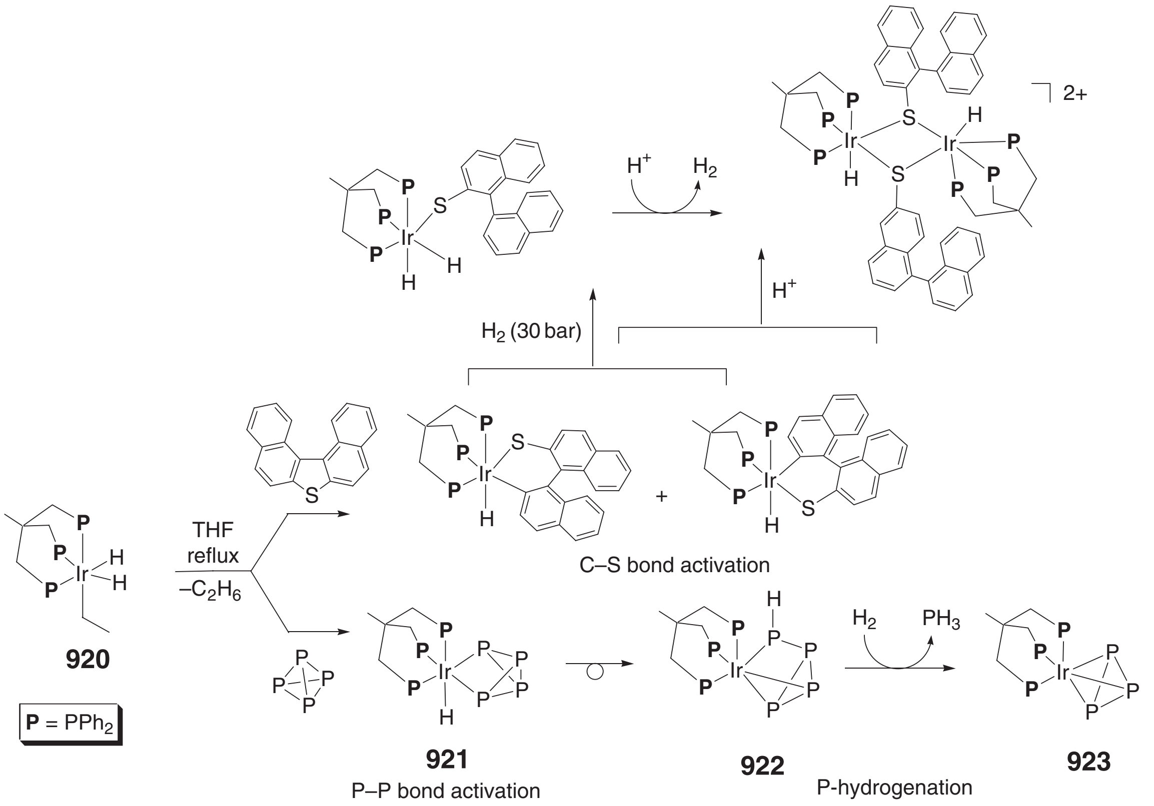


Scheme 125

The highly reactive iridium monohydride fragment [(triphos)IrH], generated *in situ* by thermolysis of [(triphos)IrH$_2$(C$_2$H$_5$)] 920 in THF (Scheme 126), has been used to activate C–S bonds from substituted thiophenes[493] and P–P bond in white phosphorus.[494] The reaction with P$_4$ has helped to unravel the mechanism of the stoichiometric hydrogenation transforming one P atom of P$_4$ into PH$_3$.[495,496] Scheme 126 illustrates this chemistry for both the P$_4$ molecule and the 1,1′-binaphthalene-2-thiol (DNT), one of the most difficult thiophenic substrates to be degraded under HDS conditions.

In the case of white phosphorus, the reaction proceeds through the following elementary steps: (i) ethane elimination, (ii) P–P bond activation at iridium forming the Ir(III) hydride [(triphos)IrH(η^2-P$_4$)] 921, (iii) isomerization of 921 to [(triphos)Ir($\eta^{2:1}$-P$_4$H)] 922 with selective delivery of the hydride atom to one of the coordinated P-atoms, and (iv) hydrogenation of the teraphosphidohydride ligand with PH$_3$ generation and formation of the known *cyclo*-P$_3$ complex [(triphos)Ir(η^3-P$_3$)] 923.

The formation of iridium hydrides is a common feature in the many processes resulting in the C–H bond activation that are promoted by coordinatively unsaturated iridium precursors. A few examples are illustrated below, while other processes featuring C–H bond breakage of an organic compound are mentioned in Section 3 of this review.



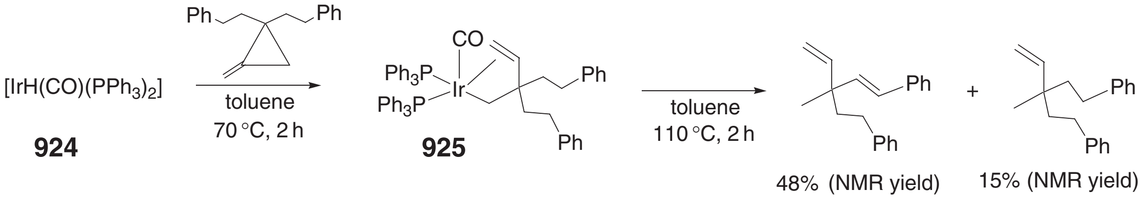
Scheme 126

β-Hydrogen elimination from iridium alkyl or alkoxide derivatives is also a general pathway to generate Ir–H species. The mechanism of the reversible β-hydrogen elimination from square-planar Ir(I) alkoxide complexes has been studied in detail by Hartwig,[497] Milstein,[498,499,500,501] and their co-workers.

Catalytic C–C bond-forming reactions are often catalyzed by iridium hydrides. As an example, the head-to-tail dimerization of acrylates and vinyl ketones is promoted by $[IrCl(cod)]_2$ in Bu^nOH in the presence of small amounts of Na_2CO_3 and $P(OMe)_3$. The alcohol and the carbonate serve to generate *in situ* an iridium hydride species which is thought to be the catalyst capable of dimerizing acrylates.[502]

A further example of C–C bond activation promoted by iridium hydrides was provided by Nishihara *et al.* who showed that the reaction of highly strained methenecyclopropanes with $[IrH(CO)(PPh_3)_2]$ **924** gives 1,3-dienes via the intermediate formation of isolable 3-butenyl complexes **925** (Scheme 127).[194a]

Water-soluble iridium hydrides containing PTA, TPPMS, and TPPTS ligands have been described and a few notes on these compounds have been presented in Section 1.1 of this review.[4] A remarkable hydrosoluble hydride is $[Cp^*Ir(bpy)H]^+$ **821** prepared by Ogo and co-workers by controlled protonation of the aquo complex $[Cp^*Ir(bpy)(H_2O)]^{2+}$ **505** with carboxylic acids.[228b] Compound **821** has been used as a robust and highly active catalyst



Scheme 127

for acid-catalyzed transfer hydrogenations of carbonyl compounds at pH 2.0–3.0 and for the highly chemoselective synthesis of α-amino acids via reductive amination of α-keto acids with NH_3 and $HCOO^-$.[503] Excited-state deprotonation and H/D exchange of this intriguing iridium hydride complex has also been described.[504] The use of low-valent iridium hydrides as alternatives to Lewis-acid and -base catalysts has been reviewed by Murahashi and Takaya.[505]

Iridium(III) complexes have been used by Bergman and co-workers for catalytic H/D exchange reactions in organic molecules. The exchange between C_6D_6 and different organic substrates has been shown to be promoted at low temperature by the Ir(III) hydride $[Cp^*Ir(PMe_3)H(CD_2Cl_2)]BAr^F$ **620**–d_2).[358] Similarly, $[Cp^*Ir(PMe_3)Cl_2]$ **926** promotes the incorporation of deuterium atoms in hydrosoluble substrates using D_2O as both solvent and D-source.[506,507] Highly selective deuterium and tritium labeling in molecules of pharmacologic interest has been achieved by using the highly electrophilic $[Cp^*Ir(PMe_3)Me(CH_2Cl_2)]BAr^F$ **293**.[508,509] The use of the Ir(V) trihydride $[Cp^*Ir(PMe_3)H_3]OTf$ **927** to catalyze the H/D scrambling between arenes and acetone-d_6 has also been reported.[509] Deuteration of aromatic substrates is promoted by a variety of *in situ* generated Ir(I) species, $[Ir(cod)(L)_2]BF_4$ ($L = PR_3$, AsR_3, SbR_3, py).[510,510a–510e] Finally, a mechanistic study of the stoichiometric and catalytic H/D exchange reactions involving cationic iridium complexes has been carried out and the collected evidence supports a monohydrido-iridium intermediate as responsible for both the stoichiometric and the catalytic isotopic exchanges.[511]

The long-lasting question about the existence of Ir(IV) paramagnetic hydrides, $[IrH_xCl_2(PPr^i{}_3)_2]$ **928**, was answered definitely by a thorough reinvestigation by magnetic measurements, IR and NMR methods, and X-ray crystallography.[512] It was concluded that this compound is a genuine TBP coordinatively unsaturated monohydride, while the originally observed paramagnetism was therefore attributed to surface impurities.

7.04.7.2 Dihydride Complexes

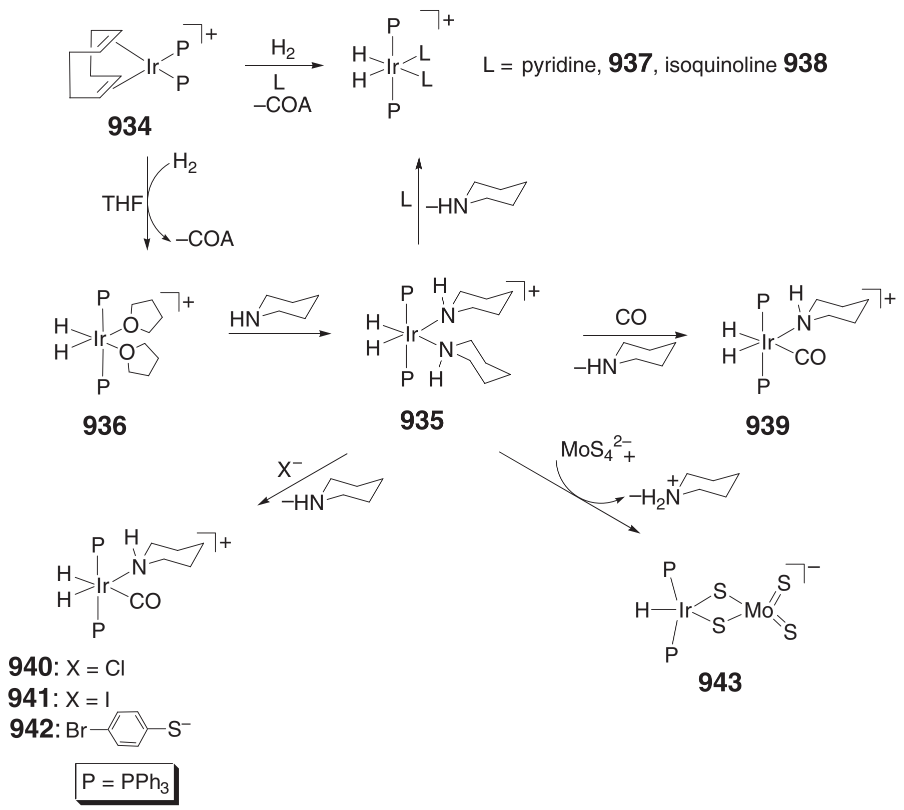
OCT Ir(III) dihydrides obtained by oxidative addition of H_2 to square-planar Ir(I) complexes have continued to be systematically studied after the publication of COMC (1995).[513] Usually, two phosphines occupy the axial positions of the coordination polyhedron lying in mutual *trans*-disposition, while two hydrides and two additional L ligands are *cis*-disposed to each other to afford complexes of formula *cis,cis,trans*-$[IrH_2(L)_2(PR_3)_2]$. Meridional arrangements of three phosphines are also known in complexes of general formula *cis,mer*-$[IrH_2(L)(PR_3)_3]$. Similar dihydrides containing ligands other than phosphines have also been reported. These include stibines,[305b] combination of stibines and phosphines,[305c,343] nitriles,[514] aminoacidic residues,[515] polydentate ligands such as diphosphines,[516,517] bipyridyls,[518] dithioethers,[227a] and the triazacyclononanes Cn and Cn*.[519]

Reversible oxidative addition of H_2 takes place at SQP iridium complexes containing chelating diphosphines. As an example, [Ir(dippe)Cl] **929** adds H_2 to afford *cis*-$[IrH_2(dippe)_2]Cl$ **930** which reversibly gives back **929** upon exposure to UV light.[516] The oxidative addition of H_2 to $[Ir(bisphosphine)(cod)]^+$ complexes was studied in detail by Landis and co-workers to model the kinetic and thermodynamic stereoselectivities of the catalytic hydrogenation of prochiral enamides.[517,520] In the case of $[Ir(chiraphos)(cod)]^+$ **931**, it was demonstrated that kinetic and thermodynamic selectivities of H_2 addition are not the same and the dominant kinetic product is thermodynamically less stable than the minor kinetic product.

The reactivity of these iridium dihydride compounds has been largely studied in both stoichiometric and catalytic processes. A few selected examples are illustrated below.

The reaction of $[Cp_2M(SH)_2]$ (M = Mo, W) with 1 equiv. of $[IrH_2(\eta^1\text{-}O\text{-}OCMe_2)_2(PPh_3)_2]PF_6$ **538** in acetone under H_2 atmosphere was shown by Hidai *et al.* to give the hydrosulfido-hydrido complexes $[Cp_2M(\mu\text{-}SH)_2IrH_2(PPh_3)_2]PF_6$ [M = Mo **932**, W **933**].[521] The two dinuclear Mo/Ir and W/Ir compounds catalyze the hydrogenation (1 atm H_2) of 1-alkynes to alkenes at room temperature.

Dihydrido complexes of formula $[IrH_2(\eta^1\text{-}N\text{-}L)_2(PPh_3)_2]PF_6$ and $[IrH_2(\eta^1\text{-}S\text{-}L)_2(PPh_3)_2]PF_6$ have been synthesized in high yield by Sánchez-Delgado and co-workers by the hydrogenation of $[Ir(cod)(PPh_3)_2]PF_6$ **934** in the presence of the appropriate *N*-aromatic[522] or *S*-aromatic compound L.[523] As an example, the reaction with piperidine yielded a mixture of products including $[IrH_2(\eta^1\text{-}N\text{-}NC_5H_{10})_2(PPh_3)_2]PF_6$ **935**. This latter was better prepared by reacting a THF solution of $[IrH_2(THF)_2(PPh_3)_2]PF_6$ **936**, previously generated by *in situ* hydrogenation of $[Ir(cod)(PPh_3)_2]PF_6$, with excess of piperidine.[524] The chemistry of these hydrides has been investigated (Scheme 128). Exchange of piperidine in **935** with pyridine and isoquinoline easily afforded **937** and **938**, respectively, while under CO the monocarbonyl complex $[IrH_2(\eta^1\text{-}N\text{-}NC_5H_{10})(CO)(PPh_3)_2]PF_6$ **939** was generated. Reaction of **935** with anionic ligands X^- (Cl, I, 4-BrC_6H_4S) gave the neutral dihydrides $[IrH_2(\eta^1\text{-}N\text{-}NC_5H_{10})(X)(PPh_3)_2]$ (X = Cl **940**, I **941**, 4-BrC_6H_4S **942**). The heterobimetallic monohydride anion



Scheme 128

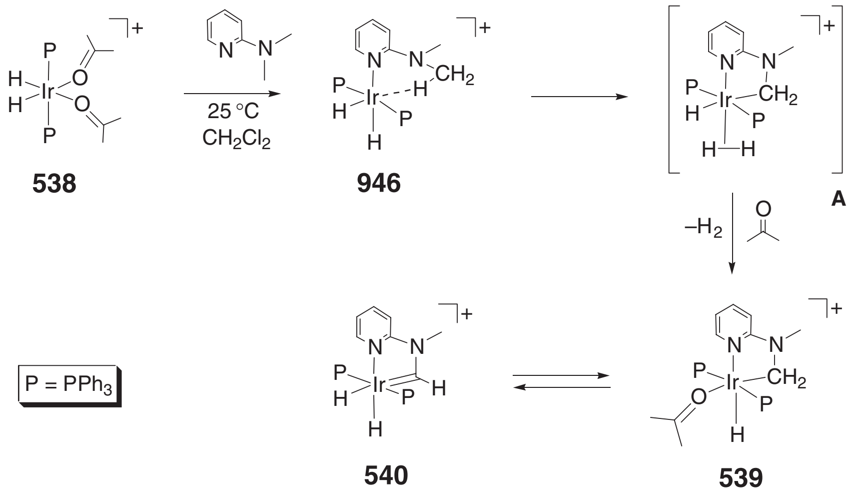
$NH_4[Ir(H)(PPh_3)_2(\mu\text{-}S)_2MoS_2]$ **943** was obtained by reaction with ammonium tetrathiomolybdate. The relevance of these hydrides as models for the chemisorption step in heterodenitrogenation catalysis was also briefly commented. A mechanism for the hydrogenation of BT involving coordination of two BT molecules and hydride migration to the coordinated heterocycle has been proposed.[523]

Selective and non-innocent ion pairing has been found to occur in solution in $[IrH_2(bpy)(PRPh_2)_2]Y$ [R = Me **944**, Ph **945**; Y = PF_6, BF_4, OTf, BPh_4] by 1D and 2D NMR methods by Macchioni *et al.*[518,525] Remarkably, the interaction is enhanced on the side of the bpy ligand, then remote from the metal and opposed to the IrH_2 moiety.

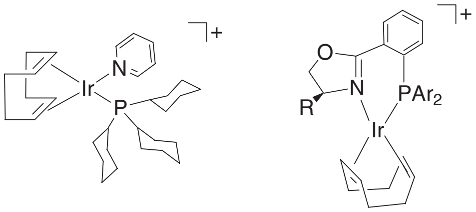
Reversible α-elimination has been described by Crabtree and co-workers in the reaction of 2-dimethylaminopyridine with $[IrH_2(\eta^1\text{-}O\text{-}OCMe_2)_2(PPh_3)_2]PF_6$ **538**.[325] The reaction, illustrated in Scheme 129, gives the chelated Fischer carbene $[IrH_2\{{=}CHN(Me)Py\}(PPh_3)_2]PF_6$ **540** and takes place via a rare double C–H activation route. Monitoring the process by low temperature NMR shows the formation of an agostic C–H···Ir intermediate **946**, which upon eliminating H_2 from a presumed η^2-H_2 intermediate **A**, eventually gives the final carbene via α-elimination. In keeping with this hypothesis, the carbene dissolves in acetone to give back the acetone adduct **539** with complete reversibility of the α-elimination step.

Dihydrido complexes containing stibines have been prepared by Werner and co-workers by the reaction of $[Ir(coe)_2Cl]_2$ with $SbPr^i_3$ in the presence of H_2.[343] The stibine ligands in $[IrH_2Cl(Sb^iPr_3)_3]$ **947** are labile and readily undergo displacement reactions. For example, the reaction with CO affords $[IrH_2Cl(CO)(Sb^iPr_3)_2]$ **948**. In contrast, the reaction of **947** with HC≡CR (R = Ph, CO_2Me) gives $[IrHCl(C{\equiv}CR)(Sb^iPr_3)_3]$ [R = Ph **949a**, CO_2Me **949b**] from which stibine is easily replaced by treatment with pyridine yielding $[IrHCl(C{\equiv}CR)(py)(Sb^iPr_3)_2]$ [R = Ph **950a**, CO_2Me **950b**].

The effectiveness of the Crabtree's catalyst $[Ir(cod)(py)(PCy_3)]$ **951** for the hydrogenation of hindered alkenes has been boosted toward impressive enantioselectivities by replacing the py/PCy_3 pair of ligands with a chiral bidentate phosphinooxazolidine (PHOX) in the cationic Pfalz's catalysts [Ir(PHOX)(cod)]Y **952** (Scheme 130).[526] A marked dependence on the nature of the counter anion for the catalytic performance of this class of excellent catalysts has been reported by several authors[281f,k,526,527] and interpreted by Pregosin and co-workers by 2D NMR diffusion



Scheme 129



951
Crabtree's catalyst

952
Pfalz's catalyst

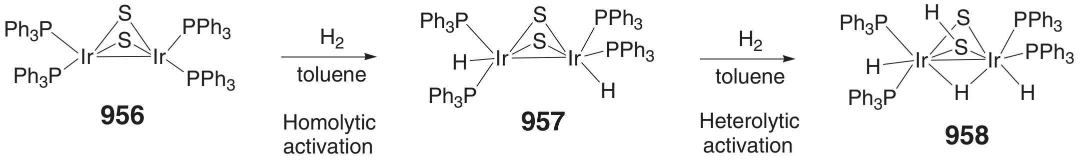
Scheme 130

techniques.[528,529] A detailed DFT analysis coupled with a kinetic study of the catalyzed reaction suggested a catalytic cycle and provided an explanation for the observed enantioselectivity.[530]

cis-[IrH_2(cod){(+)-RiSSR_2}]BF_4 **953**, containing a variety of chiral dithioether ligands derived from sugars (1,2-*O*-isopropylidene-3,5-bis(methylsulfanyl)-[(+)-RiSSMe_2], 1,2-*O*-isopropylidene-3,5-bis(isopropylsulfanyl)- [(+)-RiSS$\mathrm{Pr^i_2}$], and 1,2-*O*-isopropylidene-3,5-bis(phenylsulfanyl)-α-D-(+)-ribofuranose, [(+)-RiSSPh_2]),[226] have been successfully used to carry out the asymmetric hydrogenation of acrylic acid derivatives under mild conditions (1 bar H_2, RT).

The addition of H_2 to SQP iridium complexes has been largely studied. In particular, the successful application of *para*-hydrogen (*p*-H_2) effect for the enhancement of NMR signals has been applied by Duckett, Eisenberg and their co-workers to study the addition of H_2 to simple SQP iridium complexes such as the Vaska's compound and related complexes.[79,531,532,533,534,535,536] The use of this intriguing technique has allowed the ^{1}H NMR detection of metal-bound hydrides at significantly enhanced levels of sensitivity and, therefore, the collection of invaluable mechanistic information on H_2 addition and hydrido exchange processes. Reviews about the use of *p*-H_2 effects to unravel reaction mechanism and catalytic processes involving H_2 addition are available.[537,538] Parahydrogen (*p*-H_2) was used to unravel the mechanism of iridium carbonyl complexes promoted hydroformylation. Remarkably, although hydrogen transfer to substrate in hydroformylation is nonpairwise, *p*-H_2 effects proved useful mechanistically.[539,540] PHIP NMR spectroscopy has also been used to study the reaction of H_2 with the iridium μ-S "A-frame" complex [Ir_2(μ-S)$(CO)_2$$(dppm)_2$] **954** and the mixed metal complex [IrRh(μ-S)$(CO)_2$$(dppm)_2$] **955**. PHIP enhancement of the NMR ^{1}H signals was used to detect species not readily seen by normal NMR spectroscopy and therefore to study the mechanism of these reactions.[541]

Double addition of H_2 to the dinuclear Ir(II) sulfide complex [Ir_2(μ-S$)_2$$(PPh_3)_4$] **956** was studied by Rauchfuss and co-workers by NMR methods at low temperature and deuterium incorporation experiments.[542] Complex **956** binds



Scheme 131

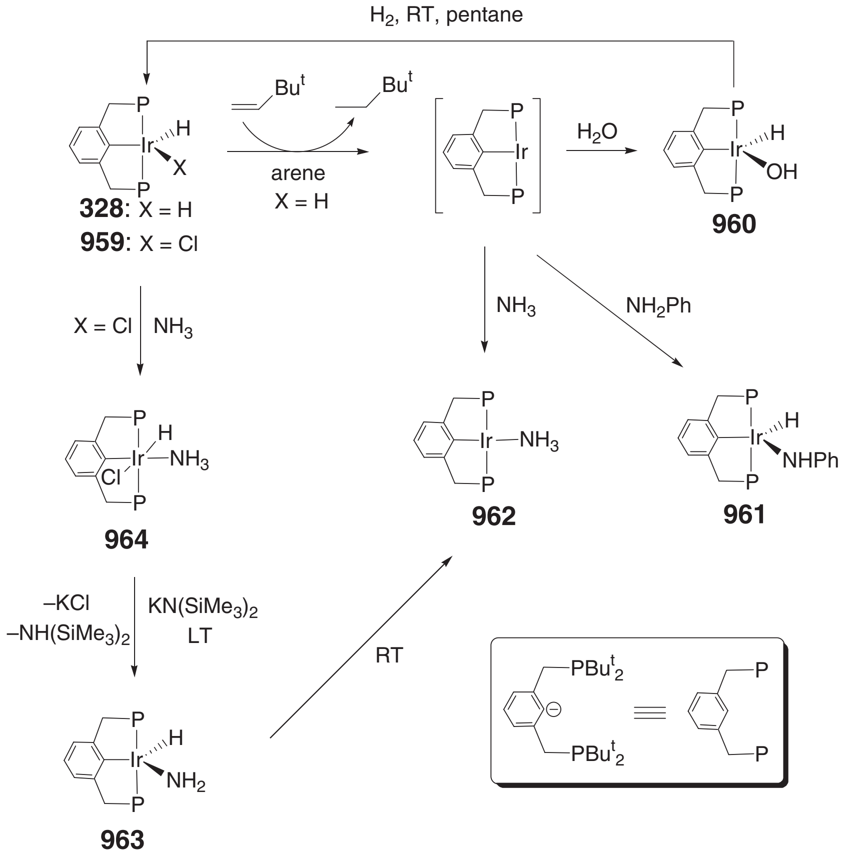
2 equiv. of H_2, via an initial homolytic process yielding $[Ir_2H_2(\mu\text{-}S)_2(PPh_3)_4]$ **957** which is followed by a heterolytic H_2 activation resulting in the stable complex $[Ir_2H_2(\mu\text{-}H)(\mu\text{-}S)(\mu\text{-}SH)(PPh_3)_4]$ **958** (Scheme 131). Questions about the mechanism governing the second dihydrogen uptake were raised by D_2 experiments. Thus, replacing H_2 with D_2 shows that the intermediate dihydride **957** absorbs the second equivalent of D_2 to generate a fully equilibrated mixture of isotopomers with the deuterium located equally in the three hydride sites as well as in the hydrosulfide position.

Pincer-type PCP ligands ($PCP = \eta^3\text{-}2,6\text{-}(R_2PCH_2)_2C_6H_3$; where R is usually a bulky organic group such as Pr^i or Bu^t) have attracted great interest in iridium chemistry since the publication of COMC (1995) and have shown very unusual reaction pathways. Particularly, the [(PCP)IrH(X)] units [X = H **328**, Cl **959**] have been used, mainly by Kaska and co-workers, as efficient catalysts for alkane dehydrogenation.[233,233a–233c,236,543,544] Selective formation of α-alkenes has been demonstrated by Goldman *et al.*[233c] who, soon thereafter, reported on the intriguing capability of these iridium pincers to cleave C–H bonds in alkenes and arenes and firstly highlighted the dynamic behavior of the activated hydrido(organyl) species.[162a] DFT/ECP electronic structure calculations suggested that the favored mechanism for the "acceptorless" alkane dehydrogenation promoted by **328** is dissociative rather than associative although the calculated energies for the two processes are very close.[545] O–H activation in water[546] and alcohols[71] was demonstrated by Jensen and co-workers. The reaction of $[(PCP)IrH_2]$ **328** with water yielded a very unusual 16e hydrido(hydroxo) species [(PCP)IrH(OH)] **960**. Reductive elimination of water from **960** was demonstrated upon exposure of a pentane solution to a H_2 atmosphere.

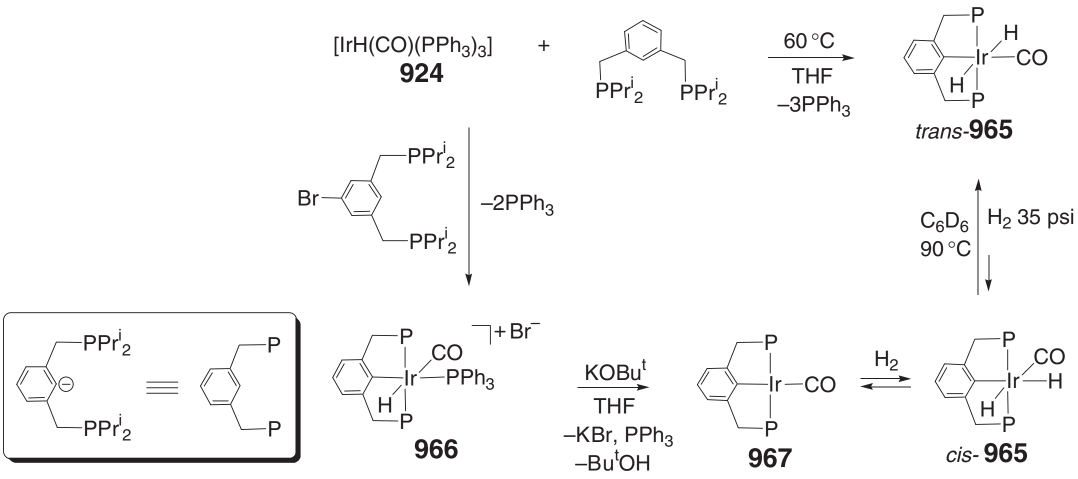
Intriguing results in the area of N–H activation of amines promoted by iridium pincer complexes have been reported.[234,234a] In particular, Hartwig showed that, while the reaction of **328** with aniline gave [(PCP)IrH(NHPh)] **961**, the analogous reaction with ammonia afforded the SQP NH_3 complex $[(PCP)Ir(NH_3)]$ **962**.[547] In a separate experiment, it was shown that the amido hydride complex $[(PCP)IrH(NH_2)]$ **963**, independently generated by deprotonation of the NH_3 complex $[(PCP)IrH(Cl)(NH_3)]$ **964** with $KN(SiMe_3)_2$ at LT, underwent reductive elimination of NH_3 at RT to form the NH_3 complex **962**. Remarkably, **963** would have been formed by oxidative addition of NH_3. Some of this intriguing chemistry is presented in Scheme 132.

The oxidative addition of H_2 to Ir(I) SQP complexes stabilized by pincer ligands (Scheme 133),[548] and the selective activation of C–H bonds have been studied in detail by Milstein and co-workers.[162a] As an example, the one-pot reaction of $[IrH(CO)(PPh_3)_3]$ **924** with DIPPX [$DIPPX = \eta^3\text{-}2,6\text{-}(Bu^t{}_2PCH_2CH_2)_2C_6H_3$] gave the *trans*-dihydride *trans*-$[IrH_2(CO)(DIPPX)]$ *trans*-**965**. The cationic complex $[IrH(PPh_3)(CO)(DIPPX)]Br$ **966**, with a *trans* aryl-Ir-PPh_3 arrangement, was obtained by the reaction of **924** with the bromo-substituted PCP ligand. The Ir(I) monocarbonyl [Ir(CO)(DIPPX)] **967** was prepared by deprotonation of **966** with $KOBu^t$. Reversible uptake of H_2 by **967** takes place at RT to give the *cis*-dihydride (*cis*-**965**) in line with the occurrence of an oxidative addition of H_2. On heating under 35 psi H_2 at 90 °C in C_6D_6, the latter completely isomerizes to the thermodynamically favored *trans*-**965** ($\Delta G_{363} \leq -3.3\,\text{kcal mol}^{-1}$). The unusual high reactivity of *trans*-**965** with a variety of electrophiles (MeI, CS_2, HTs, CPh_3BF_4, acyl chlorides etc.,) has also been considered and ascribed to the strong mutual *trans*-influence of the hydride ligands. The thermodynamic nature of the H_2 addition to pincer-ligated iridium complexes of several different geometrical and electronic configurations (three-coordinate d^8, four-coordinate d^8, and five-coordinate d^6) were investigated by computational and experimental methods.[549]

Similar or even slightly higher activity in the dehydrogenation of linear alkanes to alkenes has been obtained by Jensen by replacing bis(phosphine) PCP pincers with the thermally more robust bis(phosphinito) iridium PCP tetrahydride $[IrH_4\{C_6H_3\text{-}2,6\text{-}(OPPr^i{}_2)_2\}]$ **968**.[550] Unusual binding modes of PCP pincers may also be possible. As an example, the hexanuclear iridium complex $[\{Ir(cod)_2\}\{\eta^6\text{-}[\kappa^4\text{-}C_6H_2(CH_2PtBu_2)_2]Ir_2H_2Cl_3\}_2]$ **969** has been prepared by the reaction of $[IrCl(cod)]_2$ with the PCP–H ligand precursor.[551] Characterization by X-ray diffraction reveals that complex **969** has an unusual structure in which metallation of the pincer aryl ring has occurred at the 4- and 6-positions (Figure 66). This is in contrast to the extensive reactivity of the ligand precursor in which a single metallation typically occurs at the 2-position, thereby allowing coordination of both phosphino ends to a single metal



Scheme 132



Scheme 133

center to give the κ^3-meridional pincer coordination. The intriguing chemistry based on (PCP)Ir systems stemmed many groups to design, synthesize, and test pincer iridium complexes with modified skeletons and/or donor ends. As an example, ferrocenyl-based pincer-type ligands $[\{\eta^3\text{-}2,5\text{-}(R_2PCH_2CH_2)_2C_5H_3\}FeCp]$ were used by Koridze *et al.* to prepare SPY and OCT iridium hydrides.[552]

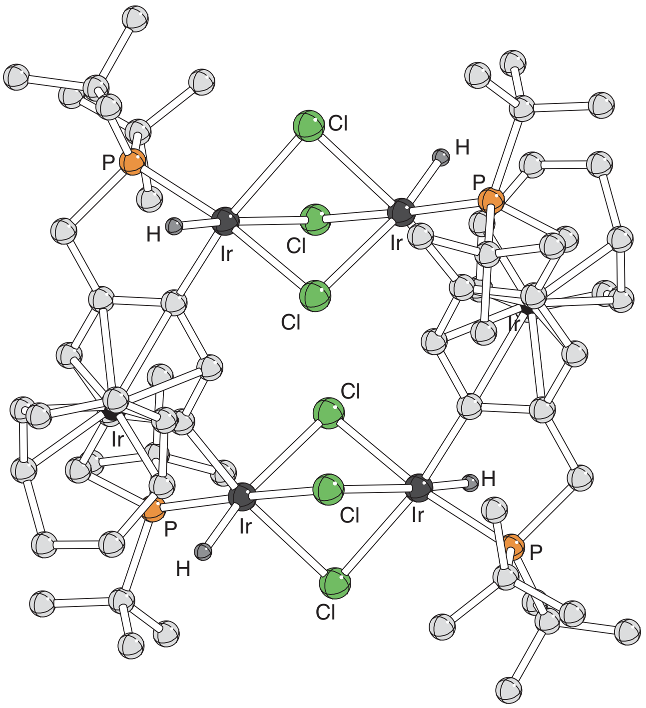
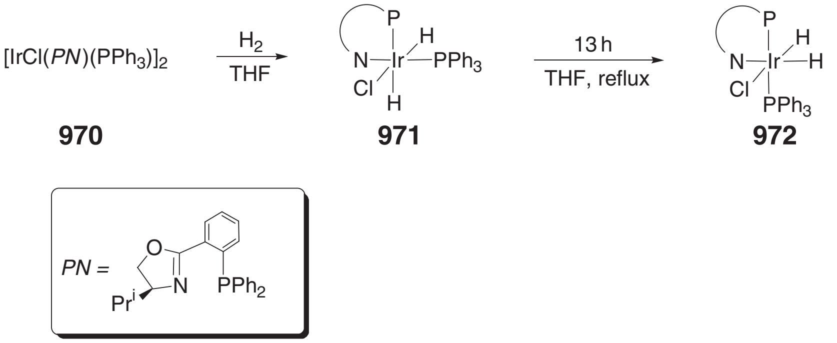


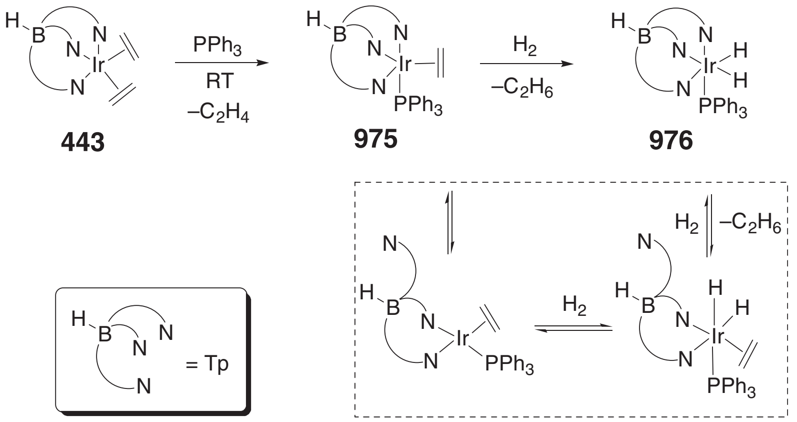
Figure 66 X-ray crystal structure of **969**. Hydrogen atoms (except for Ir–H) have been omitted for clarity.

Further unusual examples in which both the kinetically and the thermodynamically favored dihydrides may be isolated and characterized have been reported by Carmona *et al.*[553] Thus, the addition of H_2 in THF to [Ir(μ-Cl)(PHOX)(PPh_3)]$_2$ **970**, containing the chiral P,N ligand (4*S*)-2-(2-(diphenylphosphino)phenyl)-4-isopropyl-1,3-oxazoline (PHOX), is stereocontrolled and afforded the kinetically preferred dihydride *cis-P,P*-[$IrClH_2$(PHOX)(PPh_3)] **971**, while the reaction of **970** with dihydrogen in MeOH yielded only the thermodynamically preferred species *trans-P,P*-[$IrClH_2$(PHOX)(PPh_3)] **972**. The two compounds are *cis*/*trans*-isomers with respect to the coordination positions taken by the two phosphorus donors. Remarkably, **972** also formed by slow isomerization of the *cis-P,P*-adduct in refluxing THF (Scheme 134).

Dahlenburg and Götz investigated the reactivity of the aminophosphine $Ph_2PCH_2CH_2NH_2$ with *trans*-[IrCl(CO)(PPh_3)$_2$] **1**.[554] In refluxing *p*-xylene, the monohydride [IrH(Cl)($Ph_2PCH_2CH_2NH_2$)$_2$]Cl **973** was obtained. Further reaction with KOH/Pr^iOH yielded a *trans*-dihydride [IrH_2($Ph_2PCH_2CH_2NH_2$)$_2$]Cl **974**. The role of the dihydrido complex **974** in the transfer hydrogenation of acetophenone from different alcohols was briefly discussed. Enatioselective reduction of acetophenone to 1-phenylethanol was achieved with Ir complexes by using chiral versions of bidentate aminophosphines.[555]



Scheme 134



Scheme 135

Addition of H_2 to $[TpIr(PPh_3)(C_2H_4)]$ **975** afforded the *cis*-dihydride $[TpIr(PPh_3)H_2]$ **976** and free ethane.[556] A mechanism indicating reversible dissociation of a pyrazolyl arm has been invoked to account for the reaction kinetics. A sketch illustrating the arm-off process is shown in Scheme 135.

7.04.7.3 Polyhydride Complexes

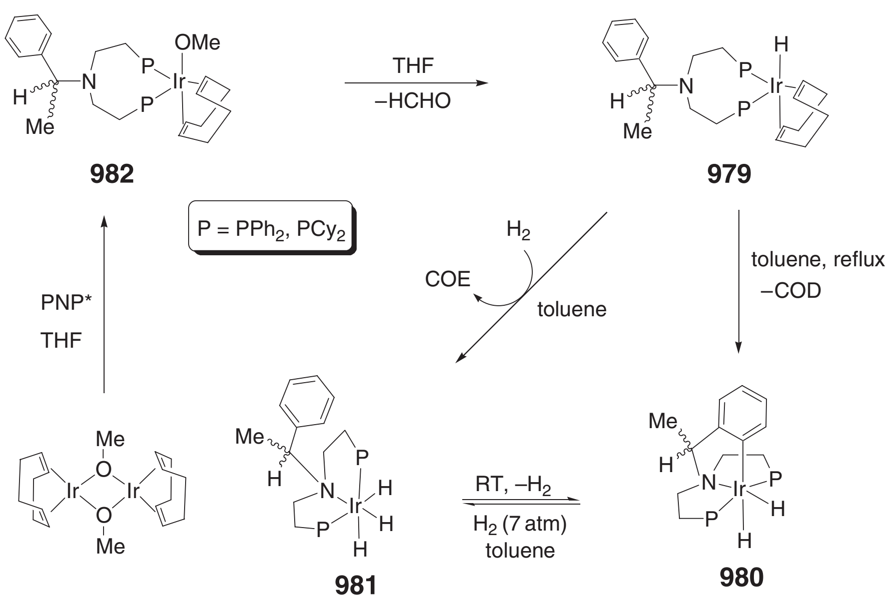
Several iridium complexes containing three, four, and five hydride ligands have been reported after the publication of COMC (1995). Selected examples are presented below. Interestingly, while IrH_3 and IrH_5 derivatives form only classical tautomers with terminally bonded hydrides, iridium tetrahydrides generally show a highly fluxional behavior with exchange between classical and non-classical hydrides. This section of the Ir–H chapter will deal only with classical polyhydrides, while iridium derivatives containing a molecular hydrogen ligand will be described in the following section.

Stable iridium trihydrides have been obtained using polydentate or cyclopentadienyl ligands. Thus, the lithium salt of the trihydride iridate complex, $Li[(PhBP_3)IrH_3]$ **977**, was obtained by Tilley *et al.* by reaction of the neutral dihalides $[(PhBP_3)IrX_2]$ (X = Cl, I **978**) with excess of $LiHBEt_3$ in THF (Scheme 125).[490]

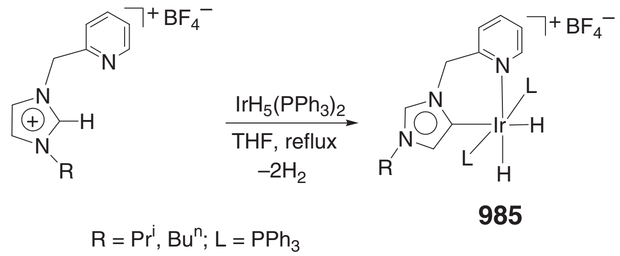
Iridium mono-, **979** di- **980**, and trihydrides **981** have been prepared by Bianchini *et al.* using chiral aminodiphosphine ligands such as bis-(2-diphenylphosphanyl-ethyl)-(1-phenyl-ethyl)-amine and bis-(2-dicyclohexylphosphanyl-ethyl)-(1-phenyl-ethyl)-amine (Scheme 136).[557] The pentacoordinate $[\kappa^2\text{-}P,P\text{-}(PNP^*)Ir(cod)(OMe)]$ **982**, which forms from $[Ir(\mu\text{-}OMe)(cod)]_2$ and PNP^*, has been intercepted. Elimination of formaldehyde form **982** affords the κ^2-*P*,*P*-monohydride $\kappa^2\text{-}P,P\text{-}[(PNP^*)IrH(cod)]$ **979**, where the *N*-donor of PNP^* is unbonded to iridium. Reflux in toluene of **979** removes the coordinated diene and gives $\kappa^4\text{-}P,N,P,C_{\text{o-Ph}}\text{-}[\{[Me(H)C(C_6H_4)]\ N(CH_2CH_2PR_2)_2\}IrH_2]$ **980** via intramolecular C–H *ortho*-metallation of the pending phenyl group. Selective incorporation of deuterium in the *ortho*-position of the metallated phenyl group confirms that the C–H activation process is fully reversible in solution. Pressurization of **980** with H_2 (7 atm) freezes out the C–H cleavage and yields the trihydride $\kappa^3\text{-}P,N,P\text{-}[(PNP^*)IrH_3]$ **981** via oxidative addition of H_2. Exposure of **979** to H_2 straightforwardly transforms the monohydride into the trihydride **981** with partial hydrogenation of COD to COE.

Cyclopentadienyl iridium(V) trihydrides $[CpIr(L)H_3]^+$ (L = various phosphine and phosphite ligands) exhibit unusual NMR properties and isotopic effects related to the quantum exchange coupling of the hydride ligands. A few papers address this argument.[558] Rotational tunneling shown by $[Cp^*Ir(PR_3)H_3]$ complexes has been interpreted by Heinekey and co-workers via a two-dimensional model accounting for hydrogen pair exchange.[559]

Among iridium polyhydrides, particular attention has been paid to mononuclear pentahydrides of formula $[IrH_5(PR_3)_2]$. An improved synthesis of the known pentahydride $[IrH_5(PCy_3)_2]$ **983** has been given.[560] Loss of H_2 from these pentahydrides is an intriguing reaction which has been used by Crabtree *et al.* to prepare iridium complexes with coordinated pyridines $[IrH_3(py')(PPh_3)_2]$ **984**.[327] The imidazolyl carbene complex $[(N\text{–}C)\text{-}IrH_2(PPh_3)_2]BF_4$ **985**, with the imidazole ring bound in the "wrong way" via C5, rather than to the expected C2, was also described from the reaction of $[IrH_5(PPh_3)_2]$ **986** with a pyridine-substituted imidazolium salt (Scheme 137).[327a] A detailed study of the binding properties of a variety of *N*,*N'*-disubstituted imidazolium salts toward the



Scheme 136



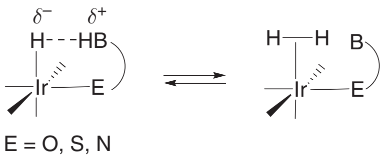
Scheme 137

IrH_2L_2 moiety was later published[327a] and the factors that affect normal (C2) versus abnormal (C5) binding of these ligands, including surprising switching effects due to the counter anion,[327c] were carefully investigated.

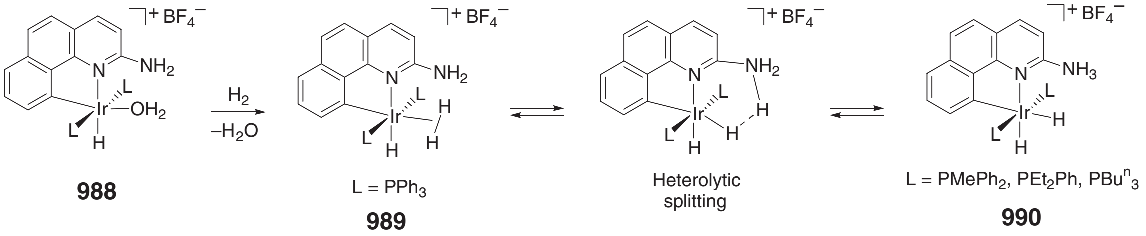
The use of $[IrH_5(PPr^i_3)_2]$ **987** as catalyst for the selective C–C bond cleavage of mono- and dinitriles has been reported.[561] This compound behaves as an ambiphilic catalyst for bringing about the one-pot three-component assemblage of alkenes, nitriles, and water resulting in the formation of glutarimides.[562]

7.04.7.4 Dihydrogen Bonding and Molecular Hydrogen Complexes

A new intramolecular proton–hydride interaction was independently discovered by Crabtree[563,564] and Morris[565,566] in iridium complexes and its relevance in mediating the heterolytic splitting of H_2 assisted by a base has been proposed.[24,567,568] Scheme 138 illustrates this intriguing H-bonding.



Scheme 138



Scheme 139

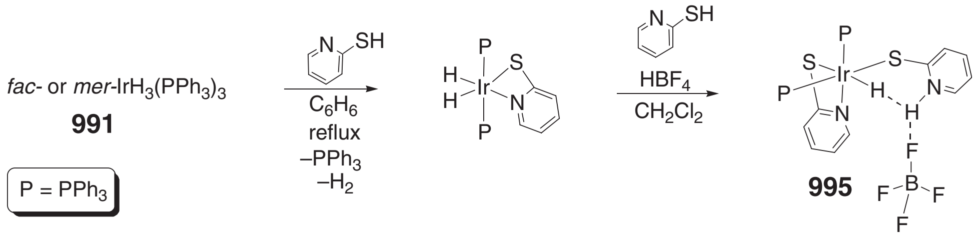
An illustration of this proton–hydride interaction is shown in the article by Lee *et al.*[569] presenting a balanced blending of experimental and theoretical facts. In fact, the reaction of H_2 with cyclometallated benzoquinolinate iridium phosphine complexes, $[IrH(bq\text{-}NH_2)(OH_2)(PR_3)_2]BF_4$ 988, bearing a pending non-ligating H-bonding functionality, depends on the basicity of the PR_3 ligands. Remarkably, non-classical $[IrH(\eta^2\text{-}H_2)(bq\text{-}NH_2)(PR_3)_2]BF_4$ 989, molecular hydrogen complexes or classical *cis*-dihydrides $[IrH_2(bq\text{-}NH_3)(PR_3)_2]BF_4$ 990, might be obtained (Scheme 139). Thus, while the less basic PPh_3 derivative gave only the hydrido(dihydrogen) complex, other phosphines ($PR_3 = P^nBu_3$, $PMePh_2$, PEt_2Ph) gave only the dihydrides via heterolytic H_2 splitting assisted by the pending NH_2 functionality. A strong N–H···H–Ir interaction has been proposed to account for the heterolytic H_2 activation on theoretical model featuring PH_xF_y ($x+y=3$) ligands.

The protonation of the trihydride *mer*-$[IrH_3(PPh_3)_3]$ 991 with HBF_4 in the presence of pyridinethione (SpyH) has been studied by Morris and co-workers.[24] The reaction affords a dihydrido SpyH complex $[IrH_2(\eta^1\text{-}SpyH)(PPh_3)_3]BF_4$ **992** which undergoes a substitution of one phosphine by a second SpyH molecule to yield $[IrH_2(\eta^1\text{-}SpyH)_2(PPh_3)_2]BF_4$ **993**. This latter eliminates dihydrogen to form a monohydrido complex $[IrH(\eta^1\text{-}SpyH)(\eta^2\text{-}Spy)(PPh_3)_2]BF_4$ **994**. The properties of the NH···HIr proton–hydride bonds for all complexes were assessed in solution by T_1 NMR measurements and in the solid state by IR measurements and single crystal X-ray diffraction analysis. The best indicators of H···H bond strength were found to be the $\Delta\nu$ values from IR and the N···Ir distance from the X-ray structures.

Elongated ${}^{\delta+}H\cdots H^{\delta-}$ interactions ranging between 1.70 and 1.90 Å have been determined in both solution and solid state for different iridium hydrides, while Milstein *et al.* authenticated by neutron crystallography an Ir–H···H–O interaction as longer as 2.40 Å in the hydrido(hydroxo) compound $[(PMe_3)_5IrH(OH)]$:[498] The mercaptopyridine complex $[IrH(\eta^1\text{-}SC_5H_4NH)(\eta^2\text{-}SC_5H_4N)(PPh_3)_2]BF_4$ 995 exhibits a unique bifurcated H-bonding interaction involving Ir–H···H(N)···F–BF_3 atoms with similar distances in the H···H and F···H units [2.0(1) Å] (Scheme 140).[570] According to proton relaxation ($T_{1(min)}$) and NOE measurements, the N–H···H–Ir interaction is maintained in solution and is responsible for the observed H/D exchange when 995 is treated with MeOD or exposed to D_2 gas.

The energy of this type of hydrogen-bonding interaction, which is approximately in the range 4–6 kcal mol^{-1}, is large enough to dictate small effects ascribable to the H-bonding interaction in product distribution. An interesting example was provided by Yao and Crabtree showing that the chelating *N,O*-pyridinaldehyde dihydride, $[IrH_2(PPh_3)_2\{\eta^2\text{-}N,O\text{-}NC_5H_4C(H)O\}]^+$ **996**, reacts with aminophenols to give a mixture of products favoring the compound containing the intramolecular H-bond.[571]

The tetrahydrides $[K(Q)][IrH_4(PR_3)_2]$ [Q = 18-crown-6 **996**, 10-diaza-18-crown-6 **997**; $PR_3 = PPr^i_3$, PPh_3, PCy_3] were prepared by Morris and co-workers by reacting $[IrH_5(PR_3)_2]$ with excess KH and 1 equiv. of Q in THF under



Scheme 140

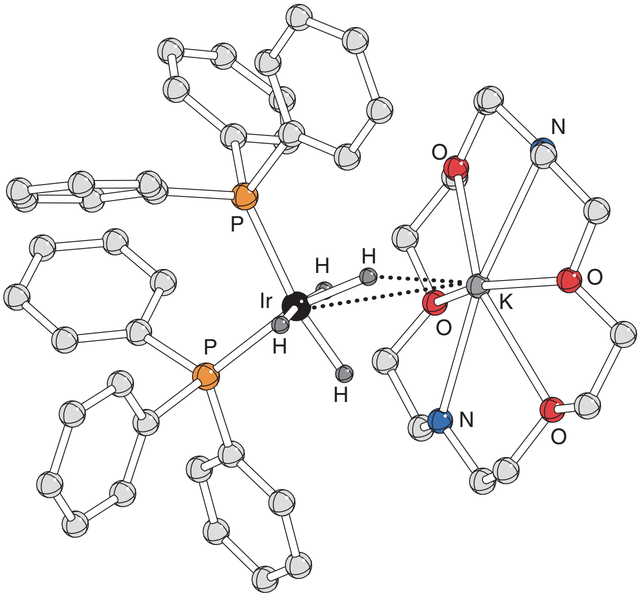


Figure 67 X-ray crystal structure of **997**. Hydrogen atoms (except for Ir–H) have been omitted for clarity.

H_2. The solid-state structures of some of these anionic tetrahydride salts have been determined showing that an extensive network of hydrogen-bonding interactions, involving the diazacrown cations and proton–hydride, $^{\delta+}H\cdots H^{\delta-}$, bonds are responsible for the 1-D chain organization and hence for the stereochemistry of these salts in the solid state.[572,573] The nature of the cation has a profound influence also on the pK_b of the tetrahydroiridate anion, $[IrH_4(PR_3)_2]^-$, which was determined against the acid $[WH_6(PMePh_2)_3]$.[573]

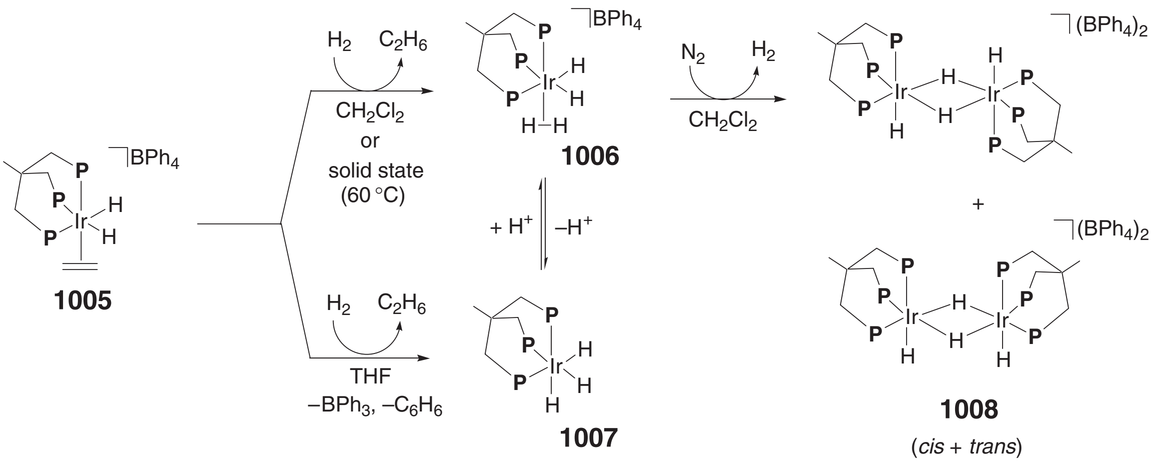
The structure of $[\{K(1,10\text{-diaza-18-crown-6})\}\{IrH_4(PPh_3)_2\}]$ $PR_3 = PPh_3$ **997** is presented in Figure 67.

The H···H distance in stretched molecular iridium dihydrogen complexes may be very sensitive to the presence of weak intra- and intermolecular interactions. In this regard, Gusev *et al.* reported, on the basis of DFT calculations and experimental spectroscopic measurements, that the complex $[IrH(H_2)Cl_2(PPr^i_3)_2]$ **998**, which contains a stretched dihydrogen ligand in the solid state,[574,575] is a trihydride in solution.[576]

Iridium polyhydrides of formulas $[IrH(H_2)X_2(PR_3)_2]$ (X = halide), $[IrH_2(L)(PR_3)_2]^+$ (L = neutral 2e- donor), and $[IrH_2(H_2)(PR_3)_2]^+$, which contain both classical and non-classical hydrides, have been largely studied during the decade 1994–2004 and have shown to be well suited to put on quantitative basis the low energy pathways responsible for both hydride scrambling and H/D exchange.[577,578,579,580,581] A combination of experimental (VT NMR) and theoretical methods have been used by Caulton and co-workers to rationalize these rapidly occurring site-exchange processes,[577] and to assess the role of the steric and electronic properties of the ancillary ligands in determining the thermodynamics of the process.[578] The low energy intramolecular dihydride/dihydrogen exchange occurring in the haloderivatives $[IrXH_2(H_2)(PPr^i_3)_2]$ X = Cl **999a**, Br **999b**, I **999c** has been studied experimentally by inelastic neutron scattering (INS) and theoretically modeled by DFT methods.[579] A fast oxidative addition/reductive elimination pathway, centered on the Ir(V) tretrahydride $[IrXH_4(PPr^i_3)_2]$, is thought to be responsible for the exchange process. A perusal of both neutron diffraction analysis and INS data on $[IrIH_2(H_2)(PPr^i_3)_2]$ **999c** suggested that the dihydride/dihydrogen interconversion is coupled with H_2-rotation without initial weakening of the dihydrogen bond.[580]

The kinetics of H_2-dissociation was studied for the complexes $[IrH(H_2)X_2(PR_3)_2]$ (X = Cl, Br; $PR_3 = PCy_3$, PPr^i_3) obtained by direct hydrogenation of $[IrHX_2(PR_3)_2]$ in toluene-d_8.[582] VT relaxation NMR measurements allowed for the evaluation of the thermodynamic parameters associated to the H_2-dissociation from both *cis*- and *trans*-$[IrH(H_2)X_2(PR_3)_2]$ isomers suggesting that the H_2-loss is strictly depending on the elongation of the H–H bond in the non-classical complex.

The neutral Ir(V) tetrahydride $[Tp^{Me}IrH_4]$ **1000** has been prepared by hydrogenation of different pyrazolylborate iridium precursors.[583] Reaction of $[Tp^{Me}Ir(C_2H_4)_2]$ **370** with H_2 affords the highest yield of **1000**.[145a] Density functional calculations on the related and simpler $[TpIrH_4]$ complex predict that there are two minimum energy



Scheme 141

structures, which are nearly isoenergetic for these species.[584] The two competing minima have a C_s edge-bridged octahedral tetrahydride structure and a C_1 η^2-dihydrogen–dihydride structure, respectively.

Important contributions for understanding the chemistry of classical versus non-classical iridium polyhydride complexes have been provided by Heineckey and co-workers.[585,586] Analysis of the isotopic shifts and J(H,D) and J(H,T) coupling constants observed after incorporation of D_2 and T_2 in the highly fluxional $[TpIr(PR_3)(H_2)H]^+$ ($PR_3 = PMe_3$ or PPh_3 **1001** indicated a preference for the heavy H isotope to occupy the hydride rather than the dihydrogen site.[585] Remarkably, $[CpIr(dmpm)H_2](BAr^F)_2$ **1002**, easily obtained by the treatment of [CpIr(dmpm)Cl]Cl **1003** with $[Et_3Si]BAr^F$ under an H_2-atmosphere, exists as a 97 : 3 equilibrium mixture between two species. The predominant isomer was tentatively assigned to the *cis*-dihydride or dihydrogen complex, whereas the minor isomer was assigned a transoid structure on the basis of NMR arguments. Analysis of a series of deuteration experiments and, particularly, of the J(H,D) coupling constants, were interpreted by hypothesizing a dynamic process between η^2-dihydrogen and *cis*-dihydride isomers.[586]

The generally observed anomalous broadening of the NMR linewidth in molecular hydrogen complexes[567,587] has been studied in $[IrH(\eta^2\text{-}H_2)(bq\text{-}H)(PPh_3)_2]BF_4$ **1004** by meticulous T_1-analysis. A rationale for this phenomenon has been proposed by assuming a slowing of H_2-rotation with quantum coupling effects making the J(H,H) very large.[588]

Hydrogenation of ethene in the dihydrido ethene complex $[(triphos)IrH_2(C_2H_4)]BPh_4$ **1005** takes place in dichloromethane at $P(H_2)$ higher than 3 atm in both solution and solid state.[589] The reaction affords the hydrido-(dihydrogen) complex $[(triphos)Ir(\eta^2\text{-}H_2)H_2]BPh_4$ **1006**, which could be isolated only from the direct solid-state hydrogenation of **1005** (Scheme 141). In THF, the reaction with H_2 produces ethane, benzene, and BPh_3 yielding the neutral trihydride $[(triphos)IrH_3]$ **1007**. Formal heterolytic splitting of H_2 from the very acidic dihydrogen ligand in **1006** is likely responsible for the degradation of the BPh_4^- anion. Complex **1006** may be reversibly deprotonated at low temperature giving back the trihydride **1007**. On raising the temperature, **1007** decomposes losing H_2 to yield the stable dinuclear tetrahydride $[\{(triphos)IrH\}_2(\mu\text{-}H)_2](BPh_4)_2$ **1008** as a mixture of geometric isomers.

The role of molecular hydrogen complexes in homogeneous catalysis has been reviewed by Oro and Esteruelas[590] and by Bianchini and Peruzzini.[591] The work includes a whole coverage, up to the year 2000, of the literature on transition metal non-classical hydrides, including iridium, which are thought to take part in catalytic reactions.

7.04.7.5 Polynuclear Iridium Hydrides

Polynuclear hydride complexes include either homodinuclear (Ir_2) and heterodinuclear (IrM) species with one, two, or three bridging hydrides. Polynuclear hydrides without H ligands in bridging position are much more unusual, an example being $[\{Cp^*Ir(CO)H\}_2]$ **203**, a compound in which the Ir–Ir bond is not sustained by any bridging ligand. A short metal–metal separation of 2.730(1) Å was determined by X-ray crystallography.[99]

Single hydrides may be located in bridging position between two identical iridium moieties. These latter are generally supported by Cp^R ligands, like in $[\{Cp^RIr[P(OR)_3]H\}_2(\mu\text{-}H)]OTf$ **1009**, $[\{Cp^*Ir(CO)\}_2(\mu\text{-}H)]^+$ **201a**, $[\{Cp^*Ir(CO)\}_2(\mu\text{-}CO)(\mu\text{-}H)\}]^+$ **201b**, $[\{Cp^*Ir(CO)H\}_2(\mu\text{-}H)]^+$ **202b**,[68] $[\{Cp^*Ir\}_2(\mu\text{-}H)(\mu\text{-}\eta^{1:1}\text{-}N_3C_2H_2)_2]^+$ **788**,

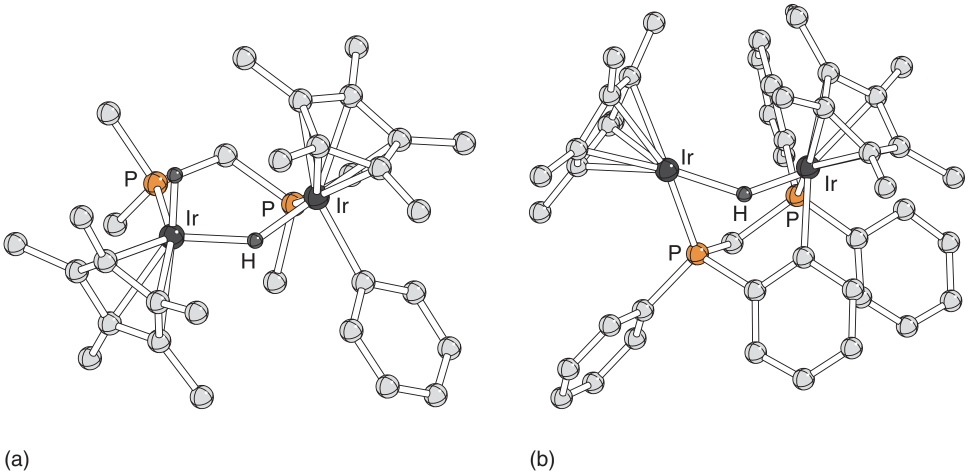
$[(Cp^*Ir)_2(\mu\text{-H})(\mu\text{-OH})(\mu\text{-HCOO})]^+$ **820**,[230b] $[\{Cp^*IrH\}_2(\mu\text{-H})B_2H_5]$ **792**, [*nido*-1,2-$\{Cp^*Ir\}_2(\mu\text{-H})B_4H_7]$ **793**,[423] and $[Cp^*Ir\{\mu\text{-1,8-(NH)}_2\text{naphth}\}(\mu\text{-H})IrCp^*]O_2CCF_3$ **759**.[409] However, ligands other than Cp^R may hold up diridium units with a bridging hydride, a nice example being the Rauchfuss's hydride $[Ir_2H_2(\mu\text{-H})(\mu\text{-S})(\mu\text{-SH})(PPh_3)_4]$ **958**.[542] Diiridium complexes featuring two bridging hydrides are also known and include the dications $[\{Cp^*Ir(CO)\}_2(\mu\text{-H})_2]^{2+}$ **202a**[68], and $[\{(\text{triphos})IrH\}_2(\mu\text{-H})_2]^{2+}$ **1008**.[589] The latter exhibits a complete fluxionality with fast exchange of terminal and bridging hydrides at RT.[589] Addition of H_2 to $[(PhBP_3)Ir(H)(\eta^3\text{-}C_8H_{13})]$ **913** yields the dinuclear tetrahydride $[(PhBP_3)Ir(\mu\text{-H})_2]_2$ **1008** in benzene and the mononuclear dihydride $[(PhBP_3)Ir(coe)H_2]$ **1009** in THF (Scheme 125).[490] Both **1008** and **1009** were structurally characterized and show Ir–Ir separations of 2.785 and 2.797 Å, respectively.

Other selected examples of polynyclear iridium hydrides include the diiridium complexes $[\{Cp^*Ir\}_2(\mu\text{-diphosphine})(\mu\text{-H})_2]^{2+}$ reported by Fujita *et al.* with a bridging dppm or dmpm ligand as tethering unit between two Cp^*Ir moieties. Thus, compounds of formula $[\{Cp^*Ir\}_2(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-X})](OTf)_2$ [X = Cl **1001a**, OMe **1001b**, OH **1001c**] have been synthesized and their poor reactivity investigated.[592] Higher reactivity is shown by the cognate derivative $[\{Cp^*Ir\}_2(\mu\text{-dmpe})(\mu\text{-H})_2](OTf)_2$ **1011** in which a less sterically demanding dmpe replaces dppm as bridging diphosphine.[593] Intermolecular aryl C–H activation takes place by the treatment of **1012** (diphos = dmpm) with $NaOBu^t$ in aromatic solvents at RT to yield the asymmetric species $[\{Cp^*Ir(H)\}(\mu\text{-dmpm})(\mu\text{-H})\{(Ar)IrCp^*\}]BPh_4$ [Ar = Ph **1013a**, *p*-Tol **1013b**, *m*-Tol **1013c**, 2-furanyl **1013d**, 3-furanyl **1013e**].[594] Refluxing $[\{Cp^*Ir(H)\}(\mu\text{-dmpm})(\mu\text{-H})\{(Ph)IrCp^*\}]BPh_4$, **1013a**, in furane affords $[\{Cp^*Ir\}(H)(\mu\text{-dmpm})(\mu\text{-H})\{(2\text{-furanyl})IrCp^*\}]BPh_4$ **1014** via reductive elimination of benzene and oxidative addition of furane to the active Ir(II)–Ir(II) (or Ir(III)–Ir(I)) species. In contrast, the reaction of the dppm-bridged diiridium complex $[\{Cp^*Ir\}_2(\mu\text{-dppm})(\mu\text{-H})_2](OTf)_2$ **1015** with a weak base (Et_2NH) results in intramolecular C–H activation of one phenyl ring of the dppm ligand to give $[\{Cp^*Ir\}(H)\{\mu\text{-PPh}(C_6H_4)CH_2PPh_2\}(\mu\text{-H})\{Cp^*Ir\}]BPh_4$ **1016** in quantitative yield. The structures of **1013a** and **1016** are presented below in Figure 68.

The dinuclear Ir(II)/Ir(II) species, $[Cp^*Ir(\mu\text{-H})]_2$ **1017**, has been described by Wakatsuki and co-workers[595] and used as an efficient catalyst for C–C bond cleavage of aromatic 1,2-diols and Michael additions under neutral and mild conditions (Scheme 142).[596]

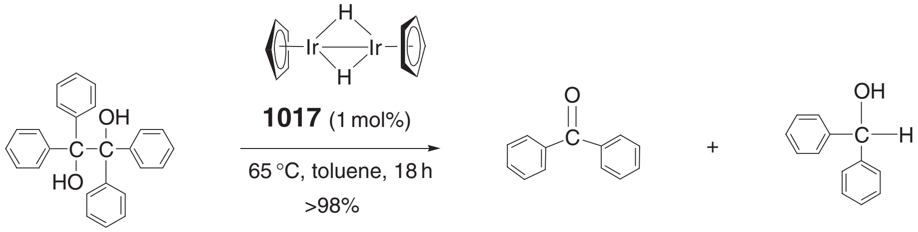
The molecular structure of the binuclear hydride $[\{Tp^{Me}Ir(H)\}_2(\mu\text{-H})(\mu\text{-}S,C\text{-}SC_4H_3)]$ **1018** has been determined (Figure 69). The dimer, obtained by the hydrogenation of $[Tp^*Ir(2\text{-thienyl})_2(SC_4H_4)]$ **1019**, contains a rare example of bridging 2-thienyl ligand.[181a]

The synthesis and reactivity of a vast class of diiridium(III) polyhydrides with both terminal and bridging hydrido and pyrazole ligands have been studied in detail by Oro and co-workers.[514,597,598,599] As an example of this type of compounds, the molecular structure of $[\{Ir(\mu\text{-Pz})(H)(\eta^1\text{-}O_2CCF_3)(CNBu^t)_2\}_2]$ **1020** is presented below in Figure 70. The molecule exhibits a central "$Ir(\mu\text{-Pz})_2Ir$" metallacycle framework, constituted by two iridium atoms bridged through two *exo*-bidentate pyrazolate ligands, adopting the typical boat conformation.[597]



(a) (b)

Figure 68 X-ray crystal structures of (a) **1013a** and (b) **1016**. In the structure of **1013a**, only the *ipso*-carbons of the bridging dppm ligand phenyls are shown; all the hydrogen atoms except the hydrides have been omitted, for the sake of clarity. In the structure of **1016**, hydrogen atoms other than the bridging one have been omitted for clarity.



Scheme 142

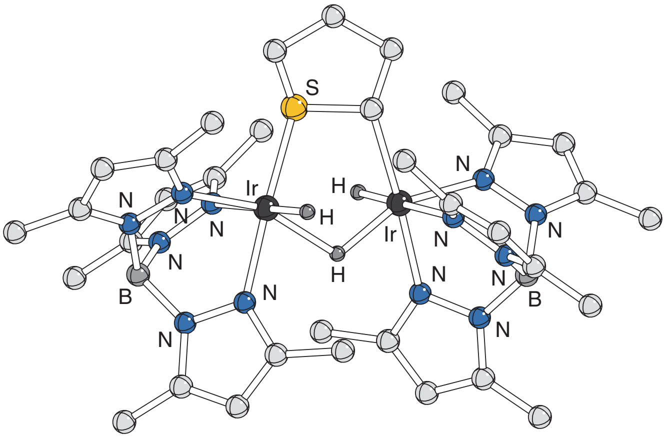


Figure 69 X-ray crystal structure of **1018**. Hydrogen atoms (except for Ir–H) have been omitted for clarity.

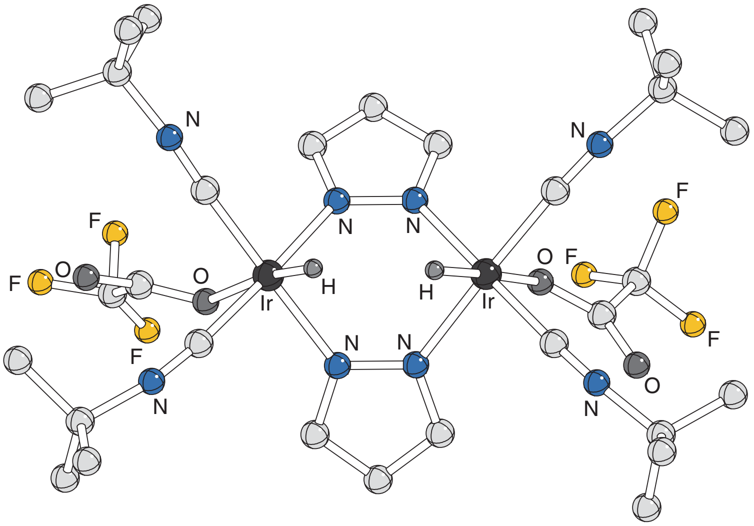


Figure 70 X-ray crystal structure of **1020**. Hydrogen atoms (except for Ir–H) have been omitted for clarity.

A review on the catalytic applications of dinuclear hydrides, mostly concerning with diiridium compounds, has been published by Oro and Sola.[600]

Transmissions of ligand *trans*-effects and influences along the backbone of the dinuclear species have been documented and the occurrence of cooperative reactivity of the two iridium centers in these systems has been demonstrated and theoretically interpreted.[601] The same group also described Ir(III)/Ir(III) "open-book" diiridium hydrido-complexes stabilized by a diamidonaphthalene bridge[602] and showed that removal of electrons from the dimer favors the C–H activation of coordinated alkenes.[603] An interpretation of this effect based on MO arguments entailing weak intermetallic interactions has been proposed. While d^8d^8 Ir_2 species do not activate apolar substrates like H_2, dihydrogen activation took place upon 2e-oxidation to d^7d^7 or d^8d^6 dimers.[604] The addition of H_2 across the diiridium(I) complex $[Ir(\mu\text{-pz})(PPh_3)(CO)]_2$ **164** afforded the 1,2-dihydrido adduct $[IrH(\mu\text{-pz})(PPh_3)(CO)]_2$ **165** which was authenticated by X-ray analysis. The crystallographic study reveals that unlike in **164** the PPh_3 ligands are axial, with the hydrids occupying *trans*-co-equatorial positions across the Ir–Ir bond (2.672 Å).[85]

Cooperative bimetallic reactivity toward dihydrogen was studied by Nocera and co-workers in dinuclear iridium and rhodium complexes stabilized by bridging diphosphazane ligands. Although dirhodium complexes capable of photocatalytically producing H_2 were the real target of this study,[605,606] the analogous Ir(0)/Ir(II) species were also of interest because, due to the higher stability of Ir–H bonds, they allowed for the stabilization of Ir(I)/Ir(III) hydrides. Thermal activation of these systems was necessary to reversibly release H_2.[607,608] DFT calculations suggest that asymmetric molecular hydrogen complexes are initially formed followed by a heterolytic H_2 bond scission within the diiridium coordination sphere.[609]

A particular class of iridium dimers with hydrides as both bridging and terminal ligands are the "A-frame" complexes described by Cowey and co-workers and already mentioned in several parts of this chapter. The reactivity of $[Ir_2H(CO)_2(\mu\text{-H})_2(dppm)_2]BF_4$ **1021** with different alkynes and alkenes has been reported and several diiridium complexes with bridging and terminal hydrides have been synthesized.[610] The analogous heterodimetallic Rh/Ir species $[RhIr(H)(CO)_2(\mu\text{-H})_2(dppm)_2]OTf$ **318** has also been reported.[158,158a]

Diiridium species with bridging hydrides have been frequently encountered in large number of studies involving iridium precursors as catalysts for the hydrodesulfurization (HDS) of thiophenes. As far as systems based on iridium catalysts are concerned, compounds pertaining to this typology have been described by Bianchini and Meli, who carefully investigated the chemistry of the system [(triphos)Ir],[611] and by Jones and co-workers, who studied the HDS of thiophene and some more sterically hindered thiophenes using $[Cp^*IrH(Cl)]_2$ **1022** and $[Cp^*IrH_2]_2$ **1023**.[612,613,614] Remarkably, **1023** showed reactivity also toward nitrogen heterocycles, such as *N*-methylpyrrole, providing useful information about the elusive HDN process.[614]

Dinuclear species with three bridging hydrides are far less known and are limited $[Cp^*{}_2Ir_2(\mu\text{-H})_3](ClO_4)_2$ **786**,[421,615] to the heteronuclear Ru/Ir dimers $[Cp^*Ru(\mu\text{-H})_3IrCp^*]$ **710** and $[Cp^{Et}Ru(\mu\text{-H})_3IrCp^*]$ **711**,[394] and to the heteronuclear Re/Ir dimers $[(CO)(PPh_3)_2Re(\mu\text{-H})_3IrH(PPh_3)_2]$ **73a** and $[(CO)(PPh_3)_2HRe(\mu\text{-H})_3IrH(PPh_3)_2]BF_4$ **1010**.[37] The dimer **73a** was prepared from the reaction of the Vaska's compound with the anionic cluster $K[ReH_6(PPh_3)_2]$. Its structure consists of two distorted octahedra sharing a face containing three bridging hydrides, with the iridium atom bonded to a terminal hydride and to two phosphine ligands. The reaction is mechanistically fascinating involving the formal transfer of carbon monoxide from Ir to Re. Further reaction of **73a** with $HBF_4{\cdot}OMe_2$ induces the formation of a rhenium–terminal hydride bond giving $[(CO)(PPh_3)_2HRe(\mu\text{-H})_3IrH(PPh_3)_2]BF_4$ **1010**.[37]

Acknowledgments

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7.05
Commercial Applications of Iridium Complexes in Homogeneous Catalysis

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7.05.1 Introduction

In the past decade, important new industrial processes employing homogeneous iridium-based catalysts have been commercialized. This chapter discusses these processes, with particular regard for the underlying mechanisms and organometallic chemistry. It will not seek to survey the numerous examples published in the literature of organic reactions mediated by iridium complexes. This topic is covered in Volumes 10 and 11 of this encyclopedia.

Iridium, as a third-row (5*d*) transition metal, is often regarded as less active in catalysis than its 3*d* and 4*d* counterparts, cobalt and (especially) rhodium. The normally lower activity results from formation of stronger metal–ligand bonds by iridium than by the lighter members of the group 9 triad. This means that some of the key reaction steps in catalytic cycles (particularly ligand migration/insertion and reductive elimination) tend to be slower on iridium than is desirable for high catalytic activity. Another outcome of the robust nature of iridium complexes is that they are often more amenable to isolation and structural characterization than analogous rhodium species, which participate in catalysis as reactive intermediates. This strategy has frequently been employed in mechanistic studies, to enable transient Rh complexes to be modeled by their iridium analogs.[1–11] In some cases, however, the stronger metal–ligand bonding of iridium can be beneficial for catalytic activity. This is particularly the case when a metal–ligand bond-forming reaction (e.g., oxidative addition) is the rate-determining step of the cycle. Oxidative addition reactions are typically at least an order of magnitude faster on iridium compared to rhodium.

The literature contains numerous examples of homogeneous catalysis by iridium complexes including hydrogenation, hydrosilylation, hydrodesulfurization, hydroamination, C–H activation, oxidation and carbonylation. However, substantially fewer studies of iridium catalysts are published by comparison with rhodium (a crude estimate based upon an electronic literature search for the period 1995–2005 indicates approximately 4–5 times more papers concerned with rhodium catalysts[12]). Substantial fluctuations in price occur for both metals, and these are not always closely correlated, but the average price for iridium (July 1992–June 2005) was ca. US$225 per troy ounce, compared with US$950 for rhodium.[13] The greater cost of rhodium (despite its higher abundance in ores) reflects a higher demand, particularly for autocatalysts. Iridium is used in a number of applications, including jewelery, electronics, and electrochemical processes, but demand has also grown significantly in recent years for use in catalysts for chemical processes. The largest of these is the BP Chemicals Cativa™ process for methanol carbonylation, but an iridium hydrogenation catalyst is also used for production of the herbicide, (S)-metolachlor, on a significant scale. These two principal applications are discussed in turn below.

7.05.2 Carbonylation of Methanol

The industrial manufacture of acetic acid by methanol carbonylation (Equation (1)) has utilized catalysts based upon all three of the group 9 metals, since the initial development by BASF of a cobalt/iodide-based system.[14,15] The BASF process required harsh conditions of temperature and pressure, and suffered from relatively low selectivity. It was soon superceded by highly selective, low-pressure rhodium/iodide-based catalysts developed by Monsanto.[16,17] The Monsanto process (and related variants operated by other manufacturers) quickly became dominant and remains one of the most successful examples of the commercial application of homogeneous catalysis.[18–22] Rhodium catalysts for methanol carbonylation are discussed in Chapter 7.03.

$$\mathrm{MeOH + CO \rightarrow MeCO_2H} \tag{1}$$

At the time when Monsanto commercialized rhodium-based catalysts, they also discovered that significant activity could be achieved using iridium.[16] Considerable studies were conducted by Forster[23–29] and others[30–32] into the iridium-catalyzed process, revealing a catalytic mechanism with similar key features but some important differences to the rhodium system. A notable difference in behavior is a change in the rate-determining step, from oxidative addition of methyl iodide to Rh(I) to migratory CO insertion on Ir(III). Interest in iridium catalysts was rekindled in the 1990s, when studies by BP Chemicals identified a number of promoters, which caused significant improvement of catalytic activity.[33–36] Resulting from this, Cativa™, an iridium/iodide-catalyzed process, which utilizes a ruthenium promoter, was commercialized in 1995, and it now operates on a number of plants worldwide (Table 1).[37–40] The Cativa™ process was initially retrofitted to an existing rhodium-based plant in Texas City (USA) and retrofitting has also been implemented on plants in the UK, South Korea, China, and India. The first new plant to employ the Cativa™ process was built in Malaysia, and further plants are currently being commissioned. In particular, new production facilities in Southeast Asia are using this technology to meet the increased regional demand, resulting from economic growth.

The following sections discuss the behavior of the iridium-catalyzed process and the details of the underlying organometallic chemistry, along with comparisons to the related rhodium system.

7.05.2.1 Process Considerations

The conditions employed for iridium-catalyzed carbonylation (ca. 180–190 °C, 20–40 bar) are comparable to those of the rhodium-based process. A variety of iridium compounds (e.g., $\mathrm{IrCl_3}$, $\mathrm{IrI_{3,4}}$, $\mathrm{H_2IrCl_6}$, $\mathrm{Ir_4(CO)_{12}}$) can be used as catalyst precursors, as conversion into the active iodocarbonyl species occurs rapidly under process conditions. In a working catalytic system, the principal solvent component is acetic acid, so the methanol feedstock is substantially converted into its acetate ester (Equation (2)). Methyl acetate is then activated by reaction with the iodide co-catalyst (Equation (3)). Catalytic carbonylation of methyl iodide formally gives acetyl iodide (Equation (4)) prior to rapid hydrolysis to the product acetic acid (Equation (5)). However, it is difficult to establish the true intermediacy of acetyl

Table 1 Summary of acetic acid plants which use (or will use) the Cativa™ process

Location	*Operator*	*Year (of commission or retrofit)*	*Approx. capacity (tonnes year^{-1})*
Texas City, USA	Sterling Chemicals	1995[a]	450k
Ulsan, South Korea	Samsung/BP	1997[a]	350k
Hull, UK	BP Chemicals	1998[a]	400k
Chongqing, China	Yaraco (Sichuan Vinylon/BP)	1998[a]	350k
Kerteh, Malaysia	BP/Petronas	2000	500k
Gujarat, India	BP/GNFC	2004[a]	100k
Taiwan	BP/Sinoco	2005	300k
Nanjing, China	BP/Formosa	2006	500k

[a] Retrofit.

iodide, and acetic acid may also arise from hydrolysis of an iridium acetyl complex. The net result of the reactions described in Equations (2)–(5) is the carbonylation of methanol (Equation (1)).

$$\mathrm{MeOH + AcOH \rightarrow MeOAc + H_2O} \tag{2}$$

$$\mathrm{MeOAc + HI \rightarrow MeI + AcOH} \tag{3}$$

$$\mathrm{MeI + CO \rightarrow MeCOI} \tag{4}$$

$$\mathrm{MeCOI + H_2O \rightarrow AcOH + HI} \tag{5}$$

The rate of iridium-catalyzed carbonylation displays a rather complicated dependence on a range of process variables such as pCO, [MeI], [MeOAc], and [H_2O].[37–39] The catalytic rate displays a strong positive dependence on [MeOAc], but is zero order in [MeI] above a limiting threshold, and independent of CO partial pressure above ca. 10 bar. A particularly notable aspect is the dependence of rate on [H_2O], which attains a maximum at ca. 5wt.% H_2O as illustrated in Figure 1. This behavior contrasts with the rhodium catalyst, for which catalytic activity attains a plateau above ca. 10wt.% H_2O. Indeed, under "conventional" high water conditions the performance of an iridium catalyst is inferior to rhodium.

The attainment of optimum rate at relatively low [H_2O] is a significant benefit for the iridium system, since it results in less costly product purification. A typical configuration for an iridium-catalyzed methanol carbonylation plant is shown in Figure 2. The feedstocks (MeOH and CO) are fed to the reactor vessel on a continuous basis. In the initial product separation step, the reaction mixture is passed from the reactor into a "flash tank" where the pressure is reduced to induce vaporization of most of the volatiles. The catalyst remains dissolved in the liquid phase and is recycled back to the reactor vessel. The vapor from the flash tank is directed into a distillation train, which removes methyl iodide, water, and heavier byproducts (e.g., propionic acid) from the acetic acid product. At the relatively high water levels used in the rhodium-catalyzed Monsanto process, three distillation columns are typically required. In the Cativa process, a lower water concentration means that the necessary product purification can be achieved with only two columns.

An advantage of iridium, compared to rhodium catalysts, is that a broad range of conditions is accessible without precipitation of IrI_3 occurring. Precipitation of a rhodium catalyst is potentially most problematic in the flash tank and catalyst-recycle system, where CO pressure and temperature are lower than in the reactor itself. Under these conditions, loss of CO from $[Rh(CO)_2I_4]^-$ can initiate a sequence of reactions, leading to precipitation of RhI_3. This is minimized by employing a relatively high water concentration to promote reduction of the problematic tetraiodide complex to the active $[Rh(CO)_2I_2]^-$. The greater stability of the iridium catalyst can be ascribed to stronger metal–ligand bonding for the third-row metal, which inhibits CO loss from the Ir center. Stronger π-backdonation from iridium to CO is evident from the lower ν(CO) values of iridium iodocarbonyl complexes compared to the rhodium analogs (Table 2).

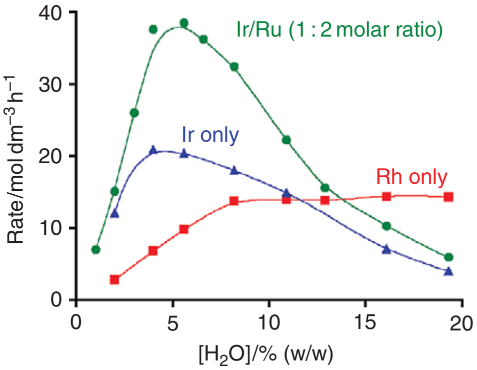


Figure 1 Effect of water concentration on catalytic rate for Rh, Ir, and Ir/Ru-catalyzed methanol carbonylation (190 °C, 28 bar). Adapted with permission from Haynes, A.; Maitlis, P. M.; Morris, G. E.; Sunley, G. J.; Adams, H.; Badger, P. W.; Bowers, C. M.; Cook, D. B.; Elliott, P. I. P.; Ghaffar, T., *et al. J. Am. Chem. Soc.* **2004**, *126*, 2847–2861. © (2004) American Chemical Society.

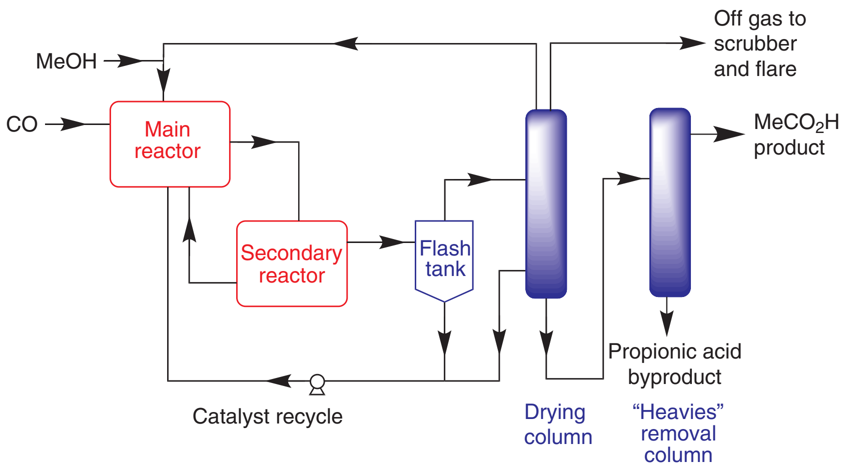


Figure 2 Schematic diagram of the main elements of a Cativa^{TM} methanol carbonylation plant.

Table 2 Comparison of ν(CO) values of Ir and Rh iodocarbonyls (in CH_2Cl_2 except where stated otherwise)

Complex	*$\nu(CO)(M = Ir)$*	*$\nu(CO)(M = Rh)$*
cis-$[M(CO)_2I_2]^-$	2046, 1968	2059, 1988
cis,fac-$[M(CO)_2I_3Me]^-$	2098, 2045	2104, 2060[a]
cis-$[M(CO)_2I_4]^-$	2112, 2067	2120, 2089
trans-$[M(CO)_2I_4]^-$	2070	2091
cis,fac-$[M(CO)_2I_3(COMe)]^-$	2110, 2062	2114, 2084
trans,mer-$[M(CO)_2I_3(COMe)]^-$	2141(w), 2064	2141(w), 2084

[a] In neat MeI.

A range of metal compounds have been discovered to enhance the activity of an iridium catalyst.[33–39,41,42] The promoters which have been patented fall into two categories: (i) carbonyl or halocarbonyl complexes of W,[34,36] Re,[35,36] Ru,[33,34,36] Os,[33,34,36] and Pt[42]; (ii) simple iodides of Zn, Cd, Hg, Ga, and In.[34,36] Addition of a promoter tends to increase the catalytic rate toward a plateau, as illustrated in Figure 3 for $[Ru(CO)_4I_2]$ and InI_3 promoters.[37–39,41] Figure 1 illustrates how the ruthenium promoter is effective over a range of water concentrations, the maximum rate being attained at ca. 5 wt.% H_2O, as in the absence of promoter. By contrast, ionic iodides such as LiI and Bu_4NI are both strong catalyst "poisons."[38,39,41] The mixed metal cluster anions, $[M_3Ir(CO)_{13}]^-$ (M = Ru, Os), have been used as catalyst precursors for methanol carbonylation on the basis that a synergistic interaction between the metals in the cluster might be beneficial for catalysis. However, under catalytic conditions, fragmentation occurs to give $[Ir_4(CO)_{12}]$ and $[M(CO)_3I_3]^-$, and the mixed-metal cluster is not considered to be significant for catalytic activity.[43]

The high activity of ruthenium-promoted iridium catalysts has allowed improved productivity by retrofitting the Cativa^{TM} process to plants which previously used rhodium catalysts.[38] For example, a 75% increase in throughput was achieved at the Samsung-BP plant in Ulsan, South Korea. Another benefit of the iridium catalyst is higher selectivity, with smaller amounts of both gaseous and liquid byproducts. The water-gas shift (WGS) reaction does occur, but at a lower rate than for rhodium, resulting in reduced formation of CO_2 and CH_4. Since the process is less sensitive to CO partial pressure, the reactor can operate with a lower vent-rate. This, as well as the incorporation of a secondary reactor prior to the purification system, which provides additional residence time for CO to react, results in an increase in CO utilization from ca 85% (Rh) to >94% (Ir). Reduced propionic acid byproduct formation and the lower water concentration employed allow for a substantial decrease in the product purification costs, with steam and cooling water requirements being reduced by 30% relative to the rhodium system. Acetaldehyde levels in the reactor are also lower than in the rhodium process, since acetaldehyde and other unsaturated species are efficiently hydrogenated by the iridium catalyst. This reduces the formation of higher organic iodides by condensation reactions, which can occur for low water rhodium systems. Organic iodides can poison downstream processes such as vinyl acetate manufacture, and their removal can require further treatment steps. All of these benefits help to reduce the environmental impact of the Cativa^{TM} process. The overall CO_2 emissions (both direct and indirect) for each tonne of product are estimated to be lowered by ca. 30% compared to the rhodium system.

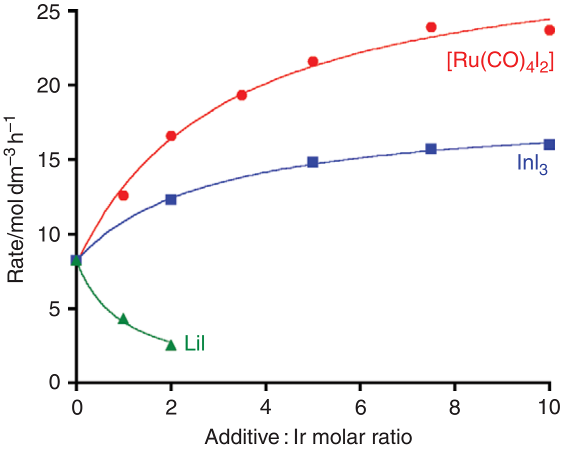


Figure 3 Effect of additive concentration on rate of iridium-catalyzed methanol carbonylation (190 °C, 22 bar). Adapted with permission from Haynes, A.; Maitlis, P. M.; Morris, G. E.; Sunley, G. J.; Adams, H.; Badger, P. W.; Bowers, C. M.; Cook, D. B.; Elliott, P. I. P.; Ghaffar, T., *et al. J. Am. Chem. Soc.* **2004**, *126*, 2847–2861. © (2004) American Chemical Society.

Some studies concerning iridium/iodide-catalyzed carbonylation of higher alcohols (e.g., ethanol to propionic acid) have been reported,[44–46] although no commercial process is in operation.

7.05.2.2 Basic Mechanism

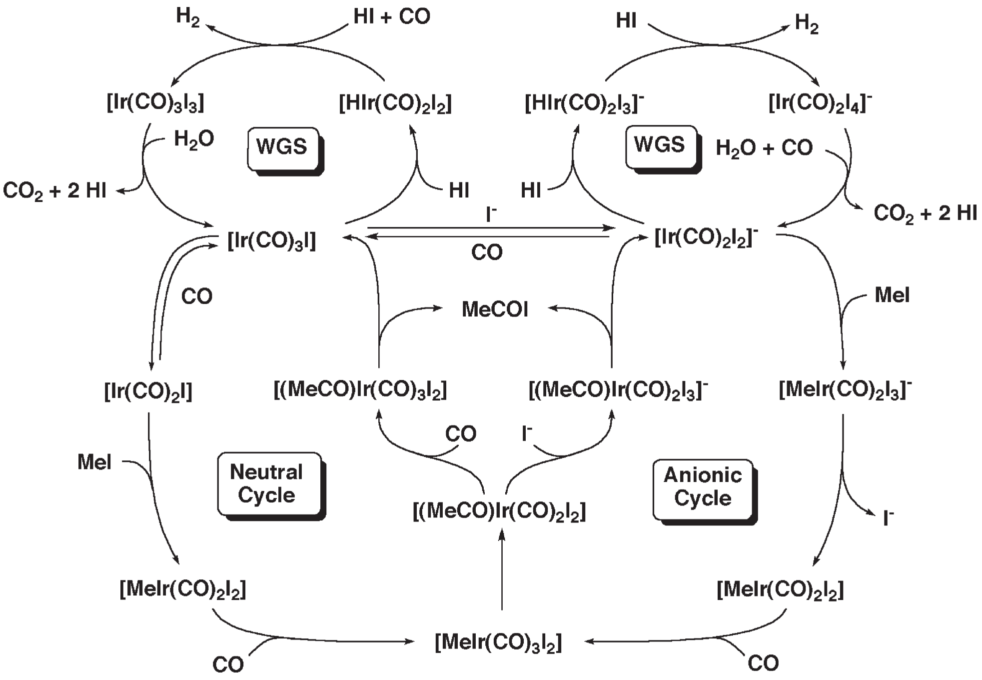
The original mechanistic investigations of iridium/iodide-catalyzed methanol carbonylation were conducted by Forster.[23–29] Some other studies were also reported in the late 1970s.[30–32] Interest in the fundamental underlying chemistry has increased in recent years due to commercialization of the Cativa^{TM} process, and a number of experimental and theoretical studies have appeared.[41,47–58]

The catalytic cycle involves the same fundamental steps as the rhodium system: oxidative addition of MeI to Ir(I), followed by migratory CO insertion to form an Ir(III) acetyl complex, from which acetic acid is derived. On the basis of spectroscopic and kinetic observations, Forster proposed that two different (but linked) cycles exist, one involving neutral iridium complexes, and the other predominantly anionic species (Scheme 1).[25] Similar cycles were also proposed for the competing WGS reaction. At low concentrations of water and iodide, the "neutral cycle" operates, with $[Ir(CO)_3I]$ as the resting state and rate-determining oxidative addition of MeI to $[Ir(CO)_2I]$ (or the solvated $[Ir(CO)_2(sol)I]$). At higher iodide concentrations, the "anionic cycle" predominates with rate-determining carbonylation of $[Ir(CO)_2I_3Me]^-$ via an iodide loss mechanism.

Under normal operating conditions, the anionic cycle operates, and *in situ* high pressure infrared (HPIR) spectroscopy indicates that the dominant Ir species are $[Ir(CO)_2I_3Me]^-$ and $[Ir(CO)_2I_4]^-$, both in the absence or presence of a promoter.[37,41,59] These two complexes are regarded, respectively, as the active and inactive forms of the catalyst, with the catalytic rate being controlled by the rate of carbonylation of $[Ir(CO)_2I_3Me]^-$. The stability of this methyl complex contrasts markedly with its rhodium analog, $[Rh(CO)_2I_3Me]^-$, which has only been detected as a transient intermediate in the reaction of $[Rh(CO)_2I_2]^-$ with MeI.[60,61] The chemistry of iridium complexes involved in the catalytic mechanism has received considerable recent attention, and is summarized in the following sections.

7.05.2.3 Reactivity of $[Ir(CO)_2I_2]^-$

Kinetic studies of the stoichiometric oxidative addition reactions[47,62] have shown that the reaction of MeI with $[Ir(CO)_2I_2]^-$ is ca. 100 times faster than that with $[Rh(CO)_2I_2]^-$, consistent with the different rate-determining steps found in the catalytic reactions of the two metals. It has also been found[63] that oxidative addition to $[Ir(CO)_2I_2]^-$ is ca. 100 times faster than to the neutral acetonitrile solvate, $[Ir(CO)_2(NCMe)I]$, demonstrating the benefit of an anionic complex for this step in the catalytic cycle. Theoretical studies[49,54,58] support an S_N2 mechanism for oxidative addition of MeI to $[M(CO)_2I_2]^-$. Nucleophilic attack by the metal center results in release of I^- from MeI via the transition state shown in Figure 4, to give the five-coordinate intermediate, $[M(CO)_2I_2Me]$. Geometrical features of the calculated transition state (e.g., deviation of the M–C–I angle from linearity) are dependent on the



Scheme 1 Catalytic cycles for iridium-catalyzed methanol carbonylation and WGS reaction. Adapted from Forster, D. *J. Chem. Soc., Dalton Trans.* **1979**, 1639–1645, with permission from The Royal Society of Chemistry.

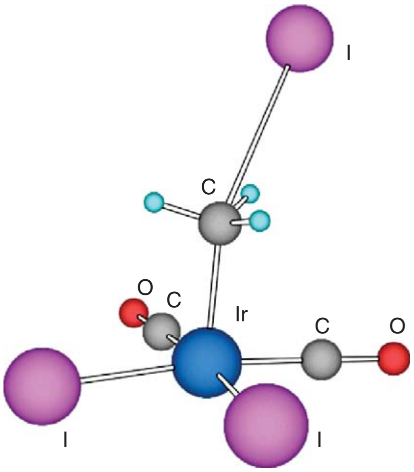


Figure 4 Transition state for S_N2 reaction of $[Ir(CO)_2I_2]^-$ with MeI.

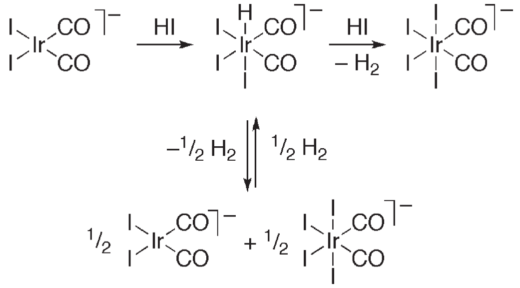
theoretical method employed. Activation barriers are predicted to be lower for Ir than for Rh, in agreement with experiment, and attributed to relativistic stabilization of the Ir–Me bond.[58] The observed small normal secondary kinetic isotope effects ($k(CH_3I)/k(CD_3I) = 1.06$ (Ir), 1.16 (Rh)) are also well reproduced by theory.[49] The reversibility of MeI oxidative addition has been demonstrated by monitoring the exchange of methyl groups between $[Ir(CO)_2I_3(CH_3)]^-$ and CD_3I at elevated temperatures.[64] Combination of activation parameters for the forward and reverse reactions indicates that MeI addition to $[Ir(CO)_2I_2]^-$ is exothermic by ca. 44 kJ mol^{-1}, and has an estimated $\Delta G_{308\ K}$ of ca. -27 kJ mol^{-1}, compared to $+14$ kJ mol^{-1} for $[Rh(CO)_2I_2]^-$.[61]

Whereas the reactivity of $[Ir(CO)_2I_2]^-$ toward MeI is very similar to that of $[Ir(CO)_2Cl_2]^-$, changing the alkyl halide has a much more dramatic effect. Kinetic measurements indicate that oxidative addition of MeCl to $[Ir(CO)_2Cl_2]^-$ is ca. 70,000 times slower (at 40 °C) than the corresponding reactions of MeI with $[Ir(CO)_2I_2]^-$ and $[Ir(CO)_2Cl_2]^-$.[64] These data support the general observation that iodide is the most effective of the halides as a co-catalyst for metal-catalyzed methanol carbonylation. Despite this, Gelin *et al.* found that MeCl is almost as effective a promoter as MeI for a vapor-phase process using a zeolite-supported iridium catalyst.[65] The rates of methyl halide elimination from the Ir(III) methyl complexes, $[Ir(CO)_2I_3Me]^-$ and $[Ir(CO)_2Cl_3Me]^-$, have also been measured, and it was found that the iodide complex eliminates MeX ca. 30 times faster than the chloride. Estimated thermodynamic data suggest that oxidative addition is more exothermic for MeI ($-44\,kJ\,mol^{-1}$) than for MeCl ($-37\,kJ\,mol^{-1}$). The experimental data were supported by *ab initio* and density functional theory (DFT) calculations.[64]

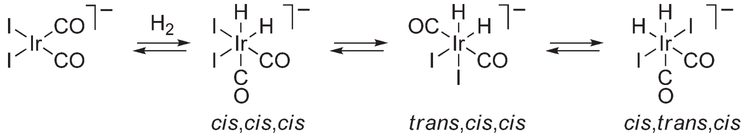
The reactivity of $[Ir(CO)_2I_2]^-$ with higher alkyl iodides has been investigated, for comparison with the MeI reaction and in relation to the carbonylation of higher alcohols.[47] Reaction with RI forms the corresponding Ir(III) alkyl complex, $[Ir(CO)_2I_3R]^-$ (R = Et, Pr^n, Pr^i, Bu^n, n-C_5H_{11}, n-C_6H_{13}), although the reaction with Pr^iI also gives progressively greater amounts of the *n*-propyl product, as the temperature is increased. Under CO, the same reaction forms exclusively $[Ir(CO)_2I_3(COPr^n)]^-$ indicating that the *n*-propyl complex can be intercepted by migratory CO insertion prior to alkyl isomerization. Kinetic studies showed that the reactions of $[Ir(CO)_2I_2]^-$ with higher alkyl iodides are much slower than with MeI, and that there is some deviation from clean second-order behavior. This was attributed to the participation of a radical pathway, which competes with the S_N2 mechanism. This was suppressed by a radical inhibitor, and the second-order oxidative addition rate constants were found to decrease in the order $k_{rel} = 1000$ (MeI), 2.3 (EtI), 0.75 (Pr^nI).

The complex $[Ir(CO)_2I_2]^-$ also undergoes facile oxidative addition of HI to give the Ir(III) hydride, $[Ir(CO)_2I_3H]^-$.[24,25,57,66] This reaction can divert iridium from the anionic carbonylation cycle into the anionic WGS cycle (Scheme 1). Although relatively stable at ambient temperature, $[Ir(CO)_2I_3H]^-$ reacts at higher temperature to form $[Ir(CO)_2I_2]^-$ and $[Ir(CO)_2I_4]^-$, as shown in Scheme 2. Churland *et al.* demonstrated that this reaction is reversible by treating a mixture of $[Ir(CO)_2I_2]^-$ and $[Ir(CO)_2I_4]^-$ with a high pressure of H_2.[66] The hydride $[Ir(CO)_2I_3H]^-$ also reacts with excess HI to release H_2 and form $[Ir(CO)_2I_4]^-$. Gautron *et al.* conducted competition experiments, in which $[Ir(CO)_2I_2]^-$ was allowed to react with mixtures of HI and MeI in CH_2Cl_2.[57] With the reactant stoichiometry 1 : 40 : 1 HI/MeI/$[Ir(CO)_2I_2]^-$, the initial rapid reaction gave $[Ir(CO)_2I_3H]^-$ as the exclusive detectable product, indicating that $[Ir(CO)_2I_2]^-$ undergoes oxidative addition of HI much faster than MeI. At high temperature, however, the same reaction mixture slowly formed $[Ir(CO)_2I_3Me]^-$ at the expense of $[Ir(CO)_2I_3H]^-$, indicating reversibility of HI addition.

Since H_2 is formed by the WGS reaction, its reactivity toward $[Ir(CO)_2I_2]^-$ is also of relevance to the catalytic process. Hasnip *et al.* employed the high sensitivity afforded by the *para*-hydrogen-induced polarization (PHIP) NMR method to detect a dihydride oxidative addition product, $[Ir(CO)_2I_2H_2]^-$.[67] The initial *cis,cis,cis*-isomer was found to undergo isomerization to a more stable *trans,cis,cis*-species (Scheme 3). Kinetic parameters ($k_{325\,K}$ $0.17\,s^{-1}$; $\Delta H^{\ddagger}$ $106 \pm 10\,kJ\,mol^{-1}$; $\Delta S^{\ddagger}$ $60 \pm 6\,J\,K^{-1}\,mol^{-1}$) for reductive elimination of H_2 from the *cis,cis,cis* isomer were



Scheme 2 Reactivity of HI with $[Ir(CO)_2I_2]^-$.



Scheme 3 Oxidative addition of H_2 to $[Ir(CO)_2I_2]^-$.

measured. Churland *et al.* used high pressure nuclear magnetic resonance (HPNMR) and HPIR to observe the same pair of dihydride species, and also detected the *cis,trans,cis*-isomer, but no evidence was obtained for any species with mutually *trans*-hydride ligands.[66] Rate and equilibrium constants for H_2 addition and complex isomerization were estimated, indicating a 5 : 1 preference for the *trans,cis,cis*-relative to the *cis,cis,cis*-isomer at 262 K. By comparison, $[Rh(CO)_2I_2]^-$ is significantly less reactive toward H_2, although evidence for small amounts of dihydride products was obtained using PHIP.[67]

The reactivity of $[Ir(CO)_2I_2]^-$ (and other $[M(CO)_2X_2]^-$ analogs) toward CO has been studied using high pressure IR and NMR spectroscopic methods. Churland *et al.* measured the rate of exchange of free and bound CO in dichloromethane solution.[68] The observed second-order kinetics and activation parameters indicated an associative mechanism. At 25 °C, the rate constant for CO exchange on $[Ir(CO)_2I_2]^-$ is smaller (by a factor of 8.6) than for $[Rh(CO)_2I_2]^-$. For both metals the rate of CO exchange follows the order of increasing halogen *trans*-effect, $Cl < Br < I$.

Higher pressures of CO result in displacement of iodide in $[M(CO)_2I_2]^-$ by CO to give $[M(CO)_3I]$ (Equation (6)).[66] Equilibrium constants for this substitution reaction were estimated by HPIR measurements. The value of the equilibrium constant (measured in $CHCl_3$) is ca. 50 times larger for the iridium complex. The greater preference for formation of the iridium tricarbonyl can be ascribed to the stronger Ir–CO backbonding. These data are consistent with the observation that, under certain conditions, $[Ir(CO)_3I]$ can accumulate as the catalyst resting state during methanol carbonylation.[37,41]

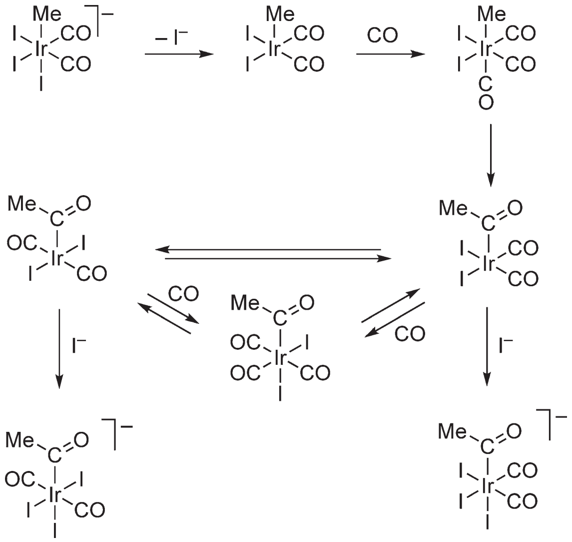
$$[M(CO)_2I_2]^- + CO \rightleftharpoons [M(CO)_3I] + I^- \qquad (6)$$

7.05.2.4 Reactivity of $[Ir(CO)_2I_3Me]^-$ and Related Ir(III) Methyl Complexes

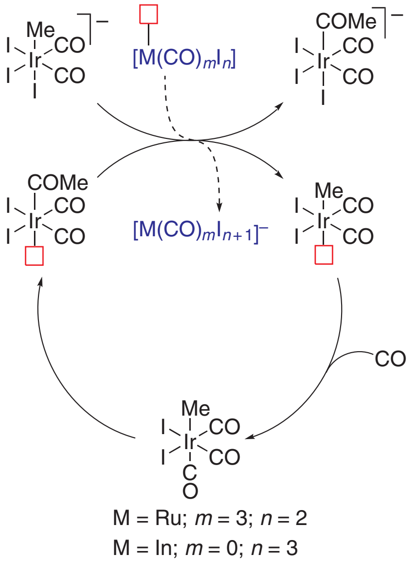
The stoichiometric carbonylation of $[Ir(CO)_2I_3Me]^-$ has been investigated as a model of the rate-determining step of the catalytic carbonylation cycle.[41,48] The reaction of $[Ir(CO)_2I_3Me]^-$ with CO can form both *cis,fac*- and *trans,mer*-isomers of $[Ir(CO)_2I_3(COMe)]^-$, the product ratio varying with the solvent and temperature used. In chlorinated solvents (e.g., PhCl), carbonylation of $[Ir(CO)_2I_3Me]^-$ is rather slow and requires temperatures >80 °C, giving a ca. 1 : 1 *cis* : *trans* product ratio. However, the presence of protic solvents (e.g., methanol) has a dramatic accelerating effect, and carbonylation can be achieved at much lower temperatures, giving predominantly the *cis*-product. For example, addition of 1% MeOH (v/v) results in an estimated rate enhancement of ca. 10^4 at 33 °C. The activation parameters also display a large solvent effect ($\Delta H^{\ddagger} = 152\ \mathrm{kJ\ mol^{-1}}$, $\Delta S^{\ddagger} = 82\ \mathrm{J\ K^{-1}\ mol^{-1}}$ in PhCl and $\Delta H^{\ddagger} = 33\ \mathrm{kJ\ mol^{-1}}$, $\Delta S^{\ddagger} = -197\ \mathrm{J\ K^{-1}\ mol^{-1}}$ in 1 : 3 MeOH/PhCl), which indicates a marked increase in associative character in the presence of methanol. This is interpreted in terms of a mechanism in which the protic solvent aids iodide dissociation by solvation. Increasing the CO pressure causes the rate to increase toward a plateau (i.e., saturation kinetics), and addition of iodide salts causes substantial rate inhibition. The behavior of the model reaction therefore closely resembles the kinetics of the catalytic carbonylation system. Scheme 4 shows the proposed reaction mechanism, involving initial dissociative substitution of iodide by CO, followed by migratory CO insertion in the neutral tricarbonyl, $[Ir(CO)_3I_2Me]$.

The effect of additives on the rate of carbonylation of $[Ir(CO)_2I_3Me]^-$ has been probed to model the effect of promoters in the catalytic cycle. The rate of carbonylation of $[Ir(CO)_2I_3Me]^-$ in PhCl is substantially enhanced by the addition of the neutral ruthenium complexes, $[Ru(CO)_3I_2]_2$, $[Ru(CO)_4I_2]$, or $[Ru(CO)_2I_2]_n$; comparable promotional effects were also found for InI_3, GaI_3, and ZnI_2.[41] Crucially, the "anionic" ruthenium species $[Ru(CO)_3I_3]^-$ or $[Ru(CO)_2I_4]^{2-}$ did not give any appreciable promotion or inhibition, indicating that the ability to accept an iodide ligand is a key property of the promoter. Activation parameters for the promoted stoichiometric carbonylation of $[Ir(CO)_2I_3Me]^-$ (e.g., $\Delta H^{\ddagger} = 90\ \mathrm{kJ\ mol^{-1}}$, $\Delta S^{\ddagger} = -63\ \mathrm{J\ K^{-1}\ mol^{-1}}$ for promotion by $[Ru(CO)_3I_2]_2$) are comparable to those measured for the Ru-promoted catalytic process ($\Delta H^{\ddagger} = 96\ \mathrm{kJ\ mol^{-1}}$, $\Delta S^{\ddagger} = -40\ \mathrm{J\ K^{-1}\ mol^{-1}}$).[41]

A proposed mechanism for the promotion of carbonylation of $[Ir(CO)_2I_3Me]^-$ is shown in Scheme 5.[41] An iodide ligand is initially transferred from $[Ir(CO)_2I_3Me]^-$ to the promoter, allowing coordination of CO to Ir to give $[Ir(CO)_3I_2Me]$, which undergoes migratory insertion to form $[Ir(CO)_2I_2(COMe)]$. Iodide transfer from the promoter back to Ir at this point is unlikely, given that InI_3 is able to abstract iodide from $[Ir(CO)_2I_3(COMe)]^-$. Instead, iodide transfer between iridium centers can give $[Ir(CO)_2I_3(COMe)]^-$ and generate another molecule of $[Ir(CO)_2I_2Me]$. The initial iodide abstraction, indicated by the dashed arrow in Scheme 5, introduces an iodide "hole" which propagates the promotion, the anion $[Ru(CO)_3I_3]^-$ or $[InI_4]^-$ remaining as a spectator. In support of this, the effect of $[Ru(CO)_3I_2]$ or InI_3 can be mimicked by addition of the neutral iridium complex, $[Ir(CO)_2I_2Me]_2$, which also



Scheme 4 Mechanism for formation of isomers of $[Ir(CO)_2I_3(COMe)]^-$ by carbonylation of $[Ir(CO)_2I_3Me]^-$. Adapted with permission from Haynes, A.; Maitlis, P. M.; Morris, G. E.; Sunley, G. J.; Adams, H.; Badger, P. W.; Bowers, C. M.; Cook, D. B.; Elliott, P. I. P.; Ghaffar, T., *et al. J. Am. Chem. Soc.* **2004**, *126*, 2847–2861. © (2004) American Chemical Society.



Scheme 5 Mechanism for promotion of carbonylation of $[Ir(CO)_2I_3Me]^-$ by iodide abstractors. The red squares represent iodide "holes." Adapted with permission from Haynes, A.; Maitlis, P. M.; Morris, G. E.; Sunley, G. J.; Adams, H.; Badger, P. W.; Bowers, C. M.; Cook, D. B.; Elliott, P. I. P.; Ghaffar, T., *et al. J. Am. Chem. Soc.* **2004**, *126*, 2847–2861. © (2004) American Chemical Society.

promotes carbonylation of the anion, $[Ir(CO)_2I_3Me]^-$. Thus, the key role of the promoter is to perturb the ratio of anionic and neutral iridium complexes. A more direct interaction between the promoter and the iridium center does not appear to be involved.

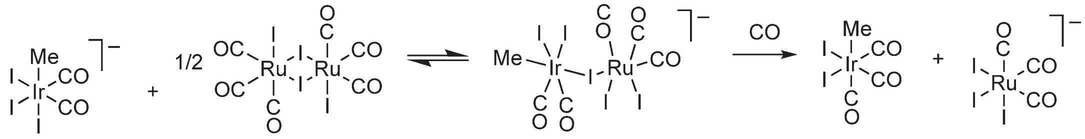
Methyl migration in $[Ir(CO)_2I_3Me]^-$ can be effected by reaction with P-donor ligands. Reactions with phosphites lead to neutral acetyl products, $[Ir(CO)L_2I_2(COMe)]$ ($L = P(OMe)_3$ or $P(OPh)_3$).[69] Kinetic studies revealed inhibition by iodide salts, promotion by methanol and a saturation dependence on [L], consistent with an iodide loss mechanism analogous to that for the carbonylation of $[Ir(CO)_2I_3Me]^-$. Addition of SnI_2 was also found to enhance the rate of carbonylation of $[Ir(CO)_2I_3Me]^-$ (although this compound is not an effective promoter for catalysis). Spectroscopic studies indicated that insertion of SnI_2 into an Ir–I bond gives $[Ir(CO)_2I_2Me(SnI_3)]^-$ which is activated toward methyl migration.[48]

Iodide transfer from iridium to the promoter is a key feature of the reaction mechanism proposed in Scheme 5, and this has been demonstrated in model stoichiometric reactions. The anion $[Ir(CO)_2I_3Me]^-$ reacts cleanly with GaI_3 and InI_3 to form $[MI_4]^-$ and the neutral iridium methyl complex, $[Ir(CO)_2I_2Me]$.[41,50,57] This five-coordinate species dimerizes through bridging iodides to give $[Ir(CO)_2I(\mu\text{-}I)Me]_2$ in non-coordinating solvents and in the solid state, but exists as a solvated monomer (e.g., $[Ir(CO)_2(NCMe)I_2Me]$) in coordinating solvents.[41] Slightly more complex behavior is observed in the reactions of $[Ir(CO)_2I_3Me]^-$ with neutral ruthenium iodocarbonyl complexes such as $[Ru(CO)_3I_2]_2$ and $[Ru(CO)_4I_2]$. In dichloromethane, IR[41] and ^{13}C NMR[56] spectroscopy indicate formation of a dinuclear iodide-bridged species. Under CO pressure, cleavage of this dimer results in formation of the anion, $[Ru(CO)_3I_3]^-$, along with $[Ir(CO)_3I_2Me]$, thus demonstrating iodide transfer from Ir to Ru as shown in Scheme 6. The dinuclear Ir–Ru complex is only observed in non-coordinating solvents in the absence of high CO pressure, and so is unlikely to be directly involved in the catalytic mechanism.

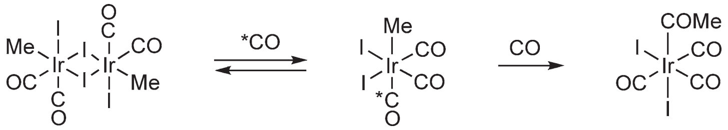
The tricarbonyl, $[Ir(CO)_3I_2Me]$, was originally proposed by Forster as a key intermediate in the carbonylation mechanism. Although not observed at that time, more recent studies by Ghaffar *et al.* have shown that $[Ir(CO)_3I_2Me]$ is formed from $[Ir(CO)_2I_2Me]_2$ under CO pressure.[41,50] HPIR and HPNMR spectroscopy, together with ^{13}CO isotopic labeling, demonstrated that $[Ir(CO)_3I_2Me]$ has a *fac*-arrangement of carbonyl ligands. The third CO ligand binds reversibly and stereoselectively *trans* to the methyl ligand (Scheme 7). At 25 bar CO, essentially complete conversion into $[Ir(CO)_3I_2Me]$ can be achieved, but release of the CO pressure results in reversion to $[Ir(CO)_2I_2Me]_2$.

Kinetic studies confirmed that $[Ir(CO)_3I_2Me]$ is carbonylated (to give $[Ir(CO)_3I_2(COMe)]$) much faster than the anion, $[Ir(CO)_2I_3Me]^-$ (by ca. 700 times at 85 °C). The increased reactivity can be ascribed to increased competition for backbonding in the tricarbonyl, which raises the electrophilicity of the CO ligands, encouraging intramolecular nucleophilic attack by the methyl ligand. A more facile migratory CO insertion in $[Ir(CO)_3I_2Me]$ is supported by theoretical calculations which predict the activation barrier for the tricarbonyl to be lower by 35–47 kJ mol^{-1}.[41,51,54] Figure 5 illustrates the reaction coordinates for methyl migration in $[Ir(CO)_2I_3Me]^-$ and $[Ir(CO)_3I_2Me]$. In both cases, the transition state involves concerted Me–C(O) bond formation, Ir–Me cleavage, and an opening of the bond angle between ligands *trans* to the methyl and CO ligands. The resulting five-coordinate products are square pyramidal with apical acetyl ligands. This explains why the kinetic products of migratory CO insertion in related Ir(III) complexes[70] have the entering ligand *trans* to acetyl, rather than *cis* as in the classic $[Mn(CO)_5Me]$ system.[71,72]

The reactivity of $[Ir(CO)_2I_3Me]^-$ with other species has also been investigated, in particular, reactions leading to methane, a known byproduct of iridium-catalyzed carbonylation.[52] Methane formation occurs on reaction of $[Ir(CO)_2I_3Me]^-$ either with carboxylic acids or with H_2 at elevated temperature. In both cases, the reaction is inhibited by the presence of CO, suggesting that CO dissociation from the reactant complex is required. For the protonolysis reaction with carboxylic acids, a mechanism was proposed (Scheme 8(a)) in which the acid coordinates to a vacant site created by CO loss, and methane is then liberated via a cyclic transition state. The hydrogenolysis reaction, which leads cleanly to $[Ir(CO)_2I_3H]^-$, could proceed via oxidative addition of H_2 or an η^2-H_2 complex as shown in Scheme 8(b).



Scheme 6 Iodide transfer from $[Ir(CO)_2I_3Me]^-$ to Ru.



Scheme 7 Reaction of $[Ir(CO)_2I_2Me]_2$ with CO.

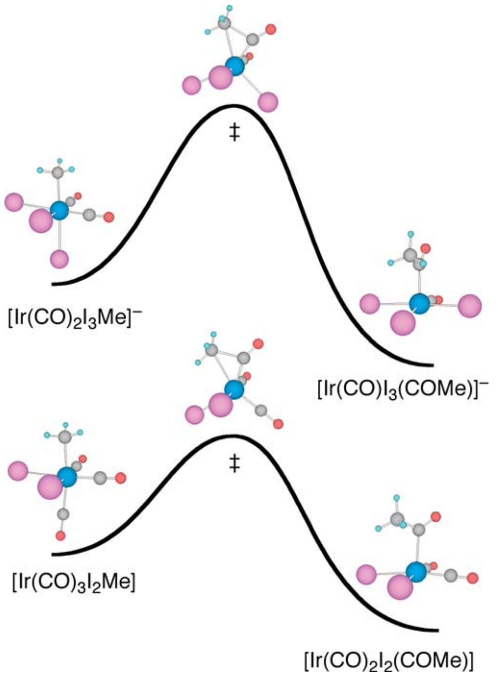
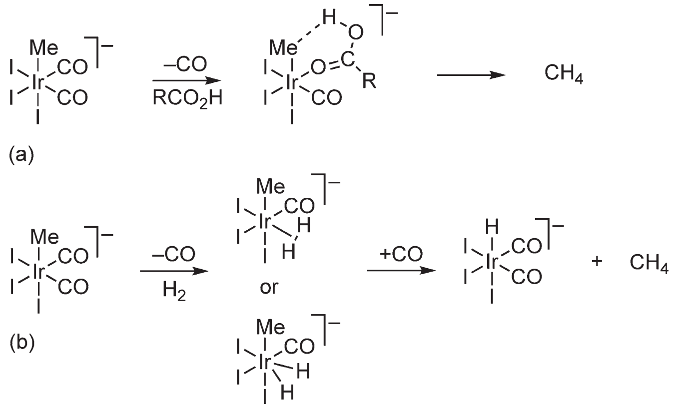


Figure 5 Reaction coordinates for migratory CO insertion in $[Ir(CO)_2I_3Me]^-$ (top) and in $[Ir(CO)_3I_2Me]$ (bottom).



Scheme 8 Proposed routes to methane formation by reaction of $[Ir(CO)_2I_3Me]^-$ with carboxylic acids or H_2.

7.05.2.5 Structural Studies of Iridium Complexes

A number of iridium iodocarbonyl species relevant to the catalytic mechanism have been characterized crystallographically in recent years, aided by the robust nature of the complexes concerned.[41,46,47,50,57] Indeed the structural data reported have made the iridium-catalyzed process one of the best characterized catalytic cycles. Some of the bond distances are compared in Table 3. All of the structures determined contain *cis*-$Ir(CO)_2$ fragments and mutually *cis*-iodide ligands. It is notable that in the octahedral Ir(III) alkyl and acetyl complexes, $[Ir(CO)_2I_3R]^-$, the *trans*-influence of R leads to a significantly longer Ir–I bond in the *trans*-position. This is likely to lead to greater lability of the iodide in this site, an important feature of the catalytic mechanism.

Although all the reported structures are *cis*-dicarbonyls, spectroscopic evidence also indicates the existence of *trans*-isomers of $[Ir(CO)_2I_3(COMe)]^-$[41] and $[Ir(CO)_2I_4]^-$.[73] In general, however, iridium complexes appear to have a stronger preference for the *cis*-dicarbonyl isomer than do the rhodium analogs, where the *trans*-isomers of $[Rh(CO)_2I_3R]^-$ (R = COMe,[74,75] H,[76] I[73,77,78]) are more stable. Theoretical calculations[51,53–55] support the greater

Table 3 Bond distances (Å) for structurally characterized iridium iodocarbonyl complexes

Complex	*References*	*Ir–I (trans to CO)*	*Ir–I (trans to R*[a]*)*	*Ir–CO*	*Ir–R*
$[Ir(CO)_2I_2]^-$	57	2.65	–	1.81	–
$[Ir(CO)_2I_4]^-$	46	2.70	2.71	1.86	–
$[Ir(CO)_2I_3Me]^-$	57	2.71	2.77	1.83	2.13
$[Ir(CO)_2I_3(n\text{-}C_6H_{13}]^-$	47	2.71	2.78	1.90	2.04
$[Ir(CO)_2I_3(COMe)]^-$	41	2.70	2.83	1.90	2.19
$[Ir(CO)_2I_3H]^-$	57	2.69	2.84	1.89	–
$[Ir(CO)_2I_3Me]_2$	41,50,57	2.69, 2.72 (μ-I)	2.80 (μ-I)	1.87	2.17

[a] R = I, H, alkyl, or acetyl.

stability of *cis*-$[Ir(CO)_2I_2]^-$, but for $[Ir(CO)_2I_3R]^-$ (R = Me, COMe) the *trans*-dicarbonyl isomers are predicted to be marginally lower in energy. Possible participation in the catalytic mechanism by the different geometrical isomers was also considered by theoretical studies.

7.05.2.6 Overall Catalytic Mechanism

A mechanism for the catalytic process is represented in three-dimensional form in Scheme 9.[41] The participating iridium complexes are grouped into three vertical triads, namely, Ir(I) species, Ir(III) methyls, and Ir(III) acetyls. The three complexes within each set are linked by equilibria involving I^- and CO, so as to place neutral tricarbonyls on the upper ring, neutral dicarbonyls on the middle ring, and anionic dicarbonyls on the lower ring. Although this representation depicts the catalytic process somewhat differently, most of the interconversions between Ir species are equivalent to those in Forster's two-cycle mechanism (Scheme 1). The dominant route for catalytic turnover is indicated in red. It is apparent in this view that $[Ir(CO)_2I_3Me]^-$ (the formal product of MeI oxidative addition to $[Ir(CO)_2I_2]^-$) lies off the main cycle as a resting state species, shown in blue. This arises since oxidative addition occurs via an initial S_N2 step to give $[Ir(CO)_2I_2Me]$, which can either be trapped by I^- or react with CO to give the productive $[Ir(CO)_3I_2Me]$. Under conditions where $[Ir(CO)_2I_3Me]^-$ is the resting state, iodide acts as a poison, since it inhibits entry to the main cycle from $[Ir(CO)_2I_3Me]^-$. Conversely, at low $[I^-]$, $[Ir(CO)_3I]$ (also shown in blue) accumulates as the resting state, as there is insufficient iodide to maintain the catalyst in an anionic form, and oxidative addition of MeI to neutral species is much slower.

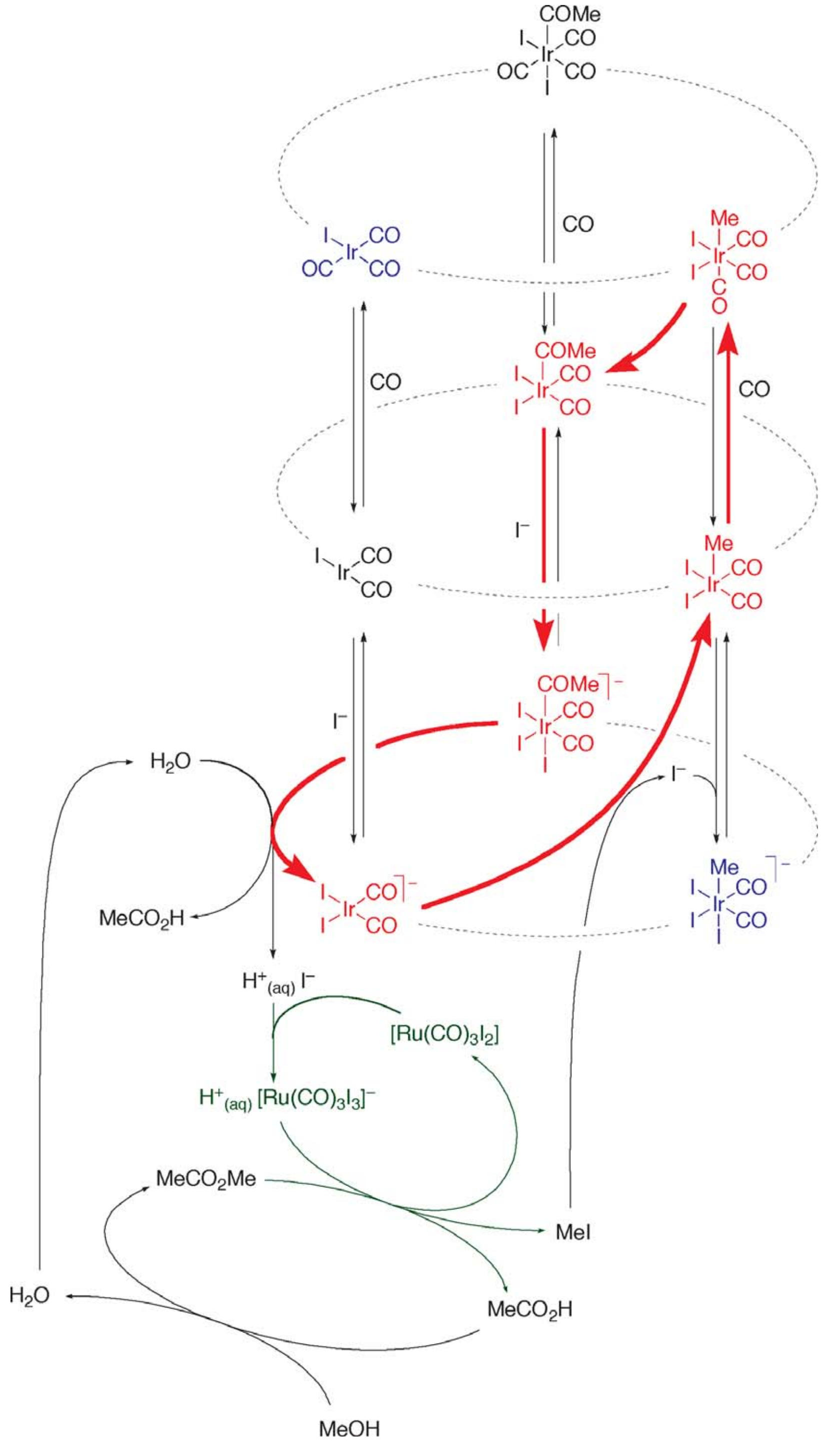
The iodide ($HI_{(aq.)}$) concentration is influenced by the water and methyl acetate concentrations (according to Equation (7)).

$$\mathrm{MeOAc} + \mathrm{H_3O^+} + \mathrm{I^-} \rightleftharpoons \mathrm{MeI} + \mathrm{H_2O} + \mathrm{AcOH} \tag{7}$$

Each turnover of the iridium cycle generates one molar equivalent of $HI_{(aq.)}$, which has to be recycled by reaction with methyl acetate to give methyl iodide, as shown in Equation (7). The steady-state concentration of "free" iodide depends on the rate of this conversion, and also plays a crucial role in the Ir cycle, where it inhibits conversion of $[Ir(CO)_2I_3Me]^-$ into $[Ir(CO)_3I_2Me]$. The HI concentration also influences the rate of the competing WGS reaction, which involves oxidative addition of HI to $[Ir(CO)_2I_2]^-$, and further reaction with HI to give the "inactive" $[Ir(CO)_2I_4]^-$.

A key function of the ruthenium promoter (and other promoter species) is to moderate the iodide concentration. *In situ* HPIR spectroscopy showed that under catalytic conditions, the ruthenium promoter exists mainly as $[Ru(CO)_3I_3]^-$, in equilibrium with smaller amounts of $[Ru(CO)_3I_2(sol)]$ and $[Ru(CO)_2I_2(sol)_2]$.[41] The presence of a high concentration of $[Ru(CO)_3I_3]^-H_3O^+$ increases the Brønsted acidity, and is thought to accelerate the reaction of methyl acetate with HI by acid catalysis. Consistent with this, the exchange of isotopically labeled methyl groups between MeI and MeOAc is catalyzed by $[Ru(CO)_3I_3]^-H_3O^+$.[41,59] The promoter therefore acts not just as an iodide abstractor, but is able to promote recycling of ionic iodide back into methyl iodide, as indicated by the green cycle in Scheme 9.

The precise mechanism of the reductive elimination step of the catalytic cycle is not known with certainty. It is often depicted as a concerted elimination of acetyl iodide from the Ir center, which has been modeled theoretically for both $[Ir(CO)_2I_3(COMe)]^-$ and $[Ir(CO)_3I_2(COMe)]$.[55] In practice, however, this is difficult to distinguish from hydrolysis of an Ir–acetyl complex to give acetic acid without the intermediacy of acetyl iodide. Indeed, solvolysis was suggested to be the rate-determining step in an early study.[31] Scheme 9 represents the elimination step as a hydrolysis of the anion,



Scheme 9 Mechanism for ruthenium-promoted, iridium-catalyzed methanol carbonylation. Alternative geometrical isomers of complexes and coordinated solvent molecules are omitted for clarity.

$[Ir(CO)_2I_3(COMe)]^-$, leading to $[Ir(CO)_2I_2]^-$ and HI, but a route via the neutral $[Ir(CO)_2I_2(COMe)]$ is also feasible (halide loss being known to facilitate other elimination reactions of Ir(III) complexes[79,80]). Quantitative kinetic data have been reported for reductive elimination of MeCOCl from the analogous iridium trichloride, $[Ir(CO)_2Cl_3(COMe)]^-$, as well as the reverse oxidative addition of MeCOCl to $[Ir(CO)_2Cl_2]^-$.[64]

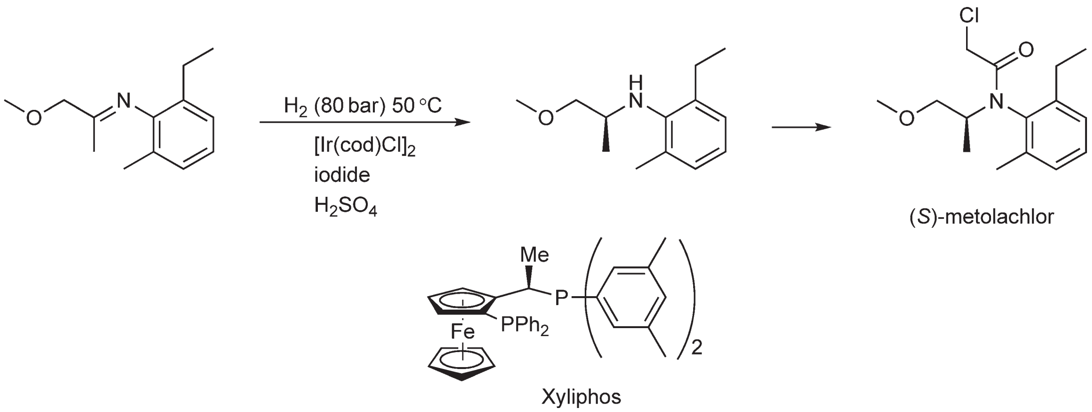
7.05.3 Enantioselective Imine Hydrogenation

Iridium complexes are effective homogeneous catalysts for a range of hydrogenation reactions. A well-cited example is the Ir(I) complex $[Ir(cod)(py)(PCy_3)]PF_6$ introduced by Crabtree *et al.*,[81] which can promote the hydrogenation of “difficult” substrates such as tri- and tetrasubstituted alkenes. Industrially, the most significant application employs an iridium diphosphine catalyst for enantioselective hydrogenation of an imine to give a precursor of the herbicide, (*S*)-metolachlor. An iridium-catalyzed imine hydrogenation process has also been operated on the pilot plant scale by Lonza for production of dextromethorphan, a cough suppressant.[82] Asymmetric catalytic reactions are dealt with in detail in Volume 10 of this encyclopedia, but the principal features of the (*S*)-metolachlor process and the underlying organometallic chemistry will be summarized here. It is particularly noteworthy that both of the major iridium-catalyzed processes discussed in this chapter employ an acidic solvent and iodide compounds as co-catalysts. The numerous effects of iodide in transition metal catalysis have recently been reviewed.[83]

7.05.3.1 Manufacture of (*S*)-metolachlor

Chiral amines are important intermediates for biologically active compounds, and enantioselective hydrogenation of C═N is an attractive route for their synthesis. Metolachlor is an *N*-chloroacetylated, alkoxyalkylated *ortho*-disubstituted aniline, which is the active ingredient of Dual®, a herbicide used for maize and other grass crops. The original synthetic route gave a racemic mixture, but 95% of the herbicidal activity arises from the stereoisomer with (*S*) stereochemistry at the chiral carbon. An enantioselective route to (*S*)-metolachlor has now been commercialized by Syngenta.[84–87] The product is marketed as Dual–Magnum®, on a scale of ca. 10,000 tonnes per annum.[88] The crucial Ir-catalyzed step in the synthesis involves enantioselective hydrogenation of an aryl imine as shown in Scheme 10. The catalyst comprises the Ir(I) dimer, $[Ir(cod)(\mu\text{-}Cl)]_2$, in combination with a chiral ferrocenyldiphosphine ligand, xyliphos, an iodide salt (Bu_4NI or NaI), and sulfuric or acetic acid. At 323 K and 80 bar H_2, the hydrogenation is reported to occur with 79% ee and an initial turnover frequency (TOF) of 1.8×10^6 h^{-1}.[88] Heterogenized versions of the catalyst, in which the xyliphos ligand is tethered to a solid support based on silica or polystyrene, have also been reported.[89] These show good enantioselectivity but suffer from somewhat lower activity (highest TOF 2×10^4 h^{-1}) and stability.

An interesting personal perspective by Blaser[90] describes the development of the (*S*)-metolachlor process by Ciba–Geigy during the 1980s and early 1990s, culminating in the first production batch in November 1996. In the initial development stages, a range of diphosphine ligands, combined with iridium, were found to give promising catalytic results, but problems were encountered concerning catalyst activity, enantioselectivity, and stability.[91–94] In 1993, promising results were obtained using some ferrocenyldiphosphine (known as Josiphos[88]) ligands, and later, in the same year, it was discovered that there was a remarkable (ca. 10×) enhancement of activity when acetic acid was employed as solvent for the Ir/xyliphos catalyst, in combination with an iodide salt promoter. The increased activity was accompanied by improved enantioselectivity, opening the way to successful commercialization. The process is currently the largest scale industrial application of enantioselective catalysis.

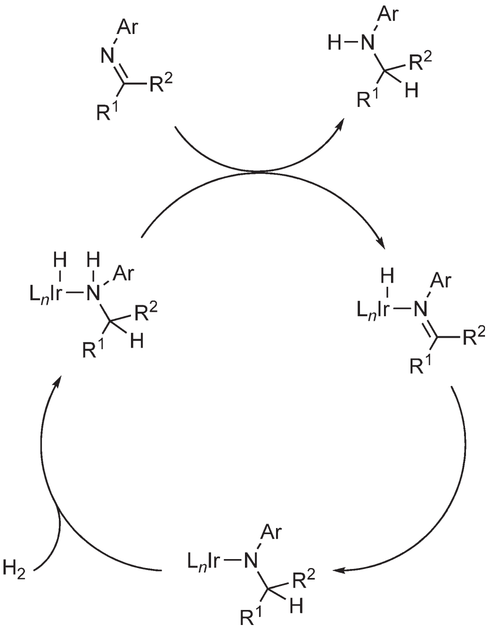


Scheme 10 Synthetic route to the herbicide, (*S*)-metolachlor.

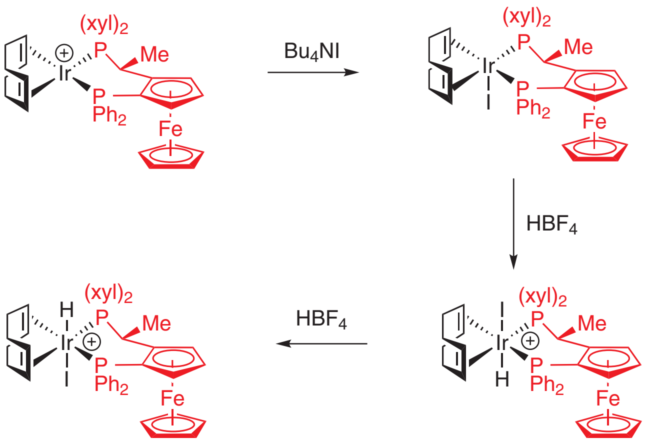
7.05.3.2 Mechanism

A catalytic cycle indicating the key steps thought to occur in iridium-catalyzed imine hydrogenation is shown in Scheme 11. Coordination of the imine and insertion into an Ir–H bond gives an amido intermediate, which activates H_2 to give a hydrido–amine complex. This liberates the amine product and binds another substrate molecule to complete the cycle.

Iridium xyliphos complexes relevant to this catalytic cycle have been investigated.[95] Reaction of $[Ir(cod)(\mu\text{-}Cl)]_2$ with the xyliphos ligand gives [Ir(cod)(xyliphos)Cl], from which chloride can be abstracted using $AgBF_4$ to give $[Ir(cod)(xyliphos)]BF_4$, which was characterized crystallographically. Since the catalytic medium is acidic and contains iodide, the reaction of $[Ir(cod)(xyliphos)]BF_4$ with HI was tested and found to give a mixture of hydride species. A cleaner result was obtained by the stepwise reaction of $[Ir(cod)(xyliphos)]BF_4$ with Bu_4NI followed by protonation (Scheme 12). An X-ray structure of the intermediate iodide complex, [Ir(cod)(xyliphos)I], revealed a square-pyramidal coordination environment with an apical iodide, oriented toward the ferrocenyl fragment of the xyliphos ligand.



Scheme 11 Schematic catalytic cycle for iridium-catalyzed aryl imine hydrogenation.



Scheme 12 Iridium (iodo) and (hydrido) (iodo) complexes containing the xyliphos ligand.

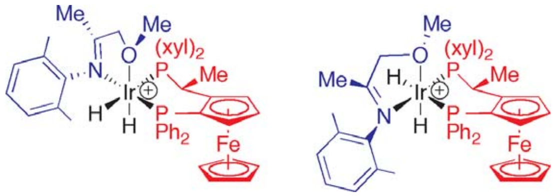
Protonation of [Ir(cod)(xyliphos)I] using HBF_4 resulted in a cationic Ir(III) hydride $[Ir(cod)(xyliphos)(H)I]BF_4$, which was found to convert into its isomer on addition of a second equivalent of HBF_4. Interestingly, both of these hydrides were identified spectroscopically in the reaction mixture formed by the normal catalyst preparation method, and they were also found to be good pre-catalysts themselves. Addition of I_2 to [Ir(cod)(xyliphos)I] gives a dinuclear Ir(III) complex, $[(Ir(xyliphos)I)_2(\mu\text{-}I)_3]I$, which was also effective as a pre-catalyst. Significantly lower activity (but similar enantioselectivity) was found when using the Ir(I) complexes [Ir(cod)(xyliphos)X] (X = Cl, I) as pre-catalysts, but very low activity was found for the halide free complex, $[Ir(cod)(xyliphos)]BF_4$.

Studies of imine binding to iridium employed a slightly simpler 2,6-dimethylphenyl-substituted imine rather than the 2-methyl-6-ethylphenyl-substituted imine of the commercial process. Treatment of $[Ir(cod)(xyliphos)]BF_4$ with the imine under H_2 resulted in displacement of 1,5-cyclooctadiene, oxidative addition of H_2, and binding of the imine in a chelate manner. The Ir(III) dihydride adduct, $[Ir(xyliphos)(MeOCH_2\text{–}C(Me){=}N(2,6\text{-}Me_2C_6H_3)H_2]BF_4$, was shown by NMR spectroscopy to exist as a mixture of four stereoisomers, each having *cis*-hydride ligands, with the methyl ether function always *trans* to hydride and the imine N *trans* to P. The two major isomers, shown in Scheme 13, are formed in almost equal amounts.

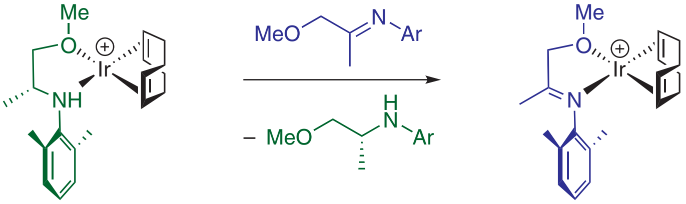
Migratory insertion of the imine C=N bond into the Ir–H bonds of these two isomers will generate the (*R*) and (*S*) amine products, respectively. Based on this observation, it was proposed that the enantioselective step is migratory insertion rather than pre-coordination of the imine. It is suggested that the enantioselectivity arises from the electronic asymmetry of the diphosphine ligand. The desired (*S*) amine results from more favorable migratory insertion in the isomer in which the more basic $P(xyl)_2$ donor group is *trans* to hydride, thus imparting higher nucleophilicity on the hydride. The imine is also more electrophilic in this isomer, being *trans* to the less basic PPh_2 donor. A further consideration is that the strongly basic amide function resulting from migratory insertion will have a preference for the coordination site *trans* to the less basic PPh_2.

Bidentate coordination of the imine was also demonstrated in crystal structures of Ir(I) bis(ethylene) and 1,5-cyclooctadiene complexes.[95,96] An analogous chelate iridium–amine adduct was also synthesized and structurally characterized. The kinetics of substitution of amine by imine (Scheme 14) were investigated to probe the mechanism of the product/substrate exchange reaction in the proposed catalytic cycle. The data were interpreted in terms of an associative mechanism in which the imine binds reversibly to Ir, prior to the release of amine. However, since the catalytic mechanism may well involve octahedral Ir(III) rather than square-planar Ir(I) complexes, a different mechanism could well operate during catalysis.

Reactions of the cationic Ir(I) complexes $[Ir(cod)(xyliphos)]BF_4$ and $[Ir(cod)(\kappa^2\text{-}ArN{=}C(Me)CH_2OMe)]BF_4$ with I_2 resulted in transformations involving C–H activation of the 1,5-cyclooctadiene ligand.[96,97] Although the current evidence does not allow precise formulation of all the species which participate in the catalytic cycle, the results summarized above provide some important observations concerning ligand-coordination modes and interconversions.



Scheme 13 Two major isomers of a catalyst–imine adduct.



Scheme 14 Amine–imine exchange on Ir(I).

7.05.4 Conclusion

Despite the common perception that third-row transition metal complexes have poor activity as homogeneous catalysts, iridium-based processes now play a significant role in industrial catalysis. Since 1995, the BP Cativa process for methanol carbonylation and the Syngenta (S)-metolachlor process have both been commercialized. Compared to rhodium-based systems, iridium catalysts can benefit from being more robust due to the stronger metal–ligand bonding. Catalyst stability and longevity are important considerations for a commercial process, particularly when operated continually such as methanol carbonylation. The prospects for developing further iridium-catalyzed processes will depend upon the success in identifying combinations of ligands, reaction conditions, and promoters, which infer the appropriate selectivity, activity, and stability for commercial operation.

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