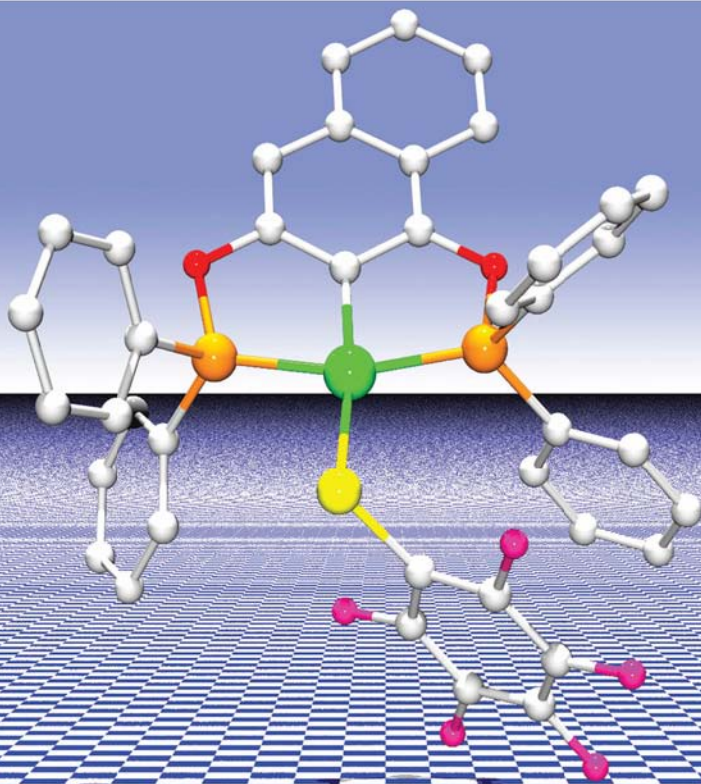




The Chemistry of Pincer Compounds

David Morales-Morales and Craig M. Jensen
(Editors)



The Chemistry of Pincer Compounds

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The Chemistry of Pincer Compounds

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Elsevier
Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands
Linacre House, Jordan Hill, Oxford OX2 8DP, UK

First edition 2007

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Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN: 978-0-444-53138-4

For information on all Elsevier publications
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Printed and bound in The Netherlands

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Contents

Preface	xv

Chapter 1 Organometallic pincer-type complexes: recent applications in synthesis and catalysis

<i>Jairton Dupont, Crestina S. Consorti and John Spencer</i>	1
1.1 Introduction	1
1.2 Preparation of Pincer Palladacycles	2
1.2.1 General Remarks	2
1.2.2 The Chloropalladation Reaction Path	4
1.3 Structural Aspects	6
1.3.1 Solution Phase Studies	6
1.3.2 Mass Spectrometry Studies	7
1.3.3 Solid-State Studies	9
1.4 Pincers as Catalyst Precursors for Cross-Coupling Reactions Involving Aryl Substrates	9
1.4.1 General Remarks	9
1.4.2 Heck Coupling	12
1.4.3 Suzuki Cross-Coupling	18
1.4.4 Sonogashira Coupling	20
1.5 Conclusions and Trends	21

Chapter 2 Synthesis and transformation of allyl- and allenyl-metal species by pincer complex catalysis

<i>K.J. Szabó</i>	25
2.1 Introduction	25
2.2 Palladium-Catalyzed Allylation of Electrophiles	26
2.2.1 Pincer Complex-Catalyzed Coupling of Allyl Stannanes with Aldehydes	27
2.2.2 Trifluoro(allyl)borate as Allylating Agent	28
2.2.3 Application of Chiral Pincer Complex Catalysts for Allylation of Sulfonimines	29
2.2.4 Mechanism of the Pincer Complex-Catalyzed Electrophilic Allylic Substitution	30

2.3	Pincer Complex-Catalyzed Synthesis of Organometallic Compounds	32
2.3.1	Synthesis of Allylboronic Acids and Allyl Boronates	32
2.3.2	Pincer Complex-Catalyzed Synthesis of Allyl Stannanes	34
2.3.3	Stannylation of Propargylic Substrates	35
2.3.4	Synthesis of Allenyl Silanes Using Pincer Complex Catalysis	36
2.3.5	Phenylselenation of Organohalides	37
2.3.6	Mechanistic Aspects of the Pincer Complex-Catalyzed Organometallic Group Transfer Processes	37
2.4	Conclusions and Outlook	41

Chapter 3 Chiral pincer complexes and their application to asymmetric synthesis

Christopher J. Richards and John S. Fossey 45

3.1	Introduction	45
3.2	The Synthesis of Chiral Nonracemic Pincer Complexes Containing Anionic Terdentate Ligands	45
3.2.1	NCN Complexes	46
3.2.2	NNN Complexes	56
3.2.3	PCP Complexes	59
3.2.4	SCS Complexes	61
3.2.5	Mixed Donor Complexes	62
3.2.6	Reactions of Chiral Pincers	62
3.3	The Application of Pincer Complexes to Asymmetric Synthesis	63
3.3.1	Imine Alkylation	64
3.3.2	Allylation, Propargylation and Allenylation	64
3.3.3	The Diels–Alder and Aldol Reactions	67
3.3.4	The Reaction of Activated Isonitriles with Aldehydes	68
3.3.5	The Michael Reaction	71
3.3.6	Reduction Reactions	73
3.3.7	Miscellaneous Reactions	74

Chapter 4 Desulfurization catalyzed by nickel PCP-pincer compounds

J. Torres-Nieto and J.J. García 79

4.1	Introduction	79
4.2	HDS Catalysts	80
4.2.1	Coordination Modes of Thiophenic Moieties	80
4.2.2	Metal Insertion into C–S Bonds	81
4.2.3	Catalytic Homogeneous Desulfurization	82
4.3	Desulfurization Catalyzed by Nickel PCP-Pincer Compounds	82

Chapter 5 Pincer systems as models for the activation of strong bonds: scope and mechanism

B. Rybtchinski and D. Milstein 87

5.1	Introduction	87
5.2	C–H vs C–C Bond Oxidative Addition in PCX-Type Systems	87

5.2.1	Insertion into a Strong C—C Bond in Solution: C—C vs C—H Activation	88
5.2.2	The Methylene Transfer Reaction	98
5.3	Metal Insertion into Unstrained C—O Bonds	101
5.4	Summary	103

Chapter 6 ‘Pincer’-carbene complexes

	<i>Eduardo Peris and Robert H. Crabtree</i>	107
6.1	Introduction	107
6.2	Pincer-Carbene Complexes of Metals from the Platinum Group	108
6.2.1	Palladium Pincer-Carbene Complexes	108
6.2.2	Rhodium and Ruthenium Pincer-Carbene Complexes	113
6.3	Pincer-Carbene Complexes of Other Metals	118
6.3.1	Pincer-Carbene Complexes of Fe, Co and Early Transition Metals	118

Chapter 7 Pincer complexes derived from benzimidazolin-2-ylidene ligands

	<i>F.E. Hahn and M.C. Jahnke</i>	125
7.1	Synthesis of Complexes with Benzimidazolin-2-ylidene Ligands	125
7.2	Complexes with <i>N</i> -allyl-Functionalized Benzimidazolin-2-ylidene Ligands	126
7.3	Coordination Chemistry of the <i>N</i> , <i>N'</i> -diallyl-Functionalized Benzimidazolin-2-ylidene Ligand at Iridium	127
7.4	Pincer Complexes with <i>N</i> , <i>N'</i> -Heteroatom-Functionalized Benzimidazolin-2-Ylidene Ligands	128
7.5	Synthesis of Pincer Complexes with Tridentate Dicarbene Ligands	130
7.6	NMR Studies on Dicarbene Pincer Complexes	134

Chapter 8 Pincer complexes of *N*-heterocyclic carbenes. Potential uses as pharmaceuticals

	<i>Matthew J. Panzner, Claire A. Tessier and Wiley J. Youngs</i>	139
8.1	Introduction	139
8.1.1	<i>N</i> -heterocyclic Carbenes	139
8.2	Silver NHC-pincer complexes	140
8.2.1	Silver Antimicrobials	140
8.2.2	Synthesis of Pyridine-Based Silver NHC-Pincer Complexes	141
8.2.3	Antimicrobial Activity of Silver NHC-Pincer Complexes	142
8.3	Rhodium NHC-Pincer Model Complexes	145
8.3.1	Synthesis of Rhodium NHC-Pincer Complexes	145
8.3.2	Ligand Modification for Targeting	147
8.4	Conclusions	149

Chapter 9 The chemistry of PCP pincer phosphinite transition metal complexes

	<i>David Morales-Morales</i>	151
9.1	Introduction	151
9.2	Synthesis of the Ligands	152
9.3	Synthesis and Reactivity of Transition Metal Phosphinite PCP Pincer Complexes	153
9.3.1	Palladium Complexes	153
9.3.2	Iridium complexes	163
9.3.3	Rhodium Complexes	170
9.3.4	Ruthenium Complexes	171
9.3.5	Platinum Complexes	174
9.3.6	Nickel Complexes	175
9.4	Conclusions	177

Chapter 10 Nitrogen-based pincers: a versatile platform for organometallic chemistry

	<i>Preston A. Chase and Gerard van Koten</i>	181
10.1	Introduction	181
10.2	Lithium Complexes	182
10.3	Early Transition Metals	185
10.3.1	Titanium	185
10.3.2	Molybdenum	186
10.3.3	Tungsten	187
10.4	Mid-Transition Metals	188
10.4.1	Group 7 (Mn–Re)	188
10.4.2	Group 8 (Fe–Os)	190
10.5	Late Transition Metals	194
10.5.1	Cobalt	194
10.5.2	Rhodium	195
10.5.3	Iridium	204
10.5.4	Group 10 (Ni–Pt)	207
10.5.5	Group 11 (Cu–Au)	220
10.5.6	Group 12 (Zn–Hg)	226
10.6	Conclusions	228

Chapter 11 S–P–S and S–C–S pincer ligands in coordination chemistry and catalysis

	<i>N. Mézailles and P. Le Floch</i>	235
11.1	Introduction	235
11.2	S–P–S Pincer Ligands	235
11.2.1	Bis(phosphinosulfide)phosphinines	235
11.2.2	Bis(thioether)phosphines	251
11.3	S–C–S (and Se~C~Se) Pincer Ligands	251
11.3.1	Thioether (N1) and Related Selenoether (N2) Derivatives	251
11.3.2	Thioamide (E) and Phosphine Sulfide (F) Derivatives	262

11.3.3	Anion (G) and Dianion (H) of the Bis-(diphenylphosphinosulfide)-methane	262
11.4	Conclusion	268

Chapter 12 Pincer ligand complexes with unusual atoms and molecular backbones

*Hermann A. Mayer, William C. Kaska, Flor Toledo Rodríguez
and Wolfgang Leis*

		273
12.1	Introduction	273
12.1.1	From Ylides to Pincers	273
12.2	Intra- vs. Intermolecular C–H Activation	275
12.3	PNP Pincer Ligand Backbone	277
12.4	Pincer Carbene Complexes	278
12.4.1	Endocyclic Pincer Carbenes	278
12.4.2	Cycloheptatriene as Ligand Backbone	280
12.5	Conclusion	284

Chapter 13 Rigid PNP pincer ligands and their transition metal complexes

O.V. Ozerov

		287
13.1	Introduction	287
13.2	Ligand Synthesis	288
13.2.1	Approaches to C–P Bond Construction	288
13.2.2	Approaches to the Diarylamine Precursors	289
13.3	Group 4 Metals: Multiple Metal–Carbon Bonds	290
13.3.1	Synthesis of Zr Alkylidenes	291
13.3.2	Synthesis of Ti Alkylidenes and Related Compounds	291
13.4	Ruthenium: CO Abstraction	293
13.5	Group 9 Metal Chemistry	294
13.5.1	Intramolecular N–H, N–C, and C–H Oxidative Addition Reactions	294
13.5.2	Competitive C–H vs. C–Hal Oxidative Addition Reactions of Haloarenes	296
13.5.3	Catalytic Alkyne Dimerization	298
13.5.4	PNP Complexes of Cobalt	299
13.6	Group 10 Chemistry	300
13.6.1	Synthesis of Various (PNP)MX Complexes	300
13.6.2	Catalytic Applications of (PNP)MX	304
13.7	Copper Complexes	306
13.8	Summary	306

Chapter 14 Pincer, chelate and spirocyclic metal carbene complexes from bis(iminophosphorano)methane ligands

Ronald G. Cavell

		311
14.1	Introduction and Overview	311
14.2	The Beginning: Pincers of Early Transition Metals	315

14.2.1	Structures	318
14.2.2	Reaction Chemistry of the Group 4 Pincers	319
14.2.3	The Nature of the M=C Bond: Theory	323
14.2.4	Other Early Transition Metals	324
14.3	Bis-Ligated Complexes	325
14.4	Early Metal-Bridging Carbenes	326
14.5	Main Group Metal Complexes	328
14.5.1	Aluminum	328
14.5.2	Zinc	331
14.5.3	Other Main Group Metals	332
14.6	Platinum Group Metals	332
14.6.1	A Triple Carbene Pincer	334
14.6.2	Orthometallation and Rearrangements	335
14.7	Bimetallic Spirocycles	336
14.7.1	Synthesis and Characterization	336
14.7.2	Reactions of Bimetallic Complexes	338
14.7.3	Reactivity of the Lithiated Spirocycle	339
14.7.4	A Ketene Complex	340
14.7.5	The Reactivity of the Ketene	341
14.8	Summary	342
 Chapter 15 Pincer and chelate carbodiphosphorane complexes of noble metals		
	<i>Ronald G. Cavell</i>	347
15.1	Introduction	347
15.2	Background	348
15.3	Metal Complexes of Hexaphenylcarbodiphosphorane	349
15.3.1	Synthesis	349
 Chapter 16 Hypervalent organotin, aluminium, antimony and bismuth Y,C,Y-chelate complexes		
	<i>R. Jambor and L. Dostál</i>	357
16.1	Introduction	357
16.2	Organotin Compounds Containing Y,C,Y-Chelating Ligands	359
16.2.1	Preparation of Organotin Compounds Containing Y,C,Y-Chelating Ligands L ¹⁻⁵	359
16.2.2	Structure, Dynamic Behaviour and Reactivity of Organotin Compounds Containing Y,C,Y-Chelating Ligands L ¹⁻⁵	361
16.3	Organoaluminium, Antimony and Bismuth Compounds Containing Y,C,Y-Chelating Ligands L ¹⁻⁴	375
16.3.1	Synthesis of Organoaluminium(III) Derivatives	375
16.3.2	Structure and Dynamic Behaviour of Organoaluminium(III) Compounds	375
16.3.3	Reactivity of Organoaluminium(III) Derivatives	376

16.3.4	Synthesis and Reactivity of Organoantimony(III) and Organobismuth(III) Derivatives	377
16.3.5	Structure of Organoantimony(III) and Organobismuth(III) Derivatives	378
Chapter 17	Stability of supported pincer complex-based catalysts in Heck catalysis	
	<i>William J. Sommer, Christopher W. Jones and Marcus Weck</i> . . .	385
17.1	Introduction	385
17.2	Studies into the Stability of Pd-Pincer Complexes	388
17.2.1	Stability of Pd-SCS Pincer Complexes	390
17.2.2	Stability of Pd-PCP Pincer Complexes	392
17.3	Conclusions	395
Chapter 18	Dendrimers incorporating metallopincer functionalities: synthesis and applications	
	<i>Preston A. Chase and Gerard van Koten</i>	399
18.1	Introduction	399
18.2	Peripherally Substituted Systems	402
18.2.1	Early Studies	402
18.2.2	Dendrimers with NCN-Ni groups	402
18.2.3	Dendritic Platinum and Palladium Pincers	411
18.3	Metallopincers Within Each Dendrimer Generation	420
18.3.1	Dendrimers Containing Pincer-Ligated Palladium and Platinum Complexes	420
18.4	Focal Point and Core-Functionalized Metallopincer Dendrons and Dendrimers	427
18.5	Conclusions and Future Perspectives	431
Chapter 19	Perspective and prospects for pincer ligand chemistry	
	<i>William D. Jones</i>	441
Index		445

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Preface

The development of chemistry including pincer-type complexes has been tremendous in the last decade. As a product of the ingeniousness of chemists around the world, these compounds have turned from mere curiosity complexes to a very interesting research topic in multiple areas of chemistry, having a strong impact on the development of other emerging areas nowadays.

Although this book does not intend to be comprehensive, it is fair to say that most of the areas in which pincer complexes have had an impact have already been covered in this text. Thus, topics such as homogeneous catalysis, enantioselective organic transformations, activation of strong bonds, the biological importance of pincer compounds as potential therapeutic or pharmaceutical agents, dendrimeric and supported materials have been boarded by some of the most influential chemists in these areas. The coverage of this book has not been limited to the typical PCP backbones. It also covers the more recent and very interesting pincer compounds having *N*-heterocyclic carbenes or phosphinite PCP pincer analogs. In addition, chapters dealing with the chemistry of SPS, SCS, NCN, and OCO pincer complexes and other pincer species with unusual backbones have been included. The extension of these chemistries has not been reserved to transition metals only, and representative elements such as Al, Sn, Sb, and Bi have also been covered. Hence, although some excellent reviews have been published regarding the chemistry of pincer compounds, we are sure that the present book will come to fill the gaps not covered by those works, turning the present text of general interest for the chemistry community to an appealing one for those interested in these fascinating compounds.

Finally, we would like to express our profound gratitude to all the co-authors who, with great dedication, agreed to share their expertise with the readers and thus made possible the realization of this book.

Fall 2006

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Organometallic pincer-type complexes: recent applications in synthesis and catalysis

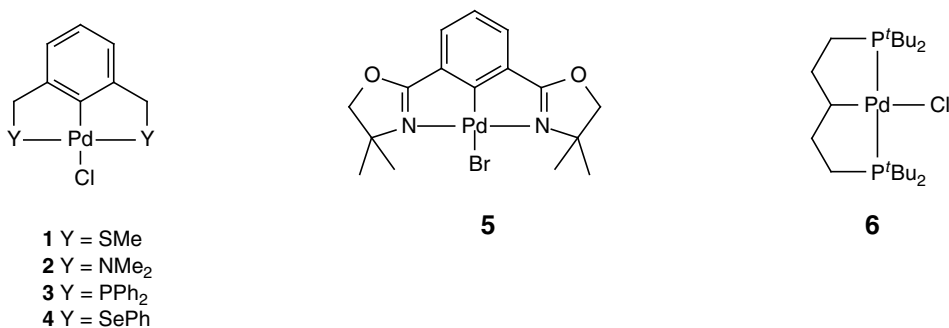
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1.1 INTRODUCTION

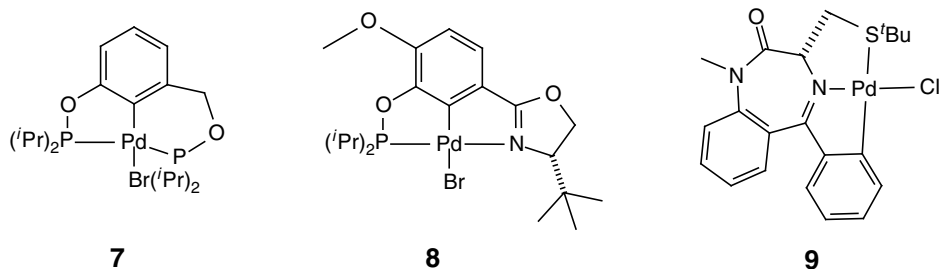
YCY pincer palladacycles, where YCY is typically an SCS, NCN, PCP, SeCSe anionic six-electron donor ligand (e.g. see **1–6**, Scheme 1.1), are a well-established family of organometallic complexes with manifold applications in catalysis, synthesis and materials science [1–24]. Their synthesis can be achieved by many routes including C–H activation, oxidative addition, transmetalation and *trans*-cyclopalladation [25].



Scheme 1.1

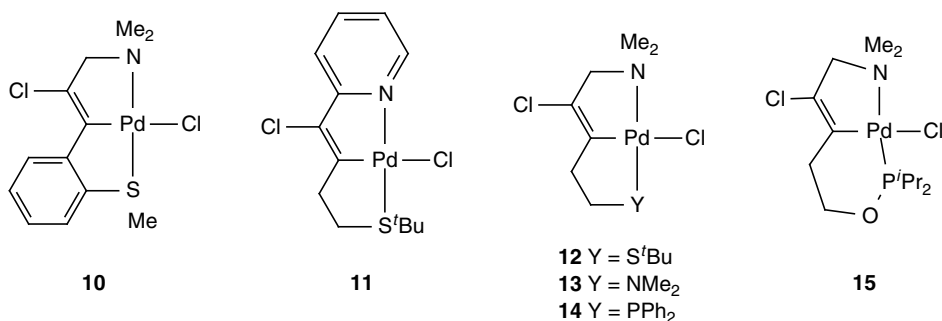
Although most pincer complexes are symmetrical, unsymmetrical YCY' pincer palladacycles are now documented (see **7–9**, Scheme 1.2) [26–28].

A further important and distinct class of symmetrical YCY and unsymmetrical YCY' pincer palladacycles is represented in Scheme 1.3 (exemplified but not limited



Scheme 1.2

to complexes **10–15**). These complexes are formed by a unique, general synthetic method involving the *trans*-chloropalladation (see Section 1.2) of easily prepared hetero-substituted alkynes and are described in a series of papers from our group [29]. These interesting metallacycles are usually easy to handle and are air- and moisture stable with a high thermal stability.



Scheme 1.3

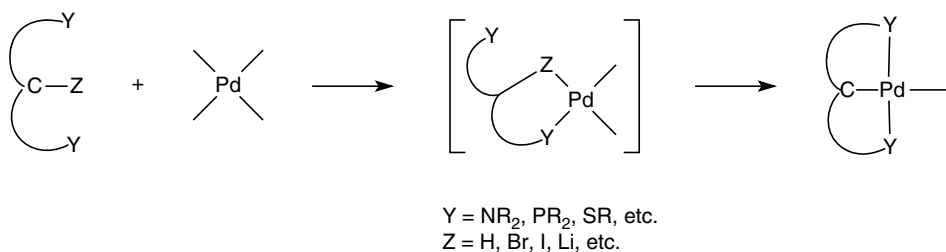
Analogues such as **7–9** (Scheme 1.2) and **10–15** (Scheme 1.3) allow one to fine-tune electronic and steric effects as well as modify reactivity and physicochemical properties of complexes combining different ring sizes and/or types of donor atom (hard and soft) *within the same molecule*. In the following subsections, we will describe the scope and limitation of the *trans*-chloropalladation routes to complexes such as **10–15**, their reactivity, properties and structural features.

1.2 PREPARATION OF Pincer Palladacycles

1.2.1 General Remarks

There are several methods available for the generation of pincer palladacycles (C–H bond activation, oxidative addition and transmetalation for instance), and often two

five-membered or to a lesser extent six-membered chelates are formed as a result of the formation of a stable Pd–C bond, assisted primarily by coordination of one of the two-electron donor groups (Scheme 1.4).



Scheme 1.4

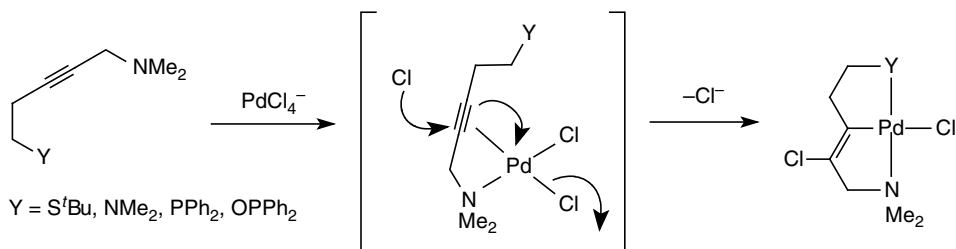
The direct chelation-assisted palladation of C–H bonds is the most simple and direct method for the construction of palladacycles. Palladation agents include tetrachloropalladated salts (often the first choice method due to cost and ease of use), with a base, palladium acetate in acetic acid or benzene. Otherwise, a ligand exchange process is employed using another palladacycle (*trans*-cyclopalladation).

The oxidative addition of aryl halides and, to a lesser extent, alkyl halides, containing two-electron donor groups, is also a useful method for the generation of various palladacycles that cannot usually be obtained by direct C–H bond activation procedures.

The transmetalation reaction is an interesting and often-used methodology for the generation of palladacycles. In most cases, the *trans*-metallating agents are organolithium or organomercurial reagents. The organolithium reagents can be prepared directly by the selective lithiation of the ligand or by Li/halogen exchange, which is usually quantitative.

Alternatively, the reaction of propargylamines or thioethers with Li_2PdCl_4 also generates palladacycles containing a Pd–vinyl bond. The product results from the nucleophilic addition of the chloride anion onto the CC triple bond. This chloropalladation reaction is an interesting method for the generation of various classes of palladacycles such as non-symmetrical pincer-type palladacycles. However, some of these palladacycles are not stable in solution, and in the case of dimeric derivatives, they can easily undergo a retro-chloropalladation reaction. Moreover, palladacycles are not formed when terminal hetero-substituted alkynes are used.

The palladium YCY' 'pincer' complexes **12–15** (Scheme 1.3) were obtained in high yields (70–95%) from the reaction of the corresponding alkynes with Li_2PdCl_4 . Thus, the addition of equimolar amounts of alkynes to a dark-red methanolic solution of Li_2PdCl_4 at 5°C leads almost instantaneously to dark-yellow solutions or the precipitation of light-yellow solids. The palladium pincer complexes are easily isolated in analytically pure form by extraction with dichloromethane and precipitation with hexanes. Various functional donor groups can be introduced in the metallated fragment, such as amines, pyridine, thioethers, phosphines and phosphinites.

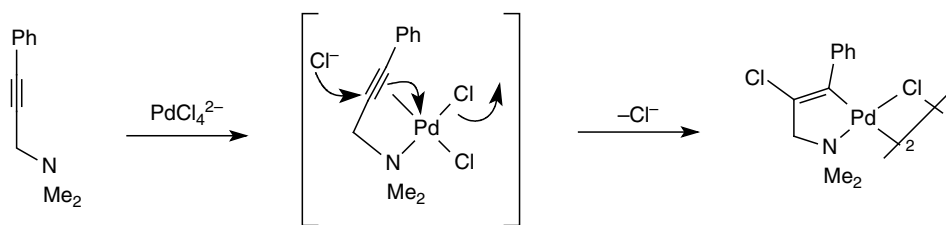


Scheme 1.5

Palladacycles **12–15** are air- and moisture-stable crystalline solids, which are highly soluble in most polar organic solvents such as dichloromethane and acetone and slightly soluble in hexanes and diethyl ether. Compounds **12–15** have relatively high thermal stabilities, starting to decompose only above 140°C.

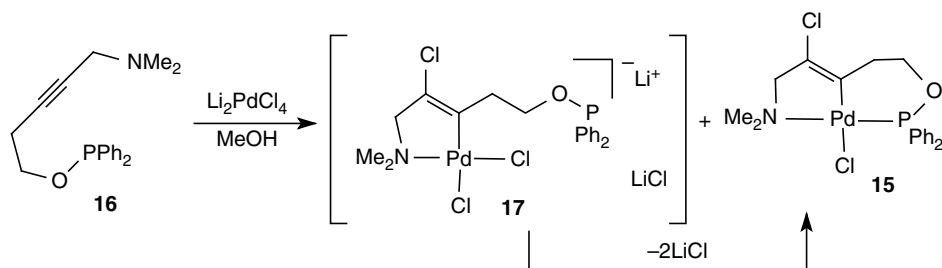
1.2.2 The Chloropalladation Reaction Path

It has been proposed earlier that the chloropalladation of hetero-substituted alkynes such as $\text{PhC}\equiv\text{CCH}_2\text{NMe}_2$ proceeds through the coordination of the N atom followed by interaction of the triple bond to the metal centre. Intermolecular selective nucleophilic attack of the chloride anion to the activated triple bond yields the thermodynamically favoured five-membered palladacycle (Scheme 1.6) [30, 31].



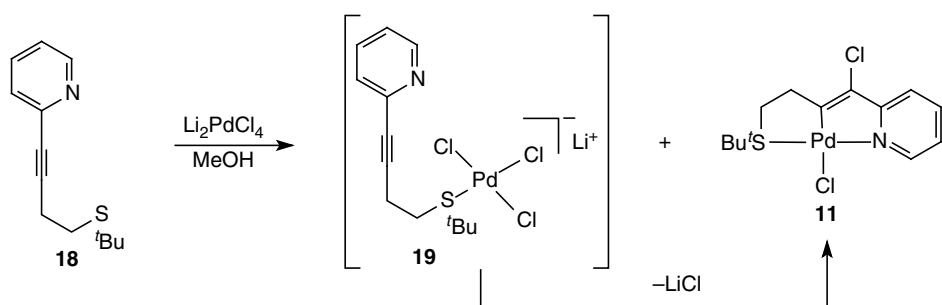
Scheme 1.6

We have observed, that in the earlier stages of the reaction of **16** with Li_2PdCl_4 , the precipitation of an intermediate compound that is gradually and quantitatively transformed into the ‘pincer’ palladacycle **15** (Scheme 1.7) [29]. Although it was impossible to isolate this intermediate in pure form, spectroscopic data allow us to propose a structure (**17**) as shown in (Scheme 1.7). The presence of a single resonance at 106.5 ppm in the $^{31}\text{P}\{-^1\text{H}\}$ NMR and a singlet at 2.81 ppm for the NMe_2 moiety in the ^1H NMR spectra is strong indication that **16** is coordinated to the Pd centre through its N atom only. IR and the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum clearly show the absence of the $\text{C}\equiv\text{C}$ bond and the presence of a $\text{C}=\text{C}$ bond.



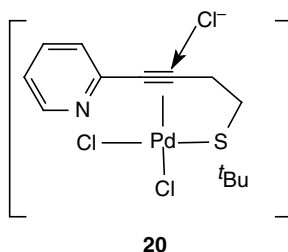
Scheme 1.7

Further evidence for the chloropalladation reaction pathway was provided by the spectroscopic data of the yellow precipitate **19** formed immediately after the addition of **18** to a methanolic solution of Li_2PdCl_4 at room temperature. This compound slowly (2–3 h) rearranges in solution and/or in suspension (methanol or dichloromethane) to afford quantitatively the pincer palladacycle **11** (Scheme 1.8). The ^1H NMR spectrum of **19**, immediately after dissolution in CDCl_3 , shows the resonances of the *ortho* H of the substituted pyridine moiety and *t*-Bu hydrogens at 8.66 and 1.71 ppm, respectively. This is a strong indication that in **19**, ligand **18** is coordinated to the Pd centre through its thioether group only. The presence of characteristic resonances of a $\text{C}\equiv\text{C}$ bond at 80.5 and 96.3 ppm in the ^{13}C NMR spectra and $\nu_{\text{C}\equiv\text{C}}$ at 2230 cm^{-1} in the IR spectra of **19** indicates that the chloropalladation has not yet taken place. These results suggest that it is likely that the chloropalladation reaction of these hetero-substituted alkynes occurs through the coordination of only one donor group to afford compounds such as **19**.



Scheme 1.8

After coordination of one donor group to the metal, coordination of the $\text{C}\equiv\text{C}$ bond to the metal centre would generate intermediates exemplified by **20** (Scheme 1.9). The intermolecular Cl^- nucleophilic addition occurs on the carbon that will generate the thermodynamically more stable palladacyclic ring, i.e. five-membered rather than six-membered ring. Finally, coordination of the pendant donor group through displacement of the chloro ligand yields the pincer palladacycle **11**.



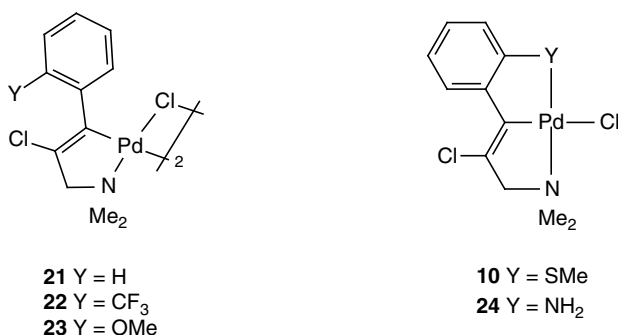
Scheme 1.9

1.3 STRUCTURAL ASPECTS

1.3.1 Solution Phase Studies

Spectroscopic investigation of these pincer complexes in solution can be very informative as already noted above (Section 1.2.2) [29]; for example, heteroatom coordination to palladium in complexes **10–13** is confirmed by a *ca.* 0.6–1 ppm downfield shift in the ^1H NMR spectra (CDCl_3) of the resonance attributed to an S^tBu , SMe or NMe_2 group compared with the free ligand. In complexes **14** and **15**, a *trans*-geometry for the NMe_2 and PR_2 groups is indicated by a $^4J_{\text{PH}} = 2.5 - 2.9$ Hz and a $^3J_{\text{PC}} = 3.0$ Hz between the P atom and the hydrogens of the NMe_2 group. The ^{13}C NMR spectra of these complexes (CDCl_3) generally exhibit two distinct signals for the two vinylic sp^2 hybridized carbons; a low field (140–150 ppm; C–Cl) and a high field resonance (110–125 ppm; C–Pd(II)). The IR spectra of complexes generally reveal a C=C bond represented by a band between 1580 and 1650 cm^{-1} .

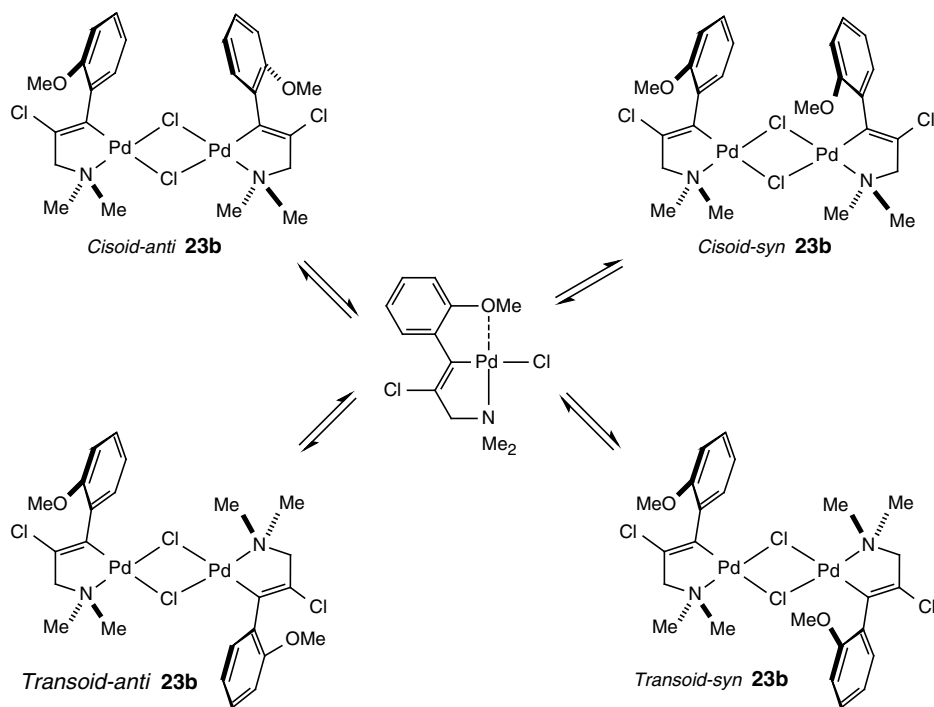
In the series of analogues **10**, **21–24** (Scheme 1.10), the coordinating nature of the group Y determines whether the complexes are dimeric palladacycles (Y does not coordinate to Pd) or monomeric pincer complexes (Y coordinates to Pd) [32].



Scheme 1.10

Although they are not pincer metallacycles per se, complexes **21** and **22** (Y = H, CF_3) merit a cursory mention as they exist as a 1:1 mixture of *cisoid* and *transoid* isomers in solution, evidenced in their ^1H NMR spectra at ambient temperature in CDCl_3 . Moreover,

the ^1H NMR spectrum for the latter analogue ($\text{Y} = \text{CF}_3$) is complicated by the existence of four isomers (1:1:1:1 ratio in ^1H NMR) because both *cisoid* and *transoid* isomers can exhibit a *syn* or *anti* conformation of the CF_3 groups. The ^1H NMR spectrum of the palladacycle **23** ($\text{Y} = \text{OMe}$) displays a singlet for the OMe group at 3.68 ppm, in the range of the free ligand, suggesting no O–Pd coordination. However, the equivalence of the methylene hydrogens and the NMe_2 groups over a temperature range of -40 to 40°C (singlets at 3.59 and 2.83 ppm, respectively) led us to propose a dynamic process involving anchimerically assisted isomerization via the monomeric pincer intermediate (Scheme 1.11). The possibility of pincer-type coordination in complex **23** ($\text{Y} = \text{OMe}$) has been further evidenced by mass spectrometry (see Section 1.3.2).



Complexes **10** ($\text{Y} = \text{SMe}$) and **24** ($\text{Y} = \text{NH}_2$) are, however, pincer complexes; this is evidenced by their lack of reactivity with external ligands such as pyridine and also by the chemical shifts of the donor groups upon coordination to palladium as discussed earlier.

1.3.2 Mass Spectrometry Studies

We have used electrospray mass spectrometry (ESI-MS) in positive mode to detect ionic palladacycle species in the gas phase after dissolution in acetonitrile [33]. The ESI(+) mass spectrum of **10** is shown in Fig. 1.1, and three cationic palladacycles **10a–10c** can be detected in the gas phase (Scheme 1.12).

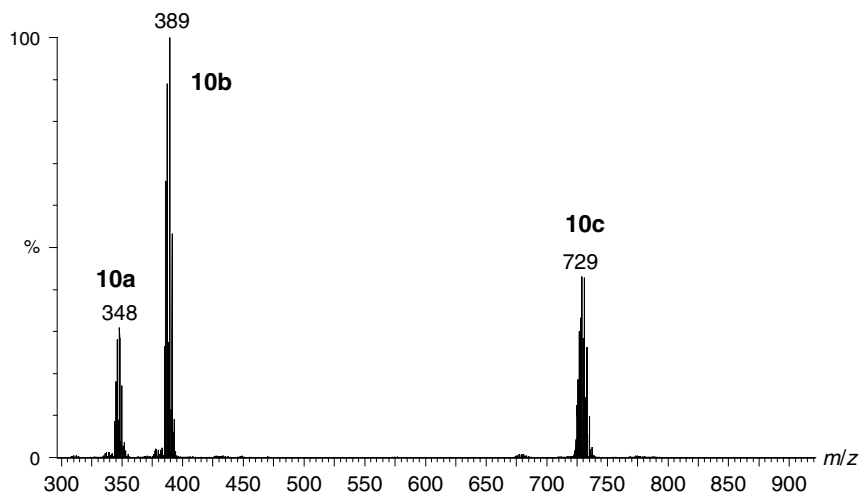
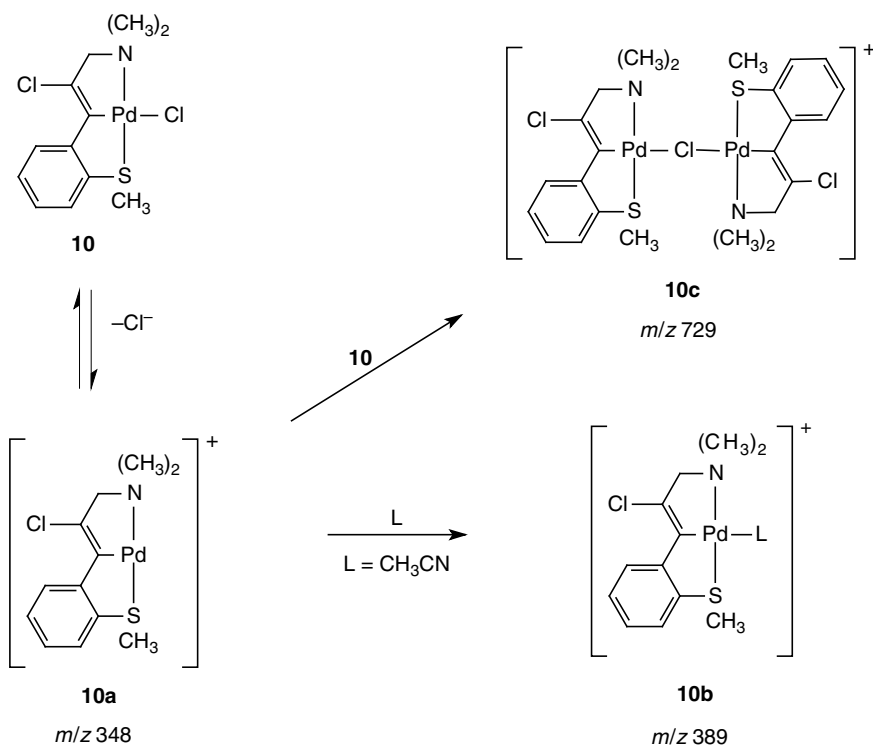


Fig. 1.1. ESI(+)-MS spectrum of the acetonitrile solution of the pincer palladium complex **10**.



Scheme 1.12

The cationic complex **10a**, for example, is detected as an isotopomeric cluster of Pd^+ ions centred at m/z 348 (for ^{106}Pd). **10b** (m/z 389) results from association with acetonitrile solvent and transfer to the gas phase, and **10c** (m/z 729) results from the association of **10** with **10a**.

Fragmentation of complexes can also be studied by ESI-MS (Fig. 1.2). For example, gaseous **10b** loses acetonitrile to afford **10a** and the latter loses HCl to afford **10d** and Pd to afford **10e**. It is interesting to note that the mass spectrum for the latter is rather simplified, due to the absence of palladium and its respective isotopomeric cluster (Scheme 1.13).

The ESI-MS of complex **23** ($\text{Y} = \text{OMe}$) is shown in Fig. 1.3, and a reaction scheme depicted in Scheme 1.14 suggests that O–Pd coordination is an important stabilizing factor in such complexes.

Such studies may be useful in rationalizing the behaviour and properties of palladacycles in solution, e.g. in catalysis.

1.3.3 Solid-State Studies

The X-ray structures of many of our pincer complexes have been determined to probe their solid-state structures [29, 34, 35]. Typical features of these complexes include a distorted square-planar geometry around palladium, a mutually *trans* arrangement of the donor groups, and the Pd–C(vinyl) bond length falls in the range between 1.99 and 2.01 Å (Fig. 1.4).

Complex **25** was found to be totally flat and exists in the solid state as pairs through π -stacking between pyridine and quinoline units (3.448 Å mutual distance) (Fig. 1.5). Weak fluorescent excimeric emission was observed in both solution and the solid state for **25** (Fig. 1.6) [36]. The C(vinyl)–Pd–Cl bond angle is 179° , although the mutually *trans*-bound pyridine units exhibit a 165° bond angle due to the small bite angles in the two five-membered rings (C(1)–Pd–N(8) 83° ; C(1)–Pd–N(17) 82°).

1.4 PINCERS AS CATALYST PRECURSORS FOR CROSS-COUPLING REACTIONS INVOLVING ARYL SUBSTRATES

1.4.1 General Remarks

The use of palladacycles as catalyst precursors for organometallic catalysis is relatively recent. In fact, the first such application was reported in the middle of the 1980s for the hydrogenation of C=C bonds by a cyclopalladated triphenylphosphite [37]. This was shortly followed by the use of cyclopalladated azobenzenes, hydrazobenzenes or *N,N*-dimethylbenzylamine in the selective catalytic reduction of nitro-aromatic compounds, nitro-alkenes, nitriles, alkynes, alkenes and aromatic carbonyl compounds [38, 39]. However, it was not until the first report on the synthesis and applications in catalytic C–C coupling reactions of the palladacycle derived from the cyclopalladation of *triso*-tolylphosphine [40] that the rich chemistry of these organopalladium compounds received a new impulse and indeed continues to flourish. Doubtless, there have been hundreds of reports in the last 10 years on the use of known and new palladacycles as catalyst precursors for C–C coupling reactions in particular of the Heck and Suzuki type. However, in the vast majority of these cases, the palladacycles serve as a source

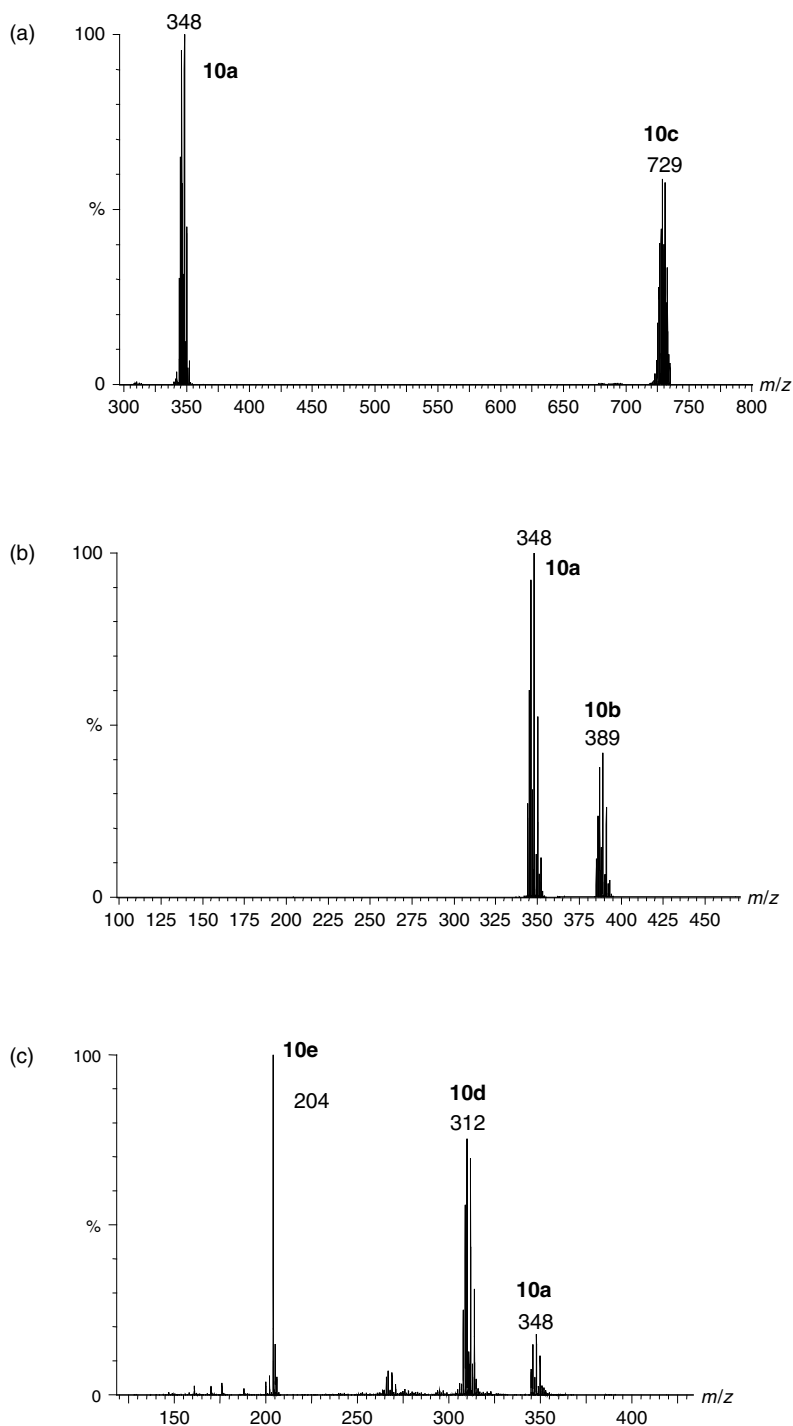
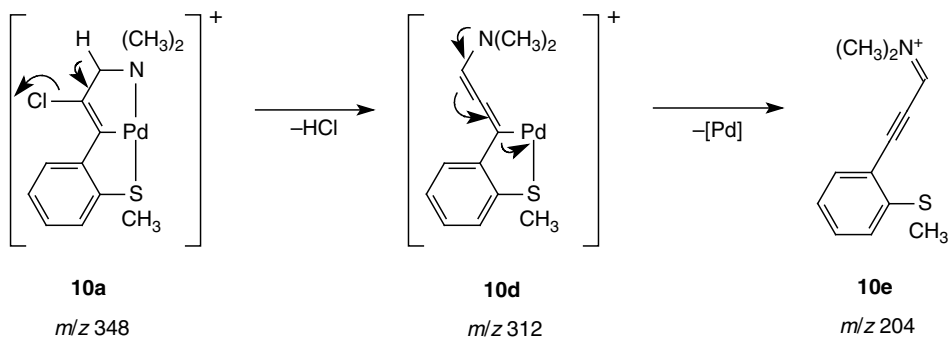
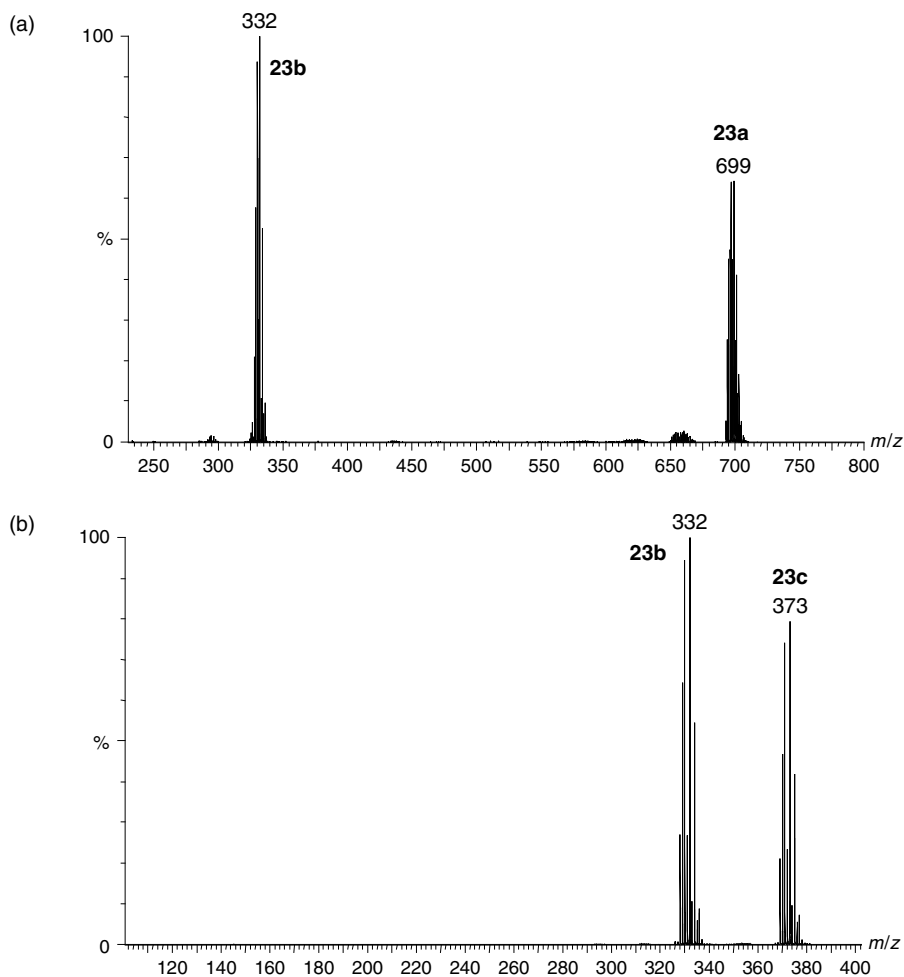
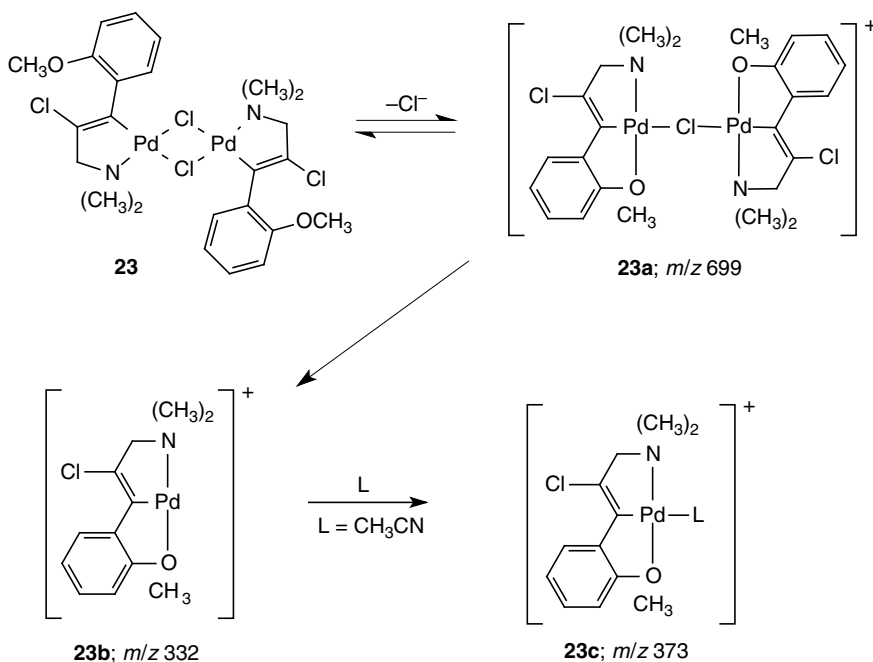


Fig. 1.2. ESI(+)-MS/MS spectra of (a) **10c** (ionic cluster centred at m/z 729), (b) **10b** (m/z 389) and (c) **10a** (m/z 348).



Scheme 1.13

Fig. 1.3. ESI-MS/MS spectra of (a) **23a** of m/z 699 and (b) **23c** at m/z 373.



Scheme 1.14

of catalytically active Pd(0) species, and this behaviour was recently addressed in an outstanding review [41]. In this manuscript, we will review the applications of pincer palladacycles as catalyst precursors for C–C coupling reactions.

1.4.2 Heck Coupling

As already pointed out, since the introduction of Herrmann's palladacycle, as a robust and effective catalyst precursor for the arylation of alkenes, a plethora of cyclopalladated compounds have been successfully used in this C–C bond coupling reaction. In fact, almost any palladacycle can promote the coupling of iodo- and bromo-arenes, with alkenes (in most of the cases, methylacrylate or styrene is used as the model alkene) at relatively elevated temperatures ($<100^\circ\text{C}$) with a base (usually tertiary amines or sodium acetate) and additives such as tetrabutylammonium bromide (Scheme 1.15).

Turnover numbers (TON) in these cases are usually in the order of 10^4 – 10^6 cycles. Phosphorus-, nitrogen- and sulphur-containing pincer palladium complexes containing mono-anionic six-electron metallated ligands (Scheme 1.16) are emerging as a new class of efficient and simple catalyst precursors for various reactions [42–46]. Indeed, pincer palladacycles with donor ligands of the type YCY ($Y = \text{NR}_2$, SR and PR_2) [2, 3, 5–7, 47–51] are among the most effective catalyst precursors for C–C couplings such as Heck and Suzuki reactions.

However, it is well known that under the reaction conditions (temperatures above 100°C), even palladium ultra-traces in reaction vessels can promote the coupling of iodo- or bromo-arenes [52]. In this respect, palladacycles are most likely to serve as

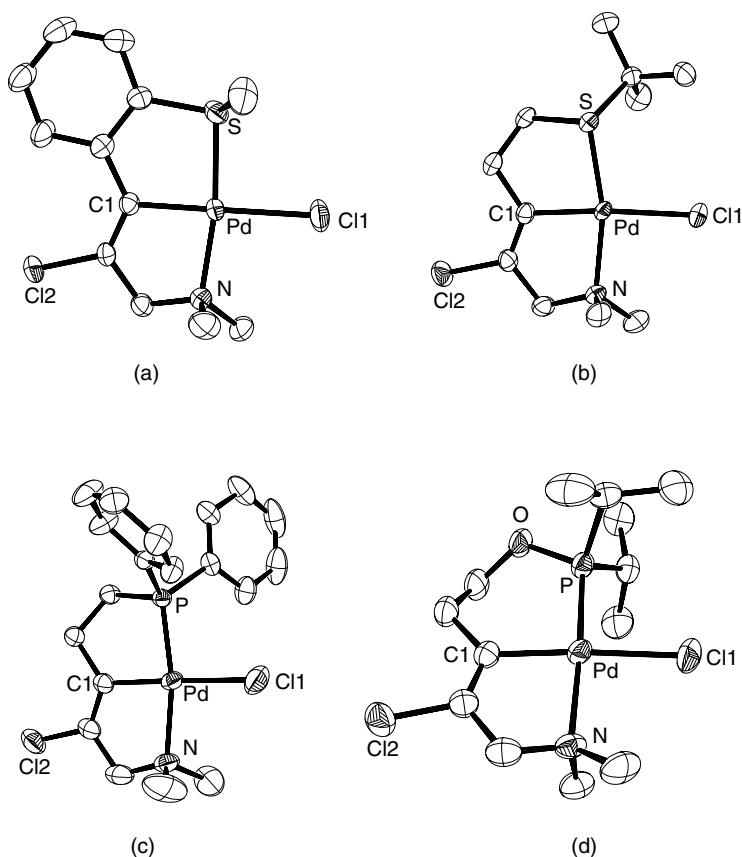


Fig. 1.4. ORTEP diagrams for palladium pincer complexes (a) **10**, (b) **12**, (c) **14** and (d) **15**. Hydrogen atoms have been omitted for clarity.

a source of catalytically active Pd(0) species that are similar to those formed in the denominated phosphine-free catalytic systems, and the reaction is likely to follow the classical Pd(0)/Pd(II) catalytic cycle [53–55]. The catalytic activity differences observed with these different palladacycle precursors have been rationalized in terms of catalyst pre-activation [56, 57]. It has been proposed that the key step in these cases is the slow release of a low-ligated active Pd(0) species. Therefore, the most efficient palladacycles will be those where the release of active Pd is neither too fast (typical of poorly thermally stable palladacycles that preferentially result in the formation of inactive metallic palladium) nor too slow (typical of thermally robust palladacycles, which would require higher temperatures to start the reaction in order to maintain a reasonable reaction rate). The catalytic performances of these pincer palladacycles are strongly dependent the nature of the donor group. For example, the phosphinito PCP pincer complex $[\text{PdCl}\{\text{C}_6\text{H}_3(\text{OP}^i\text{Pr}_2)_2-2,6\}]$ effectively promotes the coupling of deactivated chloro-arenes, such as 4-chloro-anisole, with styrene under relatively drastic reaction conditions (Table 1.1, entry 1), whereas the $[\text{PdCl}\{\text{C}_6\text{H}_3(\text{CH}_2\text{Y})_2-2,6\}]$ ($\text{Y} = \text{PR}_2$, NMe_2 and SR) analogues are only marginally active [58].

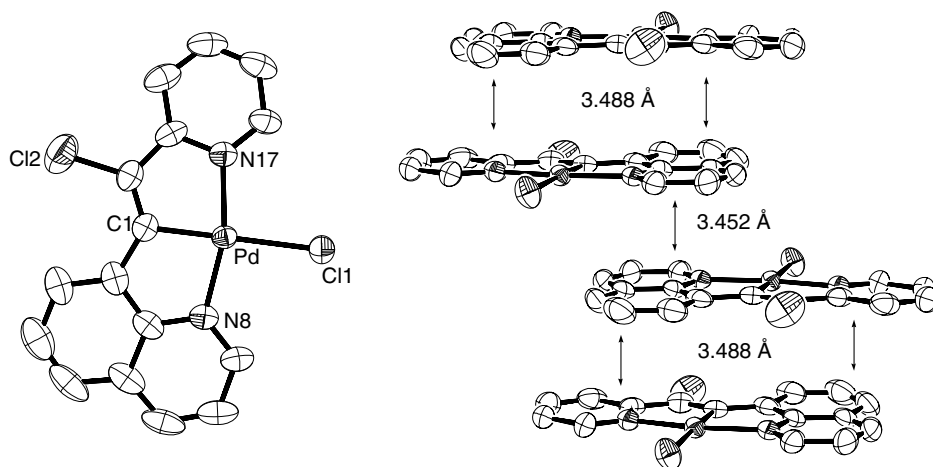


Fig. 1.5. ORTEP diagram and packing structure for palladium pincer complex **25**.

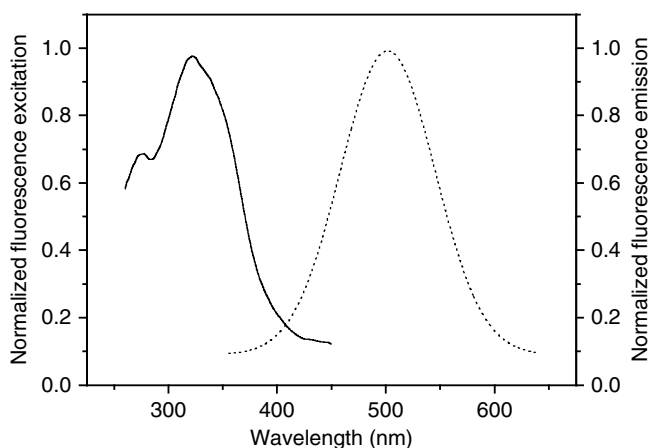
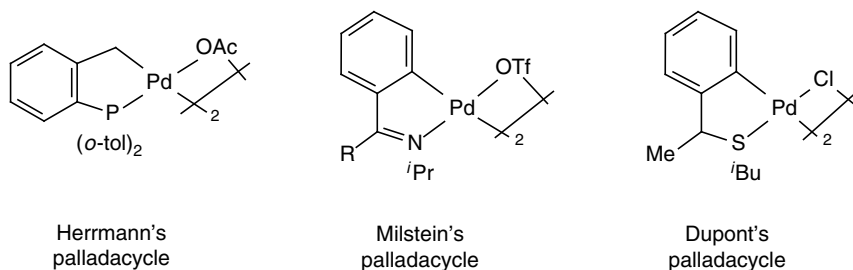
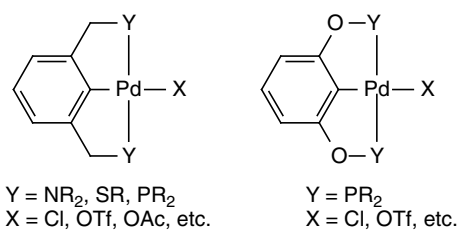


Fig. 1.6. Normalized solid state fluorescence spectra of the Pd complex.

On the other hand, the simple dimeric N-containing palladacycle derived from the chloropalladation of *N,N*-dimethyl-1-phenyl propargyl amine promotes the coupling of iodo-arenes and activated bromo-arenes (substituted with electron-withdrawing groups), with acrylates and styrene at room temperature (Table 1.1, entry 3) [59]. Moreover, it was recently reported that adducts resulting from the ciation of dimeric nitrogen-containing palladacycles with carbenes [60] or secondary and tertiary phosphines [61–63] generate highly active catalyst precursors for C–C and C–N couplings. These catalyst precursors combine the stability due to the presence of a palladated unit with the steric and electronic properties associated with phosphorus and carbene ligands. Structurally, these complexes possess two different donor groups (amine, phosphine and phosphite) connected only through the metal centre. Deactivated chloro-arenes, such as 4-chloro-anisole, can react

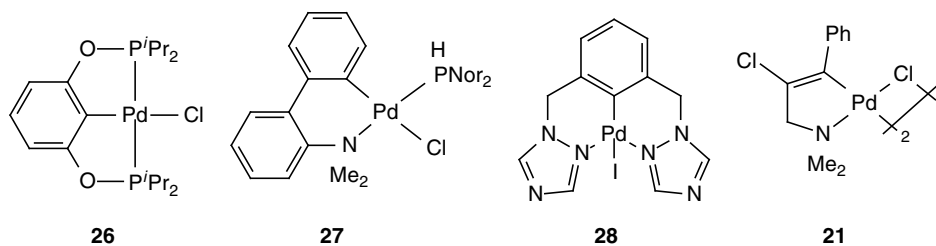


Scheme 1.15



Scheme 1.16

Table 1.1. Catalytic performance of selected palladacycles in the Heck coupling reaction



Entry	Pd (%)	Alkene	ArX	T (°C)	t (h)	Yield (%)	TON	References
1	26 (0.67)		C ₆ H ₅ Cl	180	24	99	147	[3]
2	21 (0.01)		4-NO ₂ C ₆ H ₄ Cl	150	24	100	1000	[59]
3	21 (1.0)		C ₆ H ₅ I	RT	24	100	100	[59]
4	27 (1.0)		4-MeOC ₆ H ₄ Cl	140	20	100	100	[62]
5	28 (0.5)		4-NO ₂ C ₆ H ₄ Cl	140	15	89	89	[64]

Table 1.2. Catalytic performance of unsymmetrically substituted palladium pincer complexes in the Heck coupling reaction

Entry	Pd	ArX	Base	T (°C)	Yield (%)	TON	References
1	25	4-MeC ₆ H ₄ Br	Na ₂ CO ₃	150	72	72 000	[65]
2	14	4-MeC ₆ H ₄ Br	Na ₂ CO ₃	150	100	100 000	[34]
3	11	4-MeC ₆ H ₄ Br	Na ₂ CO ₃	150	18	1800	[65]
4	15	4-MeOC ₆ H ₄ Br	Na ₂ CO ₃	150	37	3700	[65]
5	25	4-MeCOC ₆ H ₄ Cl	Na ₂ CO ₃	150	95	95	[65]
6	14	4-MeCOC ₆ H ₄ Cl	Na ₂ CO ₃	150	47	47	[34]

in the presence of these catalyst precursors giving the Heck coupling products in high yields (Table 1.1, entry 4).

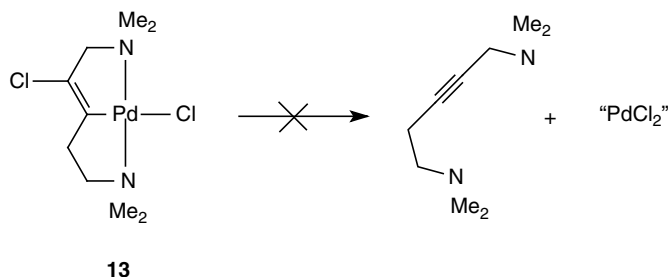
We initially investigated the catalytic performance of our palladium pincer complexes in the coupling of bromo-arenes with *n*-butylacrylate. In contrast to the well-known base/additive NaOAc/N(^{*n*}Bu)₄Br, which represents the best combination for our dimeric palladacycles, it became clear during our studies that Na₂CO₃ is a superior base and the addition of the N(^{*n*}Bu)₄Br additive has a detrimental effect on the catalytic activity of pincer complexes. Complexes **25** and **14** are quite superior catalyst precursors when compared with the sulphur and phosphinite pincer analogues **12** and **15**. Bromo-arenes substituted with both electron-withdrawing and electron-donating groups are efficiently coupled with *n*-butylacrylate using very low catalyst precursor loadings (Table 1.2, entries 1–4). This catalytic performance is similar to those obtained using, as catalyst precursors, phosphine adducts of N- and P-containing palladacycles, under comparable reaction conditions.

Although the coupling reaction can be performed using chloro-arenes substituted with electron-withdrawing groups, affording *trans*-cinnamates in modest to good yields (Table 1.2, entries 5 and 6), the reaction completely fails with non-activated and deactivated chloro-arenes such as 4-chloro-anisole.

No coupling product is observed when the reaction of iodo-arenes with alkenes is performed at room temperature using the unsymmetrically substituted palladium pincer complexes as catalyst precursors. This latter result is in sharp contrast to the catalytic behaviour of the simple dimeric palladacycle **21**, which promotes the coupling of activated bromo- and iodo-arenes with alkenes at room temperature [59]. The differences observed in the catalytic activities of different palladacycles can be correlated with the rate of the release of the catalytically active Pd(0) species [54, 56, 66]. It is highly probable that in the case of the relatively high thermally robust palladium pincer complexes (it starts to decompose only at temperatures above 140°C), a higher temperature is necessary to start the reaction and to maintain a reasonable rate [67–69].

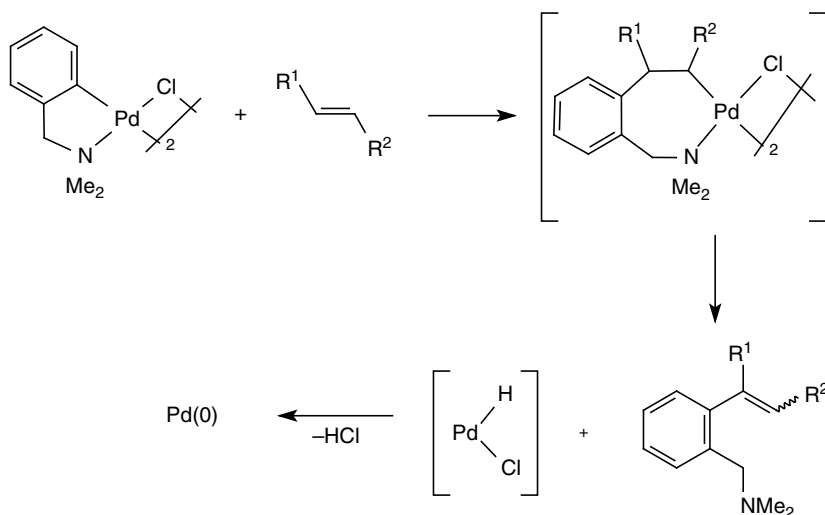
Further indication of the high thermal stability of this class of compounds was obtained through the investigation of the catalytic performance of the pincer palladacycle **13**. This compound, in opposition to **21**, is much more reluctant to undergo retro-chloropalladation under the conditions investigated (up to 120°C in DMSO) (Scheme 1.17). As expected, when using the pincer palladacycle **13**, only a 7% yield was recorded for the coupling of iodobenzene with *n*-butylacrylate at 30°C after 24 h (PhI/Pd = 100).

Although there is a legion of catalytic tests for the Heck coupling promoted by a plethora of palladacycles, little attention has been paid to the species involved and

**Scheme 1.17**

ultimately to reaction mechanism. However, observations over the years from different studies indicate that the Heck reaction promoted by palladacycles occurs through the classical Pd(II)/Pd(0) catalytic cycle. It is important to note that the formation and isolation of a Pd(IV) species through the oxidative addition of PhI with a P-containing palladacycle was claimed, but the manuscript was retracted 2 years after its publication [70].

The involvement of Pd(0) in the coupling of aryl halides with alkenes was evidenced by positive mercury poisoning tests in the reactions promoted by N- [59] and P-containing [71] palladacycles. The formation of the catalytically active Pd(0) species from palladacycles probably results from an olefin insertion into Pd–C bond of the palladacycle followed by beta-hydride elimination and reductive elimination (Scheme 1.18) [72, 73].

**Scheme 1.18**

Despite the greater stability of pincer complexes, evidence for the involvement of active Pd(0) species in the Heck reaction of phenyl halides with styrene promoted by a series of PCP palladium pincer complexes was found. Induction periods, formation

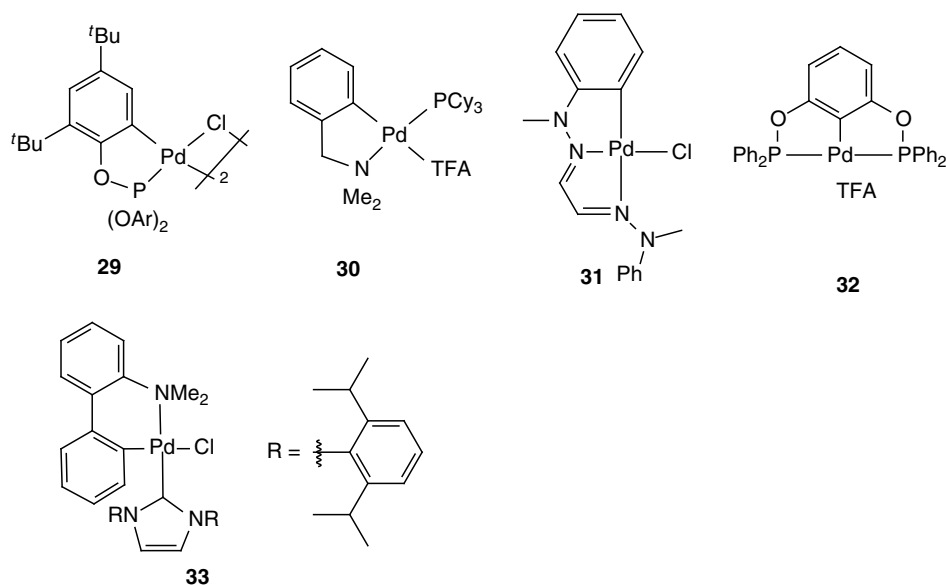
of palladium black, poisoning experiments (Hg, CS₂, thiophene and PPh₃) and NMR studies were used to show that these complexes are catalyst precursors for highly active forms of metallic palladium [71].

Recently, we have shown that pincer palladium complexes solutions in acetonitrile present appreciative amounts of cationic species that may be involved in the generation of the catalytically active species [33]. The ESI-MS/MS spectrum of gaseous cation shows a dissociation route involving HCl elimination and loss of palladium atoms. The probable decomposition pathway is described in Scheme 1.13.

Interestingly, dimeric palladacycles and palladium pincer complexes were also tested in Hammett competitive experiments in the Heck reactions of bromo- and iodo-arenes with *n*-butylacrylate [34], and no significant changes were observed for the Hammett parameters obtained with different palladium sources, indicating that the same active species are in operation. It was also demonstrated that the oxidative addition step is responsible for the substituent effect on the reaction rate in competitive experiments performed with different bromo- and iodo-arenes even if oxidative addition is not the rate-limiting step.

1.4.3 Suzuki Cross-Coupling

Palladacycles are also quite efficient catalyst precursors for the coupling of arylboronic acids and aryl halides under relatively mild reaction conditions [74, 75]. In fact, almost any palladacycle promotes the coupling of bromo- or iodo-arenes, with arylboronic acids at temperatures above 80°C depending on the nature of the base and the solvent. Of note, TONs up to 1 000 000 have been achieved in the coupling of phenylboronic acid, with 4-bromoacetophenone in toluene using K₂CO₃ as base at 110°C promoted by the phosphinito palladacycle **29** [76] (Scheme 1.19).



Scheme 1.19

Table 1.3. Catalytic activity of some pincer palladium complexes that promote the Suzuki coupling between phenylboronic acids and halo-arenes

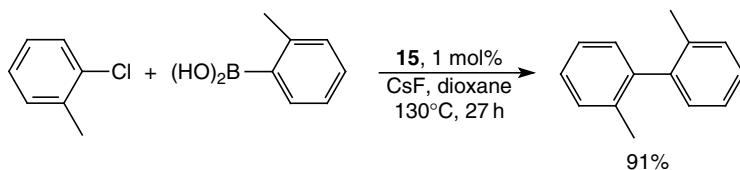
Entry	Pd	[Pd] (%)	ArX	T (°C)	t (h)	Yield (%)	TON	References
1	15	0.5	4-MeOC ₆ H ₄ Cl	130	27	85	170	[81]
2	30	0.01	4-MeOC ₆ H ₄ Cl	100	17	80	8000	[61]
3	31	2.0	4-MeOC ₆ H ₄ Br	RT	3	89	45	[82]
4	32	0.01	4-NO ₂ C ₆ H ₄ Cl	130	18	43	4300	[4]
5	26	1.0	4-MeOC ₆ H ₄ Cl	100	20	95	95	[62]
6	33	2.0	2-MeC ₆ H ₄ Cl	RT	1.5	95	47	[83]

This result is not exceptional because the Suzuki coupling involving bromo- and iodo-arenes substituted with electron-withdrawing groups is promoted by almost any palladium salt or complex such as palladium acetate even at room temperature [77]. These exceptionally high turnover numbers obtained for these substrate combinations suggest that it is not a useful benchmark to test new catalysts in Suzuki couplings [78].

The main challenges in Suzuki coupling pertain to the use of less reactive aryl halides such as chloro- and bromo-arenes substituted with electron-donating groups, under relatively mild reaction conditions, and in these cases, only a few palladium pincer complexes have displayed catalytic activity (Table 1.3). The phosphinite pincer palladium complex **32** was tested in the cross-coupling of activated chloro-arenes with PhB(OH)₂ [4] (0.01 mol% Pd, toluene, 130°C) affording poor yields, and its performance was inferior to that of simple phosphinite palladacycles.

Of note is that the best results for the coupling of arylboronic acids with chloro-arenes were obtained with phosphapalladacycles or with palladacycles modified with carbenes or phosphorus containing ligands (Table 1.3, entries 5 and 6). This could be related to the extra stability provided by these ligands towards the low-ligated catalytically active Pd(0) species involved in the main catalytic cycle [41].

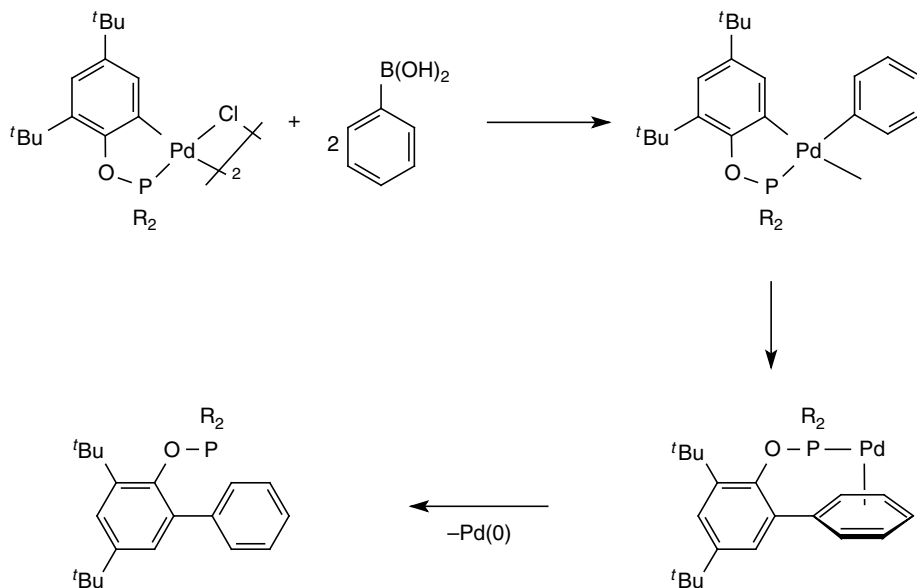
The phosphinite pincer palladium complex **15** is a highly efficient catalyst precursor for the coupling of boronic acids with chloro-arenes. Both electron-rich and electron-poor chloro-arenes are efficiently coupled in the presence of **15** to yield the corresponding biaryl products in excellent yields. A wide variety of functional groups are tolerated in both aryl chloride and aryl boronic acid, and hindered biphenyls can be synthesized with high yields (Scheme 1.20). This is one of the best reported systems in the literature, being one of the most active palladium pincer complex for Suzuki couplings.

**Scheme 1.20**

Structurally, this complex can be compared with phosphine or phosphite adducts of dimeric nitrogen-containing palladacycles [62] with an additional covalent connectivity

between the two donor groups. Apparently, this structural modification in the non-symmetrical pincer palladacycle **15** is able to lead to significantly more stable catalytic systems and better yields when compared with the analogous phosphine adducts.

As observed in Heck coupling reactions, the catalytically active species are probably Pd(0) species formed through a reductive elimination process between the palladated ligand and the arylboronic acid derivative (Scheme 1.21) [79, 80].

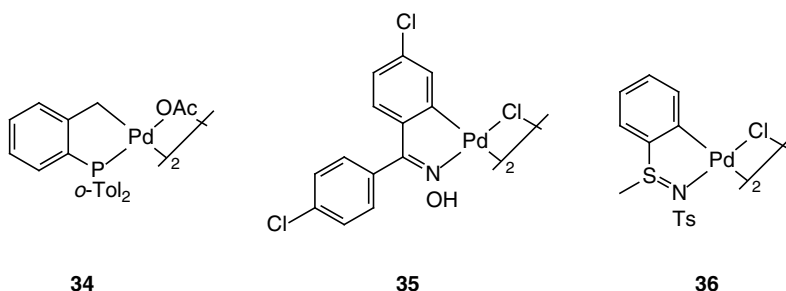


Scheme 1.21

1.4.4 Sonogashira Coupling

Palladacycles have proved to be useful and versatile catalyst precursors for the Sonogashira coupling reaction. As noted in the Suzuki reaction section, the best results for the activation of chloro-arenes were obtained with phosphapalladacycles or with imine palladacycles (Table 1.4, entries 1–5). There are only a few examples of Sonogashira coupling reactions promoted by CN palladacycles, and in these cases, only marginal catalytic activities were obtained with less reactive chloro-arene substrates. Despite the poor activity with chloro-arene substrates, CN palladacycles are exceptional catalyst precursors for promoting Sonogashira couplings with iodo- and bromo-arenes in copper-free conditions, and a huge TON of 400 000 can be achieved in the Sonogashira coupling of iodobenzene with phenylacetylene promoted by dimeric palladacycle **21** (Table 1.4, entries 6 and 7).

We have tested our palladium pincer complexes as catalyst precursors for Sonogashira couplings, and similar to the results for the Heck coupling reaction, no coupling product was observed when the reaction of iodo-arenes with acetylenes was performed at room temperature. High temperatures are necessary to activate the catalyst precursor and initiate the Sonogashira coupling reaction. Using the best reaction conditions, iodobenzene

Table 1.4. Palladacycles in catalytic C–C and C–N bond formation

Entry	Pd	Substrates	Conditions	Yield (%)	TON	References
1	36	PhI, HC≡CPh	NEt ₃ , 80°C, 12 h	84	336	[84]
2	36	PhBr, HC≡CPh	NEt ₃ , 80°C, 12 h	25	100	[84]
3	35	PhI, HC≡CPh	NMP, NBu ₄ OAc, 110°C, 24 h	72	72 000	[85, 86]
4	35	4-MeOPhBr, HC≡CSi(<i>i</i> -Pr) ₃	NMP, NBu ₄ OAc, 130°C, 1 h	85	340	[85]
5	34	4-COMePhBr, HC≡CPh	NEt ₃ , 90°C, 5 h	99	990	[87]
6	21	PhI, HC≡CPh	DMA, NBu ₄ OAc, 130°C, 24 h	82	410 000	[88]
7	21	PhI, HC≡CPh	DMA, NBu ₄ OAc, 30°C, 4 h	100	100	[88]
8	25	PhI, HC≡CPh	DMA, NBu ₄ OAc, 130°C, 24 h	97	480 000	[65]

and phenylacetylene react to give the Sonogashira product in almost quantitative yields with an unprecedented catalytic activity (Table 1.4, entry 8). Bromo-arenes and chloro-arenes fail to react under the conditions tested.

1.5 CONCLUSIONS AND TRENDS

The *trans*-chloropalladation of disubstituted alkynes is a simple and efficient method for the construction of various types of pincer palladacycles that cannot be prepared or are easily available from other synthetic methods such as C–H bond activation, oxidative addition or transmetalation. In particular, various functional donor groups can be introduced in the metallated fragment, such as amines, pyridine, thioethers, phosphines and phosphinites. This method allows the preparation of totally flat compounds that possess interesting photophysical properties in the solid state at room temperature. Pincer complexes containing both N- and P-donor groups are among the most efficient catalyst precursors that promote the C(Csp²)–C(sp²) coupling reaction involving less reactive chloro-arenes. In view of the large number and variety of disubstituted alkynes that are easily prepared from a plethora of methods and that may undergo the halopalladation reaction, the number of tailor-made pincer-type palladacycles with specific properties is almost endless.

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Synthesis and transformation of allyl- and allenyl-metal species by pincer complex catalysis

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2.1 INTRODUCTION

Palladium-catalyzed transformations have been very successfully employed for synthesis and transformation of unsaturated organometallic compounds [1–6]. Allyl and allenyl stannanes, silanes and boranes are considered as masked carbanions, and therefore, these compounds are important building blocks in advanced organic synthesis and natural product synthesis [4–6]. In fact, there are also several palladium-catalyzed transformations applying these compounds as precursors [5–7]. Because palladium complexes are able to either create or cleave carbon–metal (such as C–Sn, C–Si and C–B) bonds, control of the selectivity of these transformations is usually a complicated issue. In palladium chemistry, selectivity-related problems can be efficiently solved by employment of appropriate ligands on the metal. Certain ligand effects may lead to activation of the catalysts for carbon–metal bond formation; however, when synthesis of organometallic compounds is desired, other types of ligand effects can be employed to hinder the cleavage of the formed carbon–metal bonds. A primary requirement in these transformations is that palladium and the applied ligand are firmly kept together, otherwise the desired ligand effects cannot be efficiently transmitted to the catalyst leading to formation of organic by-products or to very slow reaction. In this respect, application of pincer complex [8–14] catalysts offers several attractive features.

The most efficient catalysts in these processes are PCP (**1–3**), NCN (**4**) and SeCSe (**5**) type of pincer complexes characterized by the following structural and electronic features: (1) There is a strong ligand–metal interaction preventing ligand exchange processes; (2) As three of the coordination sites of palladium are kept engaged by the terdentate coordination, there is only one free site available for external ligands; and (3) Under ambient conditions, the oxidation state of palladium is largely restricted to +2.

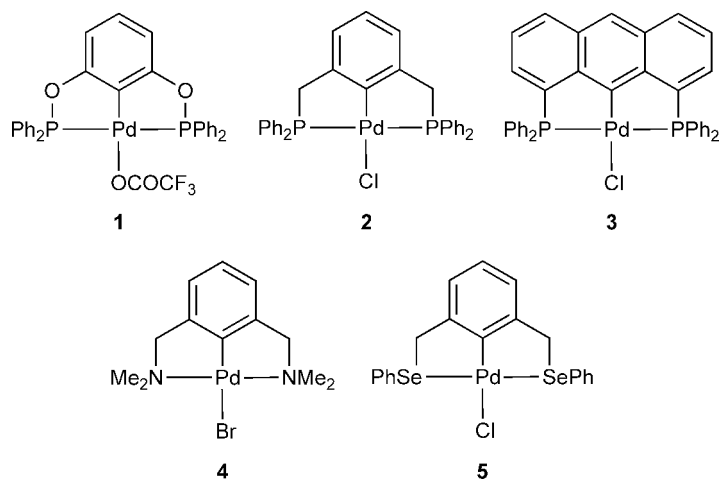


Fig. 2.1. Palladium pincer-complexes catalyzing synthesis and transformation of organometallic compounds.

This chapter describes a couple of recently developed palladium pincer complex-catalyzed reactions for allylation of aldehyde and imine substrates including asymmetric catalysis (Section 2.2), synthesis of allyl stannanes and boronates and preparation of allenyl stannanes and silanes (Section 2.3). A brief discussion of the experimental and theoretical mechanistic aspects of these reactions is also provided (Section 2.3.6).

2.2 PALLADIUM-CATALYZED ALLYLATION OF ELECTROPHILES

Although palladium-catalyzed allylation of nucleophiles is one of the most established area in transition metal catalysis [1–3], recently, allylic substitution of electrophilic reagents [7, 15–24], including aldehydes, imines and various Michael acceptors attracted a broad interest. The key step of this process (Fig. 2.2) involves an electrophilic attack on the η^1 -coordinated allyl moiety of the bis-allylpalladium intermediate (**6**) of the reaction [19], which is generated from a mono-allylpalladium complex and allyl stannane [15]. In the TS of the reaction (**8**), the nucleophilicity of the η^1 -allyl moiety is increased by the electron-supplying η^3 -allyl moiety of palladium. Accordingly, the η^3 -allyl moiety in **6** and **8** can be considered as a strongly electron-donating spectator ligand activating the η^1 -allyl group in the electrophilic substitution process.

Although the above electrophilic substitution reactions are useful transformations for catalytic carbon–carbon bond formation reactions, the diverse reactivity of bis-allylpalladium intermediates (**6**) imposes considerable limitations to the reactions. For example, the control of the regioselectivity is problematic in case of substituted allyl moieties in **6** [20, 21, 25]; and bis-allylpalladium complexes (**6**) may undergo allyl–allyl coupling instead of coupling with electrophiles [17, 26]. An efficient solution to avoid these complications would be the replacement of the η^3 -allyl (spectator) ligand of bis-allylpalladium complexes with another one possessing the same electronic properties. In this respect, application of pincer ligands represents an interesting alternative. For

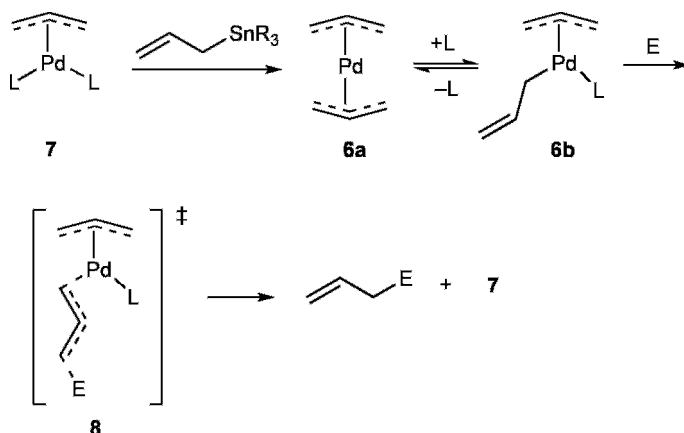


Fig. 2.2. Palladium-catalyzed electrophilic substitution via bis-allylpalladium intermediate.

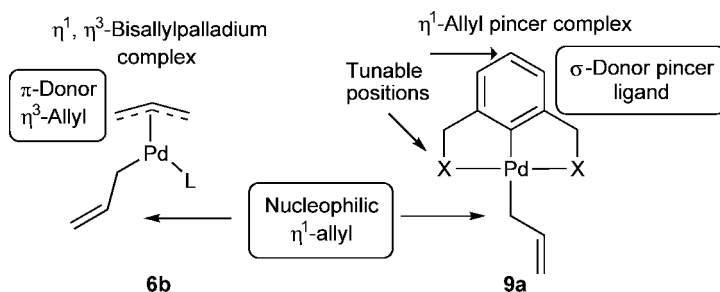


Fig. 2.3. Comparison of bis-allylpalladium and pincer-allyl complexes.

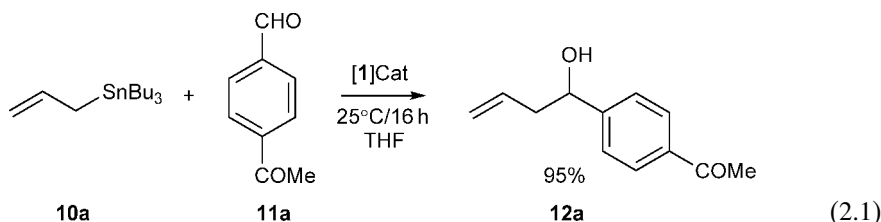
example, the pincer ligand in PCP complexes **1–3** is a good σ -donor because of the (aromatic) carbon–palladium bonding (Fig. 2.3), and therefore, it may replace the η^3 -allyl moiety of **6b** without decreasing the nucleophilicity of the η^1 -allyl moiety (**9a**).

Another advantage of using a pincer ligand in these species is that the η^1 -allyl moiety is not able to undergo dynamic $\eta^1 \rightarrow \eta^3$ rearrangements, as only a single coordination site is available on palladium in **9a**. Thus, in the pincer complex-catalyzed electrophilic allylation reactions, several limitations of the catalytic transformations via bis-allylpalladium complexes can be avoided.

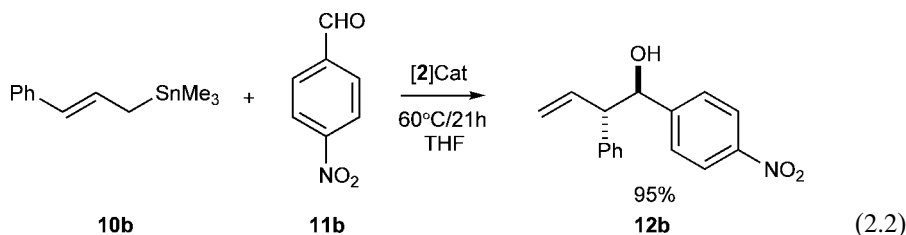
2.2.1 Pincer Complex-Catalyzed Coupling of Allyl Stannanes with Aldehydes

Several PCP pincer complexes (such as **1–3**) proved to be efficient catalysts in allylation of various aldehydes (Eqns 2.1 and 2.2) [27, 28]. Phosphite-type pincer complex **1** displayed higher catalytic activity than its phosphine analogs **2** and **3**. The reactions proceed under mild conditions, typically at 25°C with **1** and 40–60°C with **2** and **3**, without additives. Therefore, the reaction has a broad synthetic scope including the parent allyl stannane **10a** and substituted analogs (such as **10b**), as well as both aromatic

and aliphatic aldehydes. The functional group tolerance of the reaction is very high. For example, the aldehyde functionality of **11a** can be allylated in the presence of the keto group (Eqn 2.1).

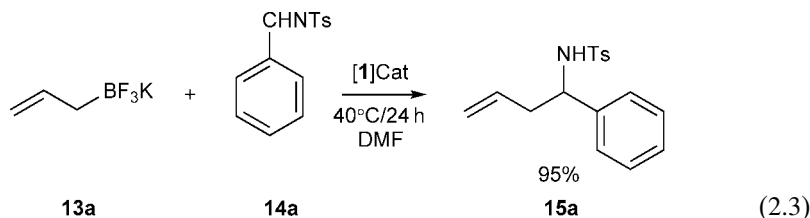


Phenyl-substituted stannane **10b** reacts with a high selectivity, providing the branched allylic product with anti-stereoselectivity. On the contrary, in the presence of less bulky substituents in the allyl stannane, such as methyl group, the regioselectivity is still high; however, the stereoselectivity of the reaction is poor [28].



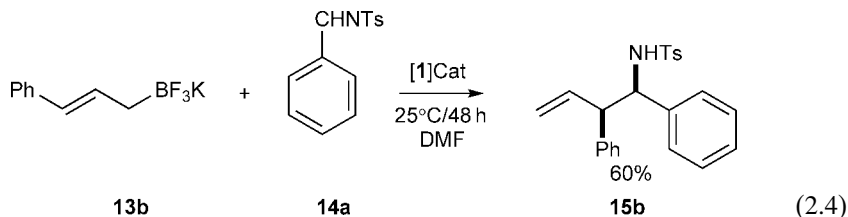
2.2.2 Trifluoro(allyl)borate as Allylating Agent

The pincer complex-catalyzed allylation reaction can be extended to sulfonimine substrates (e.g. **14a**) using trifluoro(allyl)borate (**13a–b**) substrates in place of allyl stannanes (**10a–b**). These reactions (Eqns 2.3 and 2.4) are suitable for synthesis of homo-allyl amines under mild reaction conditions [29, 30]. The reactivity of allyl trifluoro(allyl)borates is slightly higher in these reactions than in the corresponding allyl stannanes [30].



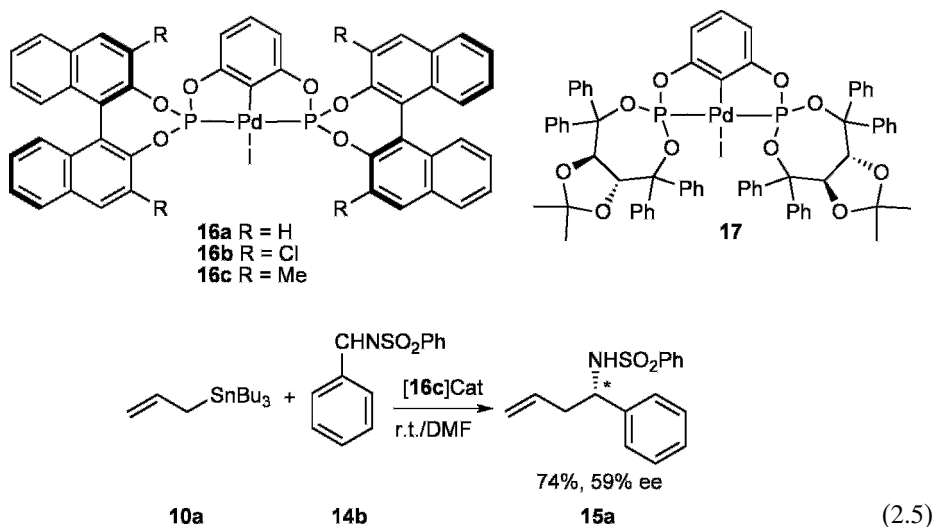
Phenyl-substituted allyl borates, such as **13b**, react with high regio- and stereoselectivity in these catalytic transformations (Eqn 2.4). Interestingly, the major diastereoisomer is the *syn* form **15b**. The different diastereoselectivity of the allylation of aldehydes

(Eqn 2.2) and sulfonimines (Eqn 2.4) suggests that the mechanism of the stereoselection (see Section 2.2.4) is different in these processes.



2.2.3 Application of Chiral Pincer Complex Catalysts for Allylation of Sulfonimines

Development of catalytic asymmetric allylation reactions is a challenging task in organic synthesis, as in these processes the stereogenic carbon is created via enantioselective carbon–carbon or carbon–heteroatom bond formation [31, 32]. Development of new methods for selective allylation of imines is particularly important, as these substrates are more difficult to allylate than aldehydes, and therefore, relatively few efficient enantioselective processes are available [16, 33–37]. As the above-presented transformations (Sections 2.2.1 and 2.2.2) create a new stereogenic carbon, asymmetric electrophilic allylation of sulfonimines is expected to occur by employment of chiral pincer complex catalysts [38]. This type of reactivity and selectivity was investigated by synthesis and application of BINOL- (**16**) and TADDOL-based pincer complexes (**17**).

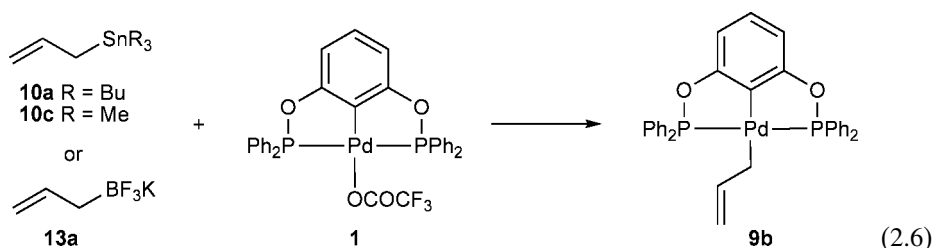


These complexes proved to be active catalysts for allylation of sulfonimine **14b** with **10a** (Eqn 2.5) [38]. Although the reaction proceeds with relatively poor enantioselectivity using the parent BINOL-based complex **16a** (20% ee) and TADDOL-based complex

17 (5% ee), the selectivity can be considerably increased by increasing the steric bulk of the substituents at the γ -position of the BINOL ligand, such as in **16b** and **16c**. So far, the highest ee was achieved using the Me-substituted analog **16c** (59% ee). The high stability of **16** is a particularly important feature. It was found that this complex survives the catalytic reaction without any decomposition, suggesting that a highly durable easily recyclable catalyst can be obtained by immobilization of **16** and its derivatives.

2.2.4 Mechanism of the Pincer Complex-Catalyzed Electrophilic Allylic Substitution

The mechanism of the pincer complex-catalyzed allylation reaction was studied by stoichiometric reactions [28, 30] involving complex **1** and allyl stannanes **10a** and **10c** as well as allyl boronate **13a** (Eqn 2.6). Analysis of the ^1H -NMR spectrum of these reaction mixtures clearly showed that η^1 -allyl-coordinated pincer complex **9b** is readily formed by transmetalation of the allyl-metal species (**10a**, **10c** and **13a**) with palladium. Interestingly, formation of **9b** from allyl stannanes **10a** and **10c** is an equilibrium process [28], whereas the corresponding transmetalation with allyl boronate **13a** is irreversible [30].



Considering the results of the above studies, the catalytic cycle of the reaction is initiated by transmetalation of **10a**, with pincer complex **1** affording η^1 -allyl complex **9b** (Fig. 2.4). Subsequently, the η^1 -allyl moiety of **9a** undergoes electrophilic attack with the aldehyde substrate **11** (or a sulfonimine substrate) to give complex **9c**, which after decomplexation provides primary product **18** and regenerates catalyst **1**.

The transfer of the allyl moiety from palladium to the organic substrate (e.g. **9b** $\rightarrow$ **9c**) is one of the most important steps of the reaction, as it determines the regio- and stereoselectivity of the allylation reactions, when substituted allyl reagents (such as **10b** and **13b**) are applied. To understand the mechanism of the allyl transfer and the development of the selectivity in these reactions, DFT modeling studies were carried out [28, 30].

As pointed out above, the stereoselectivity of the pincer complex-catalyzed allylation of aldehydes and imines is different (cf. Eqns 2.2 and 2.4). Thus, cinnamyl stannane gives predominantly the *trans* diastereomer with benzaldehyde [27, 28] (cf. Eqn 2.2) [28], whereas the *syn* diastereomer is formed in the reaction with sulfonimine **14b** (Eqn 2.4) [30]. The different stereoselectivity clearly indicates the important mechanistic differences between the two allylation processes. These mechanistic differences are

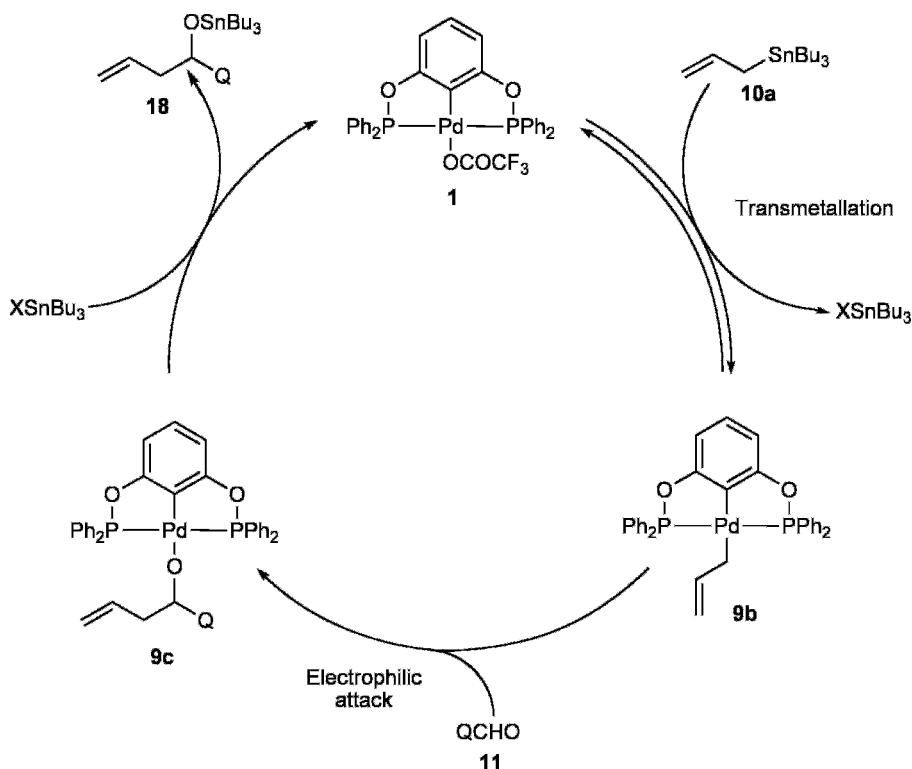
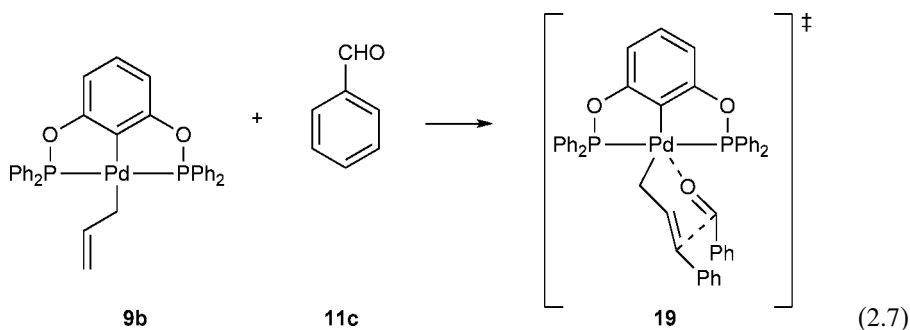
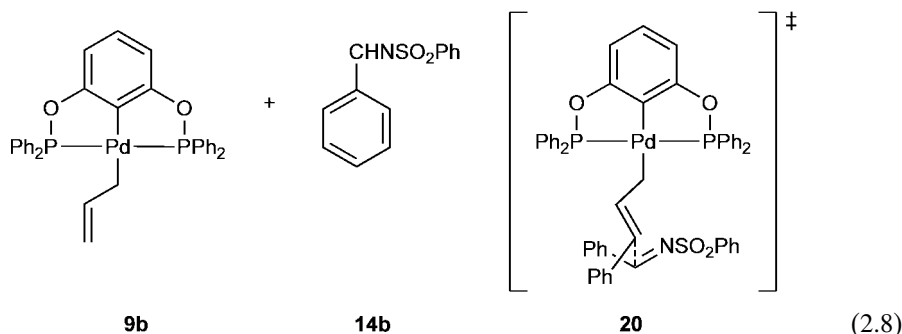


Fig. 2.4. Catalytic cycle for the pincer complex-catalyzed electrophilic allylation of aldehydes.



clearly pointed out by the DFT modeling studies. In the TS structure (**19**) of the allylation of aldehyde (Eqn 2.7), the negatively charged oxygen atom of the aldehyde unit coordinates to palladium [28]. This coordination leads to formation of a six-membered ring TS with a well-defined chair conformation. In case of allylation of the imine substrate (Eqn 2.8), the potential energy surface of the reaction is more complicated than for the allylation of aldehyde. In the lowest energy TS (**20**), the nitrogen atom of the sulfonimine unit does not coordinate to palladium because the negative charge is efficiently delocalized to the sulfonyl group [30]. Therefore, the sulfonimine substrate does not form a six-membered ring TS with the allyl moiety and palladium.



For allylation of imines, the main factor determining the stereoselectivity of the process is the steric interactions between the sulfonyl group and the pincer ligand leading to a *syn* diastereoselectivity. On the contrary, for the allylation of aldehydes, the stereoselectivity is determined by the steric interactions between the phenyl group of the benzaldehyde and the phenyl group of the allyl moiety in the six-membered TS structure favoring *trans* diastereoselectivity.

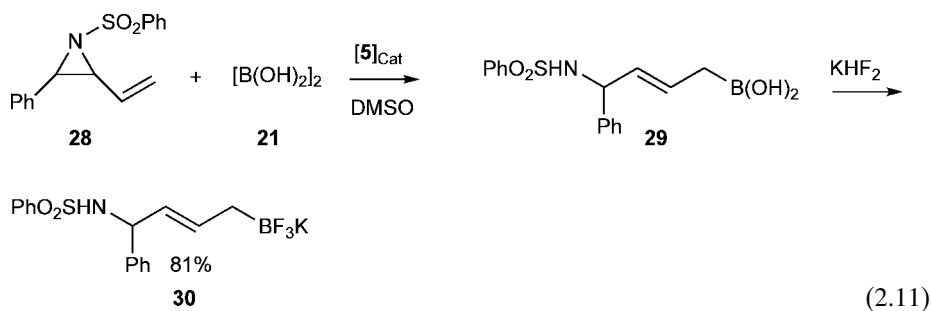
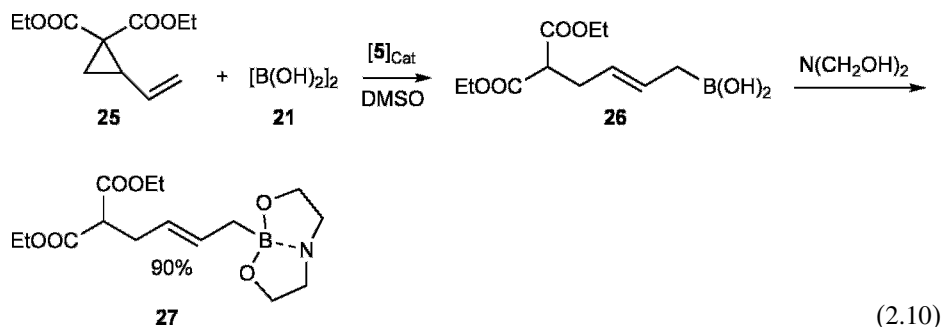
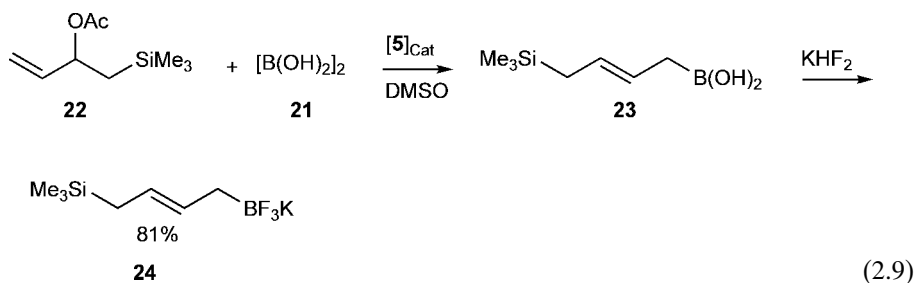
2.3 PINCER COMPLEX-CATALYZED SYNTHESIS OF ORGANOMETALLIC COMPOUNDS

Although commonly used palladium catalysts (such as $\text{Pd}(\text{PPh}_3)_4$ and $\text{Pd}_2(\text{dba})_3$) can be employed [5, 6] for synthesis of organometallic compounds, such as allyl stannanes [23, 39] and allyl boronates [40–43], a usual problem is that the employed catalyst further reacts [39, 40] with the reactive organometallic product, decreasing the yield and the selectivity of the process. As indicated above (Section 2.2), PCP complexes **1–3** are efficient catalysts for allylation of aldehydes and imines with allyl stannanes and allyl boronates involving cleavage of the carbon–tin and carbon–boron bonds (Eqn 2.6). Changing the heteroatoms in the side arms from phosphor to nitrogen (**4**), the catalytic activity for carbon–metal bond cleavage is considerably decreased [24, 28]. On the contrary, complexes **4** and **5** (Fig. 2.1) are highly active catalysts for carbon–tin and carbon–boron bond formation reactions [24, 44–47]. The different reactivity of **1–3** and **4–5** in the allylation process and metal (tin, boron and selenium) substitution reactions is an excellent example for the efficient tunability of palladium in pincer complexes by change of the heteroatoms in the side arms (Fig. 2.3).

2.3.1 Synthesis of Allylboronic Acids and Allyl Boronates

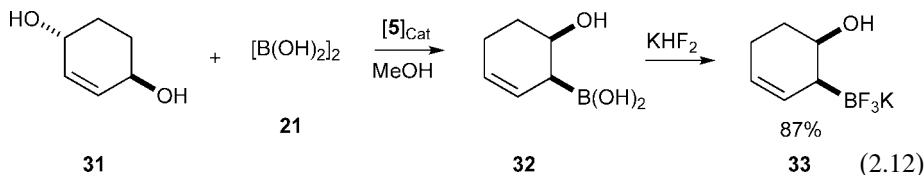
Miyaura and co-workers [40] have shown that allyl acetates can be converted to allyl pinacolboronates in the presence of bis(pinacolato)diboron using $\text{Pd}_2(\text{dba})_3$ catalyst. The allyl–allyl homocoupling of the product is a well-known side reaction of this catalytic transformation. Formation of this side-product can be explained by the reaction of allyl boronate product with allylpalladium intermediate **7** to give bis-allylpalladium complex **6**, which undergoes allyl–allyl coupling (cf. Fig. 2.2). As bis-allylpalladium complexes do

not form pincer complex intermediates, it was expected that formation of the allyl–allyl coupling product could be avoided. Indeed, SeCSe pincer complex **5** proved to be a very efficient catalyst in allylic boronation reactions using diboronic acid (**21**) as boron source (Eqns 2.9–2.12).



Functionalized allyl acetates (e.g. **22**) react smoothly with diboronic acid **21** to give allylboronic acid **23** without affecting the silyl functionality (Eqn 2.9) [46]. In this reaction, homoallyl coupling of **23** was not observed. Even activated vinyl cyclopropane (**25**) and vinyl aziridine derivatives (e.g. **28**) gave allylboronic acids under mild conditions in DMSO solvent (Eqns 2.10 and 2.11). Allylboronic acids (**23**, **26** and **29**) are

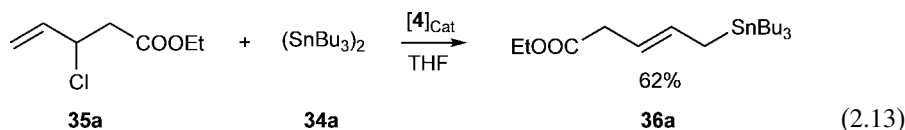
moisture- and air-stable compounds; however, they undergo rapid decomposition under solvent-free conditions [47]. Therefore, these compounds have to be used in solution directly after the boronation reaction [48], or they have to be converted to other more stable derivatives, such as trifluoroboronates (**23** or **30**) or allyl boronates (such as **27**) [46]. As shown in Section 2.2.2, trifluoroboronates can be employed in pincer complex (**1**)-catalyzed allylation of imines.



Interestingly, even allyl alcohols (such as **31**) can be employed as substrates in the boronation reactions (Eqn 2.12) [47]. The catalytic transformations can be carried out under mild conditions similar to the corresponding reactions of other substrates (Eqns 2.9–2.11); however, methanol has to be used as solvent or as a component of the reaction medium. This procedure can be exploited for synthesis of stereo- and regiodefined allyl boronates (such as **33**) from easily accessible and inexpensive allyl alcohols. An interesting feature of this reaction is that allyl alcohols are boronated faster than the corresponding allyl acetates under the same reaction conditions [47]. A possible explanation for this reactivity is that the reaction of allyl alcohols involves diboronic esters of the substrates as reactive intermediates [47].

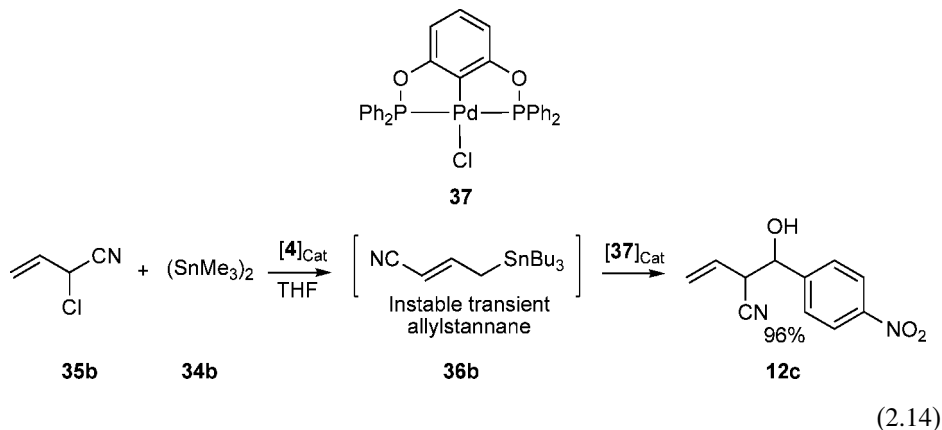
2.3.2 Pincer Complex-Catalyzed Synthesis of Allyl Stannanes

Similar to the boronation reactions, pincer complex (**4**)-catalyzed stannylation of allylic substrates can also be accomplished using hexaalkylditin (**34a**) as organotin source [24]. Using these procedures, allyl chlorides (such as **35a**), phosphonate and epoxide substrates can be converted to the corresponding allyl stannanes. The reaction shows a high functional group tolerance, providing stabilized allyl stannanes (e.g. **36a**) in relatively good isolated yield [24].



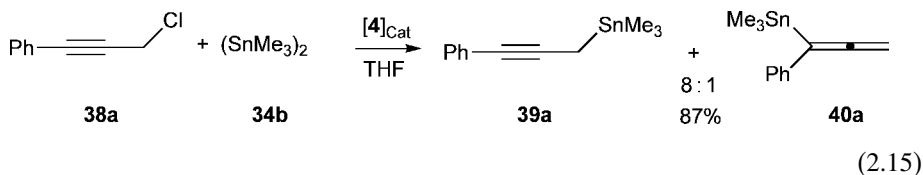
The purification of allyl-stannanes is usually rather cumbersome because of their low stability and high toxicity. In particular, allyl stannanes bearing electron-withdrawing groups in the allylic positions (e.g. **36b**) easily undergo polymerization and rapidly decompose under silica-gel chromatography. On the contrary, the NCN pincer complex (**4**)-catalyzed stannylation process can be combined with the PCP pincer complex (**37**)-catalyzed allylation of aldehyde and imine substrates (see Sections 2.2.1 and 2.2.2). This

reaction can be performed as a one-pot sequence via transient allyl stannanes (such as **36b**) providing homoallyl alcohols from allyl chlorides in high yield (Eqn 2.14).

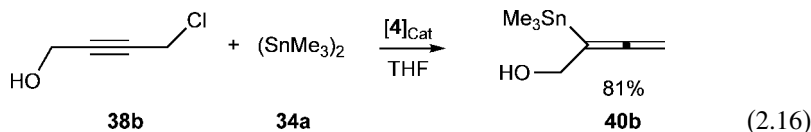


2.3.3 Stannylation of Propargylic Substrates

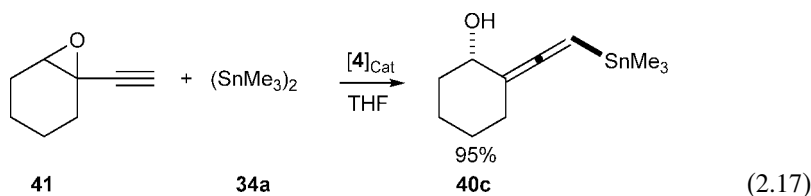
The palladium-catalyzed addition of hexaalkylditin (**34**) reagents to alkynes represents an important synthetic procedure for synthesis of vinyl distannane derivatives [49–53]. Application of usual palladium(0) catalysts (such as $\text{Pd}(\text{PPh}_3)_4$) in this process leads to oxidative addition of palladium to the tin–tin bond generating a bis-stannyl palladium(II) species [52], which then adds to the triple bond providing a disubstituted olefin product. As only a single coordination site is freely accessible on palladium in a pincer complex catalyst, formation of a bis-stannyl reagent is unlikely, and therefore, a completely different reactivity is expected. Indeed, it was found that using hexamethylditin (**34b**) with propargyl chloride (e.g. **38a**) or mesylate substrates and catalytic amounts (2.5 mol%) of pincer complex catalyst **4** leads to displacement of the propargylic-leaving group instead of addition of the trimethylstannane groups to the triple bond [44, 45]. Thus, this reaction leads to formation of propargyl or allenyl stannanes depending on the steric and electronic effects of the substituents attached to the triple bond.



In case of bulky electron supplying substituents, such as phenyl (**38a**) group, the main product of the reaction is propargylstannane **39a** (Eqn 2.15). Substrates with electron-withdrawing substituents give exclusively allenyl products. Interestingly, even subtle electronic effects have a strong influence on the regioselectivity of the stannylation process. For example, the hydroxymethylene group in **38b** has a weak electron-withdrawing effect, which is sufficient to direct the reaction toward exclusive formation of the corresponding allenyl product **40a** (Eqn 2.16).

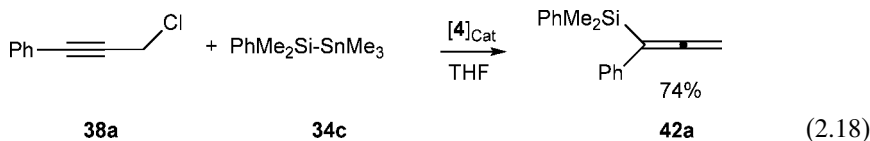


Propargyl epoxides (such as **41**) can also be employed in place of propargyl chlorides. The epoxide opening (Eqn 2.17) of cyclic substrate **41** proceeds with an excellent *anti* selectivity affording the corresponding allenyl product as a single diastereomer (**40c**). Thus, the pincer complex-catalyzed epoxide opening reaction occurs with an excellent regio- and stereochemistry, and in high yield.



2.3.4 Synthesis of Allenyl Silanes Using Pincer Complex Catalysis

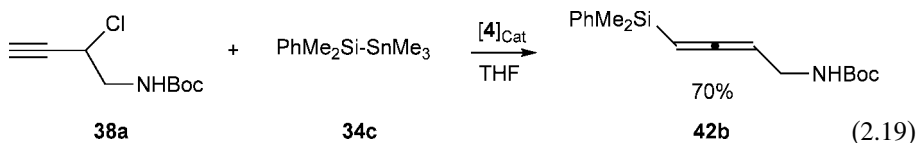
Synthesis of allenyl silanes could also be achieved using NCN-pincer complex **4** as catalyst (Eqns 2.18 and 2.19). Although employing unsymmetrical reagent **34c**, either the silyl or the stannyl group can be transferred to the propargyl substrates, the corresponding catalytic reactions afforded exclusively silylated products, such as **42a–b**.



The silylation reaction proceeds with a very high regioselectivity providing the allenyl product. The regiopreference for formation of the allenyl product is higher in the silylation reactions than in the stannylation processes. For example, propargyl chloride **38a** reacts with **34a** in the presence of pincer complex catalyst **4**, affording mainly the propargyl product **39a** and only traces of allenyl stannane **40a** (Eqn 2.15). Conversely, the same catalytic reaction with silylstannane **34c** (Eqn 2.18) yields exclusively allenyl silane **42a**.

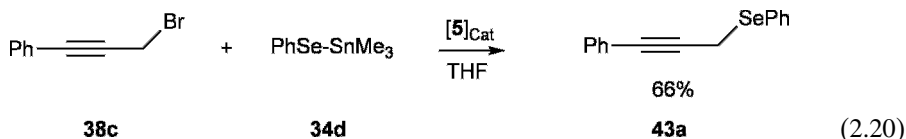
Both the stannylation and the silylation reactions are conducted under mild and neutral reaction conditions with a robust catalyst (**4**), and therefore, many functionalities including COOEt, OR, OAc, NR, NAc and even unprotected OH are tolerated (Eqns 2.16 and 2.19). Considering the high selectivity and broad substrate scope of the reaction, these

processes can be exploited to a flexible synthesis of allenyl stannanes and silanes, which are useful precursors in advanced organic synthesis and natural product chemistry [54].

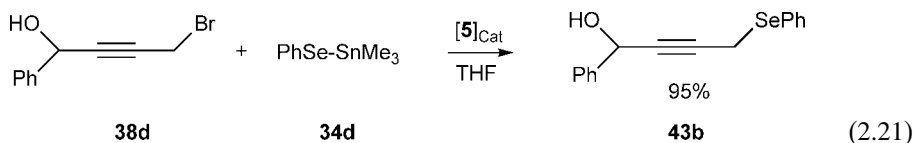


2.3.5 Phenylselenation of Organohalides

The pincer complex-catalyzed synthesis of organometallic reagents were also extended to organoselenium chemistry [55]. In these processes, trimethylstannylphenylselenide (**34d**) was used as source of the phenylselenenyl group, and SeCSe complex **5** was employed as catalyst (Eqns 2.20 and 2.21). Similar to the silylation reactions, only the phenylselenenyl group was transferred from **34d** to the organic substrate to give the corresponding organoselenide (e.g. **43a** and **43b**).



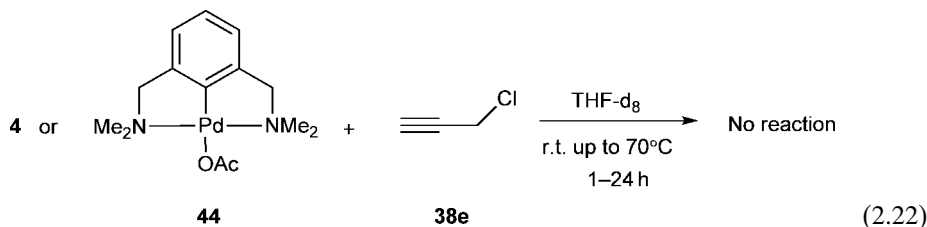
The selenation reactions displayed a pronounced regiopreference for formation of the propargyl selenyl product, such as **43a** (cf. Eqns 2.15, 2.18 and 2.20). In contrast to the stannylation reactions, electron-withdrawing groups attached to the triple bond did not change the regioselectivity of the reaction (cf. Eqns 2.16 and 2.21). The selenation reactions can be extended to allylic and benzylic substrates as well [55].



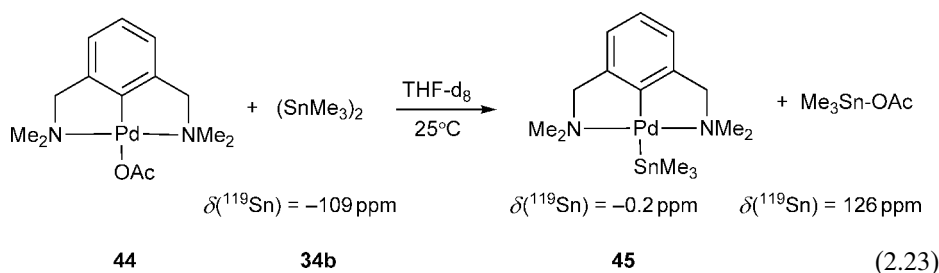
2.3.6 Mechanistic Aspects of the Pincer Complex-Catalyzed Organometallic Group Transfer Processes

The mechanistic aspects of the versatile pincer complex-catalyzed boron, tin, silicon and selenium transfer reactions from dimetallic reagents to organic substrates were discussed in several studies [28, 45, 55]. These studies are usually based on stoichiometric reactions between the pincer complex catalyst and the corresponding dimetallic substrates, as well as DFT modeling on the mechanism of the formation of the organometallic product. The

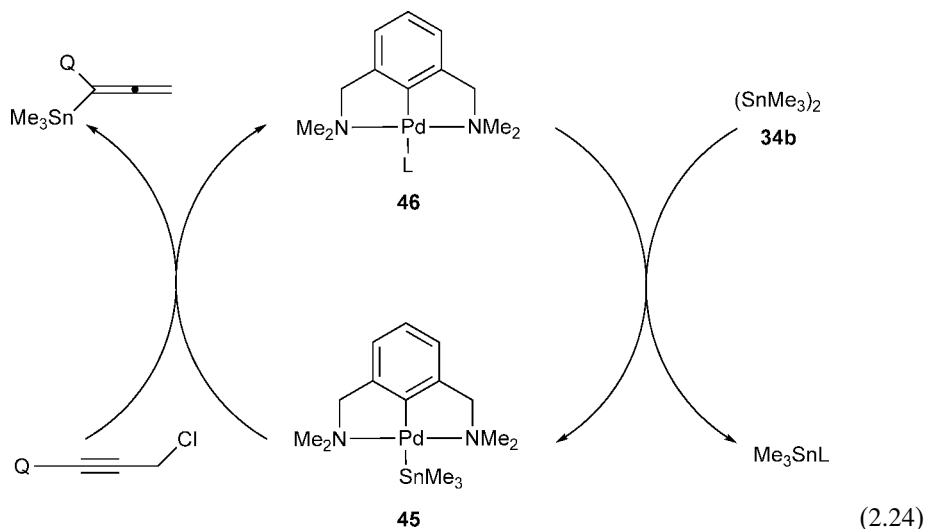
most important experimental results were obtained for the mechanism of the stannylation reactions, as the fate of the trimethylstannyl group could be followed by ^{119}Sn -NMR spectroscopy [28, 45].



It is well known that palladium(0) complexes readily undergo oxidative addition to propargyl chlorides. However, it was found that neither NCN complex **4** nor its acetate analog **44** reacted with propargyl chloride **38e** (or allyl chloride) even at 70°C for up to 24 h (Eqn 2.22). On the contrary, complex **44** reacted readily with distannane **34b** (Eqn 2.23). The progress of this reaction was clearly indicated by the systematic changes of the ^{119}Sn -NMR spectrum of the reaction mixture: the resonance peak of **34b** (-109 ppm) was decreased with simultaneous appearance of a new peak at -0.2 ppm . The latter peak was assigned to the ^{119}Sn -NMR resonance of trimethyltin-coordinated complex **45** [52, 56].



According to the stoichiometric reactions (Eqn 2.23), the catalytic cycle of the stannylation reaction is initialized by the transfer of the stannyl functionality from **34b** to the pincer complex (**46**). This transmetalation step is followed by trimethylstannane substitution of the leaving group of the propargylic substrate affording allenyl or propargyl stannane product. Considering the fact that there is no freely accessible coordination site on palladium in **45**, this process is expected to be the most unique reaction step in the above pincer complex-catalyzed metalation process. The mechanistic details of this step were explored by DFT modeling studies.



These DFT modeling studies [45] have revealed at least two important mechanistic features. The first is that the trimethylstannyl transfer takes place in a single reaction step (Fig. 2.5) without intermediates. The other interesting feature is that formation of the allenyl product (**40d**) proceeds with lower activation barrier ($20.5 \text{ kcal mol}^{-1}$) than the formation of the propargyl (**39b**) product ($33.5 \text{ kcal mol}^{-1}$).

Analysis of the TS structures **47a** and **47b** (Fig. 2.6) reveals some interesting structural and electronic aspects of the reaction. The geometry of the reaction center is similar to that of the classical $\text{S}_{\text{N}}2'$ (**47a**) and $\text{S}_{\text{N}}2$ (**47b**) reactions, in which the formation of the new bond and cleavage of the leaving group bond take place simultaneously. There is, however, a clear difference between the geometry of the TS of the classical nucleophilic substitution reactions and the presented processes (**47a–b**). In a classical $\text{S}_{\text{N}}2$ reaction, the attacking nucleophile is aligned with the reaction center and the leaving group closing an angle of 180° . However, the corresponding $\text{Sn}-\text{C}-\text{Cl}$ angle in **47b** is 132° , and furthermore, the palladium atom is also involved in the displacement of the leaving group. On the contrary, the middle point of the palladium–tin bond, the attacked propargylic carbon and the carbon–chloride bond do form an angle close to 180° in the TS structures. As a result, the palladium, tin and the attacked carbon atoms

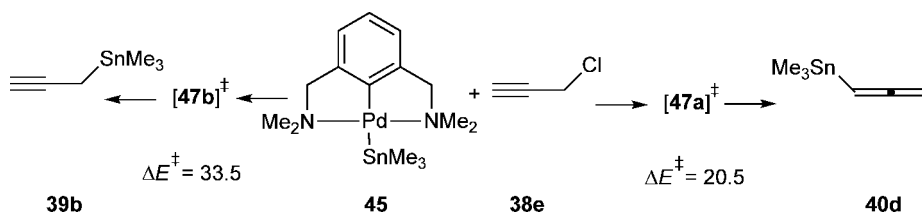


Fig. 2.5. DFT reaction profile [45] for trimethyltin transfer process. The activation energies are given in kcal mol^{-1} .

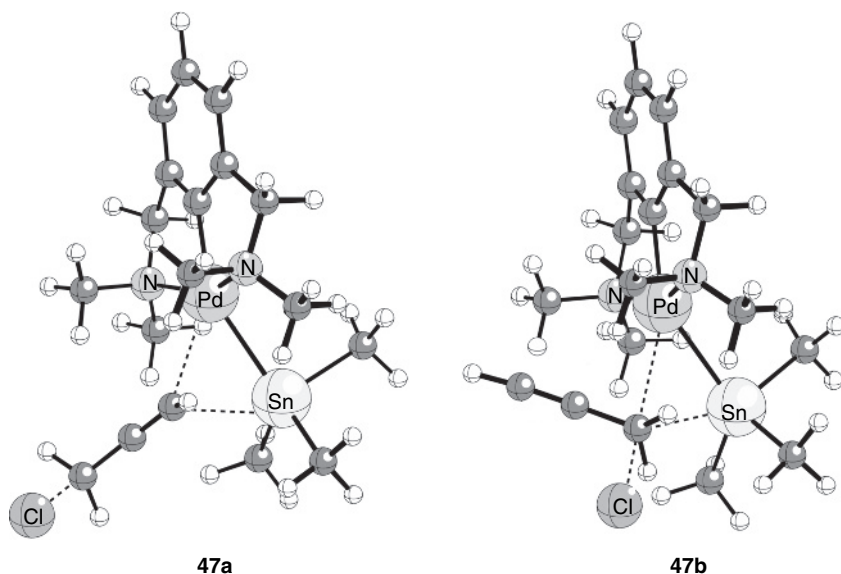


Fig. 2.6. Transition state structures for formation of allenyl stannane (**40d**) and propargyl stannane (**39b**).

create a triangular formation. This triangular geometry suggests that the electron pair of the palladium–tin σ -bond exerts a nucleophilic attack on the propargylic carbon simultaneously cleaving the carbon–chloride bond. This hypothesis can also be confirmed by inspection of the high-energy (-4.5 eV) HOMO orbital of complex **45** (Fig. 2.7),

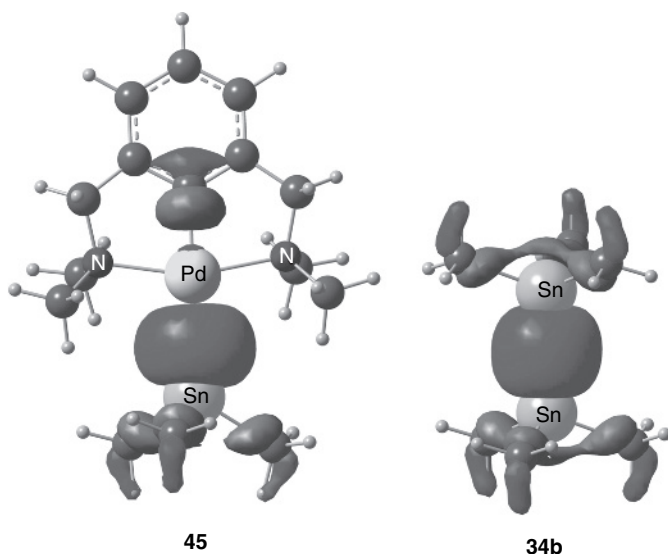


Fig. 2.7. Electronic structure of the HOMO orbitals of trimethyltin-coordinated pincer complex **45** ($\epsilon_{\text{HOMO}} = -4.5$ eV) and hexamethylditin **9a** ($\epsilon_{\text{HOMO}} = -6.3$ eV).

which is largely localized on the palladium–tin σ -bond. Thus, the electron pair of the palladium–tin σ -bond in **45** is readily available for electrophiles, such as **38e**.

It is particularly interesting to compare the HOMO of complex **45** to the corresponding HOMO of hexamethylditin (**34b**). The HOMO in **34b** has also a clear metal–metal σ -bond character; however, the HOMO energy (-6.3 eV) is considerably lower in **34b** than in **45**. Because of this low HOMO energy, **34b** is not able to perform the nucleophilic displacement of the chloride of **38e**. On the contrary, in palladium pincer complex **45**, there is a high-energy HOMO, and therefore, this complex is more nucleophilic than **34b**, which leads to a successful trimethyltin transfer to the propargylic substrate **38e** (Fig. 2.5). This also explains the necessity of employment of palladium pincer complex catalysis in the above reaction.

A further interesting structural feature of **47a** and **47b** is that the terdentate coordination of the pincer ligand is maintained in the TS of the trimethyltin transfer. The simultaneous (one-step) formation of the carbon–tin bond and the cleavage of the palladium–tin bond can probably be ascribed to the fact that only a single coordination site is available for the catalytic process.

The experimental mechanistic investigation of the pincer complex-catalyzed boronate and selenyl group transfer is more cumbersome than the above organostannane transfer, and therefore, much less experimental data are available for these processes [47, 48, 55]. However, considering the similarity of the catalysts and the dimetallic reagents applied in these processes, it can be assumed that the boronation and selenylation processes also occur via boronate and selenide analogs of **45**.

2.4 CONCLUSIONS AND OUTLOOK

This chapter has demonstrated that palladium pincer complexes can be employed as effective catalysts for synthesis and transformation of allyl boronates, allyl stannanes, allenyl stannanes, allenyl silanes as well as propargyl selenids. Chiral pincer complexes are promising catalysts for asymmetric allylation of sulfonimines. The presented catalysts are highly moisture and air stable. Therefore, relatively low catalyst loadings can be employed, and in many cases, the pincer complex catalysts can be recovered unchanged after the catalytic processes. Because of their high stability and selectivity, pincer complex catalysts can be efficiently employed in one-pot reactions proceeding via allyl- and allenyl-metal intermediates. As the above-described pincer complexes are highly durable species under catalytic conditions, easily recyclable robust catalyst systems can be obtained by their immobilization. The future catalytic studies will probably be directed to development of new type of boronation and silylation methods and further development of the selectivity of chiral pincer complexes. Furthermore, considerable efforts will be invested to immobilize pincer complex catalysts on solid support to obtain robust, recyclable catalyst systems.

ACKNOWLEDGMENT

This work was supported by the Swedish Natural Science Research Council (VR) and the IDECAT Network of the European Communities.

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Chiral pincer complexes and their application to asymmetric synthesis

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3.1 INTRODUCTION

In this chapter pincer complexes are defined as containing anionic terdentate ligands with the formal negative charge lying on the central atom attached to the metal. For example, the anionic *Phebox* ligand structure **1**, which forms organometallic complexes, features heavily, whereas the neutral forerunner *Pybox* **2** that forms terdentate coordination complexes lies outside the remit of this discussion (Fig. 3.1) [1].

3.2 THE SYNTHESIS OF CHIRAL NONRACEMIC PINCER COMPLEXES CONTAINING ANIONIC TERDENTATE LIGANDS

Terdentate anionic chiral pincer complexes are available by much the same techniques as their achiral counterparts, and architectures incorporating a range of ligand and metal variations have been synthesised by methods broadly falling into three main categories. (i) *Transmetallation*: A ligand bearing an initial metal–carbon bond is exposed to a second metal in the required oxidation state, a transmetallation event furnishes the desired product.

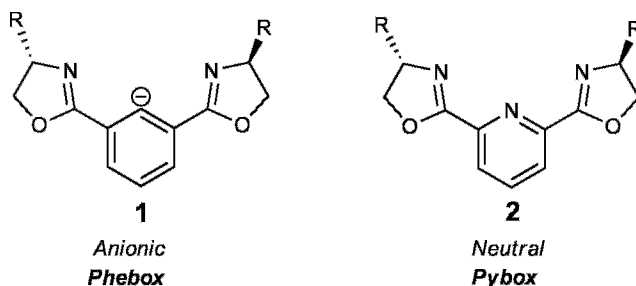


Fig. 3.1. Anionic and neutral bisoxazoline ligands.

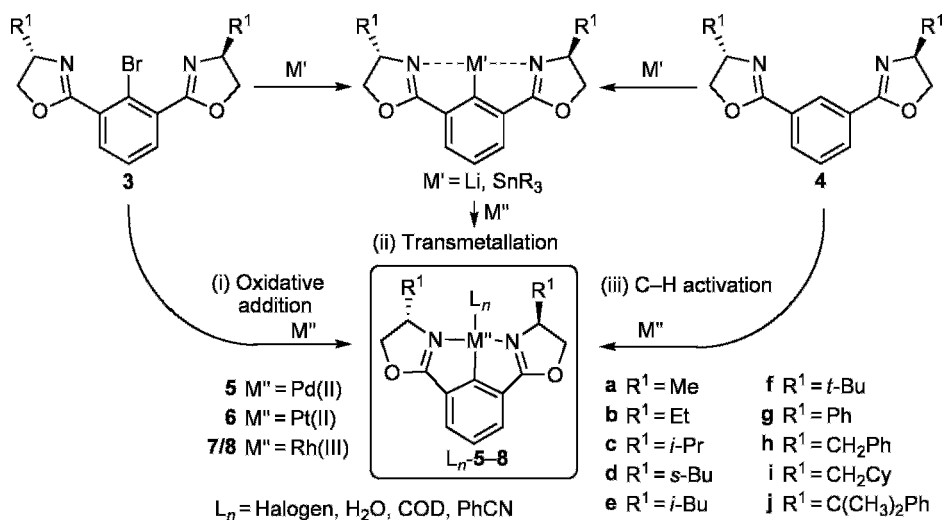
(ii) *Oxidative addition*: Ligand precursors with a suitably positioned halide substituent undergo oxidative addition of the required metal to furnish the corresponding metallo-halide pincer complex. (iii) *Direct C–H activation*: The pincer ligand precursors *trans* donor atoms flank a central C–H group which is activated by the metal and subsequently becomes part of the pincer construct. The suitability of each method strongly depends upon the nature of the ligand and metal. The focus of Section 3.2 is the synthetic step which introduces a metal, i.e. the chiral pincer construction step. This section provides a comprehensive compendium of chiral pincer complexes and their syntheses. As the majority of chiral pincer complexes are C_2 -symmetric, the commonly employed ECE abbreviation conveniently classifies complexes for the purpose of this section.

3.2.1 NCN Complexes

Chiral and achiral nitrogen containing pincer complexes are of interest in a wide range of applications not directly related to synthesis including materials science and small molecule sensing. This material has been reviewed elsewhere [2]. NCN pincer complexes are divided still further by the nature of the nitrogens in the system.

3.2.1.1 Bisoxazoline complexes

Bisoxazoline pincers can be divided into two subclasses based on the fused metalocycle ring size. First the most common is where two five-membered metalocycles form the pincer (e.g. *Phebox*- $M L_n$ **5–8**), the second are the less studied fused six-membered metalocyclic rings found in the *Benbox* series **16**. The three main synthetic routes to pincer complexes are exemplified by bisoxazolines (Scheme 3.1, Table 3.1).



Scheme 3.1 Routes to chiral *Phebox* pincers.

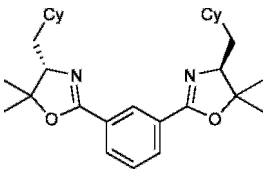
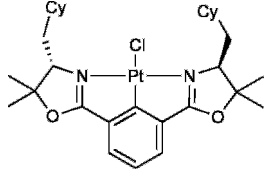
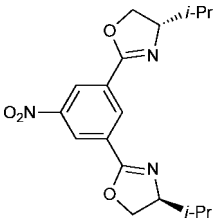
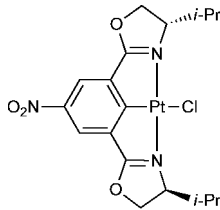
Whilst some 36 different syntheses of chiral *Phebox* pincers have been reported only palladium, platinum and rhodium metals have been incorporated into these chiral complexes [16, 17].

Table 3.1. Syntheses of *Phebox* pincer complexes

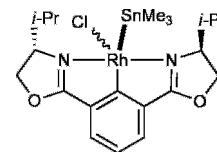
Entry	Ligand	Route ^a	M'	M''	Product <i>R</i> ¹ - <i>Phebox</i> -ML _{<i>n</i>}	Yield (%) [Ref.]
1	3c	(ii)	i, <i>n</i> -BuLi; ii, Me ₃ SnCl	Cl ₂ Pd (NCPPh) ₂	Cl- 5c	96 [3, 4]
2	4c	(ii)	LDA, TMEDA	Br ₂ Pd(1,5-COD)	Br- 5c	29, 41 [5, 6]
3	4e	(ii)	LDA, TMEDA	Br ₂ Pd(1,5-COD)	Br- 5e	21 [6]
4	4f	(ii)	LDA, TMEDA	Br ₂ Pd(1,5-COD)	Br- 5f	18, 24 [5, 6]
5	4i	(ii)	LDA, TMEDA	Br ₂ Pd(1,5-COD)	Br- 5i	41 [5]
6	3h^b	(i)	–	Pd ₂ (dba) ₃ ·2H ₂ O	Cl- 5h	74 [7]
7	3f^b	(i)	–	Pd ₂ (dba) ₃ ·2H ₂ O	Cl- 5f	87 [7]
8	3j^c	(i)	–	Pd ₂ (dba) ₃ ·2H ₂ O	I- 5j	75 [7]
9	3c	(ii)	i, <i>n</i> -BuLi; ii, Me ₃ SnCl	K[PtCl ₃ (C ₂ H ₄)]·H ₂ O	Cl- 6c	88 [8]
10	3g	(ii)	i, <i>n</i> -BuLi; ii, Me ₃ SnCl	K[PtCl ₃ (C ₂ H ₄)]·H ₂ O	Cl- 6g	86 [4]
11	3h	(ii)	i, <i>n</i> -BuLi; ii, Me ₃ SnCl	K[PtCl ₃ (C ₂ H ₄)]·H ₂ O	Cl- 6h	86 [4]
12	3d	(ii)	i, <i>n</i> -BuLi; ii, Me ₃ SnCl	K[PtCl ₃ (C ₂ H ₄)]·H ₂ O	Cl- 6d	88 [4]
13	3f	(ii)	i, <i>n</i> -BuLi; ii, Me ₃ SnCl	K[PtCl ₃ (C ₂ H ₄)]·H ₂ O	Cl- 6f	40 [4]
14	4f	(iii)	–	K ₂ PtCl ₄	Cl- 6f	35 [9]
15	4i	(iii)	–	K ₂ PtCl ₄	Cl- 6i	9 [9]

(Continued)

Table 3.1. Continued

Entry	Ligand	Route ^a	M'	M''	Product <i>R</i> ¹ - <i>Phebox-ML_n</i>	Yield (%) [Ref.]
16	9 	(iii)	—	K ₂ PtCl ₄	12 	22 [9]
17	10 	(iii)	—	K ₂ PtCl ₄	13 	21 [9]
18	4c	(iii)	—	RhCl ₃ ·3H ₂ O	Cl ₂ (H ₂ O)- 7c	56, 64, 56 [3, 10, 11]
19	3c	(ii)	i, <i>n</i> -BuLi; ii, Me ₃ SnCl	RhCl ₃ ·3H ₂ O	Cl ₂ (H ₂ O)- 7c	45 [3]

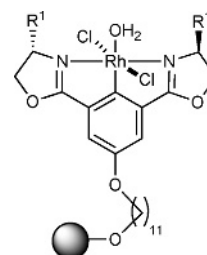
20	3c	(ii)	i, <i>n</i> -BuLi; ii, Me ₃ SnCl	[(<i>c</i> -octene) ₂ RhCl] ₂ ^d	Cl ₂ (H ₂ O)- 7c	67, 67 [12, 13]
21	3c	(ii)	i, <i>n</i> -BuLi; ii, Me ₃ SnCl	[(<i>c</i> -octene) ₂ RhCl] ₂ ^e	Cl ₂ (H ₂ O)- 7c	75 [13]
22	4c	(iii)	—	[(<i>c</i> -octene) ₂ RhCl] ₂ ^f	Cl ₂ (H ₂ O)- 7c	46 [11]
23	4d	(iii)	—	RhCl ₃ ·3H ₂ O	Cl ₂ (H ₂ O)- 7d	52 ^g [11]
24	4e	(iii)	—	RhCl ₃ ·3H ₂ O	Cl ₂ (H ₂ O)- 7e	53 ^g [11]
25	4f	(iii)	—	RhCl ₃ ·3H ₂ O	Cl ₂ (H ₂ O)- 7f	24 ^g [11]
26	3g	(ii)	i, <i>n</i> -BuLi; ii, Me ₃ SnCl	RhCl ₃ ·3H ₂ O	Cl ₂ (H ₂ O)- 7g	16 [12]
27	3g	(ii)	i, <i>n</i> -BuLi; ii, Me ₃ SnCl	[(<i>c</i> -octene) ₂ RhCl] ₂ ^d	Cl ₂ (H ₂ O)- 7g	64, 64 [12, 13]
28	4g	(iii)	—	RhCl ₃ ·3H ₂ O	Cl ₂ (H ₂ O)- 7g	50 ^g [11]
29	3h	(ii)	i, <i>n</i> -BuLi; ii, Me ₃ SnCl	RhCl ₃ ·3H ₂ O	Cl ₂ (H ₂ O)- 7h	0 [13]
30	3h	(ii)	i, <i>n</i> -BuLi; ii, Me ₃ SnCl	[(<i>c</i> -octene) ₂ RhCl] ₂ ^d	Cl ₂ (H ₂ O)- 7h	50, 50 [12, 13]
31	4h	(iii)	—	RhCl ₃ ·3H ₂ O	Cl ₂ (H ₂ O)- 7h	52 ^g [11]
32	3f	(ii)	i, <i>n</i> -BuLi; ii, Me ₃ SnCl	[(<i>c</i> -octene) ₂ RhCl] ₂ ^d	Cl ₂ (H ₂ O)- 7f	24, 43 [12, 13]
33	3a	(ii)	i, <i>n</i> -BuLi; ii, Me ₃ SnCl	[(<i>c</i> -octene) ₂ RhCl] ₂ ^e	Cl ₂ (H ₂ O)- 7a	61 [13]
34	3c	(ii)	i, <i>n</i> -BuLi; ii, Me ₃ SnCl	[(<i>c</i> -octene) ₂ RhCl] ₂	Cl(SnMe ₃)- 8c	6 ^h [14]



(Continued)

Table 3.1. Continued

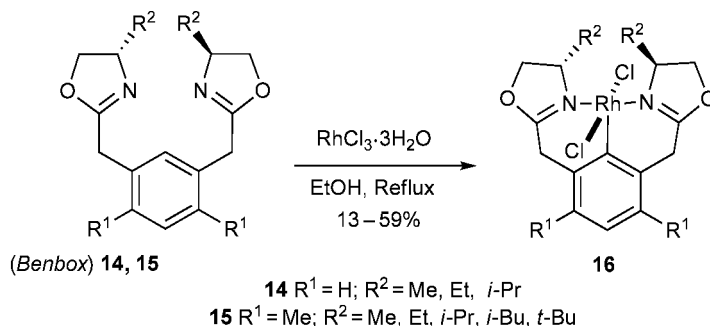
Entry	Ligand	Route ^a	M'	M''	Product R ¹ - Phebox-ML _n	Yield (%) [Ref.]
35	3f	(ii)	i, <i>n</i> -BuLi; ii, Me ₃ SnCl	[(<i>c</i> -octene) ₂ RhCl] ₂	Cl(SnMe ₃)- 8f	3 ^h [14]
36	Polymer supported 4	(iii)	–	RhCl ₃ ·3H ₂ O	Cl ₂ (H ₂ O)- 11a-c, h	[15] ⁱ

Polymer
bound **7**

^a See Scheme 3.1. ^b Chloride pre-pincer used. ^c Iodide pre-pincer used. ^d CCl₄ as chlorinating agent. ^e CuCl₂(H₂O)₂ as chlorinating agent. ^f CHCl₃ as chlorine providing agent. ^g One of two reported procedures. ^h NMR yield, mixture of isomers. ⁱ ~0.1 mmol/g Rh loading IPC analysis.

Amino acid-derived oxazolines **4** are more readily synthesised than the corresponding 1,2,3-trisubstituted benzenes **3**, so direct metallation routes to pincers (route iii) are the most desirable. It should be noted that the yields quoted in Table 3.1 are for the metal insertion step and do not account for the relative ease or difficulty of ligand preparation. Both platinum and rhodium are effective for the C–H activation route to pincers, whereas palladium *Phebox* pincers require the oxidative addition or transmetallation routes (i and ii) [18, 19]. In a detailed study of transmetallation intermediates, Stol et al. showed Li species to be involved in pincer-like structures but Sn was not bound by the neutral donor ligands [20]. Nishiyama reported most of the chiral Rh *Phebox* pincers and successfully applied them to asymmetric catalysis, discussed later [21, 22].

The second class of chiral bisoxazoline pincers (*Benbox*) are those where the pincer part of the molecule consists of two fused six-membered rings (Scheme 3.2) [23, 24].



Scheme 3.2 Synthesis of chiral *Benbox* pincers [23, 24].

Despite the use of nonanhydrous rhodium chloride in the synthesis of **16**, water does not coordinate to the apparent vacant coordination site (as drawn). Crystallography revealed that Rh/H interactions from hydrogens contained within R^2 stabilises these structures. *Trans*-chelated $\text{Rh}^{\text{II}}\text{Cl}_2$ complexes were also identified in some cases.

3.2.1.2 Diamine complexes

Chiral diamine NCN pincers may be divided into three classes depending on the position of their stereogenic centres (Fig. 3.2). (i) *Chirality on the pincer*: Compounds

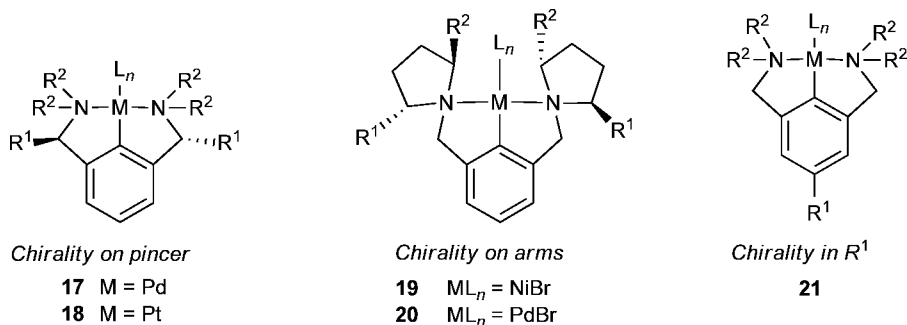


Fig. 3.2. Chiral diamine pincers.

17 and **18** have stereogenic centres in the metallocyclic ring, one atom away from nitrogen. (ii) *Chirality in arms*: Compounds **19** and **20** have stereogenic carbons which are not part of the metallocycle but are only one atom away from nitrogen. (iii) *Chirality in R¹*: Pincer complexes **21** have stereogenicity remote from the pincer motif.

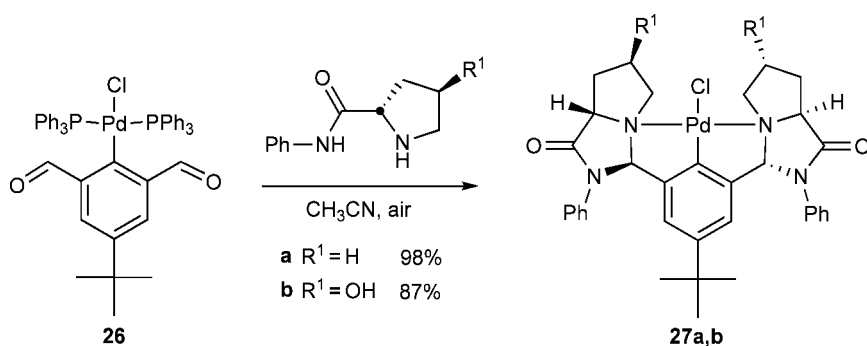
Table 3.2 summarises chiral diamine pincer syntheses by referring to the same synthetic methods as the bisoxazolines of Scheme 3.1 (i and ii) and uses the numbering scheme of Fig. 3.2. Direct C–H activation (route (iii), Scheme 3.1) has not been used to synthesise chiral bisamine pincer complexes and transmetallation (ii) has been used in only a few cases. By far the most common method for the synthesis of chiral bisamine pincers is oxidative addition of Pt(0) or Pd(0) to 2-halo pre-pincer ligands affording the corresponding M(II) pincer complexes in good yield.

An additional element of chirality is considered by Gosiewska et al. where the diastereomeric nature of nitrogen coordination in pincers **19** is examined [25]. The isolation (and use in asymmetric catalysis) of Pd complexes of ethylene diamine derivatives that are chiral by nitrogen coordination only, reported by Gagné and co-workers, demonstrates the importance of nitrogen-centred chirality in these potentially stereofluxional compounds [26]. Oxidation of **19a** to give chiral Ni(III) pincers has also been reported [27–29].

Although not directly within the remit of this section, an achiral *para*-functionalised Pt pincer complex has been introduced into a chiral environment by nano-encapsulation after support in a chiral medium (hyperbranched polyglycerols) [30].

3.2.1.3 Other nitrogen donors

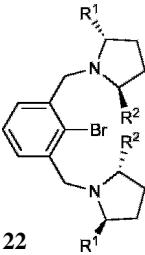
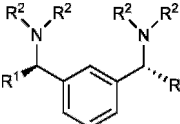
Takenaka et al. coined the phrase ‘ligand introduction route’ for their pincer syntheses [31, 32]. Preformation of a Pd–C bond (**26**), followed by subsequent reaction of the noncoordinating aldehyde moieties, afforded novel pincer complexes **27a** and **b** in high yield (Scheme 3.3). Importantly these syntheses did not suffer any detrimental effects when carried out exposed to air.



Scheme 3.3 Ligand introduction route to chiral NCN pincers [31, 32].

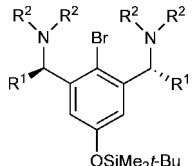
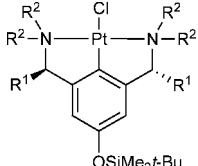
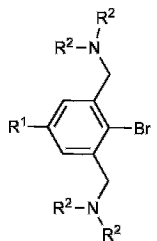
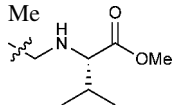
Chiral bisimine pincer complexes **30** derived from (*S*)- α -methylbenzylamine were prepared by two independent routes, oxidative addition of Pd(0) to **28** or direct C–H activation by Pt(II) on **29** (Scheme 3.4) [38]. Previous reports by the same authors

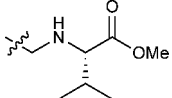
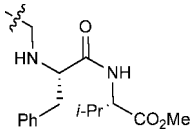
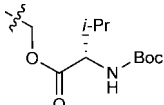
Table 3.2. Synthesis of NCN amine pincers

Entry	Ligand	Route ^a	R ¹	R ²	M'	M''	Product ^b	Yield (%) [Ref.]
1	 22	(i)	CO ₂ <i>i</i> -Pr	H	–	Ni	Br- 19a	48 [33]
2	22	(i)	Me	H	–	Ni	Br- 19b	40 [33]
3	22^c	(i)	Me	Me	–	Ni	Br- 19c	37 [33]
4	22	(i)	CO ₂ Me	H	–	Pd ₂ dba ₃ ·CHCl ₃	Br- 20a	90 [25]
5	22	(i)	CO ₂ CH ₂ Ph	H	–	Pd ₂ dba ₃ ·CHCl ₃	Br- 20b	65 [25]
6	 23	(ii)	Et	Me	<i>n</i> -BuLi	Cl ₂ Pt(SEt ₂) ₂	Cl- 18a	27 [34]

(Continued)

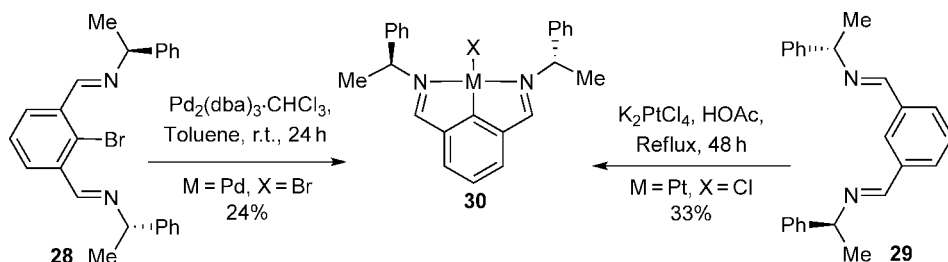
Table 3.2. Continued

Entry	Ligand	Route ^a	R ¹	R ²	M'	M''	Product ^b	Yield (%) [Ref.]
7	23	(ii)	Et	Me	<i>t</i> -BuLi	Cl ₂ Pt(SET ₂) ₂	Cl- 18a	60 [35]
8	24 	(ii)	Me	Me	<i>n</i> -BuLi	Cl ₂ Pt(SET ₂) ₂	 Cl- 18b Br- 18b	78 [35]
9	24	(i)	Me	Me	—	[Pt(SET ₂)(<i>p</i> -tol) ₂] ₂	Br- 18b	43 [35]
10	24	(i)	Me	Me	—	Pd(dba) ₂	Br- 17b	52 [35]
11	25 	(i)		Me	—	[Pt(SET ₂)(<i>p</i> -tol) ₂] ₂	PtBr- 21a	59 ^d [36]

12	25	(i)		Me	–	$\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$	PdBr- 21a	79 [37]
13	25	(i)		Me	–	$\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$	PdBr- 21b	40 [37]
14	25	(i)		Me	–	$\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$	PdBr- 21c	76 [37]

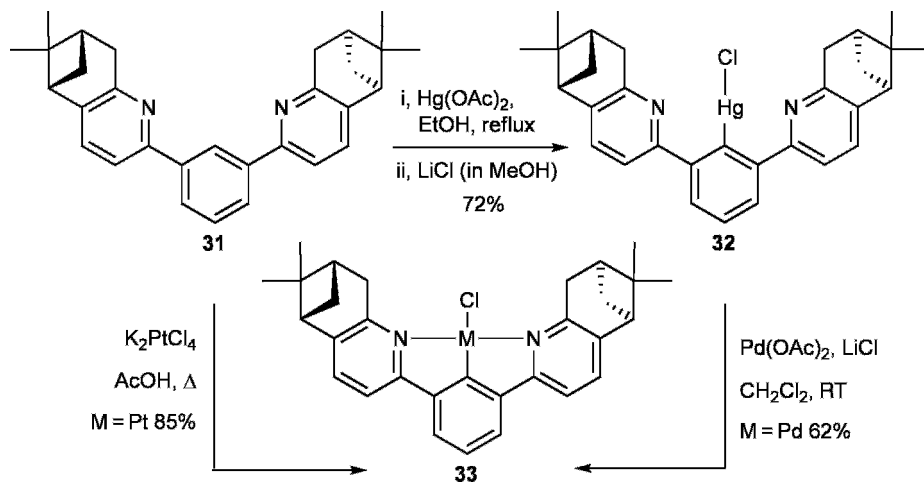
^a See Scheme 3.1. ^b See Fig. 3.2. ^c Opposite enantiomer used. ^d A 64% yield of the same complex was obtained when an achiral pincer was functionalised with a valine derivative.

detailed direct platination of achiral analogues and noted the reaction's strong dependency on rigorously dried HOAc as solvent. Under the same conditions direct addition of Pd was not possible [39, 40].



Scheme 3.4 Synthesis of chiral Pt and Pd bisimine piners by direct platination or oxidative palladium addition [38].

Scheme 3.5 depicts chiral variants of Cárdenas et al.'s achiral bispyridyl piners [41], synthesised by Soro et al. [42]. Additionally, and in contrast to earlier reports, these workers successfully introduced palladium via a direct C–H activation route (**31**, Na_2PdCl_4 , HOAc, reflux) in 87% yield.

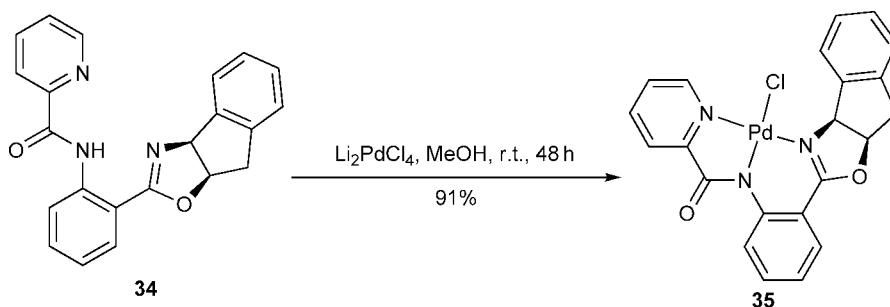


Scheme 3.5 Chiral bispyridine Pt and Pd piners derived by C–H activation or transmetalation [42].

3.2.2 NNN Complexes

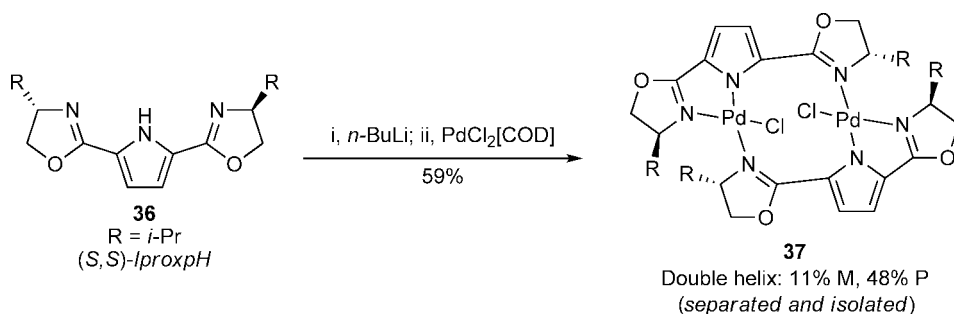
In this section anionic NNN pincer complexes are discussed where the central nitrogen is covalently bonded to a metal displaying the classic pincer orientation of flanking neutral donor atoms.

Chiral oxazoline containing, pre-pincer ligand **34** was stirred at room temperature for 2 days with lithium tetrachloropalladate. Amide deprotonation and palladium–nitrogen bond formation gave the unsymmetrical pincer complex **35** in 91% yield (Scheme 3.6) [43].



Scheme 3.6 A non- C_2 -symmetric NNN chiral pincer complex [43].

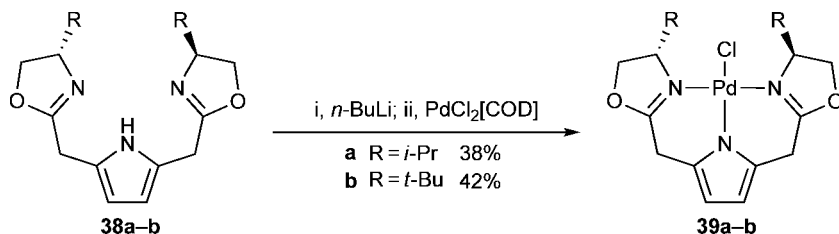
Mazet and Gade studied (*R,R*)- and (*S,S*)-*IproxpH* **36** in detail and noted the similarities and differences of 2,5-bis(oxazoliny)pyrrole-derived ligands to *Pybox* and *Phebox*. Owing to the helical nature of the nonpincer binuclear complexes formed (general formula **37** – Scheme 3.7), they isolated five distinct products from their different experiments with the two enantiomers of **36** [44]. Whilst these workers did not isolate pincer complexes, this is an important study which formed the basis of their later work [45].



Scheme 3.7 *Iproxp* forms binuclear double helices rather than pincers complexes [44].

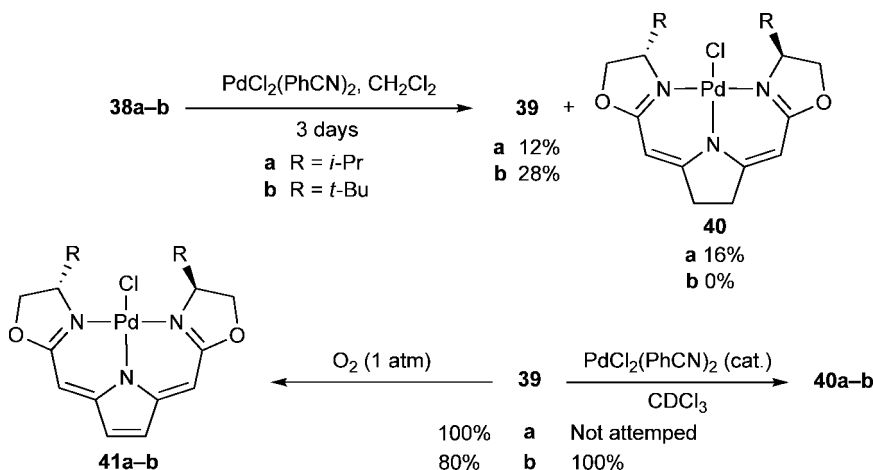
Reasoning that the ligand geometry of **36** was the cause of the failure to give pincer constructs, Mazet and Gade later successfully altered the ligand architecture to that of a pyrrole analogue of *Benbox* [46]. Lithiation of **38** followed by transmetalation with $\text{PdCl}_2[\text{COD}]$ resulted in desired pincer complexes **39** (Scheme 3.8).

During the course of their investigations a new metal-induced isomerisation was discovered. First complexation reactions with $\text{PdCl}_2(\text{NCPh})_2$ were shown to give a mixture of products **39** and **40** (Scheme 3.9). Then exposure of **39b** to $\text{PdCl}_2(\text{NCPh})_2$



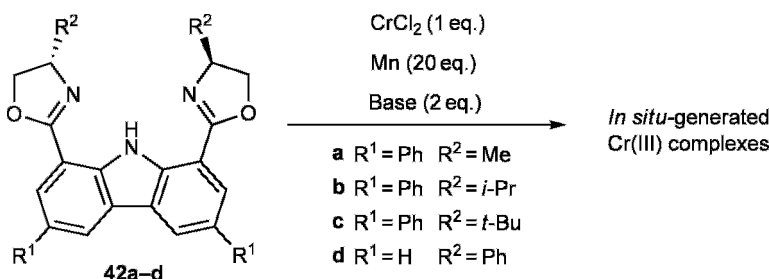
Scheme 3.8 A lithiation, transmetalation route to chiral pyrrole bisoxazoline NNN pincer complexes [46].

quantitatively converted it to **40b**. Exposure to an atmosphere of oxygen led to complete conversion of **39a** to **41a** in 14 h. A longer reaction time was required for an 80% conversion of **39b** to **41b** (16 days).



Scheme 3.9 Isomerisation and oxidation of **39** [46].

Nakada and co-workers have employed a series of in situ-generated chromium complexes derived from ligands of general formula **42** (Scheme 3.10) in a series of Nozaki–Hiyama reactions (discussed in Section 3.3.2) [47–50].



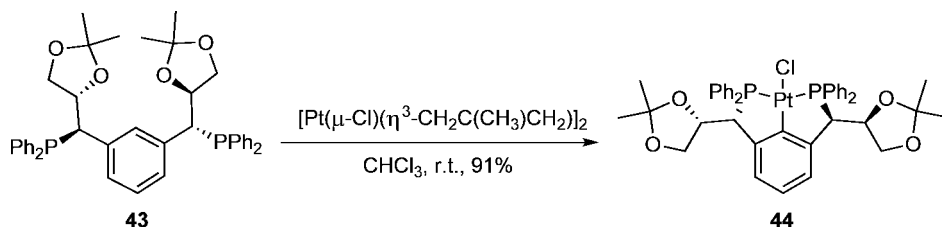
Scheme 3.10 Chromium NNN pincer complexes generated in situ [47–50].

3.2.3 PCP Complexes

Historically bisphosphine PCP complexes are of great significance as the first reported pincer was of this class [51]. The chiral PCP pincers reported to date can be classified into three groups (discussed separately) where: (i) the metal-bound carbon is aromatic and chirality exists in the ligand backbone (Section 3.2.3.1), (ii) the metal-bound carbon is aromatic and the complex contains P-chirogenic phosphine ligands (Section 3.2.3.2) and (iii) the carbon attached to the metal is part of a chiral aliphatic framework with pendant dialkyl phosphines (Section 3.2.3.3).

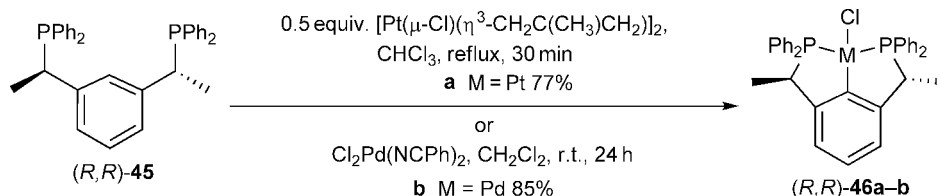
3.2.3.1 Aromatic, C-stereogenic pincers

Venanzi and co-workers synthesised *rac* and *meso* 1,3-bis[1',1'-(diphenylphosphino)ethyl]benzene **45** derived PCP pincer complexes akin to NCN pincers **17** and **18** [52]. This work was rapidly followed up by the synthesis of enantiomerically pure **44** (Scheme 3.11) [53].



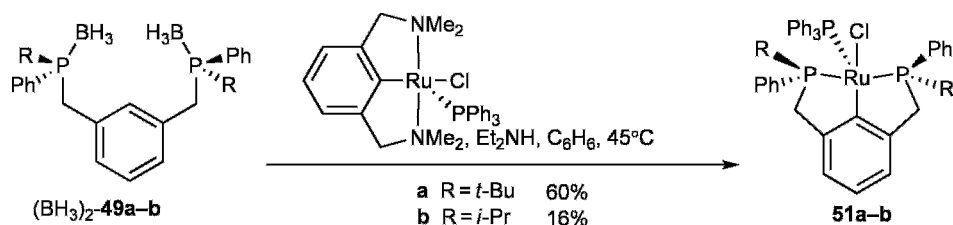
Scheme 3.11 C–H activation by Pt(II) gives chiral PCP pincer **44** [53].

Zhang and co-workers reported a facile synthesis of enantiomerically pure bisphosphine **45** [54] and used the *R,R* enantiomer to synthesise and isolate Pt and Pd complexes **46a** and **b**, respectively (Scheme 3.12) [55]. Dani et al. revealed that Ru(II) could be introduced into **45** via direct C–H activation or by transcyclometallation (from an NCN pincer complex) [35, 56].



Scheme 3.12 Facile C_2 -symmetric Pt and Pd PCP pincer syntheses [55].

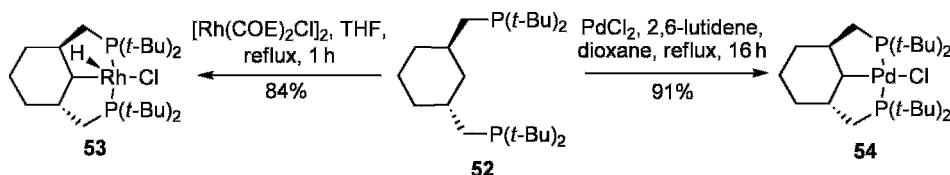
Chiral Pd phosphonite PCP pincers incorporating BINOL **48a–c** and TADDOL **48d** motifs were prepared by oxidative addition of Pd(0) to aromatic iodide precursors **47a–d** (Scheme 3.13) [57].



Scheme 3.15 Transcyclometallation route to *P*-stereogenic pincer complexes [60].

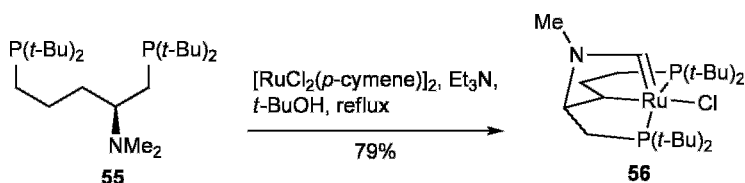
3.2.3.3 Aliphatic, *C*-stereogenic pincers

A cyclohexyl ligand backbone was used by Gusev and co-workers in their synthesis of Rh and Pd pincer complexes. They studied chiral (*trans*) **52** and achiral (*cis*) 1,3-disubstituted cyclohexane ligands. Scheme 3.16 shows the metallation steps employed with substrate **52** [62].



Scheme 3.16 Metallation of a chiral alkyl PCP pincer ligand [62].

Gusev and co-workers had previously discovered that a chiral alkyl pincer with a pendant carbene donor **56** was available in one step from **55** in 79% yield (Scheme 3.17) [63].

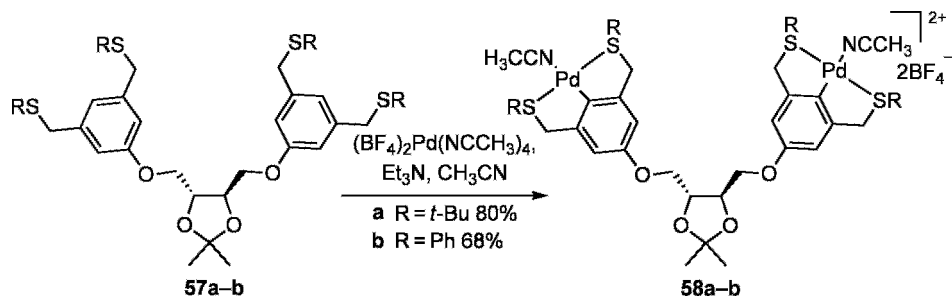


Scheme 3.17 Chiral pentane PCP pincer with pendant carbene arm [63].

3.2.4 SCS Complexes

Chiral sulfur-containing pincers are relatively rare, but a number of researchers have observed the relative stereochemistry of SCS sulfide pincers where chirality exists at the sulfur atoms. Coordination of one of sulfur's lone pairs to a metal imparts chirality at sulfur [64–66]. Sulfur-only chirality is often fluxional and has not yet been exploited with success in any asymmetric synthetic sequence and so is not discussed further here.

Chiral binuclear pincer complexes **58a** and **b**, where an acetal-protected chiral diol links two pincer motifs, have been synthesised (Scheme 3.18). Following the attachment



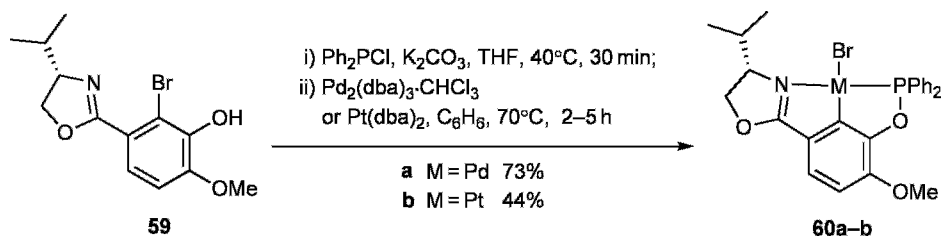
Scheme 3.18 Binuclear SCS pincer complexes with remote chirality [67].

of these complexes to a silica support, the catalytic activity of the complexes was determined [67].

Pincer complexes of a *rac/meso* mixture of sulfoxides resulted in mixtures of (*R,R*), (*S,S*) and difficult to isolate *meso S*-ligated pincers. Whilst not formally an asymmetric synthesis, this work demonstrates the potential of chiral sulfoxide pincers for synthesis [68, 69]. Additionally achiral SCS (and NCN) pincers have been attached to an enzyme resulting in formally chiral pincer complexes [70].

3.2.5 Mixed Donor Complexes

Motoyama et al. reported the synthesis of the first chiral, nonracemic, nonsymmetrical pincer complexes **60a** and **b** (Scheme 3.19) [71].

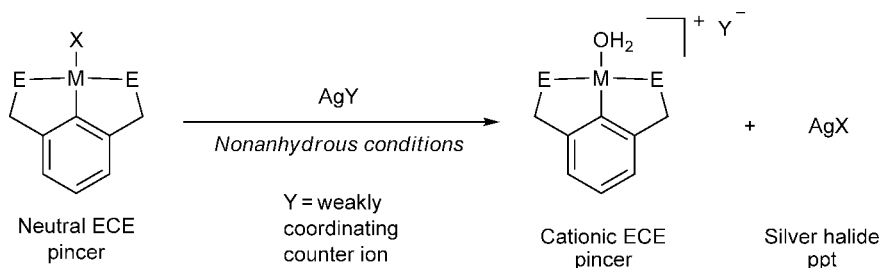


Scheme 3.19 Synthesis of (*i*-*Pr*-*Phemox*-*OPPh*₂)-Pd **60a** and -Pt **60b** via oxidative addition [71].

3.2.6 Reactions of Chiral Pincers

The principle objective of Section 3.2 was to provide a compendium of the syntheses of chiral pincers within the remit of the earlier definition and where the metal introduction steps were considered in detail. Variable oxidation states of the pincer-bound metals allow access to a considerable range of structures not detailed here. Most of the *at metal* reactions performed on chiral pincers were first exemplified on their achiral analogues and detailed discussion of this is available elsewhere. However, a particularly noteworthy reaction is silver-mediated halide abstraction. Many neutral halide-containing pincers

can be activated as cationic Lewis acids by treatment with a suitable silver salt (protected from light). Scheme 3.20 outlines one of the most commonly employed pincer activation methods used in many of the reports quoted above.



Scheme 3.20 Activation of halide complexes with silver salts.

3.3 THE APPLICATION OF PINCER COMPLEXES TO ASYMMETRIC SYNTHESIS

The majority of chiral nonracemic pincer complexes are C_2 -symmetric such that they may be represented by the general structures shown in Fig. 3.3. In both square-planar and octahedral complexes an initial substitution reaction takes place at position Z, *trans* to the ligand's anionic carbon (or nitrogen) atom. As a consequence, introduction of a reactant in either a stoichiometric process or a pincer-catalysed reaction takes place such that the resulting coordination axis of the reactant is also the C_2 -axis of the complex. In general such coordination results in either: (i) enhanced electrophilicity and activation towards nucleophilic attack, or (ii) a reduction in pK_a leading to the formation of a coordinated enol or enolate. Provided there is sufficient influence from the nonracemic dissymmetric

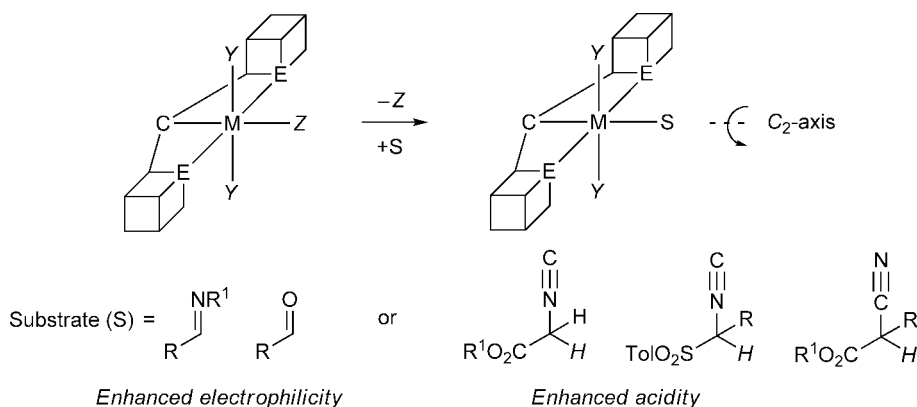
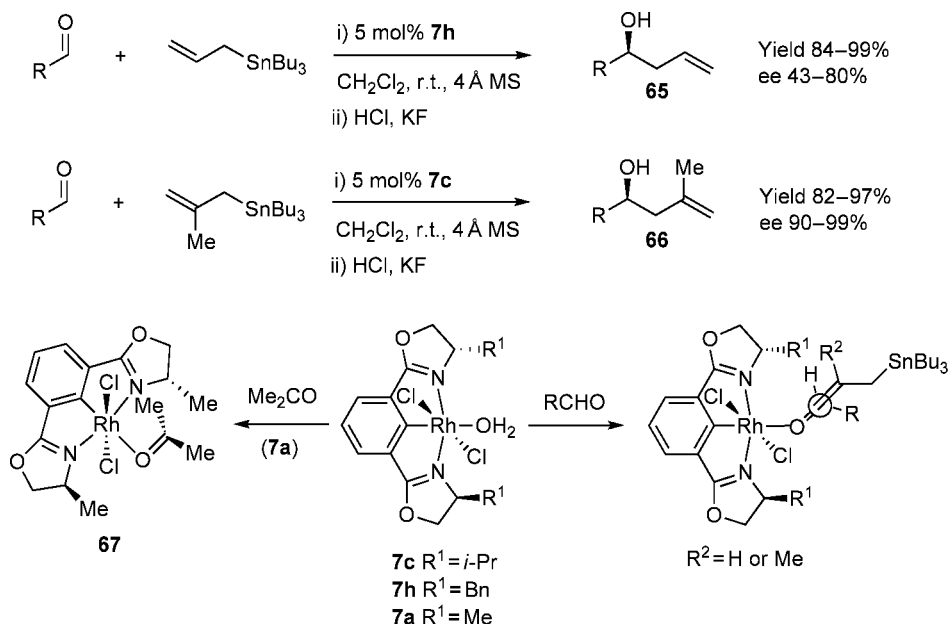


Fig. 3.3. Generalised structure of C_2 -symmetric pincer complexes and the position of substrate coordination.



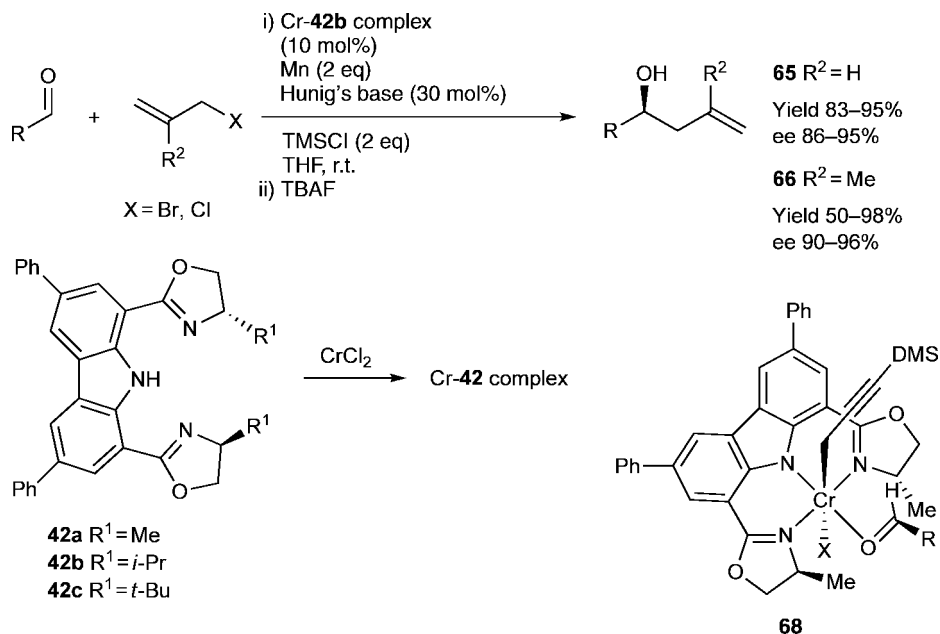
Scheme 3.22 Catalysis of aldehyde allylation by rhodium pincer complexes.

by the use of methallyltributyltin in place of allyltributyltin to give the related alcohols **66** [72]. Use of (*E*)-crotyltributyltin with catalyst **7c** resulted in a 71:29 *anti/syn* selectivity with an ee of 57% for the major diastereoisomer. Solid supported and recyclable variants of these catalysts **11** have also been developed and applied to the synthesis of **65**, albeit with a significant reduction in ee (max = 48%) [15].

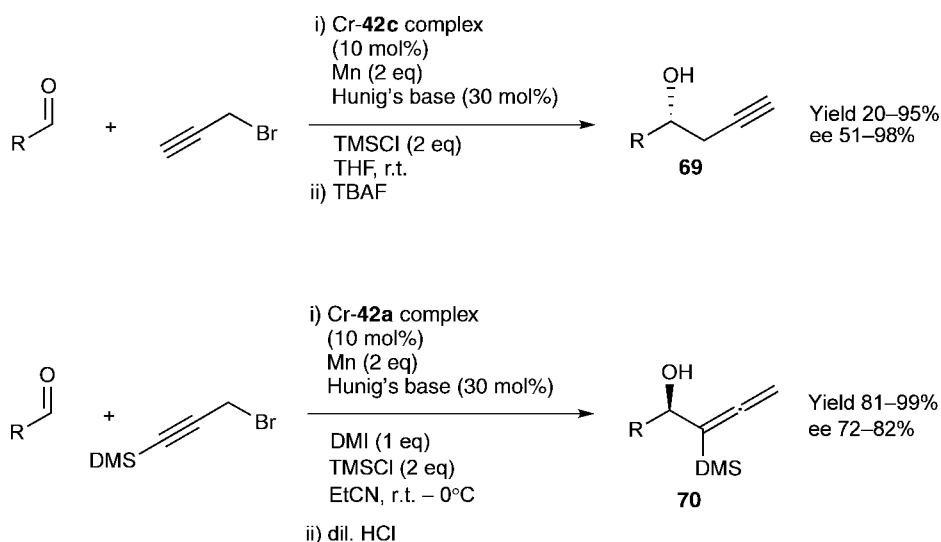
The origin of enantioselection is based upon an X-ray crystal structure analysis of the acetone complex **67** where the plane of the coordinated carbonyl is half-way between the two planes containing Cl–Rh–Cl and N–Rh–N of the octahedral complex [13]. NMR studies support a similar σ -type complex for coordinated aldehydes. Approach of the nucleophile to the exposed *si*-face opposite the adjacent oxazoline R^1 substituent accounts for the observed configuration of the predominant enantiomer.

Addition of ligands **42a–c** to CrCl_2 in the presence of manganese and Hünig's base is thought to give rise to pincer complexes containing a σ -bond to the carbazole nitrogen and two coordination bonds to the oxazoline nitrogens [47, 48]. The resultant complex is an excellent catalyst for the Nozaki–Hiyama allylation and methallylation of both aromatic and aliphatic aldehydes and the chromium–ligand species can be recycled with no loss of enantioselectivity. Use of crotylbromide with benzaldehyde resulted in an 86:14 *anti/syn* selectivity with an ee of 75% for the major diastereoisomer (Scheme 3.23).

The method is applicable to the propargylation of aldehydes to give **69** though with somewhat reduced enantioselectivity [49], and the use of 1-dimethylsilyl-3-bromopropyne with the additive 1,3-dimethyl-2-imidazolidinone (DMI) results in clean allenylation of aromatic and aliphatic aldehydes to give **70** (Scheme 3.24) [50]. The *si*-face selectivity observed in this latter reaction with ligand **42a** is rationalised as resulting from aldehyde coordination to the equatorial position to give **68** followed by



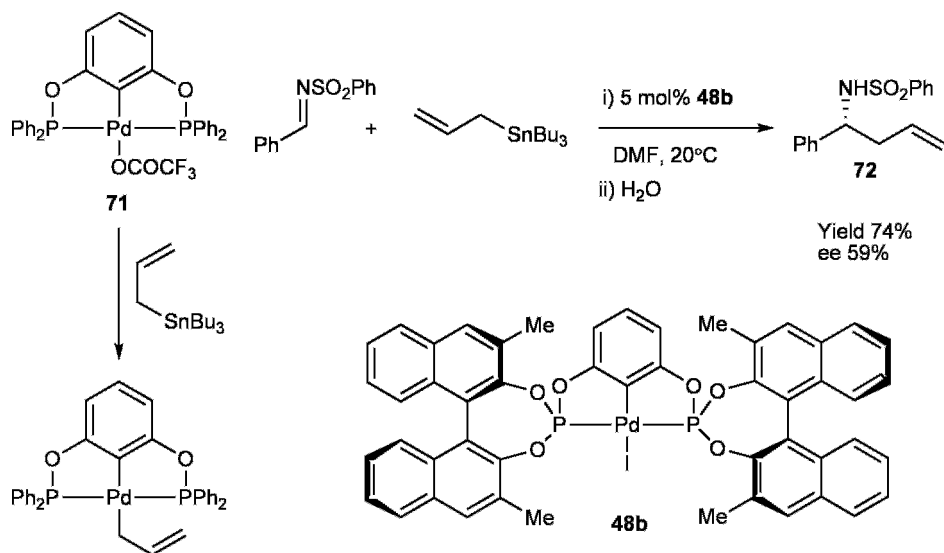
Scheme 3.23 Catalysis of aldehyde allylation by a chromium pincer complex.



Scheme 3.24 Catalysis of aldehyde propargylation and allenylation by chromium pincer complexes.

intramolecular allenylation. The *re*-face selectivity observed with **42c** is accounted for by a reversal of the equatorial and axial coordination modes of the reacting fragments. However, it must be stressed that the chromium-ligand complexes used in this work have yet to be characterised and that other explanations of facial selectivity are possible.

Palladium pincer complexes can catalyse the allylation of aldehydes and imines via an alternative mechanism involving an initial transmetalation reaction between a catalyst such as **71** and allyltributyltin to give a monoallylpalladium intermediate. Electrophilic attack by an aldehyde or imine co-reactant then leads to C–C bond formation [73]. For aldehydes, calculations point to this reaction proceeding via a cyclic six-membered transition state in which the tridentate coordination of the pincer ligand is maintained [74]. The first asymmetric variant of this reaction was reported in 2006, the C_2 -symmetric PCP complex **48b** leading to the highest ee obtained in this study for the product homoallyl amine **72** (Scheme 3.25) [57].

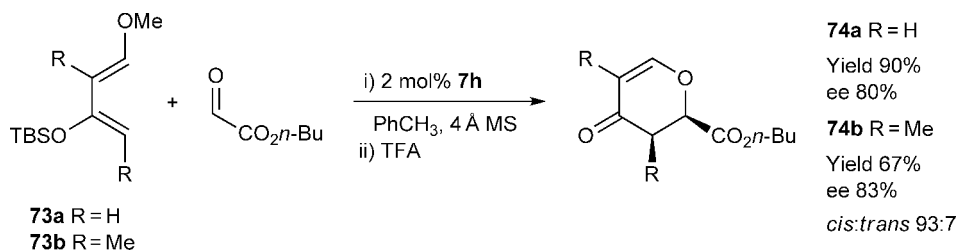


Scheme 3.25 Catalysis of imine allylation by a palladium pincer complex.

3.3.3 The Diels–Alder and Aldol Reactions

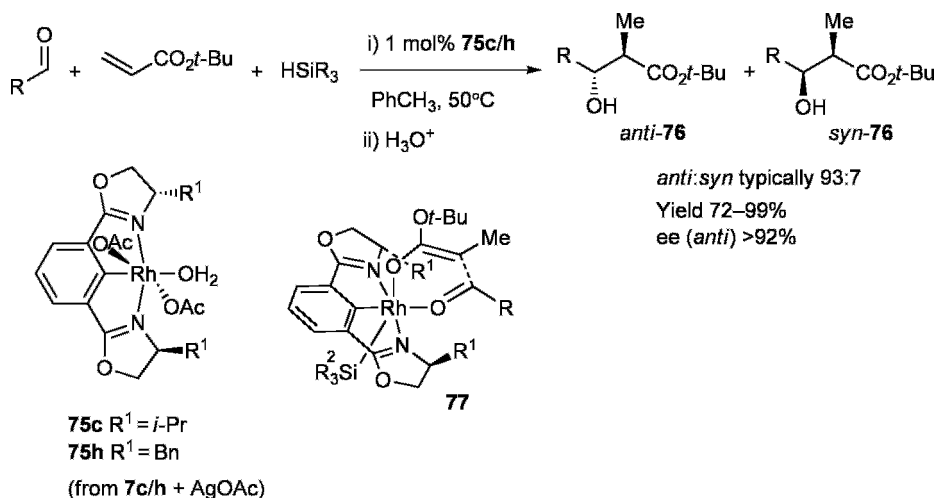
The ability of the rhodium(III) pincer complexes **7** to activate carbonyl groups is further illustrated by catalysis of the hetero Diels–Alder reaction of Danishefsky's dienes **73a/b** with *n*-butyl glyoxylate (Scheme 3.26) [75]. The dibromo and difluoro analogues of **7h** also catalyse the formation of **74a** (82 and 84% ee, respectively). The formation of the *cis* product as the major diastereoisomer with diene **73b** reveals an *endo* selective process with addition occurring to the *re*-face of the coordinated carbonyl.

The reductive aldol reaction of various aldehydes with hydrosilanes and *tert*-butyl acrylate is efficiently catalysed by the diacetate rhodium complexes **75c/h**



Scheme 3.26 Catalysis of the Diels–Alder reaction by a rhodium pincer complex.

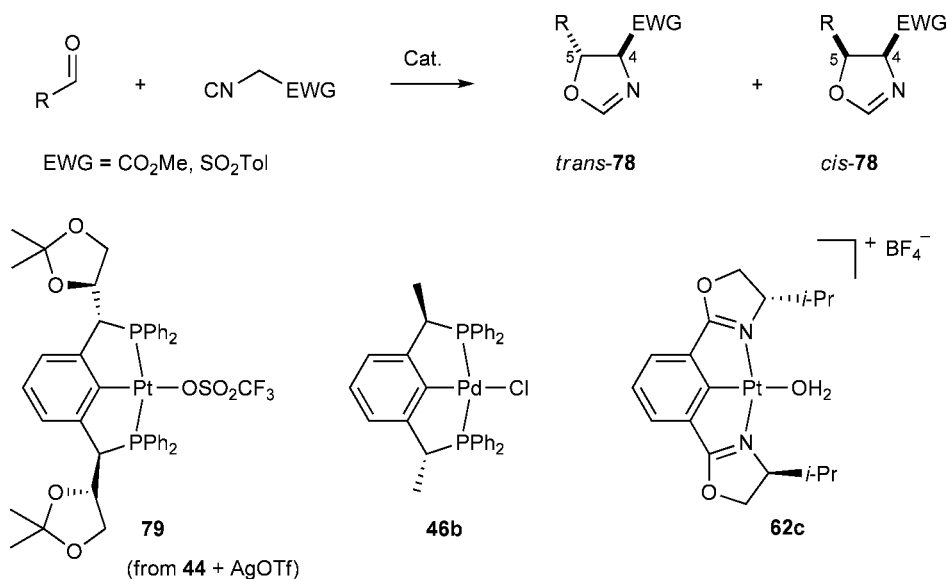
(Scheme 3.27) [76]. It is thought that the starting point of the catalytic cycle is a pincer-ligated Rh(I) species that undergoes oxidative addition of hydrosilane to give a rhodium-hydride which in turn reacts with the *tert*-butyl acrylate leading to the key intermediate **77** after aldehyde coordination. The high *anti* selectivity for the product **76** is consistent with a Zimmerman–Traxler chair-like transition state, the absolute configuration arising from addition to the *si*-face of the coordinated aldehyde. Release of the product by reductive elimination regenerates the starting catalyst.



Scheme 3.27 Catalysis of the reductive aldol reaction by rhodium pincer complexes.

3.3.4 The Reaction of Activated Isonitriles with Aldehydes

An alternative to the activation of aldehydes and imines to nucleophilic attack is the activation of the nucleophile itself through metal coordination. This occurs in the catalysis of the aldol reaction between activated isonitriles and aldehydes resulting in the formation of 4,5-disubstituted oxazolines **78** (Scheme 3.28). These are valuable intermediates in the synthesis of β -hydroxy- α -amino acids (with EWG = CO₂Me).



Scheme 3.28 Catalysis of the aldol reaction by platinum and palladium pincer complexes.

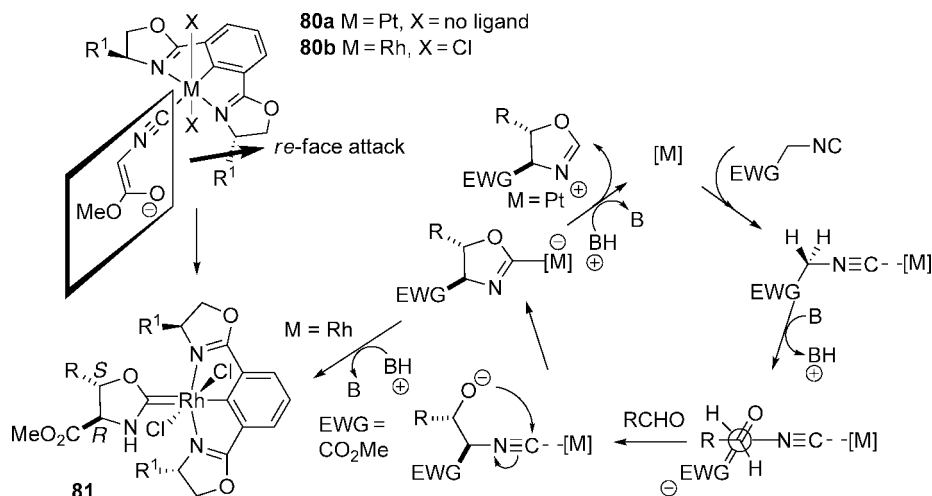
The first application of a pincer complex to this reaction was with the platinum complex **79** (Table 3.3, entry 1) [53]. A similar PCP palladium complex **46b** was found to give better diastereoselectivity than the corresponding platinum species **46a** [55], albeit with significantly lower enantioselectivity for the major *trans* isomer compared to the product obtained with **79** (entry 2). Application of the NCN cationic complex **62c** to the aldol reaction of methyl isocyanoacetate and benzaldehyde gave a *trans/cis* ratio of 86:14 and an enantiomeric excess of only 14% for the major diastereoisomer. Much better results with this catalyst were obtained with tosylmethyl isocyanide (TosMIC – entry 3) [4]. Further studies with catalyst **79** on several *para*-substituted benzaldehydes

Table 3.3. The addition of activated isonitriles to benzaldehyde

Entry	Catalyst (mol %)	Base (mol %)	EWG	Solvent/ temp. (°C)	<i>Trans</i> : <i>cis</i>	ee <i>trans</i> (config.)	ee <i>cis</i> (config.)
1	79 (1.5)	NEt(<i>i</i> -Pr) ₂ (12)	CO ₂ Me	CH ₂ Cl ₂ /20	70:30	65% ^a (4 <i>S</i> ,5 <i>R</i>)	3% (4 <i>R</i> ,5 <i>R</i>)
2	46b ^b (1)	NEt(<i>i</i> -Pr) ₂ (10)	CO ₂ Me	THF/0	78:22	31% ^c (4 <i>R</i> ,5 <i>S</i>)	77% ^c (4 <i>S</i> ,5 <i>S</i>)
3	62c (2)	NEt(<i>i</i> -Pr) ₂ (10)	SO ₂ Tol	THF/0	> 99:1	68% ^d (4 <i>S</i> ,5 <i>S</i>)	–

^a Highest ee of 19 examples with **79**, *trans* (13–65% ee), *cis* (3–32% ee). ^b Catalyst generated in situ with AgOTf. ^c Highest ee of 18 examples with **46b**, *trans* (0–31% ee), *cis* (42–77% ee). ^d One of the seven examples (25–75% ee).

revealed a good correlation between the rate of the reaction and σ_p in a subsequent Hammett plot ($\rho = 1.6$), indicating an increase in electron density at the carbonyl carbon in the transition state of the C–C bond forming step [53]. This and other qualitative similarities to Au(I)-catalysed reactions [77, 78] suggest a very similar mechanism in which electrophilic attack of an uncoordinated aldehyde to the coordinated isocyano enolate is the rate-determining step (Scheme 3.29). For catalyst **62c** the transition state assembly **80a** (with the EWG = SO₂Tol rather than CO₂Me) is used to account for the observed 4*S*,5*S* enantioselectivity. In this model the plane of the platinum-coordinated enolate is perpendicular to the square-plane of the catalyst with approach of the attacking aldehyde occurring to the exposed *si*-face of the former.



Scheme 3.29 The reactions of activated isonitriles with platinum and rhodium pincer complexes.

Use of the rhodium(III) complexes **7** as catalysts for this reaction in conjunction with tertiary amine bases did not result in oxazoline formation. However, addition of potassium *tert*-butoxide to preformed isonitrile complexes yielded Fischer carbene complexes **81** (Scheme 3.29), the highest diastereoselectivities occurring with the benzyl-substituted oxazoline complex **7h** (4*R*,5*S*:4*S*,5*R* = 91:9). Use of TosMIC with **7h** resulted in a reversal of diastereoselectivity (4*S*,5*S*:4*R*,5*R* = 31:65) [79]. The mechanism of this reaction is presumably the same as that for oxazoline formation except that protonation of the metalated oxazoline intermediate occurs on nitrogen rather than at the 2-position.

A number of other cationic pincer complexes have been applied as catalysts to the aldol reaction of methyl isocyanoacetate with low or negligible enantioselectivities (Fig. 3.4). These include the NCN complexes **82** (12% ee) [35], **83** (16% ee) [25] and **84** (0% ee) [42], together with the chiral-at-phosphorus C₂-complex **85** (11% ee) [58]. The complexes **21a–c** (+AgBF₄) and **58a/b** containing remote stereogenic centres all

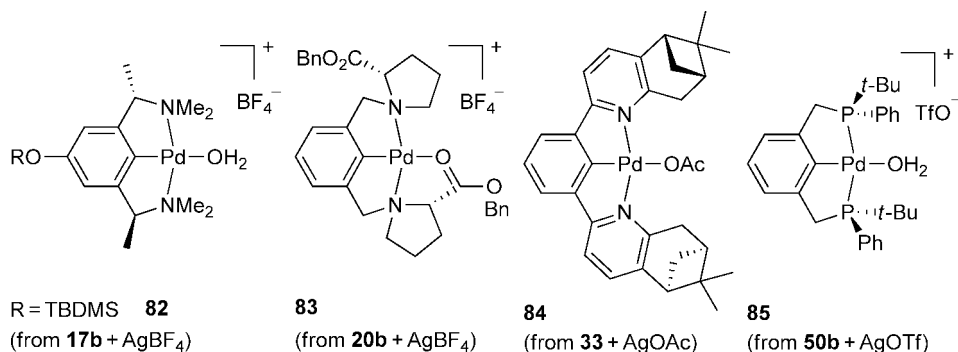


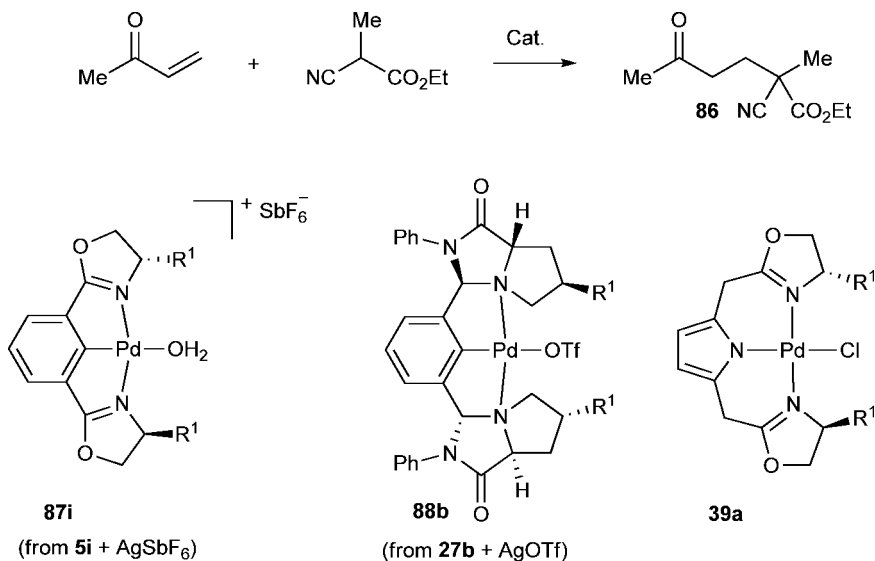
Fig. 3.4. Pincer complexes applied as catalysts for the aldol reaction.

gave racemic products [37, 67]. The absence of enantioselectivity with **84**, due at least in part to the small rate enhancement observed over the background reaction, illustrates the importance of having a good leaving group such as H₂O *trans* to carbon.

3.3.5 The Michael Reaction

Activated nitriles have also been used as substrates in pincer-catalysed reactions in conjunction with a substoichiometric quantity of base. In the presence of an unsaturated ketone electrophile a Michael reaction results which when catalysed by the palladium complex **87i** can proceed with an enantiomeric excess of up to 34% for the formation of **86** (Scheme 3.30) [5, 6]. In the absence of Hünig's base no reaction takes place, nor is any product observed when diethyl malonate is used in place of the activated nitrile. These observations suggest that the reaction proceeds in an analogous manner to the aldol reaction described in Section 3.3.4, that is via initial nitrile coordination followed by deprotonation or base-promoted enolisation, followed by addition to the Michael acceptor. Like the aldol reaction described in the previous section, the new stereogenic centre is formed three bonds away from the metal and as a consequence the longer methylenecyclohexyl oxazoline substituents of catalyst **87i** gave higher enantioselectivities than *tert*-butyl or isopropyl substituents. Preliminary investigations into the use of a related reaction catalysed by **87i** for the asymmetric synthesis of aminogluthethimide have also been reported [80].

A higher ee was achieved with catalyst **88b** provided the pyrroloimidazolone R¹ substituents are hydroxyl groups (Table 3.4, entry 2). With R¹ = H, OMe or OTBDMS, the Michael adduct **86** was isolated with enantiomeric excesses of only 8, 6 and 9%, respectively [31]. These results point to the importance of hydrogen bonding between the R¹ hydroxyl substituent(s) and the coordinated enolate, and/or the Michael acceptor, for the attainment of high asymmetric induction [32]. A bis(oxazolinylmethyl)pyrrole catalyst generated in situ from **39a** gave a low yield of **86** in 43% ee (and 29% ee where R¹ = *t*-Bu) [46]. This catalyst is reported to have relatively low activity resulting in significant competition from the nonselective background reaction, as revealed by the decrease in enantioselectivity with increased reaction times. Finally, catalysis of the Michael reaction with achiral platinum NCN pincer complexes, covalently immobilised



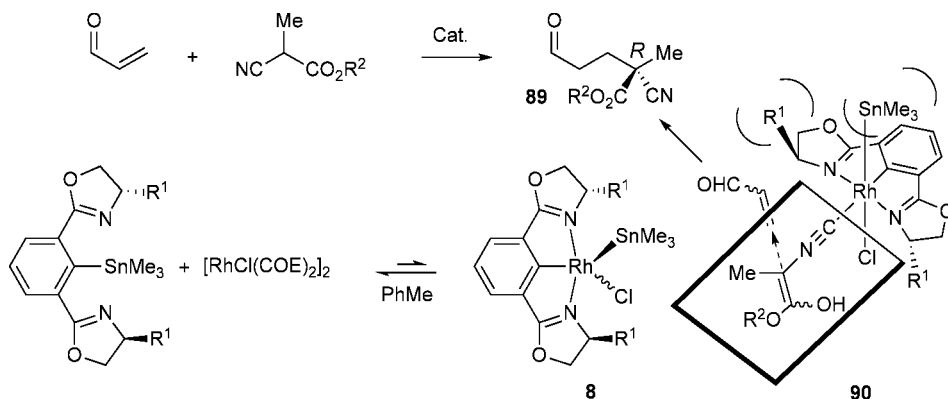
Scheme 3.30 Catalysis of the Michael reaction by palladium pincer complexes.

Table 3.4. The Michael reaction between ethyl isocyanoacetate and methyl vinyl ketone

Entry	Catalyst (mol%)	Base (mol%)	R ¹	Solvent/ temp.	Yield of 86 (%)	ee (%) (config.) of 86
1	87i (1)	NEt(<i>i</i> -Pr) ₂ (10)	CH ₂ Cy	PhMe/RT	86	34 (<i>R</i>)
2	88b (0.5)	NEt(<i>i</i> -Pr) ₂ (10)	OH	PhH or PhMe/25 °C	89	81 (<i>S</i>)
3	39a /AgBF ₄ (1)	NEt(<i>i</i> -Pr) ₂ (10)	<i>i</i> -Pr	PhMe/25 °C	14	43 (ND)

to scalemic hyperbranched polyglycerols, resulted only in the formation of racemic **86** [30].

Combination of an aryltrimethylstannane and [RhCl(c-octene)₂]₂ in D₆-benzene results in a low (3–9%) conversion to the oxidative addition products **8** as a mixture of isomers (5:1 with R¹ = *i*-Pr, >98:2 with R¹ = *t*-Bu – Scheme 3.31). These Rh(III) species are active catalysts for the Michael reaction between α-cyanopropionates and acrolein under neutral conditions. Taking into account the low yield of the oxidative addition reaction (3% with R¹ = *t*-Bu), a catalyst loading of 0.0083 mol% and a yield of 91% corresponds to a turn over number in excess of 10 000. The highest enantioselectivities were achieved with **8f** (R¹ = *t*-Bu), (*R*)-**89** being formed with an ee of 69% with R² = Et. Varying the ester substituent R² increased the ee up to 85% (R² = 2,6-(*i*-Pr)₂C₆H₃). The observed *R* stereochemistry is accounted for by model **90** in which the coordinated enol lies in the plane of the NCN chelate resulting in exposure of the *re*-face to the approaching Michael acceptor.



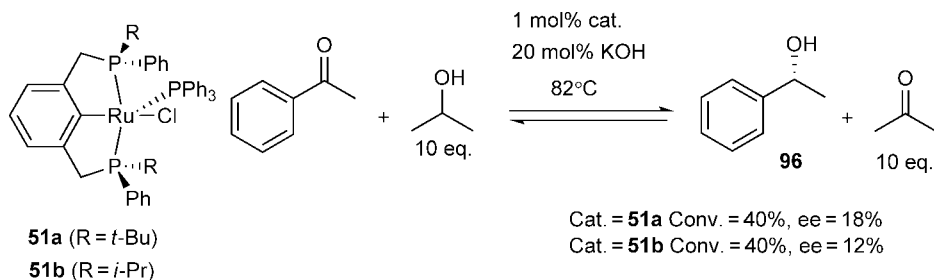
Scheme 3.31 Catalysis of the Michael reaction by rhodium pincer complexes.

3.3.6 Reduction Reactions

The one other major class of reactions to which chiral pincer complexes have been successfully applied is alkene reduction with alkoxyhydrosilanes. Addition of the latter to the rhodium complex **7c** (with or without the addition of silver tetrafluoroborate) is reasoned to give a rhodium(I) species as the active catalyst in which the integrity of NCN ligation is maintained (see also Section 3.3.3.). Oxidative addition of further alkoxyhydrosilane gives a rhodium-hydride intermediate which hydrometallates certain styrene derivatives with good facial selectivity but poor regioselectivity. The products are produced by subsequent reductive elimination, regenerating the catalyst. The enantioselectivity was determined following Tamao oxidation of the chiral silyl adducts to the corresponding secondary alcohols **91** (Scheme 3.32) [81].

Application of this reduction methodology to β,β -disubstituted α,β -unsaturated ketones and esters results in efficient asymmetric conjugate reduction, where the majority of the substrates employed are reduced with high enantioselectivity to give saturated ketones **92** and esters **93** (>90% ee) [10, 11]. Following hydride addition to the β -carbon, the intermediate rhodium-enolate undergoes reductive elimination to give a ketene silyl-acetal which is hydrolysed to an ester on work-up. The facial selectivity for both styrene and unsaturated carbonyl reduction is rationalised by the models **94** and **95** in which the α -hydrogens are preferentially orientated towards the oxazoline isopropyl substituent (Fig. 3.5).

The chiral-at-phosphorus ruthenium complexes **51a/b** have been tested as catalysts for the asymmetric hydrogen transfer reaction of acetophenone with propan-2-ol. After a reaction time of 15–17 h (*R*)-1-phenylethanol **96** was obtained in up to 18% ee (Scheme 3.33). Prolonging the reaction time to 4 days led to the isolation of a racemic product with both catalysts [60]. Similarly, the ruthenium complex derived from **45** resulted in a product alcohol of 14% ee [35]. Hydrosilylation of styrene with trichlorosilane catalysed by the chiral-at-phosphorus palladium complex **50a** gave **96** in 6.5% ee after oxidation of the product silane with hydrogen peroxide [59].



Scheme 3.33 Transfer hydrogenation catalysed by a ruthenium pincer complex.

be expected to be lost. Other potentially asymmetric reactions catalysed by scalemic pincer complexes that yield racemic products include the addition of trimethylsilylcyanide to benzaldehyde catalysed by **5i**/AgOTf [40] and the cyclopropanation of (*E*)-ethyl cinnamate by diazomethane catalysed by **5f** and cationic derivatives thereof [7].

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Desulfurization catalyzed by nickel PCP-pincer compounds

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4.1 INTRODUCTION

The composition of crude oil (petroleum) is very complex. It consists of a mixture of mainly hydrocarbons, but other components containing heteroatoms such as sulfur, nitrogen, oxygen and metals are also present, the particular constitution depending mostly on the site where the petroleum feedstock has been extracted and the class of petroleum being treated.

The most abundant heteroatom present in petroleum feedstocks is sulfur, having concentrations that vary from 0.1% wt (light oil) to 5% wt (heavyweight oil), the variety of organosulfur compounds present in petroleum being very wide. These types of compounds are summarized in Fig. 4.1 [1].

Nowadays, the light oil reserves, which contain low levels of heteroatoms, are quickly decreasing, making it necessary to depend more on the use of heavyweight oil. Sulfur compounds should be removed from petroleum feedstocks because they are released into the atmosphere as sulfur oxides during fuel combustion, causing atmospheric pollution (e.g., acid rain). Moreover, organosulfur compounds poison the precious metal catalysts used in refining reactions, such as catalytic reforming and catalytic cracking [2].

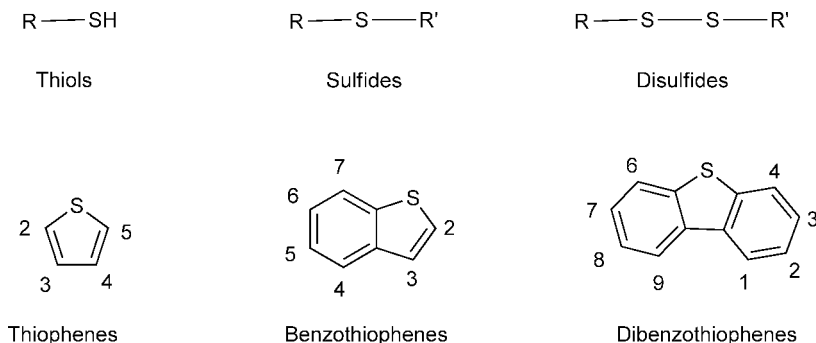


Fig. 4.1. Organosulfur constituents of petroleum and its distillates.

Having in account these problems, the United States government through the Environmental Protection Agency (EPA) and the European Union have gradually established lower sulfur limits in transportation fuels. The sulfur content in gasoline and diesel fuel will be reduced from the current levels of 300–500 ppm to meet the market limits in the United States of <30 ppm in 2006 and in Europe of <10 ppm by 2008 [3].

4.2 HDS CATALYSTS

Hydrodesulfurization (HDS) is the process by which sulfur is removed from organosulfur compounds through a reaction with hydrogen, releasing H_2S . This process is performed at high H_2 pressures (>200 atm) and temperatures (300–450 °C) (see Fig. 4.2).

There are many formulations for HDS catalysts, and the selection depends on the kind of oil being treated. Still, one of the most used consists of a mixture of Mo and Co sulfides supported on alumina. Other examples include mixtures of Ni and Mo or Ni and W [4].

Several models exist, that give an explanation to the way thiophenic moieties are coordinated on the solid catalysts. The most generally accepted model is the so-called *Co-Mo-S Model* proposed by Topsøe. In this model the catalyst is proposed to be formed by a single layer of MoS_2 , having Co or Ni at edge planes. Other phases may be present in this model, but the catalytic activity has been mainly associated to the Co-Mo-S phase having vacancies in the cobalt atom as an explanation for the HDS process [2b].

4.2.1 Coordination Modes of Thiophenic Moieties

All the thiophenic molecules, present two sites with high electronic density, these being the lone pair over the sulfur atom and the $\text{C}=\text{C}$ bond, either of which are likely to interact with the metal centers in the catalysts, and thus a number of coordination modes with the latter may be established. In fact, a large number of examples of metal thiophene complexes have already been identified and characterized (see Fig. 4.3) [5]. It is known that some of these coordination modes are involved in hydrogenation and hydrogenolysis processes; moreover these types of coordination can be applied to benzothiophene (BT) and dibenzothiophene (DBT).

The most common coordination modes in thiophenic molecules are the $\eta^1\text{S}$ and the η^5 . An important observation in the $\eta^1\text{S}$ coordination is that the sulfur atom presents an sp^3 hybridization, all examples of this mode showing the thiophene lying in a different plane from that of the metal, a feature that is distinctive to all the thiophenic moieties [5, 6]. It has been acknowledged that the binding ability increases with the number of methyl groups over thiophene ring, even though all these compounds are weakly coordinated to the metal center. Relevant to the argument at hand, it has been observed that the thiophene (T) is actually displaced by the other methyl-substituted thiophenes.

The η^5 coordination is often exhibited by metals with d^6 electron configurations [5, 6b, 6c], although BT and DBT in general prefer η^6 coordination to η^5 [7].

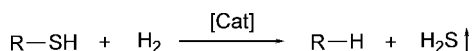


Fig. 4.2. The hydrodesulfurization reaction.

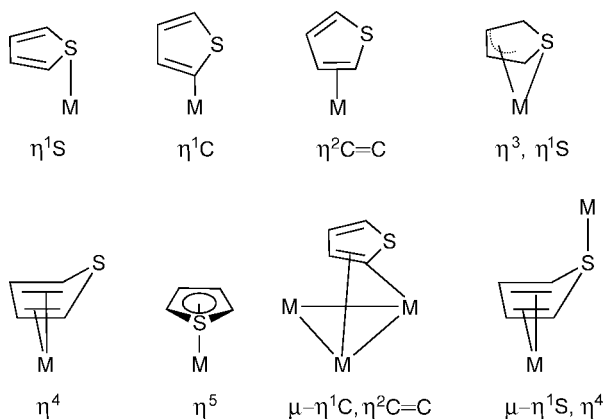


Fig. 4.3. Common coordination modes in thiophenes.

4.2.2 Metal Insertion into C–S Bonds

Usually, when coordinatively unsaturated, electron-rich metal complexes are used in reactions involving thiophenic moieties, the oxidative addition of the C–S bond to the metal center to give a metallacycle, is observed (see Fig. 4.4). The importance of the study of this type of compounds relies in that they have been proposed as key intermediaries in the HDS process.

The first metallacycle was reported by Stone and co-workers in 1960 [8]. Since then, a great number of examples using metallic complexes in low oxidation states has been reported.

Jones and Dong have made an extensive study on the C–S insertion using rhodium complexes [9]. T, BT and DBT and some methylated analogs were used in their study, and a C–S insertion into metal centers with or without previous coordination of the thiophenic fragment was established. Jones and Vicic have also reported the reversible formation of thiametallacycles using thiophenes and Ni-diphosphine complexes, typically dinuclear complexes. Also, they have found that the stability of the respective metallacycle complexes is given as: T > BT > DBT [10].

In addition to the systems above mentioned, numerous examples of metallacycles involving other metals such as Co [11], Ir [12], Fe [13], Ru [14], Zr [15], Mo [16] and Pt [17], have also been reported.

Commonly if the thiametallacycles formed are six membered, the resultant rings are planar. However, the methyl substitution over the thiophenic ring seems to have a significant effect in the geometry of the complex, as the resultant thiametallacycles



Fig. 4.4. Schematic representation of the C–S bond cleavage reaction leading to the formation of metallacycles.

distort from planarity as the number of methyl substituents over the thiophenic moiety increases. Additionally, molecular orbital studies on these type of complexes have found that the planarity is mainly due to steric effects rather than to electronic factors [18].

4.2.3 Catalytic Homogeneous Desulfurization

Considering the urgency of use of heavyweight oils, the study of the DBT activation along with and the more hindered analogs of it (those with alkyl groups in the 4 and 6 positions, 4-RDBT and 4,6-R₂DBT, respectively) has become a major goal, as these compounds constitute the bulk of the remaining sulfur compounds in petroleum feedstocks [19].

Recent studies have developed the first examples of catalytic homogeneous desulfurization of DBT and 4,6-Me₂DBT using nickel compounds. Hayashi and co-workers reported a variety of Ni(0) catalysts mediating the formation of chiral 1,1'-binaphthyls in the asymmetric cross-coupling of dinaphtho[2,1-b:1',2'-d]thiophene with Grignard reagents, which has expanded the use of 1,9-disubstituted DBTs [20].

Recently our group has developed the first catalytic example for the desulfurization of 4,6-Me₂DBT using nickel-phosphine compounds and Grignards reagents to yield the cross-coupled sulfur-free products [21]. The intermediacy of thianickelacycles, such as the ones reported by Vicic and Jones [10], participating in the catalytic cycle has been proposed (see Fig. 4.5).

Additionally in this work, different types of phosphines (mono and diphosphines, containing different hindered substituents) were used. It was observed that when the bite angle in the phosphine is increased the catalytic behavior is diminished, a feature that has been detected particularly with the hindered DBT analogs. Also it has been observed that when a Grignard reagent susceptible to carry out β -elimination is used, the latter process occurs.

4.3 DESULFURIZATION CATALYZED BY NICKEL PCP-PINCER COMPOUNDS

Nickel PCP-pincer compounds (see Fig. 4.6) have been largely used in a wide number of transformations, for instance to develop Heck reactions [22]. Recently our group has started to use this type of compounds to desulfurize thiophenic fragments (DBT and 4,6-Me₂DBT) due to their expected good resistance to high temperatures, obtaining encouraging results.

The reactivity of the above-depicted nickel pincer compounds has been compared with the nickel phosphine-containing compounds, the desulfurization of DBT using MeMgBr found to be quite similar with both types of compounds (see Fig. 4.7). Still, when either EtMgBr or iPrMgCl is used, the reactivity of the pincer compounds is drastically diminished due to the higher sterical effect. In the case of the diphosphine compounds, the latter effect indeed occurs, but in a minor extent; and in the case of monophosphines such effect is not significant (see Fig. 4.7).

The desulfurization of Me₂DBT has been found to be extremely susceptible to sterical effects, in that both the nickel-diphosphine and nickel-pincer compounds showed lower or no reactivity at all, in contrast to the case of DBT. Still, when monophosphines were

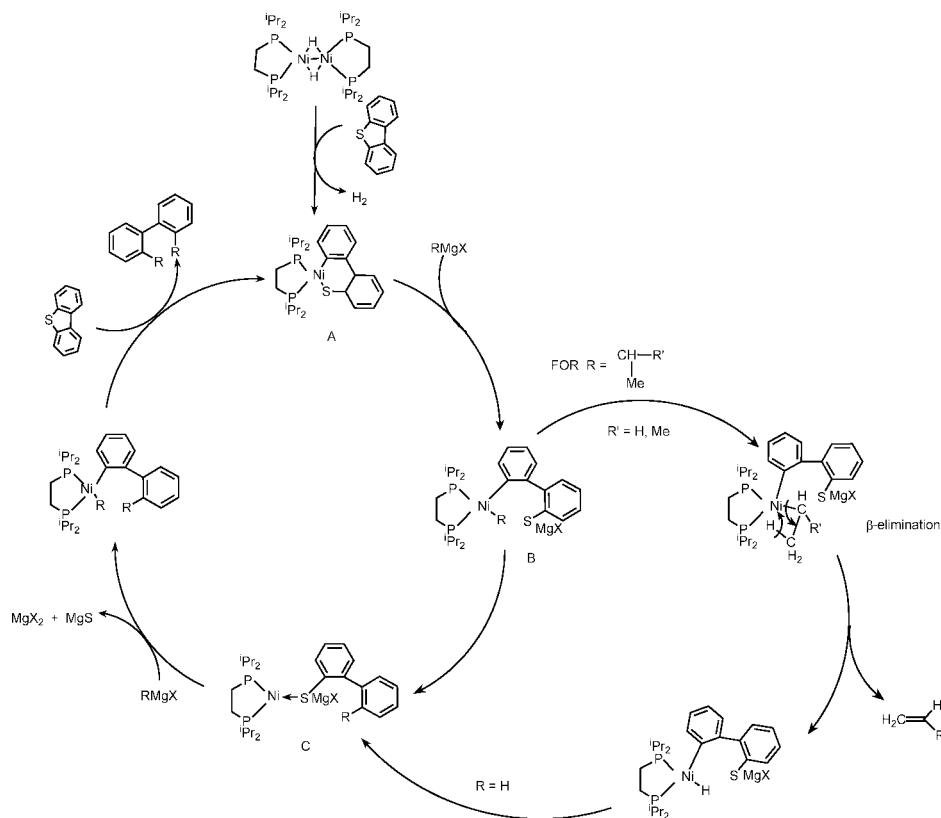


Fig. 4.5. Mechanistic proposal for the catalytic desulfurization of DBT with nickel-phosphine compounds.

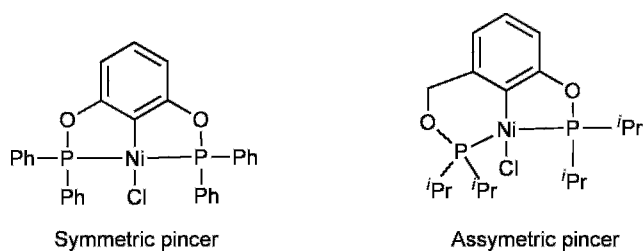


Fig. 4.6. PCP-pincer compounds used to desulfurize thiophenic fragments.

used, such as $[\text{Ni}(\text{PEt}_3)_4]$, the extent of desulfurization was found to increase. In this process in particular, when EtMgBr and $i\text{PrMgCl}$ were used no desulfurization was observed whatsoever (see Fig. 4.8).

In the light of the latter results, it was concluded that the susceptibility of nickel-pincer compounds to sterical effects during the desulfurization process is greater than that presented by nickel-phosphine compounds.

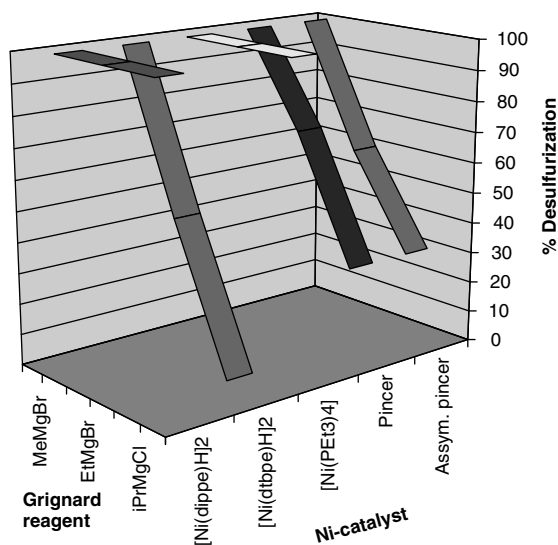


Fig. 4.7. Desulfurization of DBT mediated by Ni compounds at 100°C.

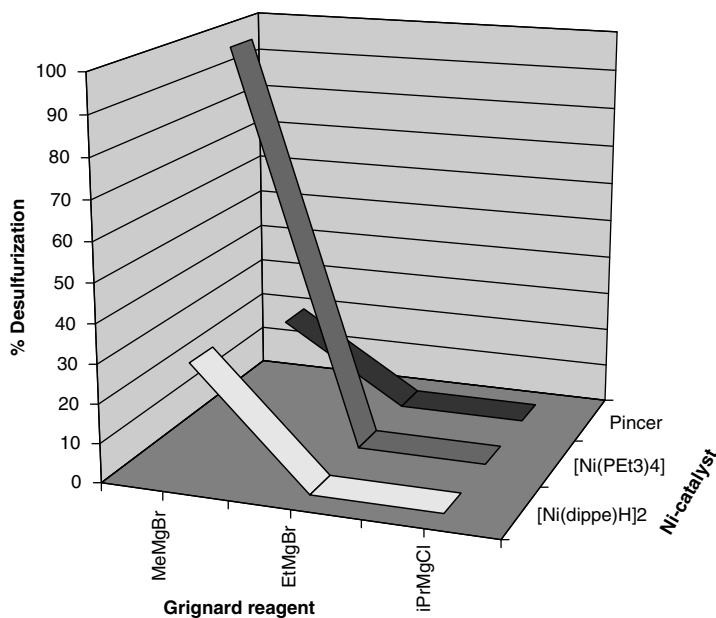


Fig. 4.8. Desulfurization of Me₂DBT mediated by Ni compounds at 100°C.

Several experiments varying temperature conditions were carried out and in these, it was found that when temperature was increased, the reactivity of either type of nickel compounds (pincer and phosphine derivatized) diminished (see Fig. 4.9). Noteworthy, the nickel-pincer complexes are more greatly affected by the temperature than the

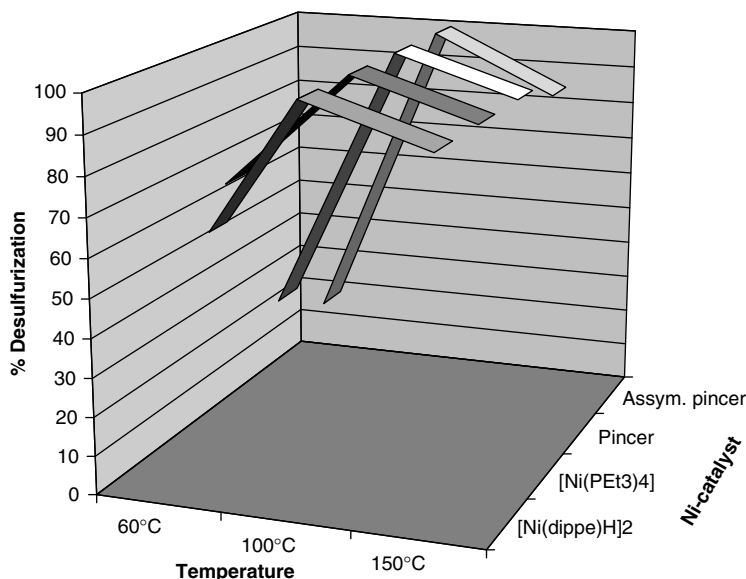


Fig. 4.9. Temperature effect in the desulfurization of DBT.

nickel-phosphine ones. It was thus concluded that the low thermostability of both nickel-pincer and nickel-phosphine compounds is due to the formation of the key metallacycle-like intermediaries, which may not be stable at the higher temperatures. It is important to mention that although pincer compounds are not better catalysts than the phosphine analogs, the versatility of this type of complexes is quite impressive, considering the increasing range of reactions in which the pincer compounds are used other than HDS itself, an area in which these type of compounds could result in assistance in promoting the development of other novel HDS catalytic systems.

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Pincer systems as models for the activation of strong bonds: scope and mechanism

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5.1 INTRODUCTION

Metal complexes with pincer ligands show excellent stability and reactivity which can be conveniently controlled by systematic ligand modifications and variation of the metal center. The process by which bis-chelating pincer systems are generated imposes reactivity patterns characterized by facile activation of various bonds located between the chelating arms of a pincer ligand [1–3]. As we have observed, extremely facile metal insertion into strong chemical bonds that are normally inert can take place in pincer systems, resulting in unequivocal demonstration and mechanistic evaluation of metal insertion into unstrained C–C and C–O bonds in solution. Herein we present an overview of intramolecular C–C and C–O bond activation in pincer systems. We also describe here C–H and O–H bond activation processes that occur concurrently with C–C and C–O cleavage in most of the studied pincer complexes.

5.2 C–H VS C–C BOND OXIDATIVE ADDITION IN PCX-TYPE SYSTEMS

In general, thermodynamic and kinetic factors favor C–H over C–C activation in solution. However, appropriate design can render C–C bond activation in solution thermodynamically feasible; for example, C–C bond activation by soluble metal complexes can be driven by strain relief or aromatization [4–8]. Another approach can be based on the fact that M–C_{Aryl} bonds are strong for M = Rh and Ir, sometimes stronger than M–H bonds; therefore, aryl–aryl or aryl–alkyl bond cleavage can be thermodynamically favorable [7]. Unlike thermodynamics, kinetics is a severely limiting aspect of C–C activation. Kinetic factors favoring C–H over C–C bond activation include (a) an easier approach of the metal center to C–H bonds, (b) the statistical abundance of C–H bonds, and (c) a higher activation barrier for C–C vs C–H oxidative addition due

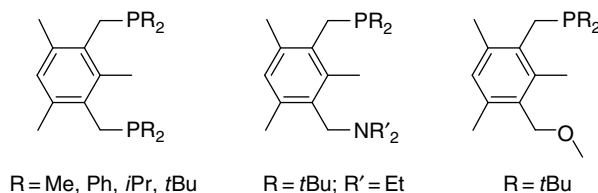


Fig. 5.1. PCX ligand structures.

to the more directional nature of the C–C bond [6, 7]. For recent examples of strong unstrained C–C bond cleavage, see references [9–18].

To achieve favorable thermodynamics and kinetics in C–C bond activation, we employed bis-chelating PCX (X = P, N, O) ligand systems (see Fig. 5.1). Notably, the $\text{C}_{\text{Me}}\text{--C}_{\text{Aryl}}$ bonds of PCX ligands are very strong (e.g., bond dissociation energy $\text{BDE}(\text{C}_6\text{H}_5\text{--CH}_3) = 101.8 \pm 2 \text{ kcal/mol}$), stronger than the competing benzylic C–H bonds (e.g., $\text{BDE}(\text{C}_6\text{H}_5\text{CH}_2\text{--H}) = 88 \pm 1 \text{ kcal/mol}$ [19]).

C–H and C–C activations in these systems are competitive processes, allowing direct comparison of the two.

5.2.1 Insertion into a Strong C–C Bond in Solution: C–C vs C–H Activation

5.2.1.1 C–C activation: demonstration of the process employing various PCP-metal systems. Scope of the reaction and influence of metal choice

The first example of metal insertion into an unstrained, unactivated C–C bond in solution was demonstrated employing Ph-PCP and $[\text{HRh}(\text{PPh}_3)_4]$ [20]. Reaction of this metal complex with the Ph-PCP ligand at room temperature resulted in H_2 elimination and formation of the kinetic C–H activation product (Fig. 5.2). The C–H activation process can be reversed by heating of this product under mild hydrogen pressure, resulting in quantitative C–C cleavage and methane elimination.

As the C–C activated complex does not react with methane, the overall C–C activation process is irreversible and thermodynamically more favorable than the C–H activation sequence.

Aryl- CF_3 and aryl-Et activation. Aryl- CF_3 bonds are among the strongest C–C bonds with $\text{BDE}(\text{Ph-}\text{CF}_3) = 108.9 \text{ kcal/mol}$ [21]. Metal insertion into such bond was observed for the first time by utilizing a PCP ligand bearing a CF_3 group between the chelate phosphine moieties. Upon the reaction of the ligand with $[\text{RhL}_2\text{Cl}]_2$ (L = ethylene, cyclooctene), oxidative addition of aryl- CF_3 bond to a rhodium metal center occurs (Fig. 5.3) [22, 23].

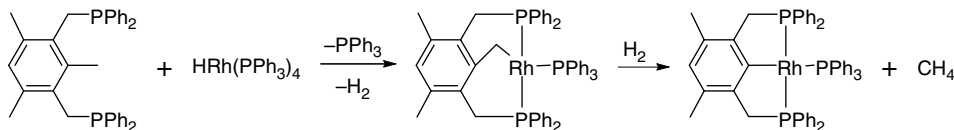
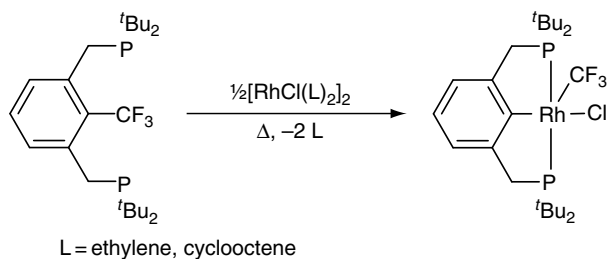
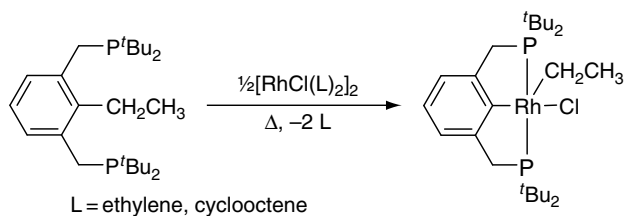
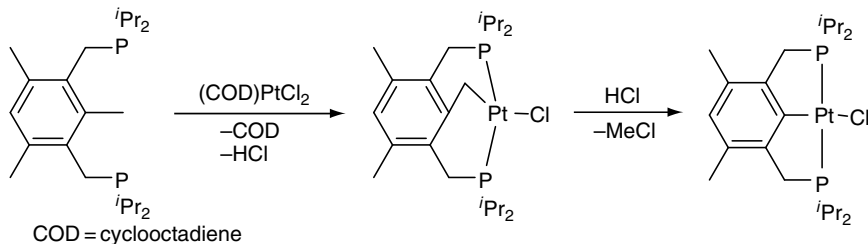


Fig. 5.2. Selective hydrogenolysis of a C–C bond.

**Fig. 5.3.** Aryl- CF_3 bond oxidative addition.**Fig. 5.4.** $\text{C}_{\text{sp}^3}\text{--C}_{\text{sp}^3}$ vs $\text{C}_{\text{sp}^3}\text{--C}_{\text{sp}^2}$ bond cleavage.

The possibility of competitive activation of $\text{C}_{\text{sp}^3}\text{--C}_{\text{sp}^3}$ vs $\text{C}_{\text{sp}^3}\text{--C}_{\text{sp}^2}$ bonds was studied with a PCP ligand containing an aryl-Et moiety [24, 25]. Remarkably, direct $\text{C}_{\text{sp}^3}\text{--C}_{\text{sp}^2}$ bond activation was observed (Fig. 5.4). Although the $\text{Ar-CH}_2\text{CH}_3$ bond is substantially stronger than the $\text{ArCH}_2\text{--CH}_3$ bond (compare BDE values of $\text{Ph-CH}_2\text{CH}_3$, 96.3 kcal/mol, and $\text{PhCH}_2\text{--CH}_3$, 71.8 kcal/mol), selective insertion into the Ar-C bond takes place, indicating that this process is product controlled, and it is likely that $\text{BDE}(\text{Ar-M} + \text{M-CH}_2\text{CH}_3) - \text{BDE}(\text{ArCH}_2\text{--M} + \text{M-CH}_3) > 20$ kcal/mol (see Section 5.2.1.4 for the discussion on thermodynamic and kinetic aspects of C-C activation).

C-C vs C-H activation by Pt. The C-C bond in PCP ligand systems was also cleaved by Pt(II) (see Fig. 5.5) [26, 27]. The kinetic C-H activation product was quantitatively converted into the C-C activation product by the addition of HCl, forming methyl chloride.

**Fig. 5.5.** C-C bond activation mediated by platinum.

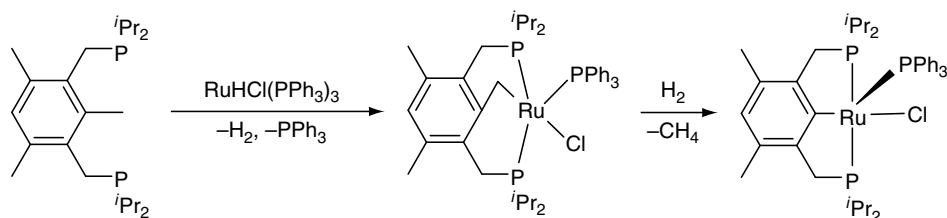


Fig. 5.6. C–C bond activation mediated by ruthenium.

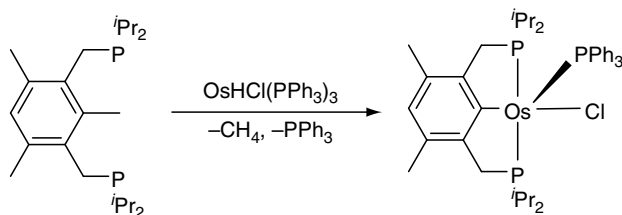


Fig. 5.7. C–C bond activation mediated by osmium.

C–C vs C–H activation by Ru and Os. When a ruthenium hydride complex is reacted with the *i*Pr-PCP ligand, C–H bond activation takes place [26]. The product of C–H bond activation upon heating under hydrogen atmosphere is converted to the C–C activation product similarly to the above-mentioned systems (Fig. 5.6).

Interestingly, the analogous Os complex shows exclusive C–C activation in the absence of hydrogen (Fig. 5.7) [28]. Such selectivity may be due to a specific orientation of osmium toward the Ar–CH₃ bond (see below).

C–C vs C–H activation by Ni. C–H and C–C bond activation mediated by nickel is shown in Fig. 5.8 [29, 30].

Notably, in the Ar–Et PCP–nickel system, only the C–C bond activation product is observed, whereas in Ar–Me PCP system, both C–H and C–C activation products are formed. A side equilibrium leading to reversible C–H activation in the former system cannot be ruled out.

5.2.1.2 Revealing the thermodynamics of the C–C vs C–H activation

Employment of hydrogen or other ‘methylene releasing’ agents masks the relative thermodynamic stability of the C–H and C–C activation products. In a Me–PCP/Rh system, no such agent was necessary. Heating the Me–PCP ligand with [Rh(PEt₃)₃Cl] led to the product of direct C–C activation quantitatively [31]. The C–H activation product, which was prepared by an independent route, is quantitatively converted into the C–C activation product on heating (Fig. 5.9), unambiguously proving that *Rh(I) insertion into the C–C bond in this system is thermodynamically more favorable than its insertion into the C–H one.*

The C_{Me}–C_{Aryl} bond in PCP ligands is much stronger than the C_{Benzyl}–H bond (see above), indicating that conversion of the C–H activation product into the C–C activation one is product controlled and that BDE(Rh–aryl + Rh–CH₃) > BDE(Rh–CH₂aryl + Rh–H). Formation of the strong Rh–aryl bond most probably is a driving force for

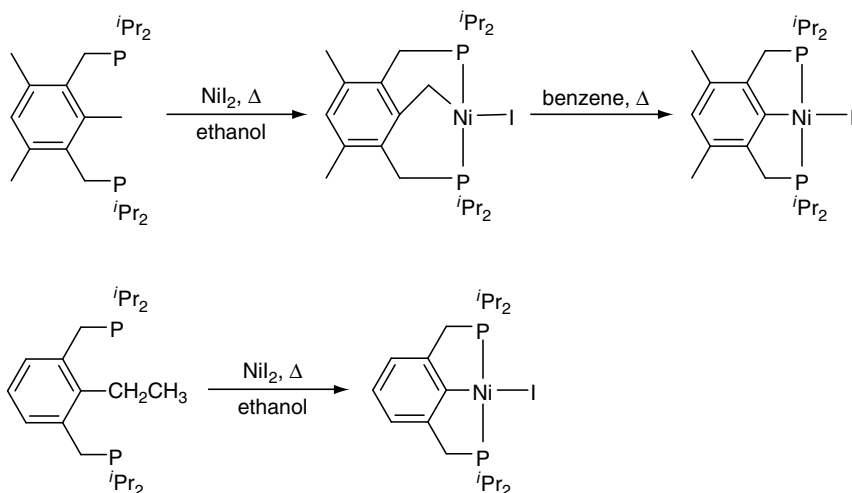


Fig. 5.8. C–C bond activation mediated by nickel.

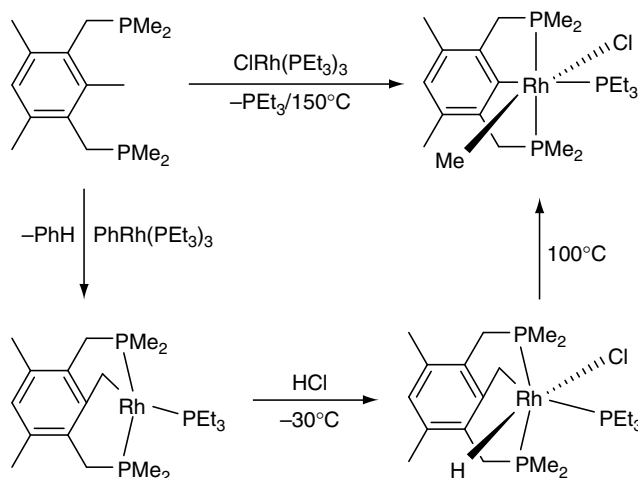


Fig. 5.9. Thermodynamic preference of C–C over C–H bond oxidative addition.

the reaction. The expected slightly lower stability of the six-membered chelate ring in the C–H activation complexes, as compared to the five-membered ring in the C–C activation complexes, may also influence their relative stability.

5.2.1.3 Selective C–C activation as a function of pincer ligand, solvent, or auxiliary ligand choice

Solvent choice. A cationic metal center in PCX-based systems exhibits specific reactivity and selectivity due to lower electron density and coordination of solvent ligands. A *t*Bu-PCP/cationic rhodium system shows exclusive activation of C–C or C–H bonds

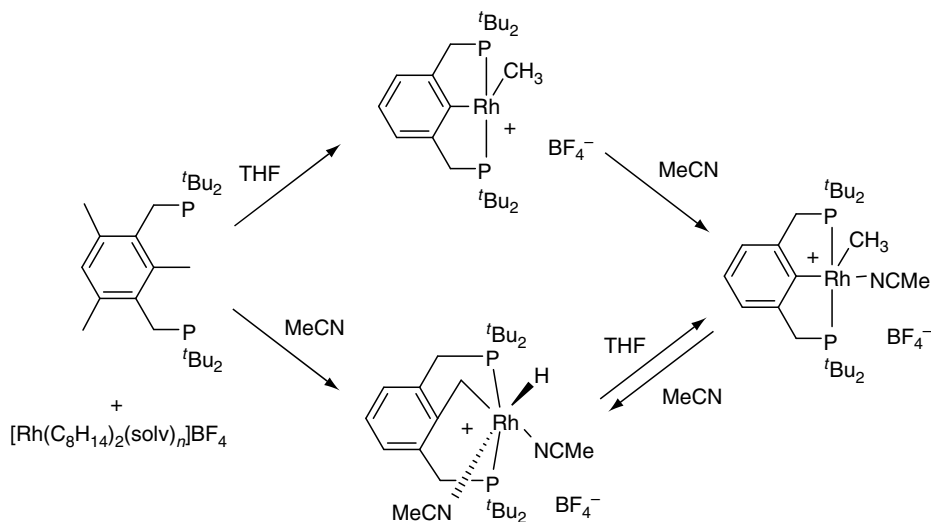


Fig. 5.10. Solvent-controlled C–C vs. C–H oxidative addition.

at room temperature as a function of solvent choice [32]. Thus, in acetonitrile, exclusive C–H activation occurs, whereas in THF, the C–C bond activation product was quantitatively formed (see Fig. 5.10). Solvent control over metal insertion into strong C–H vs C–C bonds is a consequence of solvent coordination. In THF, an unsaturated intermediate, possessing a vacant coordination site, is accessible. In the case of the better-coordinating acetonitrile, solvent coordination blocks vacant coordination sites and generates an intermediate too bulky for insertion into the sterically more hindered C–C bond. Thus, unlike its neutral counterpart that does not bind solvent molecules, the cationic rhodium center shows excellent selectivity in C–C vs C–H activation as a function of the reaction medium.

Pincer ligand choice. The PCN–Rh system demonstrates very high selectivity toward C–C vs C–H bond activation: no C–H activated products are observed in this system (see Fig. 5.11) [33]. Such preference for C–C bond activation is most probably due to the optimal metal positioning for the insertion into the C–C bond. Thus, as both C–H and C–C activations are observed in most PCP systems mentioned above, changing of one phosphine arm for an amine results in preferential C–C activation, demonstrating that the C–C vs C–H reaction aptitudes can be controlled by pincer ligand choice.

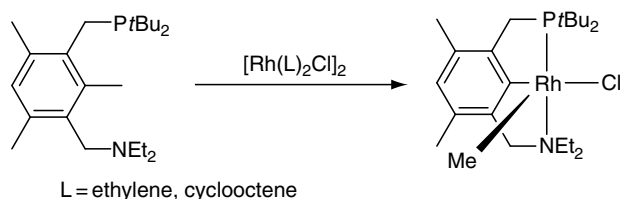


Fig. 5.11. Selective C–C bond oxidative addition in PCN system.

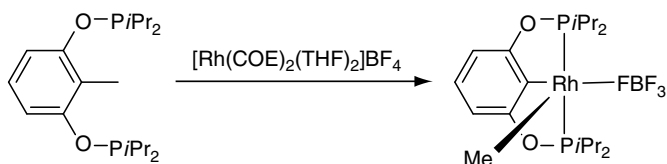


Fig. 5.12. Selective C–C bond oxidative addition in POCOP system.

This concept is further exemplified by a POCOP ligand. The POCOP–Rh system demonstrates remarkable selectivity toward C–C activation (Fig. 5.12) [34]. No parallel formation of the C–H activation product is observed. This is probably a result of coordinative unsaturation and specific orientation of the metal toward the C–C bond (see below).

Auxiliary ligand choice. Using the PCN system, control over C–C vs C–H bond activation and vs formation of an agostic C–C complex can be achieved by choice of cationic $\text{Rh}(\text{CO})_n$ -based ($n = 0, 1, 2$) precursors. When $n = 0$, the C–C activation product is obtained exclusively, whereas with the dicarbonylrhodium complex ($n = 2$), the C–H-activated compound is formed, a process promoted by protonation of the hemilabile amine arm (see Fig. 5.13) [35]. Apparently, the $\text{Rh}(\text{CO})_2$ complex undergoes electrophilic C–H activation. The monocarbonyl cationic Rh species ($n = 1$) affords an agostic C–C compound. These observations demonstrate the influence of π -accepting auxiliary ligands on the relative aptitudes of C–C and C–H activation.

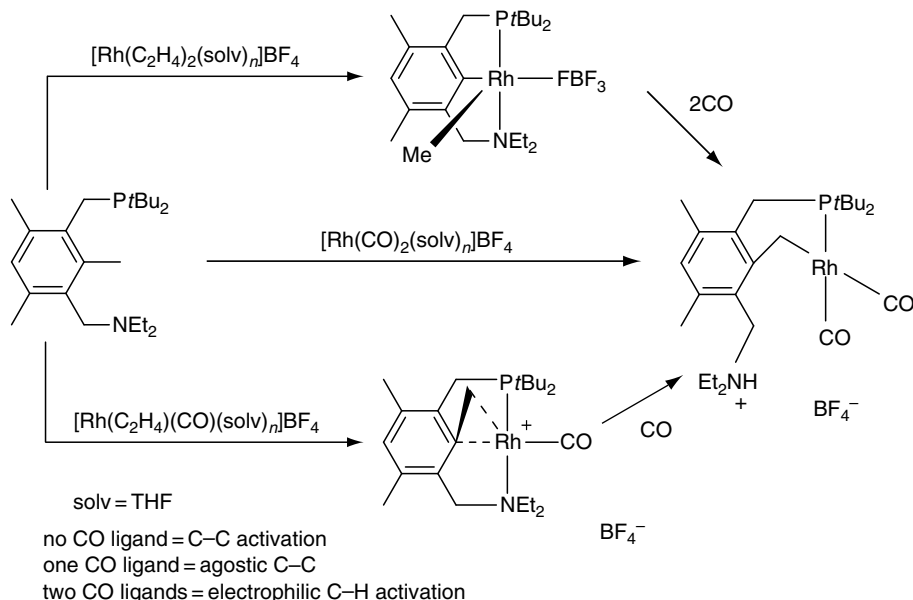


Fig. 5.13. C–C vs. C–H activation controlled by the number of CO ligands.

5.2.1.4 C–C vs C–H activation: mechanistic insight

Bulky phosphines are advantageous ligands for the study of oxidative addition processes, especially cyclometallation, since upon coordination to a metal center, they generate a species with a shielded vacant coordination site and a congested conformation. Remarkably, when the *t*Bu-PCP ligand is reacted with rhodium olefin dimers at room temperature, direct rhodium insertion into one of the strong aryl–carbon bonds takes place, yielding the product of C–C oxidative addition (see Fig. 5.14) [36]. Parallel formation of the C–H activation product is also observed, and this product is quantitatively converted to C–C activation one at room temperature. These observations indicate that the C–H activation product undergoes C–H reductive elimination, followed by rapid metal insertion into the C–C bond in the case of rhodium.

Increasing the steric bulk of the alkene ligand in the $[\text{RhL}_2\text{Cl}]_2$ (L = ethylene, cyclooctene, *t*Bu ethylene) complex results in a large decrease in the overall reaction rate. The reaction is very fast with the ethylene complex and slow with the *t*Bu ethylene one. This reactivity order indicates that associative displacement of the alkene by the phosphine takes place and that the *initial coordination of the diphosphine ligand to the rhodium olefin complex is the rate-determining step for the entire process* rather than the C–C or C–H activation steps.

Concurrent formation of the C–H and C–C oxidative addition products occurs in the reaction of $[\text{Ir}(\text{cyclooctene})_2\text{Cl}]_2$, with the *t*Bu-PCP ligand at room temperature. The product of C–H activation is quantitatively converted into C–C activation product upon moderate heating (see Fig. 5.14) [36]. Whereas the C–H activation product in the case of rhodium is unstable at room temperature, the iridium C–H activation product is stable up to 60°C, facilitating the comparison between C–H and C–C activation at lower temperatures.

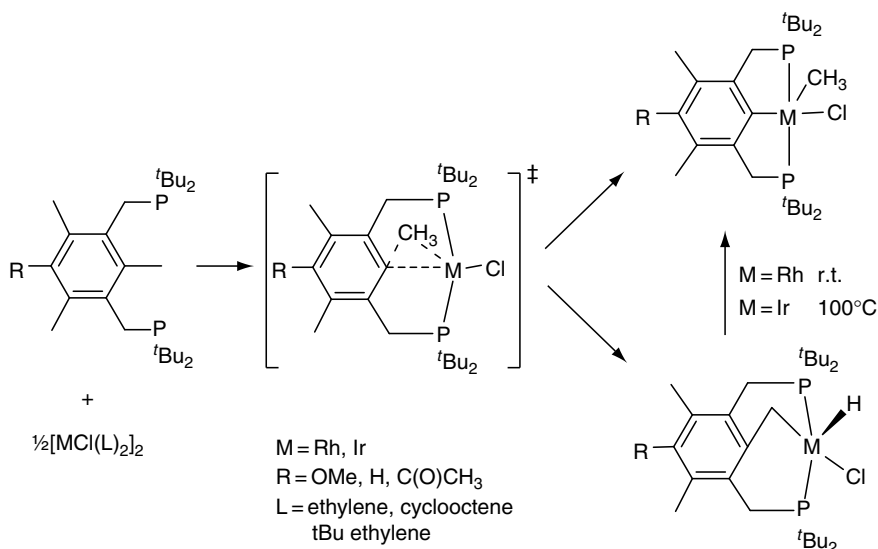


Fig. 5.14. Mechanistic insight into C–C vs. C–H bond oxidative addition in *t*Bu-PCP system.

In the case of iridium, the ratio between the products of C–C and C–H activation is constant at different temperatures during the reaction course and remains the same after the reaction is complete (C–H : C–C is 1.75 ± 0.07 in benzene and 2.29 ± 0.08 in THF). The C–H and C–C insertion products are formed irreversibly within the temperature range of 20–60°C, indicating that the C–C and C–H activation processes are kinetically controlled, while the constant ratio demonstrates that the complexes are formed in two independent concurrent processes. Thus, the C–H activation product is not an intermediate in the C–C activation process, as verified by the observation that it does not convert to C–C under the reaction conditions. Both the C–C and C–H activation processes proceed through a common intermediate with the two phosphine arms coordinated to the metal center. Thus, taking into account that the product ratio is temperature independent and that three C–H bonds per one C–C are accessible for activation, we obtain $\Delta\Delta H_{\text{CH-CC}}^\ddagger = 0$ kcal/mol and $\Delta\Delta S_{\text{CH-CC}}^\ddagger = -1.07 \pm 0.05$ eu. Surprisingly, the kinetic barrier for C–C oxidative addition is slightly lower than that for C–H ($\Delta\Delta G_{\text{CH-CC}}^\ddagger(293) = 0.342$ kcal/mol, Fig. 5.4).

The similarity of the activation parameters for C–C and C–H activation processes and the fact that they are not much affected by variation in solvent polarity (benzene and THF) or by the use of a *para*-methoxy- and *para*-carboxy-substituted derivatives of the *t*Bu-PCP ligand indicates that similar nonpolar transition states are involved in both processes. Thus, the C–C bond oxidative addition in our system appears to proceed through a three-center nonpolar transition state similar to the one postulated for aliphatic C–H bond activation.

Theoretical studies of the oxidative addition of C–C vs C–H bonds to neutral Rh(I) and Ir(I) complexes with PCP-type ligands have been carried out utilizing various DFT methods [37, 38]. According to the calculations, C–H activation is the kinetically favored process, whereas C–C activation is thermodynamically favorable. C–H addition is a reversible process in the case of Rh(I). Bulky substituents are found to increase the barrier for C–H activation relative to that for C–C activation, whereas coordinative unsaturation greatly facilitates both C–C and C–H oxidative addition, proceeding through nonpolar three-centered transition states. For the Ir–PCP system, direct metal insertion into the C–C bond is not only thermodynamically favored but also kinetically competitive with C–H bond oxidative addition [38]. Overall, the computational studies are in agreement with our experimental findings.

Further insight into the C–C bond activation mechanism was obtained by kinetic evaluation of a single-step metal insertion into a carbon–carbon bond in solution in the PCN–Rh system. In this case, pincer ligand coordination is not rate-determining, allowing the direct study of the C–C activation process. The 14e intermediate **Y** (Fig. 5.15),

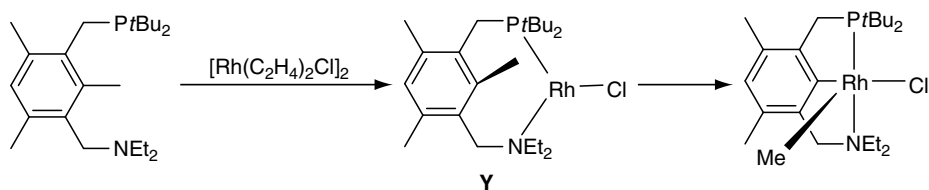


Fig. 5.15. Directly observed 14e intermediate in C–C oxidative addition in PCN system.

a frozen intermediate in the process, was formed and fully characterized at low temperature (-80°C) [39]. Using the corresponding isotopically labeled $^{13}\text{CH}_3$ complex, no interaction between the methyl group and metal center was observed. The compound **Y** undergoes clean oxidative addition of the C–C bond, allowing the direct measurement of the activation parameters: $\Delta H^{\ddagger} = 15.0 \pm 0.4 \text{ kcal/mol}$, $\Delta S^{\ddagger} = -7.5 \pm 2.0 \text{ eu}$, and $\Delta G^{\ddagger}(298) = 17.2(\pm 1.0) \text{ kcal/mol}$. The same values were observed for two solvents (toluene and 3-fluorotoluene), indicating that solvent coordination does not play a role in the process. As expected for a concerted oxidative addition process, the activation entropy is negative. The fact that it is only moderately negative indicates that the intermediate is fairly ordered toward the insertion step. Thus, our kinetic study supports a three-centered, nonpolar transition state for $\text{C}_{\text{Ar}}\text{--C}$ oxidative addition to Rh(I). The obtained activation parameters are the first data for an apparent single-step carbon–carbon bond activation by a metal complex. Notably, C–C activation in this system commences at temperatures as low as -70°C !

Our attempt to extend the scope of C–C activation to a mono-dentate PC system (see Fig. 5.16) resulted in exclusive C–H bond activation under various conditions [40]. Following this observation, a bis-chelating PCO-type ligand (Fig. 5.1) was designed to probe the apparently critical role of the chelating effect.

The PCO–Rh system undergoes C–H bond activation at room temperature, forming products with an open and closed methoxy arm (see Fig. 5.17) [41]. C–C bond activation takes place on heating. Significantly, whereas C–H activation of the two methyl groups is observed, only the C–C bond between the chelating arms is activated, demonstrating that the chelating methoxy ligand is both essential and sufficient for C–C activation. An attempt to isolate the C–H activation products led to an intriguing observation: removal of the solvent from a solution of the C–H activation complexes under vacuum at room temperature resulted in conversion of the C–H to the C–C activation product. Thus, C–H vs C–C bond activation can be controlled just by the presence or absence of the solvent. This effect appears to be due to the preferential coordination of the BF_4 counter anion to the metal center of the C–C activation product upon solvent evaporation.

Apparently, the chelate effect influences both the kinetics and the thermodynamics of the process. An important kinetic factor is the bonding of the metal center by the two ligand arms, which brings the metal into proximity of the C–C bond to be cleaved. The resulting C–C activation product is also stabilized by the presence of two five-membered chelate rings, contributing to the thermodynamic driving force of the reaction. Further insight regarding these factors was obtained from a computational DFT study of the Rh–PCO system.

The DFT study reveals that Rh(I) 14e species are significant for both C–C and C–H activation, the calculated barriers being the lowest for the 14e intermediates,

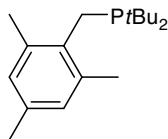


Fig. 5.16. Monodentate PC ligand.

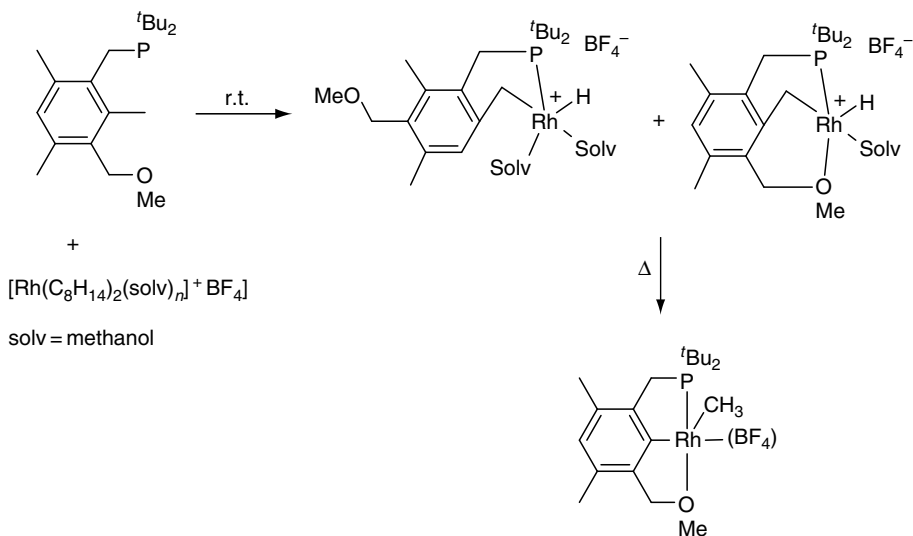


Fig. 5.17. C–H and C–C oxidative addition in PCO system.

A and **B** (Fig. 5.18) [41]. The fact that the metal center coordinates solvent molecules to achieve a 14e configuration demonstrates the general importance of this electronic structure for C–H and C–C bond activation. Both thermodynamics and kinetics favor C–H over C–C activation in the ‘open-arm’ PCO case. In the ‘closed-arm’ system, calculations show that C–H activation is kinetically preferred over C–C activation, while the C–C activation product is thermodynamically more stable (Fig. 5.18), in accord with the experimental study. Careful examination of the geometry of the intermediates and transition states showed that to achieve C–C oxidative addition, the metal must be closer to the bond than in the case of C–H activation. It seems to be a general factor, which is most probably due to the more directed character of the C–C bond in comparison to the C–H one. Hence, steric requirements for C–C bond activation are more restrictive than those for the C–H one, rendering bis-chelation essential for C–C cleavage. On the contrary, the electronic requirements for both C–C and C–H oxidative addition are very similar and 14e intermediates play a key role in both activation processes.

Overall, in the PCO–Rh system, C–C bond activation is a facile process: it can be achieved at moderate heating or at room temperature upon solvent evaporation. Importantly, a general mechanistic conclusion can be made: *steric limitations play a critical role in C–H vs C–C bond activation aptitudes, electronic requirements being very similar.*

5.2.1.5 Catalytic C–C activation

An unstrained, strong aryl–C bond can be catalytically cleaved by a metal complex in solution. Thus, reaction of $[\text{Rh}(\text{cyclooctene})_2\text{Cl}]_2$ with excess of the *i*Pr-PCP substrate in dioxane under mild H_2 pressure or with an excess of $\text{HSi}(\text{OEt})_3$ results in a catalytic selective cleavage of one of the C–C bonds in the diphosphine [42]. Although the

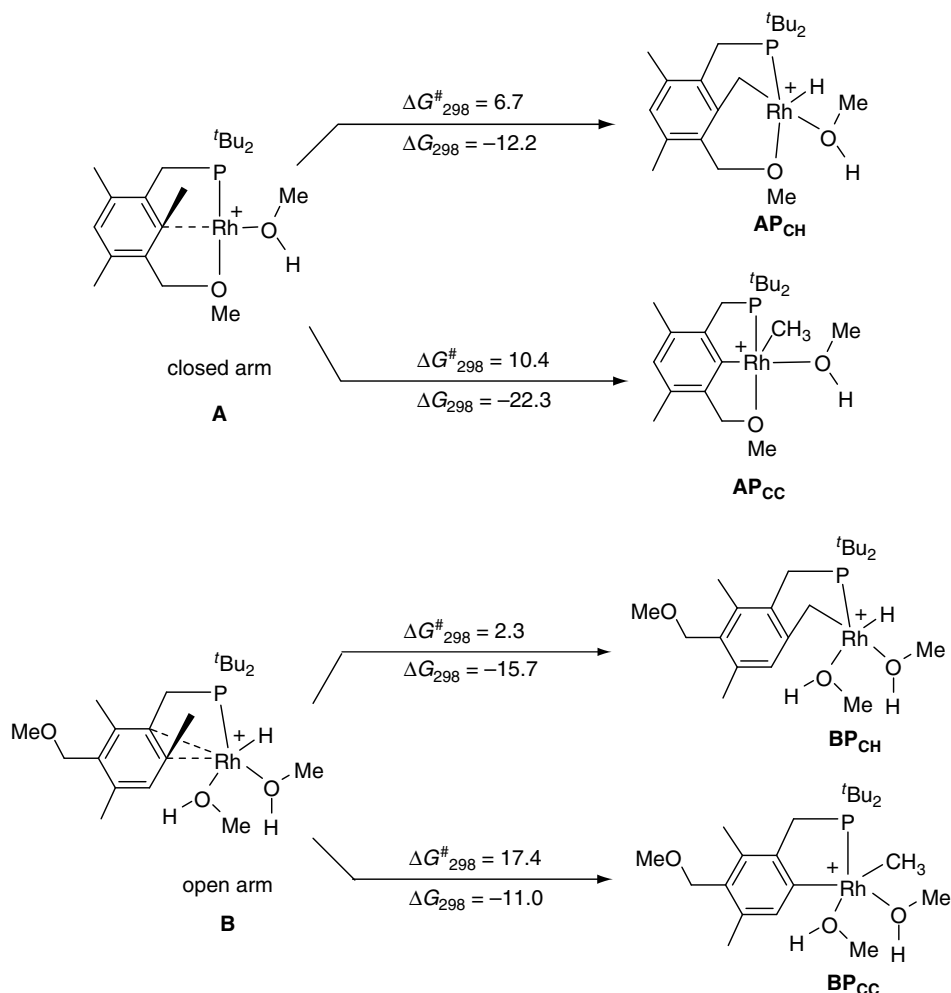


Fig. 5.18. C–C and C–H oxidative addition in PCO system: intermediates and reactions elucidated from computational studies.

catalytic reactions were not optimized, more than 100 turnovers were observed in the case of H_2 (Fig. 5.19).

5.2.2 The Methylene Transfer Reaction

The ability to insert a metal into an unactivated C–C bond raises a possibility that a hydrocarbon could serve as a source of methylene groups. If the inserted metal center is capable of binding and activating an additional substrate, the result could be selective insertion of the CH_2 group into another chemical bond. Indeed, the methylene group in the ‘methylene-bridged’ complexes can be abstracted not only by H_2 but by a variety of reagents. Thus, the CH_2 group was inserted into Si–H, Si–Si and $\text{C}_{\text{Aryl}}\text{–H}$

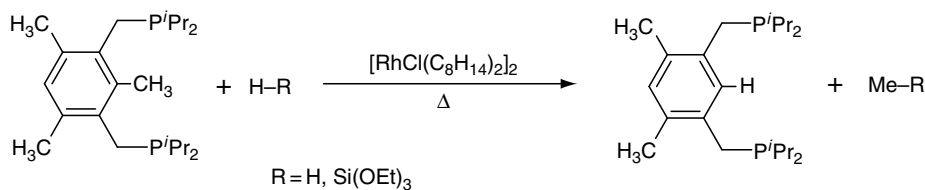


Fig. 5.19. Catalytic C–C bond activation.

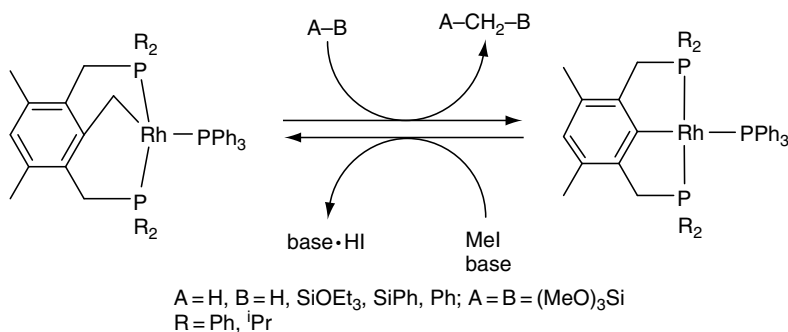


Fig. 5.20. Methylene transfer reaction.

bonds (Fig. 5.20), representing a conceptually new process in organometallic chemistry, combining C–C cleavage, methylene group transfer, and its selective incorporation into other bonds [43]. Interestingly, the methylene group can be regenerated by treatment of the C–C cleaved complex with methyl iodide and a base, representing a two-step process in which a CH₂ group is extruded from MeI and selectively incorporated into an Si–Si bond (Fig. 5.20).

A mechanism accounting for the methylene group transfer was suggested to include a substrate oxidative addition step with subsequent migration of the cleaved group to carbon, followed by C–C bond cleavage by a three-coordinate Rh(I) intermediate and, finally, product release by reductive elimination.

To gain mechanistic insight into the methylene transfer reaction and extend the scope of possible transformations, the reaction sequence shown in Fig. 5.21 was performed [44]. Initially, C_{Aryl}–I oxidative addition occurs, followed by C–C reductive elimination and oxidative addition steps. The net result is an intramolecular arene-to-arene transfer of a methylene group. Kinetic studies reveal that the C–C reductive elimination step is rate-determining, with a nonpolar three-centered early transition state characterized by the following activation parameters: $\Delta S^\ddagger = -23 \pm 4$ eu and $\Delta H^\ddagger = 17 \pm 3$ kcal/mol.

The process described in Fig. 5.21 was studied computationally in the model system (H–PCP–CH₂)Rh(Ph)(I) (see Fig. 5.22) [45]. DFT calculations support the experimental conclusion that the rate-determining step in the methylene transfer sequence is the initial C–C reductive elimination rather than the C–C activation step. The η^2 arene complex **E2**, which is formed in the process, is a key intermediate, participating

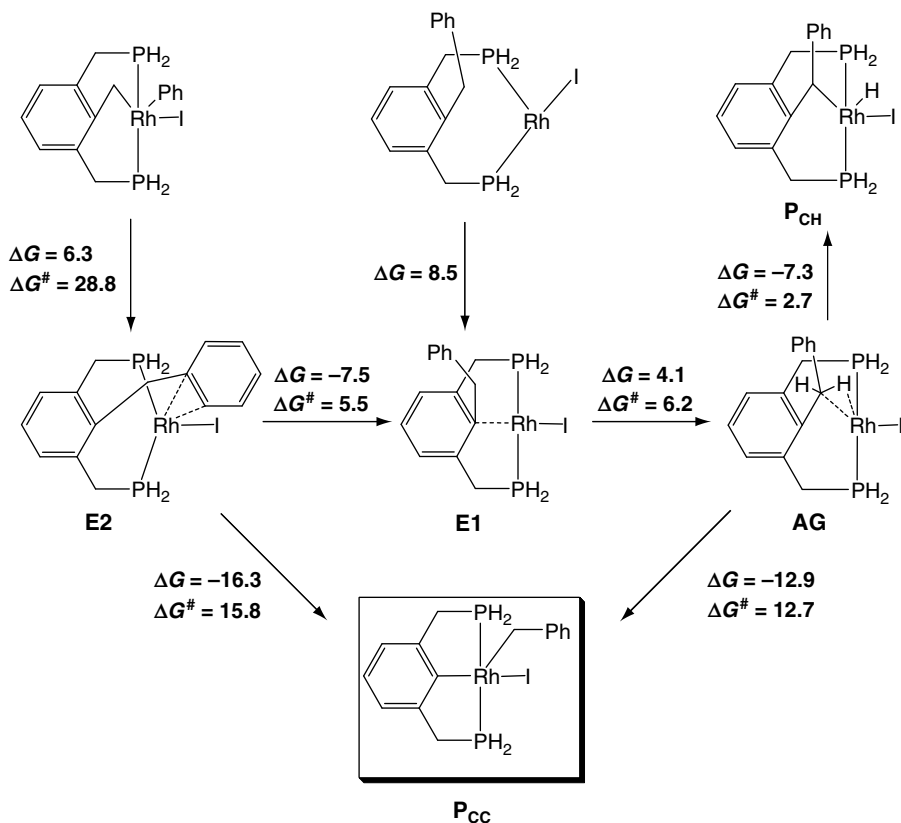


Fig. 5.22. Mechanism of a methylene transfer reaction as elucidated by a computational study.

in all pathways found for the following C–C activation reaction. The lower energy route proceeds through the η^1 complex **E1** that is converted to the agostic C–H complex **AG** capable of both C–H and C–C bond oxidative addition (producing **P_{CH}** and **P_{CC}**, respectively). The other route proceeds *directly* from the η^2 complex **E2** to give the C–C activation product.

5.3 METAL INSERTION INTO UNSTRAINED C–O BONDS

Direct activation of unstrained strong C–O bonds by metal complexes in solution is rare [12, 46–53], and mechanistic information regarding these processes is scarce [52, 53]. Employing PCP ligand systems, we have demonstrated, for the first time, that metal insertion into the strong aryl–oxygen single bond of an aromatic ether and a phenol under mild homogeneous conditions is possible (see Fig. 5.23) [30, 54]. Although in all cases studied a d^8 metal is used, the nucleophilic Rh(I) complex selectively activates the very strong aryl–O bond, whereas the more electrophilic Pd(II) or Ni(II) complexes preferentially cleave the alkyl–O single bond (BDE values of $\text{Ph–OCH}_3 = 91$ kcal/mol, $\text{PhO–CH}_3 = 80$ kcal/mol). Moreover, the alkoxy group can be transferred to silanes,

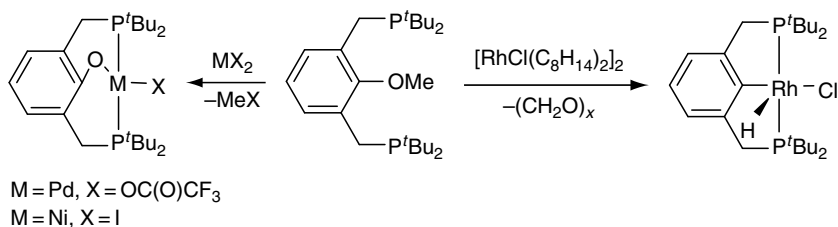


Fig. 5.23. Aryl–O vs. Me–O bond cleavage.

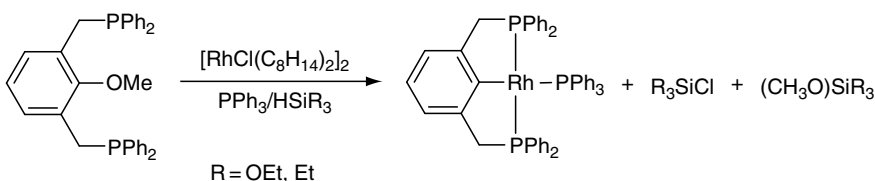


Fig. 5.24. Alkoxy group transfer from carbon to silicon.

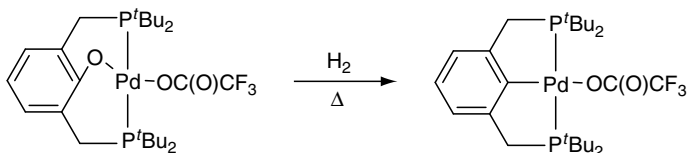


Fig. 5.25. Aryl–O bond hydrogenolysis mediated by palladium.

providing a rare example of hydrosilation of an unstrained C–O bond (see Fig. 5.24). C–O cleavage by a Pd center can be achieved using hydrogen (see Fig. 5.25).

Thus, it is possible to influence the selectivity of the kinetically controlled $\text{sp}^2\text{--sp}^3$ vs $\text{sp}^3\text{--sp}^3$ C–O bond activation by proper choice of metal precursor or the alkyl group. Our observations show that a nucleophilic metal favors direct aryl–O bond activation, whereas electrophilic metals are likely to promote alkyl–O bond cleavage (see Fig. 5.23) [30, 54]. Significantly, we observed that the phenoxy complexes are neither intermediates in the $\text{sp}^2\text{--sp}^3$ C–O bond activation processes nor involved in side equilibria. Our results provide evidence that metal complexes can be designed to selectively activate and functionalize unstrained C–O single bonds under mild homogeneous conditions.

An additional example of metal-controlled reactivity in aryl–O vs Me–O bond activation is the reaction shown in Fig. 5.26. In this PCP system, O–H activation followed by aryl–O activation is observed under mild conditions in the case of Rh(I), whereas reaction of the PCP–OH ligand with Ir(I) precursor results in exclusive O–H activation product formation [55]. The Ir O–H activation product is stable on prolonged heating. Remarkably, in the case of rhodium, we observed parallel formation of an

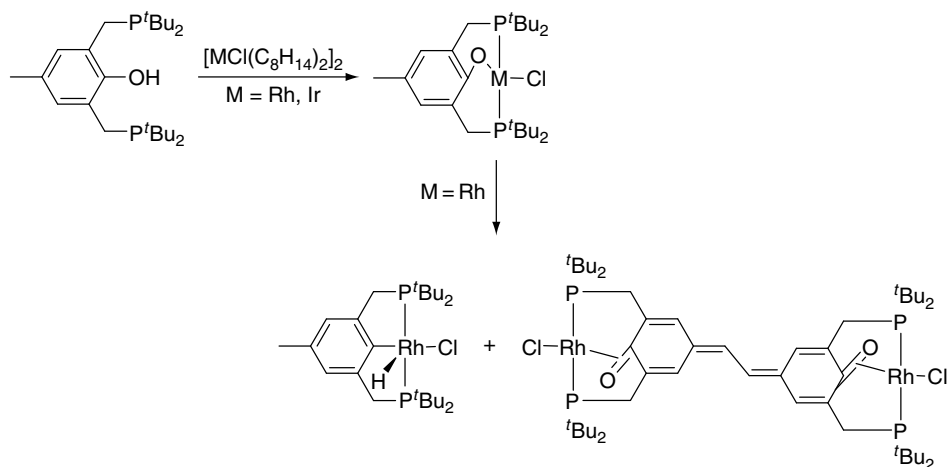


Fig. 5.26. Aryl–O bond cleavage by rhodium and formation of bimetallic stilbene quinone.

aryl–O cleavage product and a product of self-oxidation, a unique bimetallic stilbene quinone, the ratio being 3:1, respectively.

Activation of O–H bond that is not followed by aryl–O activation was also observed in an analogous iridium/PCP–OH system [56]. The difference in reactivity between Rh and Ir metal centers in aryl–O bond activation may be attributed to a higher stability of Ir(III) O–H activation products.

5.4 SUMMARY

PCX–metal systems proved to be excellent models for strong bond activation studies. Intramolecular bond activation in PCX systems is very facile, resulting in activation of very strong unstrained C–C and C–O bonds. This was demonstrated for the first time employing PCX ligands and a variety of late transition metals including Rh, Ir, Ru, Os, Ni, and Pt. PCX systems provided mechanistic insight into the activation of strong C–C bonds. In most PCX–metal systems, C–C oxidative addition is thermodynamically more favorable than competing C–H activation processes. C–C activation can proceed directly and does not require prior C–H activation. In cases where the primary C–C oxidative addition is unfavorable, C–C cleavage may be accomplished by the use of a subsequent energy-releasing reaction, such as hydrogenolysis. The C–C oxidative addition process by Rh(I) involves a 14e intermediate (directly observed in the PCN/Rh system) and proceeds via a three-centered nonpolar transition state, similar to the one involved in C–H activation. Specific orientation of the metal center toward the C–C bond is essential for C–C oxidative addition, more so than for C–H oxidative addition, due to more directional nature of the C–C bond. The activation parameters for a single-step C–C oxidative addition, which can proceed even at -70°C , were obtained for the first time. The C–C activation step was incorporated into a methylene transfer sequence, leading to a useful synthetic protocol. The scope of this conceptually new reaction is quite broad: the CH_2 group is readily introduced into typical Si–H, Si–Si, and C–H bonds,

resulting in facile syntheses of various compounds. Benzylidene group transfer was also demonstrated. Similar to C–C activation, C–O bond activation is facile in PCP–metal systems. Insertion of metals into C–O bonds is controlled by their nucleophilicity. Alkoxy transfer reaction, analogous to methylene transfer, can be utilized in various synthetic schemes.

ACKNOWLEDGMENT

We thank the members of the Milstein group whose work is cited in this review. Their dedication, creativity, and hard work resulted in the unique contribution to the fields of C–C and C–O bond activation. This research was supported by the Israel Science Foundation, Jerusalem, Israel, The Minerva Foundation, Munich, Germany, the DIP program for German–Israeli Cooperation and by the Helen and Martin Kimmel Center for Molecular Design. D.M. holds the Israel Matz Professorial Chair of Organic Chemistry. B.R. holds the Abraham and Jennie Fialkow Career Development Chair.

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'Pincer'-carbene complexes

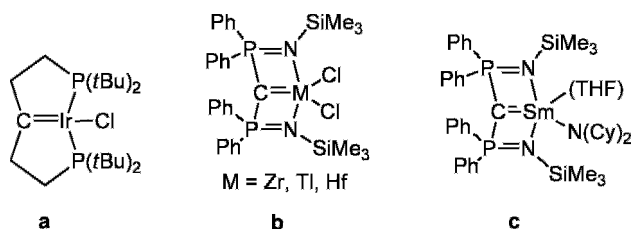
Eduardo Peris^a and Robert H. Crabtree^b

^a*Dpto. de Química Inorgánica y Orgánica, Universitat Jaume I, Av. Vicente Sos Baynat, s/n. 12071 Castellón, Spain*

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6.1 INTRODUCTION

Chelate ligands are often classified according to the heteroatom donor and the chelate ring size. The incorporation of a third donor atom in the backbone provides η^3 -coordinated ligands improving the stability of organometallic species and high or unprecedented catalytic activity. Pincer ligands are those terdentate ligands coordinating in the η^3 -*mer* form [1]. The stabilization of carbene–metal bonds by incorporating the carbene into the ligand backbone is a long-known strategy. An early example, reported by Shaw and coworkers in 1982 [2], was the pincer-diphosphino-carbene complex of Ir(I) depicted in Scheme 6.1a. Other examples of the use of this strategy to stabilize alkylidene complexes of late transition metals were described more recently [3], but most of the pincer-alkylidene complexes reported to date involve early transition metals [4, 5] or lanthanides [4] (Scheme 6.1b and c).



Scheme 6.1

Although *N*-heterocyclic carbene ligands (NHCs) have been known since 1968 [6], it is only much more recently that they have been widely recognized as being able to act as efficient spectator ligands, leading to their chemistry attracting steadily increasing interest [7]. The easy synthetic routes to imidazolylidene ligand precursors (mainly imidazolium salts) have allowed many research groups to provide a large library of ligands including mono- [8], bis- [9, 10] and tris-carbenes [9–11], and their topological

versatility has given access to a large number of metal complexes with many different geometries. The introduction of chirality has also afforded new ligands for asymmetric catalysis [12]. With the rise of NHCs, pincer versions were eagerly explored. The incorporation of NHCs into the architecture of a pincer ligand provides extraordinarily stable compounds due to the combination of the entropic stabilizing effect of pincer coordination together with the inherent strength of the M–NHC bond.

In this review, we will focus our attention on the most relevant examples of pincer NHC complexes, classified according to metal. The synthetic procedures, relevant structural features and catalytic applications are discussed.

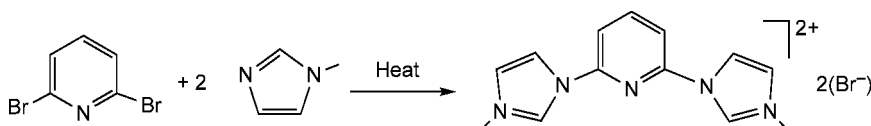
6.2 PINCER-CARBENE COMPLEXES OF METALS FROM THE PLATINUM GROUP

Most of the pincer-carbene complexes of metals from the platinum group involve Pd compounds [13–21], while the examples from rhodium [20, 22, 23] or ruthenium [24–27] are still scarce. Pincer NHC complexes of iridium, platinum and osmium have not been reported so far. Reviews on the preparation and catalytic properties of such complexes have been published [10, 28].

6.2.1 Palladium Pincer-Carbene Complexes

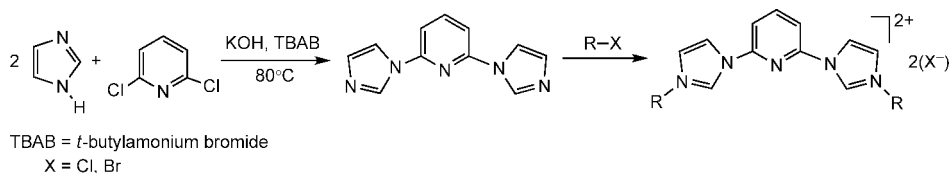
6.2.1.1 Preparation and properties

Most CNC-pincer-carbene complexes reported so far are prepared from pyridine-bisimidazolium salts. The simplest preparation of these ‘bis-carbene precursors’ consists of the direct reaction between two equivalents of an alkylimidazole and 2,6-dibromopyridine (Scheme 6.2) [29].



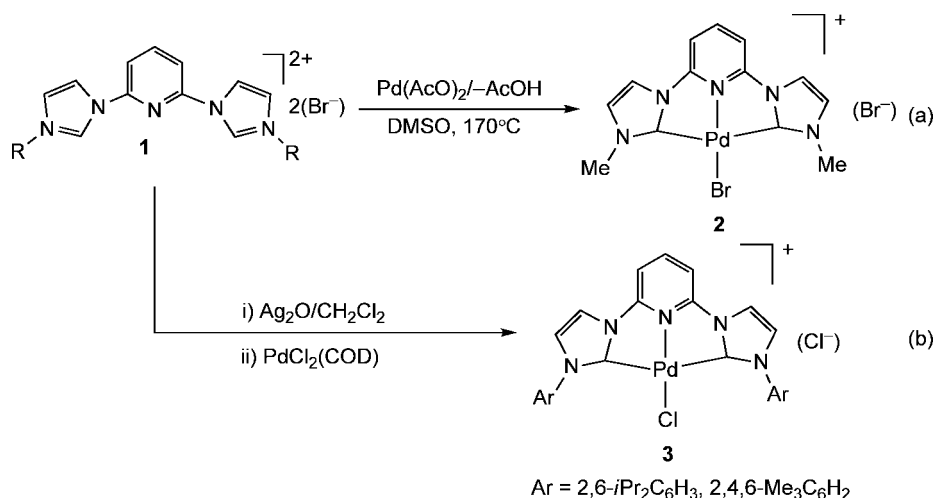
Scheme 6.2

Alternatively, the neutral 2,6-bis-*N*-imidazole(pyridine) can first be obtained, allowing subsequent functionalization of the azole rings by quaternization of the nitrogen atoms with an alkyl halide (Scheme 6.3) [30].



Scheme 6.3

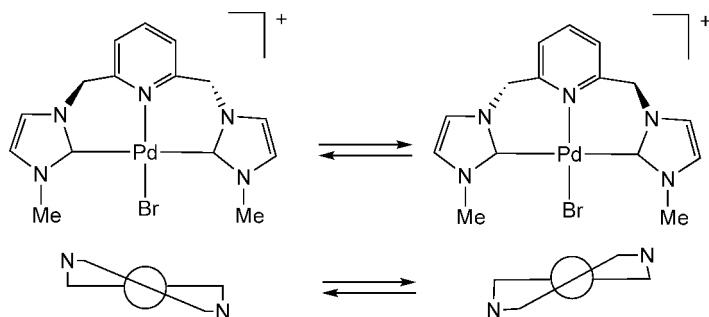
Initially, these NHC precursors were coordinated to Pd, to give pseudosquare planar complexes of Pd(II). Crabtree, Peris [14] and Danopoulos [13] almost simultaneously obtained the first Pd(II) complexes by two different procedures. The reaction of the ligand precursor **1** with palladium acetate at 170°C affords the coordination of the biscarbene ligand in the pincer form, with loss of acetic acid (Scheme 6.4a) [14]. The high temperature at which this complex is obtained shows its exceptionally high thermal stability. A similar complex can be obtained under much milder reaction conditions by transmetalating the carbene from the corresponding silver-NHC complex (prepared by reaction of the pyridine-bisimidazolium salt with Ag₂O in CH₂Cl₂) to PdCl₂(cod) (Scheme 6.4b) [13].



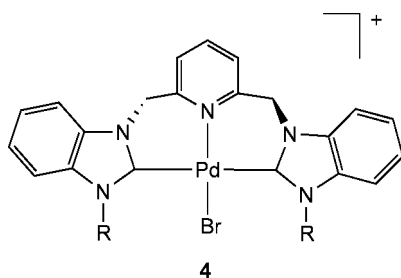
Scheme 6.4

The introduction of a CH₂ spacer between the pyridine and the azole rings enhances the solubility of the complexes, presumably by avoiding the stacking that arises from the flat geometry of **2** and **3** [13, 15]. Interestingly, a direct combination of the puckering of the two six-membered chelate rings and the presence of bulky aromatic substituents on the imidazolylidene rings affords a helical structure with a C₂ proper axis coinciding with the N–Pd–Cl vector, providing a complex with axial chirality [13]. For the less-hindered *N*-methyl-substituted analog, the two atropisomers are in equilibrium in solution, and the kinetic parameters of the dynamic process can be determined by variable temperature NMR experiments (Scheme 6.5) [15]. A similar complex was obtained by Youngs and coworkers with a chloride instead of the bromide ligand [20], and the bis(benzimidazolylidene) analog (**4**, Scheme 6.6) was described only very recently [21]. Danopoulos and coworkers made a detailed study of the structural features of this type of pincer complexes based on X-ray diffraction studies [18].

CCC-pincer-carbene complexes are far less common than their CNC analogs. The reaction of the bis-imidazolylidene precursor, **5**, with Pd₂(dba)₃ in the presence of Na₂CO₃ afforded the first pincer CCC complex reported to date (Scheme 6.7) [15].

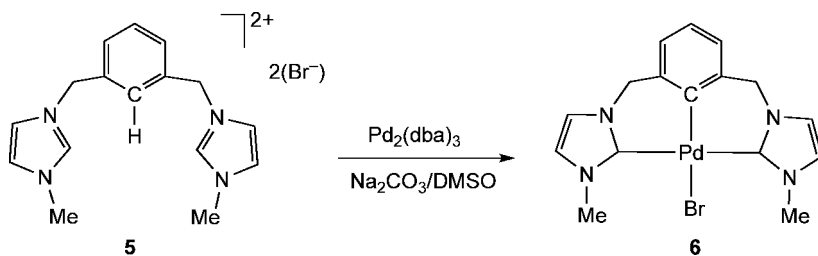


Scheme 6.5



Scheme 6.6

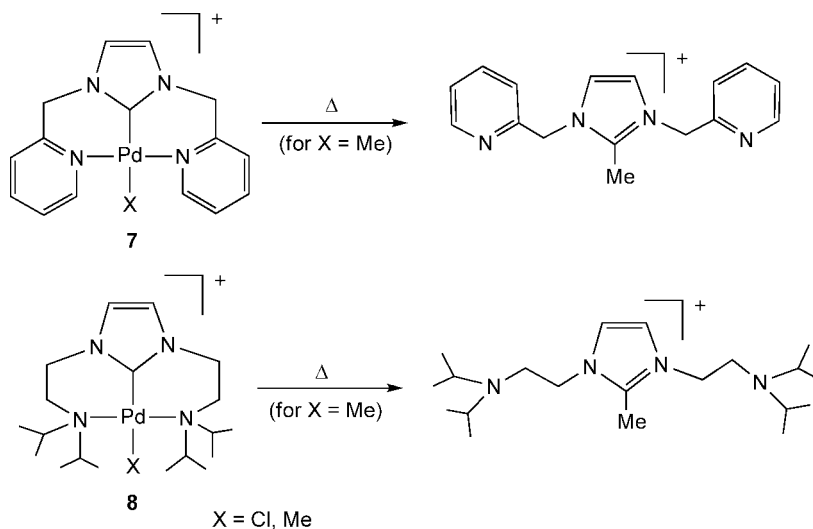
This complex displayed a similar atropisomerization to that shown by the CNC analog of Scheme 6.5.



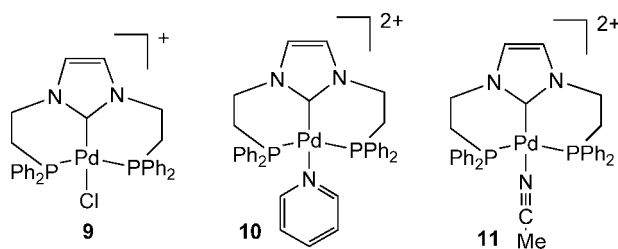
Scheme 6.7

NCN-pincer-carbene Pd(II) compounds were also reported by Cavell and coworkers [31]. These complexes consist of a pincer tridentate ligand with a central imidazolylidene ring having two wingtip substituents containing nitrogen donor fragments, such as pyridine (as in complex 7, Scheme 6.8) or diisopropylethylamine (as in complex 7, Scheme 6.8). A methyl or a chloride ligand completes the coordination sphere around Pd(II). The thermal stability of these species is lower than that for the CCC and CNC pincer Pd(II) analogs. For example, these species decompose at temperatures more than

100°C and Pd(0) is deposited. For the Pd–Me species, the decomposition pathway leads to the formation of the 2-methylimidazolium salts (Scheme 6.8), clearly due to a reductive elimination of the methyl and imidazolylidene groups [31]. PCP-pincer carbenes have recently been reported and also contain a central imidazolylidene ring. The complexes were obtained by the now-standard route of conversion to the silver carbene with Ag₂O, followed by transmetalation. In this case both wingtips of the central imidazolylidene ring are –CH₂CH₂PPh₂. The molecular structures of the complexes **9–11** (Scheme 6.9) reveal the chiral twist conformation of the imidazole rings, similar to the case shown in Scheme 6.5.



Scheme 6.8

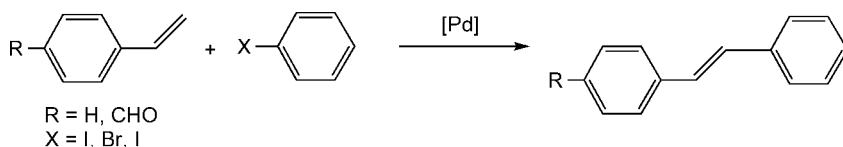


Scheme 6.9

6.2.1.2 Catalytic applications

Pd(II)-based carbene-pincer complexes have been mainly tested in catalytic reactions involving C–C bond formation. Compound **2**, tried in standard Heck reactions (Scheme 6.10), showed activities much like those seen for other Pd(II) catalysts. However, unlike other catalysts, the stability of **2** allowed the Heck reactions to be carried out in the presence of air, hence simplifying reaction workup [14]. The introduction

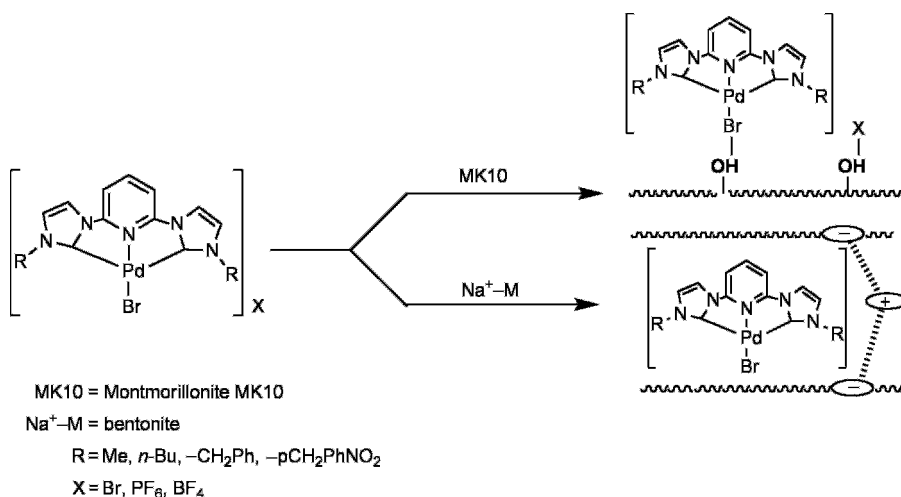
of a CH₂ spacer between the heterocyclic rings of the pincer ligand or the substitution of the methyl wingtips by *n*-butyl groups results in an increase of the solubility of the complexes [15, 16]. This has provided very active Heck catalysts that even show excellent activities for aryl chlorides. The TONs of 47 500–75 000 h⁻¹ obtained for the *n*-butyl analog of **2** are among the highest yet reported for C–Cl activation [16]. A key mechanistic problem in Pd chemistry is the potential for precipitation of colloidal Pd, which can itself be an excellent catalyst. The catalysts described above retained activity in the presence of Hg(0), thus arguing against the presence of heterogeneous Pd(0).



Scheme 6.10

The same catalysts have also been tested in the Suzuki reaction between 4-bromoacetophenone and phenylboronic acid, yielding the substituted biphenyl in high yield [16]. High conversions are seen for the Sonogashira coupling between iodobenzene and phenylacetylene. Both reactions are unaffected by air [16].

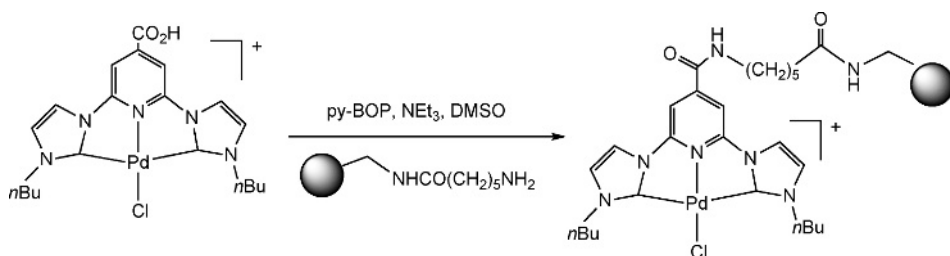
The high stability of these complexes was soon exploited in the preparation of recyclable catalysts. Immobilization of CNC-pincer Pd(II) complexes onto montmorillonite and bentonite clays by the solvent impregnation method (Scheme 6.11) afforded a series of heterogenized catalysts that showed high efficiency for the Heck [17] and Sonogashira reactions [32]. The catalysts so prepared showed a catalytic activity similar to that of



Scheme 6.11

the homogeneous counterparts. After optimization of the reaction conditions, removal of the supported catalyst by filtration and repetition of the C–C coupling reaction after recycling showed that the catalytic activity remained unchanged for many cycles. Leaching of the palladium complex was negligible; the amount of Pd(II) (determined by elemental analysis and XPS) in the solid before and after the catalytic experiments was essentially unchanged [17].

The pincer catalyst can also be covalently bound onto a polymer, providing heterogenized systems that are active in the Heck and Suzuki reactions. The immobilization of the catalyst is performed by coupling the carboxylic-functionalized complex **6** with an amino-terminated Tenta Gel® (Scheme 6.12). The catalysts can be recycled up to 14 times without apparent loss of activity [33].



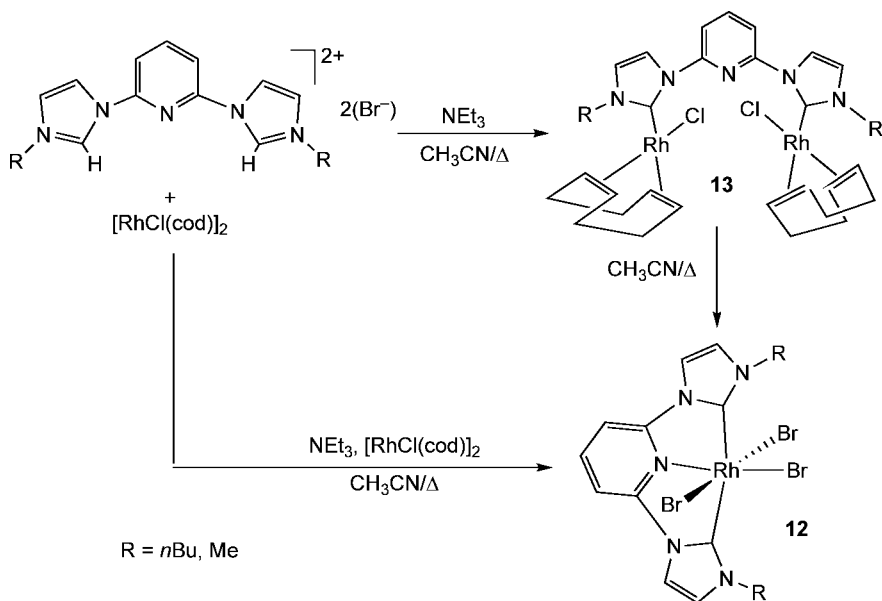
Scheme 6.12

6.2.2 Rhodium and Ruthenium Pincer-Carbene Complexes

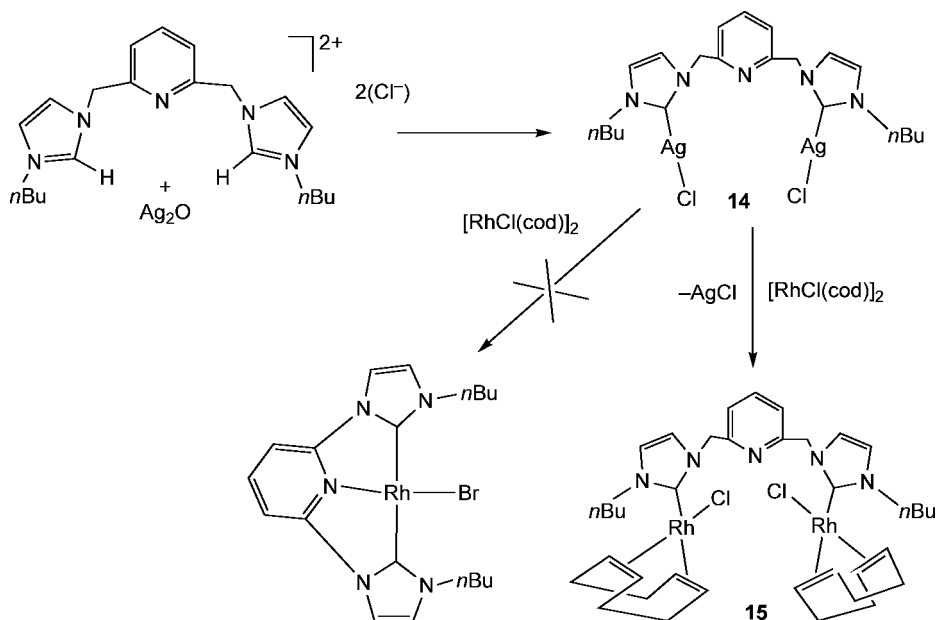
6.2.2.1 Preparation and properties

Extension of the coordination of pincer-carbene ligands to Rh and Ru has afforded new complexes that proved active for several other homogeneous-catalyzed reactions. The preparation of the CNC-Rh(III) complex **12** from the corresponding pyridine-bisimidazolium CNC pro-ligand proceeds through a dimetallic complex of Rh(I), **13**, in which the biscarbene ligand is bridging the two metal units (Scheme 6.13) [22]. Youngs and coworkers used a similar ligand precursor with a CH₂ spacer between the pyridine and the azole rings, which was coordinated to Rh by transmetalation from the corresponding silver-NHC species, **14** (Scheme 6.14). Attempts to obtain a CNC-pincer complex of Rh(I) were unsuccessful, but instead gave the bimetallic complex **15** [20].

A very convenient method for the preparation of pincer-CCC complexes has been recently described. The method consists of the reaction of the Zr-amido complex Zr(NMe₂)₄ with a phenylene-bridged bis(imidazolium) salt [34]. The complex Zr(NMe₂)₄ acts as both base and electrophile and provides the corresponding pincer-CCC-Zr complex (see Section 6.3.1.1) that can be used in situ as a transmetalating agent with an appropriate Rh source and eventually some other metal sources. The electrophilic character of the Zr center is needed in order to achieve the activation of the aryl C–H bond. This methodology afforded the preparation of the monometallic and dimetallic species **16** and **17**, respectively, shown in Scheme 6.15 [34, 35].

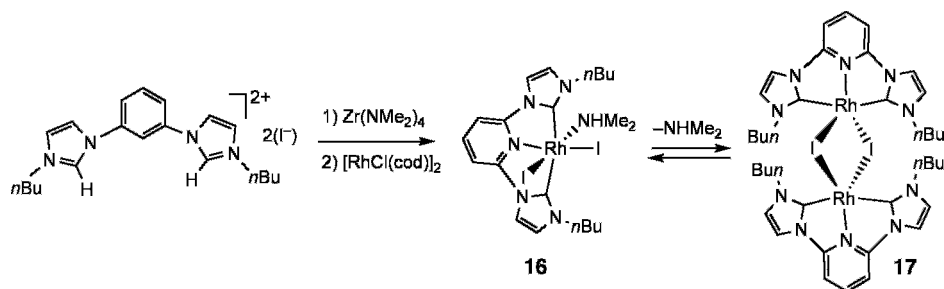


Scheme 6.13



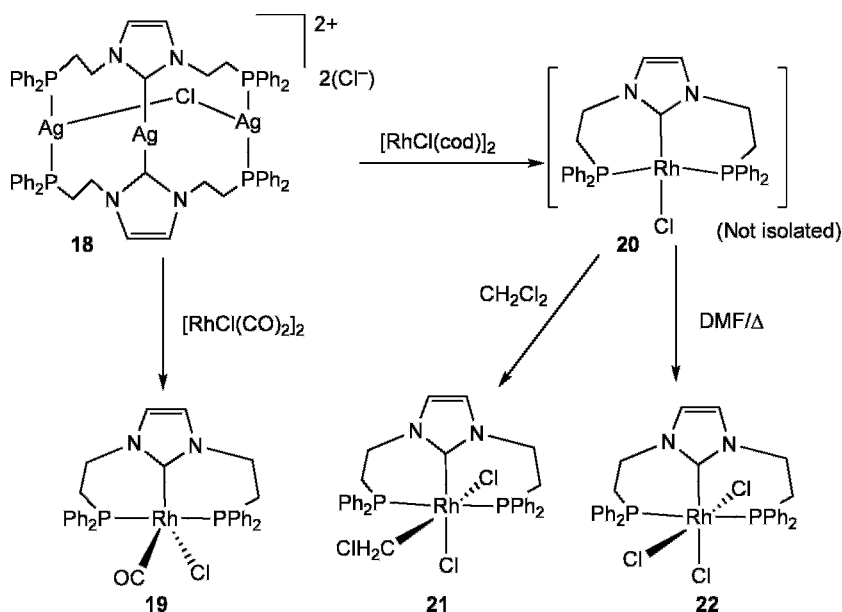
Scheme 6.14

A series of PCP-pincer carbene complexes of Rh(I) and Rh(III) were recently prepared by Lee and coworkers [23]. Transmetalation from the silver-carbene compound **18** to $[\text{RhCl}(\text{CO})_2]_2$ provided the pentacoordinate Rh(I) complex **19** with a pincer structure. A similar reaction with $[\text{RhCl}(\text{cod})]_2$ was intended to produce the electron-rich complex



Scheme 6.15

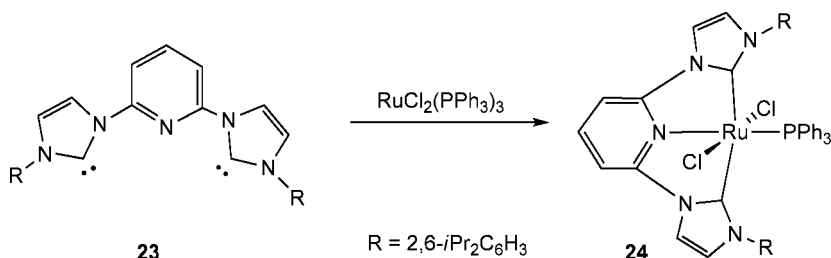
(PCP)Rh^ICl, **20**, but this compound could not be isolated because it rapidly underwent oxidative addition with solvent CH₂Cl₂ affording the Rh(III) species **21**. The reaction was also tried in DMF to avoid the presence of chlorinated solvents, but the reaction proceeded to the Rh(III) species **22** (Scheme 6.16).



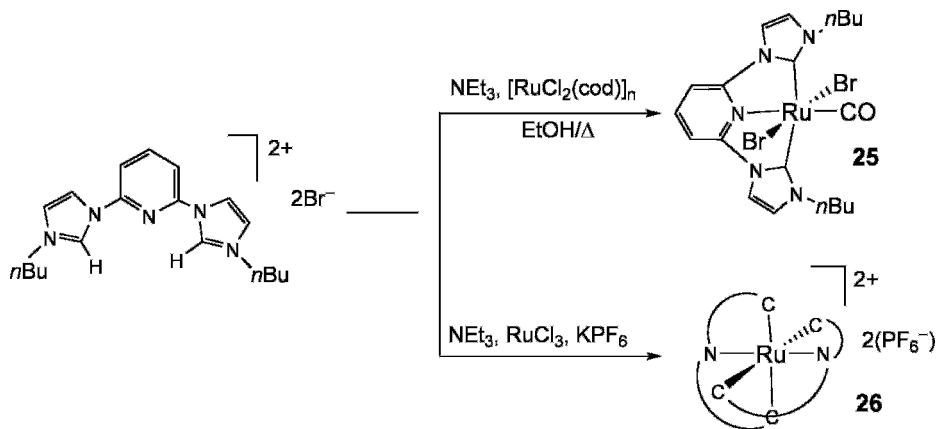
Scheme 6.16

The first ruthenium CNC-pincer carbene complex was obtained by Danopoulos and coworkers in 2002 [25]. The reaction of the free pyridine-bis(imidazolylidene) **23** (whose crystal structure was determined) and RuCl₂(PPh₃)₃ afforded the preparation of the (CNC)-Ru complex **24** in high yield (Scheme 6.17). The reaction of a pyridine-bisimidazolium salt and [RuCl₂(cod)]_n also gave an Ru(II) complex with pincer coordination of the biscarbene ligand (**25**) [24]. In this complex, the presence of the CO ligand

was explained as a consequence of the oxidative addition of CH_3CHO to the metal during the reaction, with subsequent CH_3 migration and elimination of CH_4 . The CH_3CHO may have been produced by oxidation of EtOH during the reaction. The reaction with RuCl_3 afforded complex **26** (Scheme 6.18), in which two pincer CNC ligands saturate the coordination sphere about the $\text{Ru}(\text{II})$ atom [24]. This latter compound (**26**) has shown interesting photoluminescence in water [27].



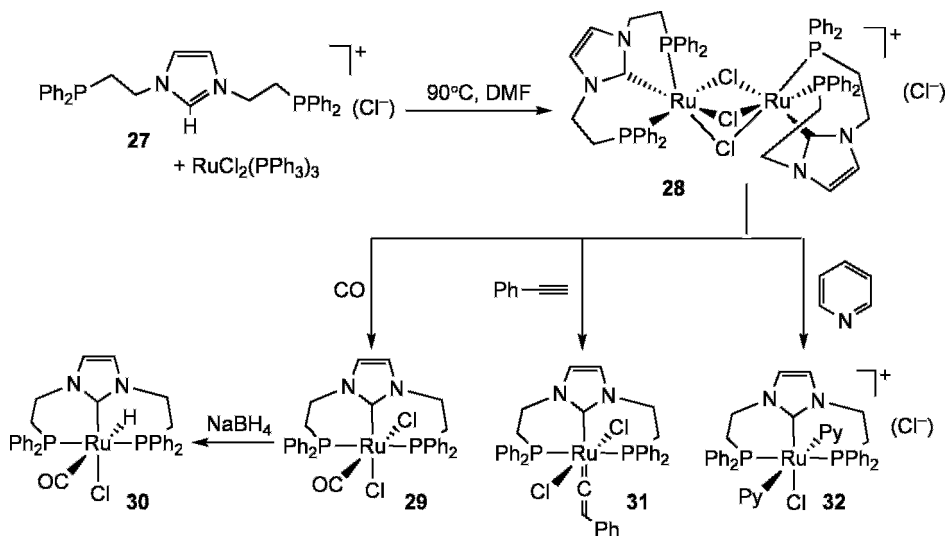
Scheme 6.17



Scheme 6.18

The bisphosphino-imidazolium salt **27** can react with $\text{RuCl}_2(\text{PPh}_3)_3$ in the absence of any base to provide the dimetallic complex **28**, in which the bisphosphino-imidazolylidene ligand is coordinated to the $\text{Ru}(\text{II})$ atoms in a *fac* tripodal arrangement. This compound can react with a series of two-electron donor ligands to provide monometallic compounds of $\text{Ru}(\text{II})$ in which the PCP ligand adopts a pincer coordination mode (Scheme 6.19) [26]. The reaction of **28** with CO affords the pseudooctahedral complex **29**, which displays a dynamic interconversion between the left- and right-handed twisted conformers in solution, similar to that seen for the palladium complexes **9–11** (Scheme 6.9). The addition of NaBH_4 to **29** yields a monohydride species, **30**, this being

the first example of a Ru(NHC)H complex prepared from the reduction of an Ru(NHC) halide [26]. Compound **28** also reacts with phenylacetylene providing the vinylidene complex **31**. The reaction of **28** with pyridine yields the pyridine adduct **32**.



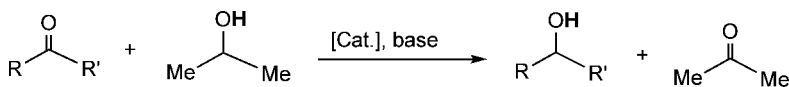
Scheme 6.19

6.2.2.2 Catalytic applications

The coordination of pincer-NHC ligands to Rh and Ru afforded a series of complexes that showed similar or even higher catalytic activities than some analogous phosphine complexes. One of the advantages of these systems is that the pincer coordination of the ligand gives the complexes high thermal stability, and in most cases, the catalytic reactions can be carried out in the presence of air without any special precautions being taken.

The rhodium complexes, **19**, **21** and **22** (Scheme 6.16), were tested in the catalytic hydrosilylation of alkynes with hydrosilanes, producing isomers of the alkenylsilanes. Slow isomerization of the *Z*-alkenylsilanes to the *E*-isomers is also observed after long reaction times [23]. The fact that all three complexes display similar activities suggests the involvement of **20** as the active species in a common catalytic cycle. In fact, most accepted catalytic mechanisms for hydrosilylation involve Rh(I) species that undergo oxidative addition of the silane in the first step of the catalytic cycle [36], so probably both **21** and **22** undergo loss of CH_2Cl_2 and the Cl ligands, respectively, prior to their participation in the catalytic cycle. Remarkably, **21** affords the quantitative production of alkenylsilane in only 15 min, this being the most efficient catalyst so far reported [23]. Compound **16** (Scheme 6.15) also showed high activity toward the hydrosilylation of terminal and internal alkynes, with a clear preference in the generation of the *Z*-alkenes [35].

Complex **12** (Scheme 6.13) has been tested in the homogeneous catalytic transfer hydrogenation from *i*PrOH to ketones (Scheme 6.20) [22], showing good activities, with TONs as high as $11\,000\text{ h}^{-1}$ [22]. The hydrogenation of aromatic ketones is faster than that shown for aliphatic ones. Some of the pincer complexes of ruthenium have also shown very good activities in this reaction; for example, **24** (Scheme 6.17) showed turnovers up to 9000 h^{-1} in the hydrogenation of cyclohexanone [25], whereas **28** (Scheme 6.19) shows a moderate activity [26]. The best result obtained so far in terms of catalytic activity of a pincer-carbene complex is the one shown by complex **25** (Scheme 6.18), with TONs as high as $1.26 \times 10^5\text{ h}^{-1}$ for the hydrogenation of cyclohexanone with a catalyst loading of $7 \times 10^{-3}\text{ mol\%}$ [24]. The same complex was an active catalyst in the oxidation of olefins to aldehydes using NaIO_4 as oxidant. Interestingly, no side products were observed from overoxidation or diol formation. On the other hand, the bis-pincer complex **26** (Scheme 6.18) was almost completely inactive in any of the catalytic reactions tested (transfer hydrogenation and olefin oxidation), probably due to the blocking of all the coordination sites of the metal by the two pincer ligands, which in fact remain bound even under the harsh reaction conditions used for the catalytic experiments [24].



Scheme 6.20

6.3 PINCER-CARBENE COMPLEXES OF OTHER METALS

Although the use of pincer-NHC ligands in transition metal chemistry is relatively recent, a broad range of metals have been involved, giving new possibilities for catalytic application. Although most of the examples reported so far are from Pd, Rh and Ru (see Section 6.2), a few examples are known of pincer-carbene complexes of iron [37, 38], cobalt [39], chromium [40, 41] and early transition metals [41]. This section summarizes the more relevant examples of pincer-carbene complexes of these metals.

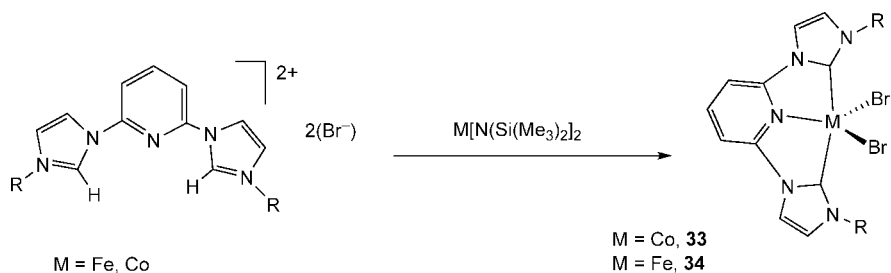
6.3.1 Pincer-Carbene Complexes of Fe, Co and Early Transition Metals

6.3.1.1 Preparation and properties

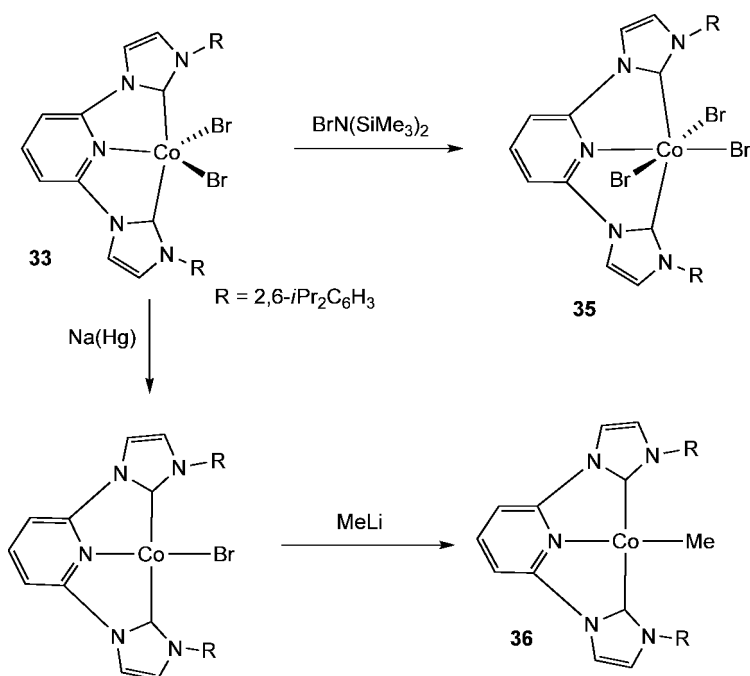
Danopoulos and coworkers have obtained N-heterocyclic pincer biscarbene complexes of Fe(II) [38] and Co(II) [39] by aminolysis of $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$ ($\text{M} = \text{Fe}, \text{Co}$), as shown in Scheme 6.21.

The $\text{Co}^{\text{II}}(\text{CNC})$ complex, **33**, can be reduced with $\text{Na}(\text{Hg})$ to afford the corresponding methylated complex of Co(I) (**35**, Scheme 6.22) after reaction with MeLi [39]. Complex **33** can also be oxidized to the corresponding Co(III) complex, **36**, by reaction with $\text{BrN}(\text{SiMe}_3)_2$ [39]. These reactions, summarized in Scheme 6.23, illustrate how the pincer-CNC ligand is capable of stabilizing different oxidation states of the same metal.

Complex **34** has also shown its versatility in terms of reactivity. Reduction with $\text{Na}(\text{Hg})$ affords $(\text{NCN})\text{Fe}^0$ complexes capable of forming a stable N_2 adduct, **37**, which



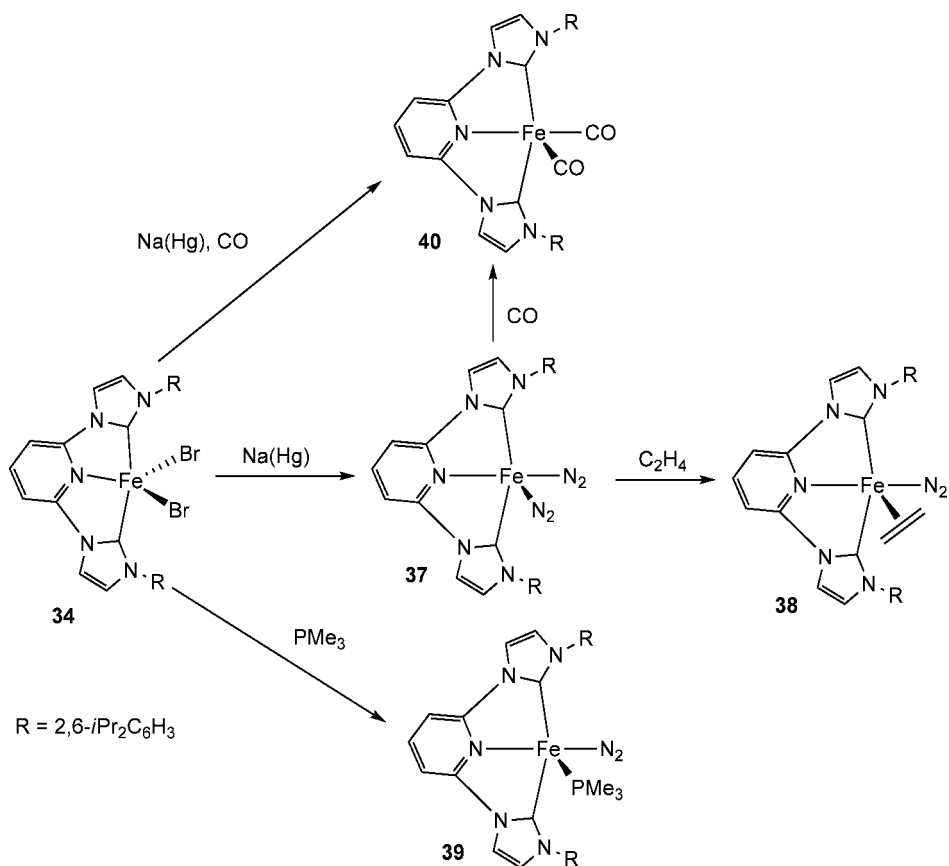
Scheme 6.21



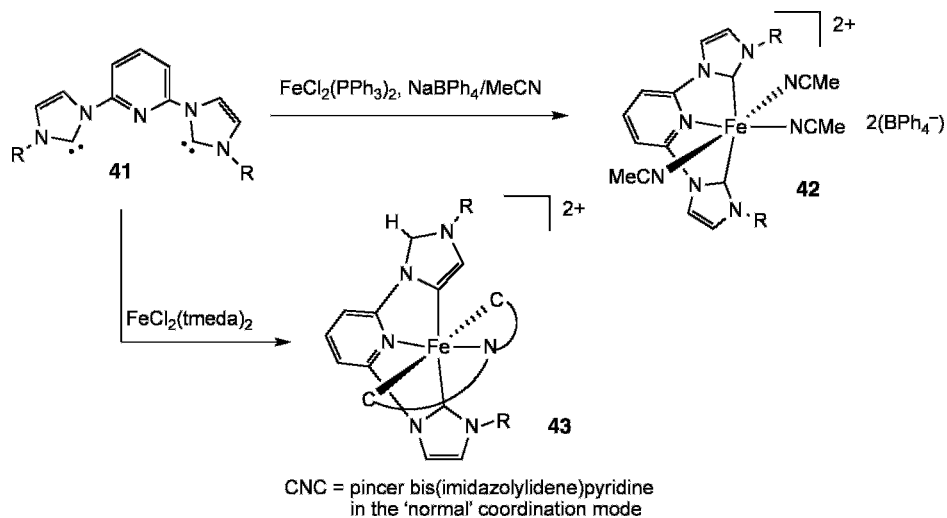
Scheme 6.22

is a valuable precursor to other pincer complexes of the type $\text{Fe}(\text{CNC})(\text{N}_2)\text{L}$ (L = C₂H₄, **38**; L = PMe₃, **39**), and also $\text{Fe}(\text{CNC})(\text{CO})_2$, **40**, as shown in Scheme 6.23 [37].

Interestingly, the coordination of the same pincer-CNC ligand to Fe can lead to a complex in which the normal C-2 and abnormal C-5 coordination modes of the imidazolyliene coexist on the same metal center [38]. Crabtree and coworkers were the first to describe the C-5 coordination mode of NHCs, when preparing NHC complexes of Ir(III) by reaction of $\text{IrH}_5(\text{PPh}_3)_2$ with picolyl- and pyridine-imidazolium salts [42]. The reaction of the preformed free biscarbene 2,6-bis(imidazolyliene)pyridine, **41**, with $\text{FeCl}_2(\text{PPh}_3)_2$ and $\text{FeCl}_2(\text{tmeda})_2$ affords the $(\text{CNC})\text{Fe}^{\text{II}}$ complexes **42** and **43**, respectively (Scheme 6.24). Complex **43** is specially interesting both because the two pincer ligands adopt both coordination modes, normal and abnormal, and because it is one



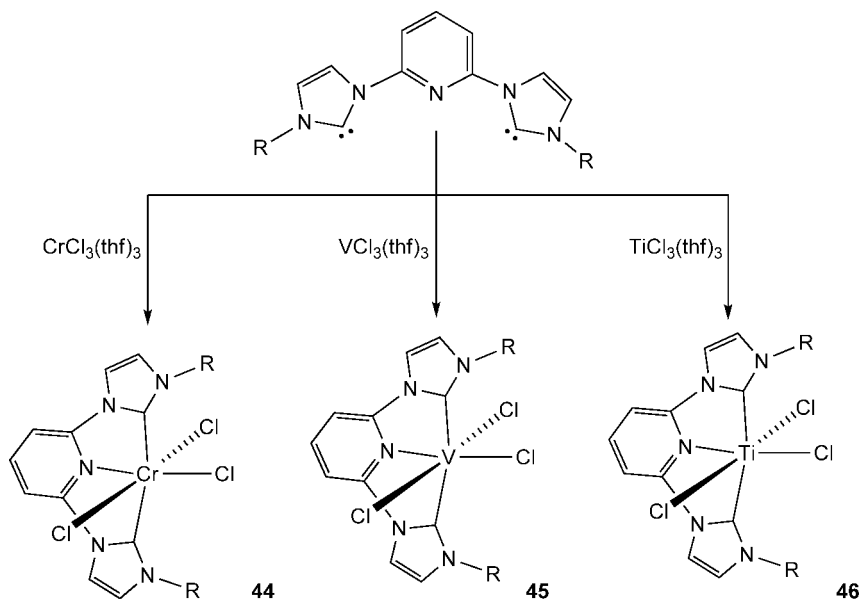
Scheme 6.23



Scheme 6.24

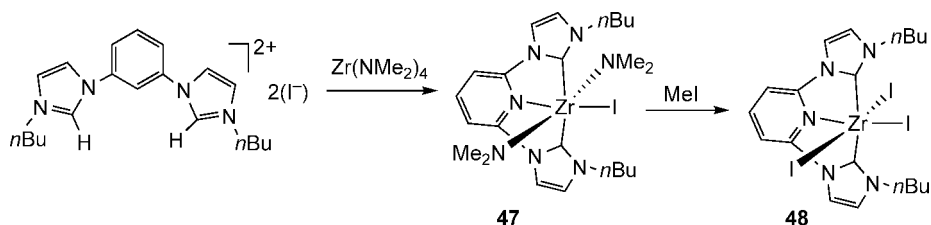
of the few homoleptic Fe(II) carbenes [43]. A similar homoleptic Fe(II) complex with normal binding of the two pincer ligands was recently reported [41].

Preformed pincer-NHCs can also be used for the preparation of complexes with metals unable to π -back-donate, such as the high oxidation states of the early transition metals. Carbenes of these metals are normally only considered possible for the Schrock type, but the high stability of the Fischer-type NHCs has broadened our understanding by affording new series of early and middle transition metal complexes. In this sense, Gibson and coworkers have prepared a series of pincer-biscarbene complexes of Cr, Ti and V (Scheme 6.25) [40, 41].



Scheme 6.25

The reports employing $\text{Zr}(\text{NMe}_2)_4$ to prepare Zr-NHC complexes [44] inspired Hollis and coworkers to use the same precursor to obtain CCC-Zr pincer species [34]. The complex $\text{Zr}(\text{NMe}_2)_4$ can react with a phenylene-bridged bis(imidazolium) salt affording complex **47**, which reacts with MeI to provide the tri-iodide complex **48** (Scheme 6.26) [34]. Complex **47** can be obtained and used in situ as a carbene-transmetalating agent, as in the reaction shown in Scheme 6.16 with an Rh source.



Scheme 6.26

6.3.1.2 Catalytic applications

The Co and Fe complexes **33**, **36** (Scheme 6.22) and **34** (Scheme 6.23) were tested for the catalytic polymerization of ethylene, in view of the structural analogies with compounds of the type [bis(imino)pyridine]MCl₂ (M = Fe, Co) which are very active for this reaction [45]. All the pincer complexes were completely inactive toward this reaction, however, the reasons possibly being (i) the much stronger basicity of the NHC compared to the imine functionalities and (ii) the coordination inert nature of the M–carbene bond in comparison to the M–imine bond [39].

The earlier transition metal complexes **44–46** (Scheme 6.25) showed extremely high activities for the ethylene polymerization and oligomerization [40, 41], and the Cr-system (**41**) showed a clear influence by the nature of the wingtips attached to the pincer ligand [40]. The catalytic activity of the later transition metal complexes for this reaction remains to be studied [41].

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Pincer complexes derived from benzimidazolin-2-ylidene ligands

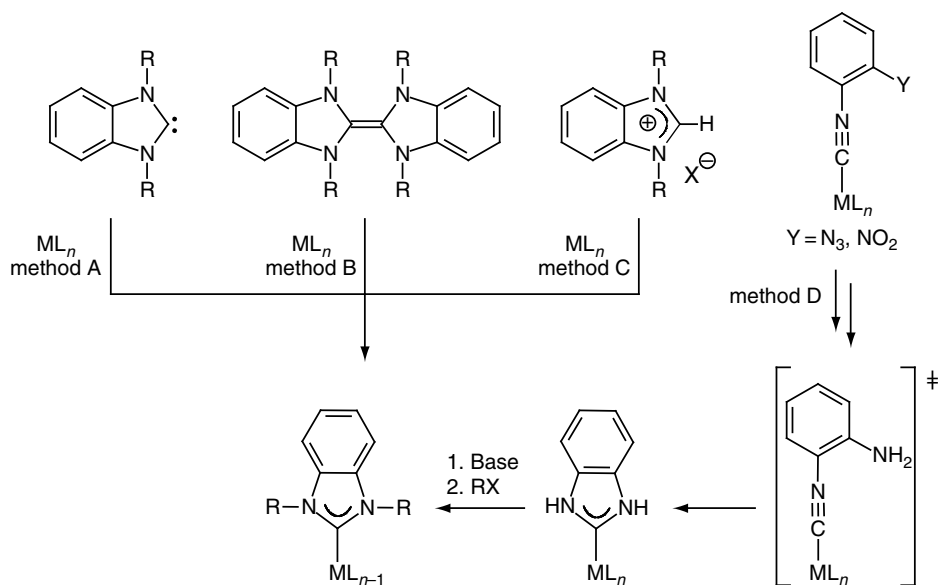
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7.1 SYNTHESIS OF COMPLEXES WITH BENZIMIDAZOLIN-2-YLIDENE LIGANDS

In the years following the isolation of the first stable *N*-heterocyclic carbene (NHC) by Arduengo et al. in 1991 [1] a large number of NHC ligands and their metal complexes have been prepared [2]. Particularly complexes with imidazolin-2-ylidene ligands have attracted much interest due to the simple access to these ligands and numerous applications of complexes with these ligands in various catalytic processes [3].

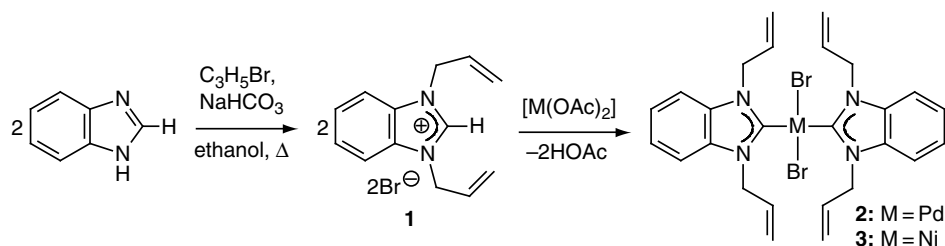
Less attention has been directed towards benzimidazolin-2-ylidene ligands. This type of NHC exhibits a different behaviour compared to the imidazolin-2-ylidenes owing to its intermediate position between saturated and unsaturated *N*-heterocyclic carbenes [4]. A variety of procedures for the synthesis of complexes with benzimidazolin-2-ylidene ligands have been reported. Among those are the reaction of the stable carbene [4a, 5] and the cleavage of a dibenzotetraazafulvalene [4b, 6] with coordinatively unsaturated transition metals (Scheme 7.1, methods A and B). In addition, the reaction of benzimidazolium salts with complexes bearing basic ligands such as metal acetates [7] or silver oxide [8] affords the corresponding carbene complexes (Scheme 7.1, method C). The template-controlled cyclization of β -functionalized phenyl isocyanides results in complexes with *NH,NH*-stabilized benzimidazolin-2-ylidene ligands [9]. *N*-alkylation of such carbene ligands allows the introduction of various functional groups (Scheme 7.1, method D). Based on the variety of synthetic methods for the preparation of benzimidazolium salts [10] and stable benzimidazolin-2-ylidenes [4a, 11] we initiated a programme to study the preparation of complexes with pincer-topology which contain benzimidazolin-2-ylidene donor groups.



Scheme 7.1 Preparation of benzimidazolin-2-ylidene complexes.

7.2 COMPLEXES WITH *N*-ALLYL-FUNCTIONALIZED BENZIMIDAZOLIN-2-YLIDENE LIGANDS

Several carbene complexes with *N*-allyl functionalized NHC ligands have been prepared [7c, 7d, 9a–9c, 9f, 11b, 12, 13]. However, only a few examples are known, where the *N*-allyl functions coordinate to the metal centre [11b, 12a, 12d, 12e, 13]. Complexes with the potentially tridentate diallyl-functionalized benzimidazolin-2-ylidene ligand have been derived from β -functionalized phenyl isocyanides at electron-poor transition metal centres [9b, 9c]. Alternatively, palladium and nickel complexes with the *N,N'*-diallylbenzimidazolin-2-ylidene ligand have been obtained from *N,N'*-diallyl-functionalized benzimidazolium bromide **1** [10a] and nickel [7c] or palladium acetate [7d] (Scheme 7.2).



Scheme 7.2 Preparation of complexes **2** and **3**.

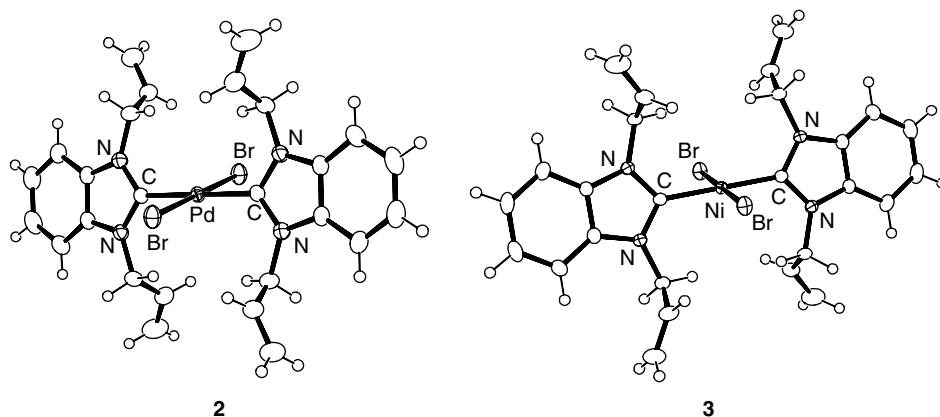


Fig. 7.1. Molecular structures of **2** and **3**.

After coordination of the carbene carbon atom in **2** and **3** (Scheme 7.2) the *N*-allyl substituents are in principle capable to bind also to the metal centre. However, no olefin coordination was observed in the nickel or palladium complex. Even halide abstraction with AgBF_4 did not lead to metal coordination of the allyl substituents [7d]. Complexes **2** and **3** have been crystallized and their molecular structures have been determined by X-ray diffraction (Fig. 7.1). They are built in a square-planar fashion and exhibit a *trans* arrangement of the ligands. The structure analyses confirmed the presence of uncoordinated allyl groups in both complexes.

7.3 COORDINATION CHEMISTRY OF THE *N,N'*-DIALLYL-FUNCTIONALIZED BENZIMIDAZOLIN-2-YLIDENE LIGAND AT IRIIDIUM

Compared to the nickel and palladium complexes **2** and **3**, a different behaviour of the *N*-allyl groups was observed in iridium(I) complexes with the *N,N'*-diallylbenzimidazolin-2-ylidene ligand [13]. Reaction of the *N,N'*-diallyl-functionalized benzimidazolium salt **1** with $[\text{Ir}(\mu\text{-OMe})(\text{cod})_2]_2$ gave the carbene complex **4**. The benzimidazolin-2-ylidene ligand in this iridium complex coordinates in a bidentate fashion exhibiting Ir–C bonds to the carbene carbon atom and to one of the allyl groups (Fig. 7.2). The second allyl substituent does not coordinate to the metal centre. Upon bromide abstraction, this second allyl substituent coordinates to the iridium centre leading to the pincer-type iridium complex $[\mathbf{5}]\text{BF}_4$ (Fig. 7.2).

The molecular structures of both **4** and $[\mathbf{5}]\text{BF}_4$ have been determined. The structure analyses confirmed that pentacoordinated iridium centres had formed. The coordination geometry at iridium is best described as trigonal-bipyramidal. Complex $[\mathbf{5}]\text{BF}_4$ resembles an armchair with the coordinated allyl functions as armrests and the carbene plane as backrest. Comparison of the two complexes revealed a significantly shorter Ir–C_{carbene} bond length for $[\mathbf{5}]\text{BF}_4$ relative to **4**. This shortening most likely results from the overall positive charge of complex cation $[\mathbf{5}]^+$ which causes the carbene ligand to act as stronger σ -donor than in **4**.

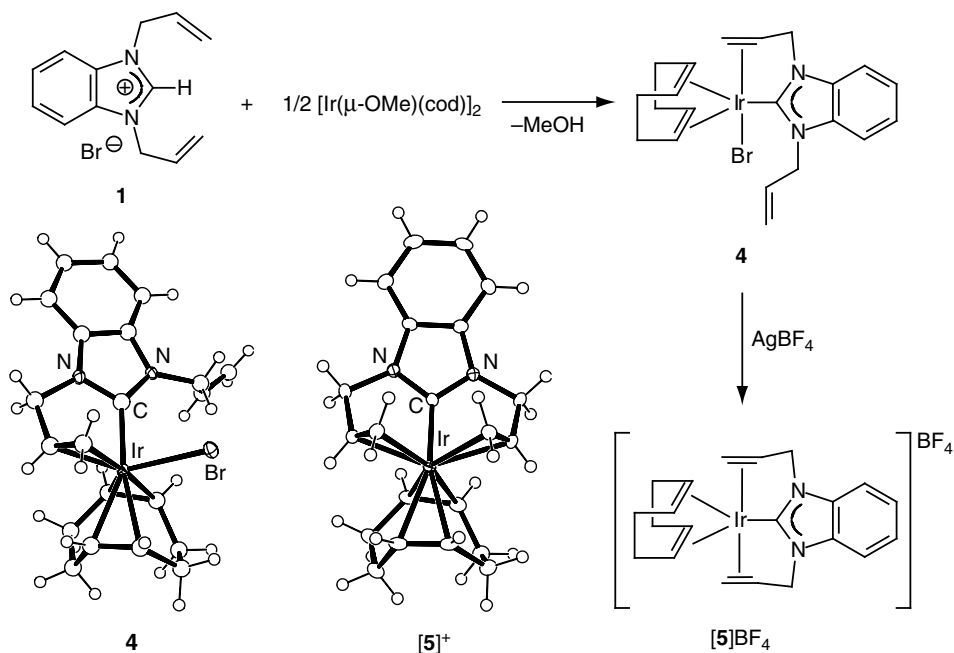
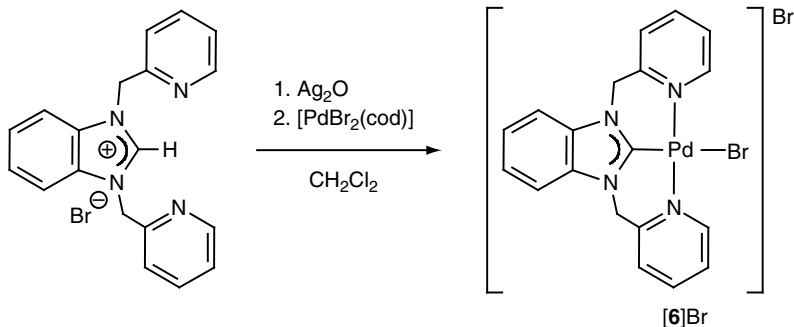


Fig. 7.2. Stepwise coordination of the allyl groups in iridium complexes **4** and **[5]⁺** and molecular structures of **4** and **[5]⁺**.

7.4 PINCER COMPLEXES WITH *N,N'*-HETEROATOM-FUNCTIONALIZED BENZIMIDAZOLIN-2-YLIDENE LIGANDS

Several pincer-type complexes with a central benzimidazolin-2-ylidene donor and peripheral 'classical' group 15 donors such as picoline (Scheme 7.3, **[6]Br**) or phosphines (Fig. 7.3, **[7]Cl**, **[8]Cl** and **[9](BF₄)₂**) have been prepared. These ligands are capable of



Scheme 7.3 Preparation of **[6]Br** containing an *N,N'*-dipicoline-functionalized benzimidazolin-2-ylidene ligand.

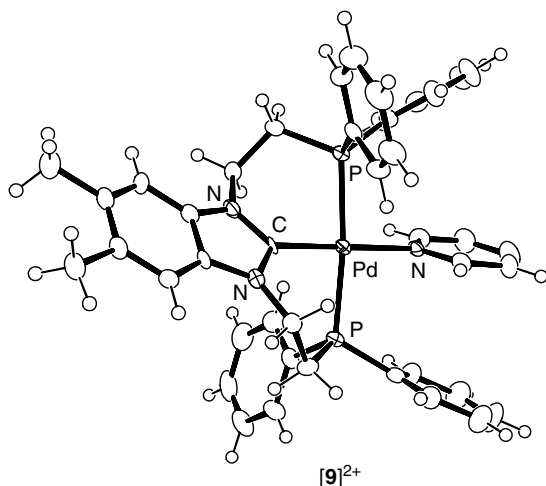


Fig. 7.3. Palladium and platinum complexes with a diphosphine-functionalized benzimidazolin-2-ylidene ligand and molecular structure of **[9]**²⁺.

forming a stable metal–carbene bond in addition to two weaker bonds to the group 15 donor functions. The ligand design was based on the intention that during a catalytic cycle the weaker metal–donor bonds could break thereby creating vacant coordination sites for substrate binding at the metal centre.

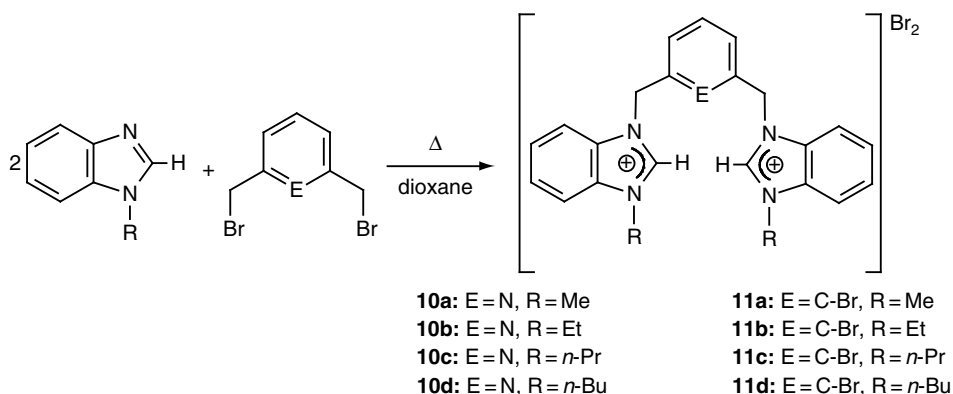
The palladium compound **[6]Br** with the *N,N'*-dipicoline-functionalized benzimidazolin-2-ylidene ligand has been obtained in a two-step reaction sequence (Scheme 7.3). Reaction of the appropriate benzimidazolium salt with silver oxide **[8]** gave initially the silver dicarbene complex, which was isolated as a red solid. Subsequent ligand transfer to palladium(II) produced the pincer-type palladium complex **[6]Br**.

In analogy to a procedure reported by Lee et al. [14] we prepared complexes derived from a diphosphine-functionalized benzimidazolin-2-ylidene ligand (Fig. 7.3) [15]. Both, the palladium complex **[7]**Cl and the platinum complex **[8]**Cl were obtained in good yield.

Reaction of the palladium complex **[7]Cl** with silver tetrafluoroborate in pyridine gave the palladium complex **[9](BF₄)₂** with a neutral pyridine donor instead of the bromo ligand. The palladium centre in **[9]²⁺** is coordinated in a square-planar fashion. The plane of the carbene ligand is rotated out of the PdL₄ plane to facilitate the coordination of both phosphorus donors. Pincer complexes with heteroatom-functionalized benzimidazolin-2-ylidene ligands like **[6]Br** and **[7]Cl** have been tested in Heck and Suzuki C–C coupling reactions [15]. They have shown good conversion rates for the coupling of several *para*-functionalized aryl bromides with styrene or butyl acrylate.

7.5 SYNTHESIS OF Pincer Complexes with Tridentate Dicarbene Ligands

Crabtree, Danopoulos and Cavell have described the preparation and applications of pincer complexes with pyridine- or phenylene-bridged bis(imidazolin-2-ylidene) ligands [16]. Based on these results the preparation of pincer complexes bearing two benzimidazolin-2-ylidene donors was attempted. It was hoped that the introduction of these donors would lead to a modification of the catalytic properties of pincer-type complexes. Ligand precursors carrying two benzimidazolium units were prepared from 2,6-dibromo lutidine or 2,6-di(bromomethyl)-1-bromobenzene and *N*-alkyl-substituted benzimidazole derivatives (Scheme 7.4).



Scheme 7.4 Preparation of bridged bisbenzimidazolium salts of types **10** and **11**.

Preparation of the ligand precursors of types **10** [17] and **11** [18] was carried out as described for the corresponding imidazolium derivatives [16]. The reaction of one equivalent of the dibromo-functionalized spacers with two equivalents of *N*-alkyl-substituted benzimidazoles gave the bridged bisbenzimidazolium salts (Scheme 7.4), which were obtained in good yield after workup.

The molecular structures of two representative bisbenzimidazolium salts (**10a**, **11c**) were determined (Fig. 7.4). These molecular structures show that the rotation around the methylene bridge is sterical not hindered. Indeed the observed conformations in the solid state can be rationalized in terms of crystal packing forces.

The preparation of pincer-type dicarbene complexes starting from ligand precursors of type **10** or **11** required different procedures depending on the spacer group. Pincer-type palladium complexes with lutidine-bridged bis(benzimidazolin-2-ylidene) ligands have been obtained from palladium acetate and ligand precursors of type **10** following the protocol published first by Crabtree [16e] for the generation of pincer complexes with lutidine-bridged bis(imidazolin-2-ylidene) ligands. Complexes of type **[12]Br** formed by coordination of the in situ-generated dicarbene ligands to the palladium centre (Scheme 7.5) [17].

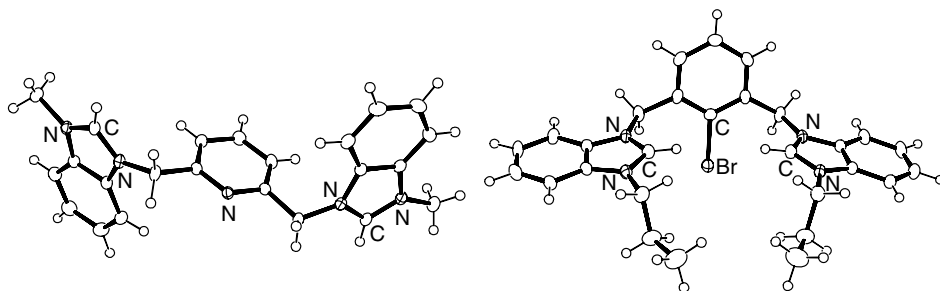
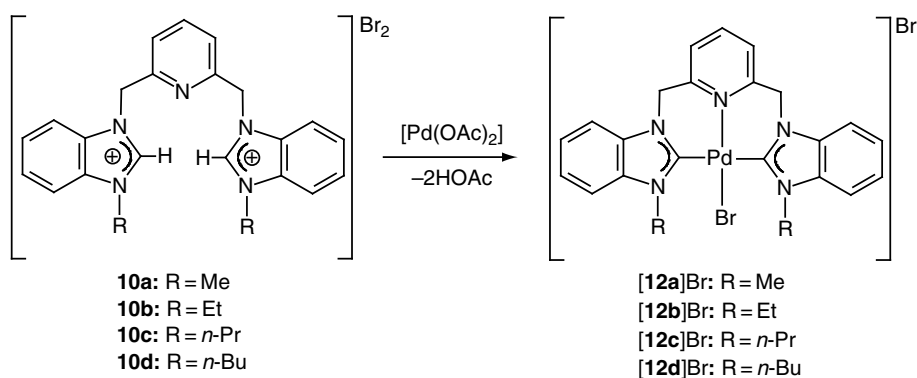


Fig. 7.4. Molecular structures of the bridged bisbenzimidazolium dications in **10a** (left) and **11c** (right).



Scheme 7.5 Preparation the lutidine-bridged pincer-type dicarbene complexes **[12a]Br**–**[12d]Br**.

Molecular structures of the two representative compounds **[12b]Br** and **[12c]Br** have been determined (Fig. 7.5). The cationic palladium pincer complexes of type **[12]⁺** are built in a distorted square-planar fashion with a *trans* orientation of the carbene donor functions. The Pd–C bond lengths (2.025(3)–2.040(3) Å for **[12b]⁺** [**17a**]) fall in

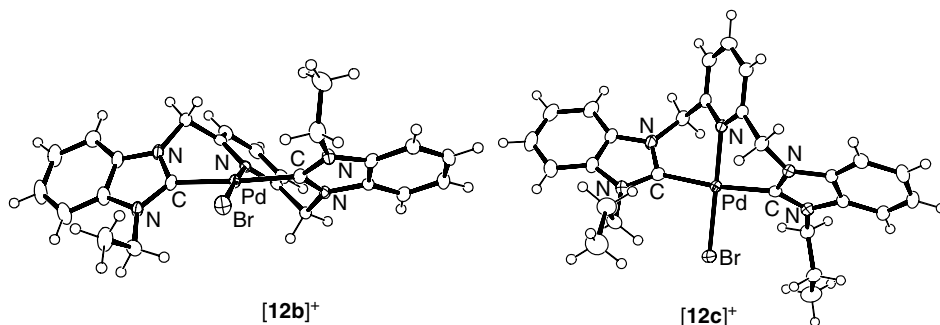


Fig. 7.5. Molecular structures of the cationic pincer complexes **[12b]⁺** and **[12c]⁺**.

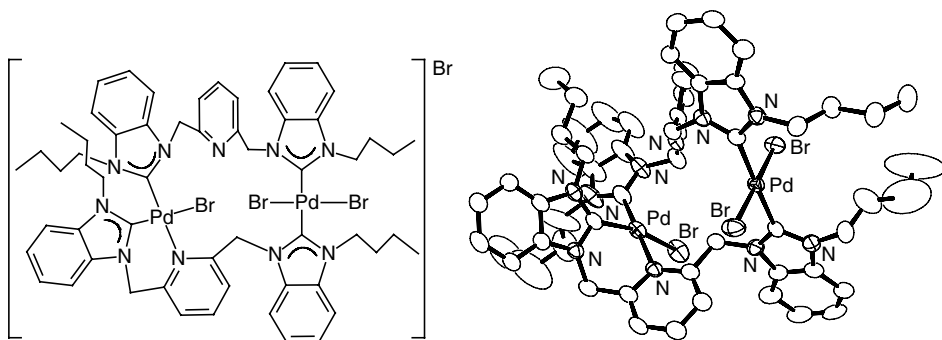


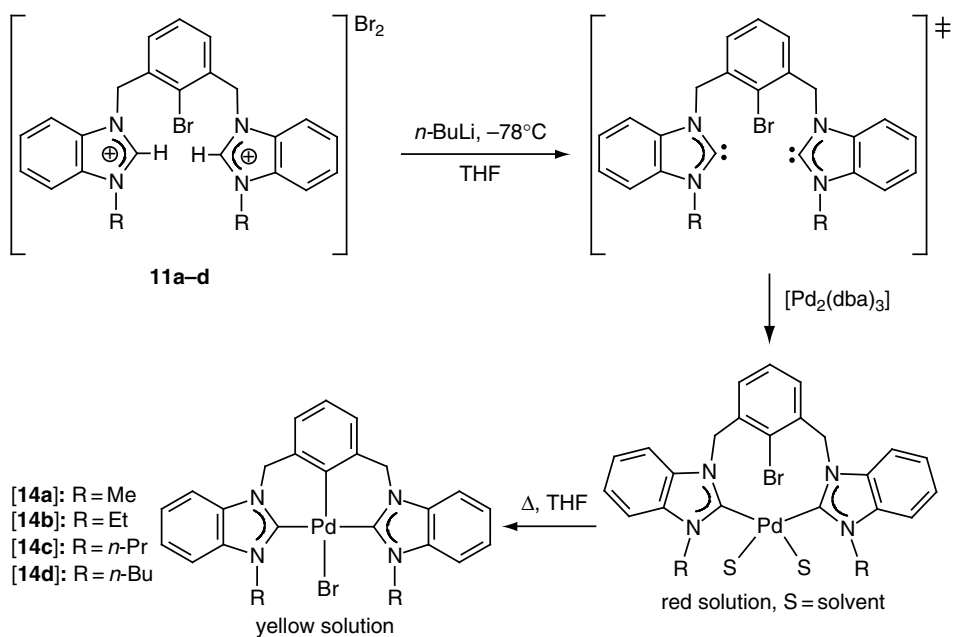
Fig. 7.6. Schematic drawing and molecular structure of the dinuclear cationic complex $[13]^+$.

the range observed for other palladium bis(benzimidazolin-2-ylidene) complexes with a *trans* orientation of the carbene ligands [7b, 7d]. They are, however, longer than those found in bis(benzimidazolin-2-ylidene) complexes with a *cis* arrangement of the benzimidazolin-2-ylidene donors (1.987(4)–1.991(7) Å [7a], 1.982(5)–1.988(5) Å [6a], 1.972(3)–1.983(4) Å [6c]).

An unusual coordination behaviour was observed for ligand precursor $[12d]Br$ after deprotonation with $[Pd(OAc)_2]$ and coordination to palladium. The dinuclear complex $[13]Br$ (Fig. 7.6) with two ligands acting as bridges between two metal centres was obtained. One palladium atom is surrounded by two carbene donors and two bromo ligands in *trans* configuration, while the other palladium atom is coordinated by two carbene donors in *cis* configuration in addition to a pyridine donor and a bromo ligand. In spite of the differences in donor sets for the two palladium atoms, longer Pd–C distances were observed for the carbene ligands in *trans* positions (2.022(4)–2.024(6) Å) compared to the Pd–C distances for carbene ligands in *cis* positions (1.967(7)–1.990(6) Å).

In addition, platinum complexes with lutidine-bridged dicarbene ligands have been obtained by in situ deprotonation of bisbenzimidazolium salts of type **10** with platinum acetylacetonate using a protocol described recently [19]. Such complexes are also accessible from the bisbenzimidazolium salts via the silver(I) carbene complexes [8b, 16b, 16f] followed by ligand transfer. However, the yields in this reaction sequence are generally lower compared to the in situ deprotonation with metal acetates or acetylacetonates.

The method for the preparation of pincer complexes with carbanionic dicarbene ligands differs from the previously described synthesis for pincer complexes of type $[12]Br$ with neutral dicarbene ligands. The preparation of complexes of type **14** started with the deprotonation of suitable bisbenzimidazolium salts of type **11** with *n*-butyl lithium at $-78^\circ C$ in THF (Scheme 7.6). The phenylene-bridged dicarbene species obtained in this way were not isolated. The acidity of the methylene protons of the spacer can lead to undesirable side reactions during the deprotonation of the azolium salt with strong bases [11, 20]. The intermediately formed dicarbene species was then trapped by palladium(0). This led to the formation of a red solution. The palladium(0) complex was not isolated, but heated under reflux for several hours. During this period the colour of the solution turned yellow indicating the formation of a complex of type **14**. Heating of the reaction mixture containing the Pd^0 complex proved essential for the oxidative



Scheme 7.6 Synthesis of the pincer-type palladium complexes [14a]–[14d].

addition of the C–Br bond to Pd^0 to proceed. The neutral palladium complexes of type [14] were obtained in reasonable yields (60–70%). They are not sensitive towards air or moisture.

The molecular structure of complex [14d] has been determined by X-ray diffraction (Fig. 7.7). The $\text{Pd}-\text{C}_{\text{carbene}}$ bond lengths (2.047(4) and 2.036(4) Å) fall in the range described for *trans* bis(benzimidazolin-2-ylidene)palladium complexes [7b, 7d]. The $\text{Pd}-\text{C}_{\text{phenylene}}$ distance measures 2.025(5) Å which is typical for such pincer complexes

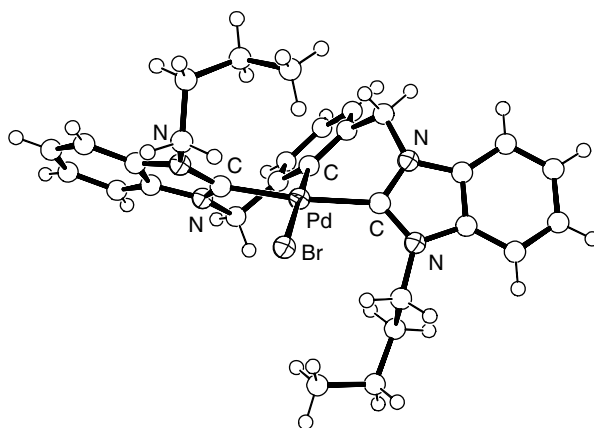


Fig. 7.7. Molecular structure of complex [14d].

(cf. 2.014(8) Å [16a] and 2.033(3) Å [16f]). Complex [14d] is built in a square-planar fashion with the $C_{\text{carbene}}-\text{Pd}-C_{\text{carbene}}$ angle ($169.50(14)^\circ$) showing the greatest deviation from a perfect square-planar arrangement.

7.6 NMR STUDIES ON DICARBENE Pincer complexes

The ^1H NMR spectra of the dicarbene palladium complexes [12a] $^+-[12d]^+$ and [14a] $^+-[14d]^+$ exhibit different signals for the protons of the bridging methylene groups. At ambient temperature, these methylene protons in the lutidine-bridged complexes [12a] $^+-[12d]^+$ appear as broad signal at $\delta \approx 6.1$ ppm, those of the phenylene-bridged complexes [14a] $^+-[14d]^+$ were observed as two doublets at $\delta \approx 5.5$ and 5.2 ppm (Fig. 7.8 for complexes [12c] $^+$ and [14d] $^+$).

The broadening of the methylene resonance signal in complexes of type [12] $^+$ is indicative of a dynamic process [16a, 16g]. The complex cations can adopt two twisted configurations (**A** and **C**, Scheme 7.7). Fast interconversion between the two possible conformations results in an average structure **B** with C_{2v} symmetry. This structure possesses equivalent methylene protons giving the observed broad singlet in the ^1H NMR spectra.

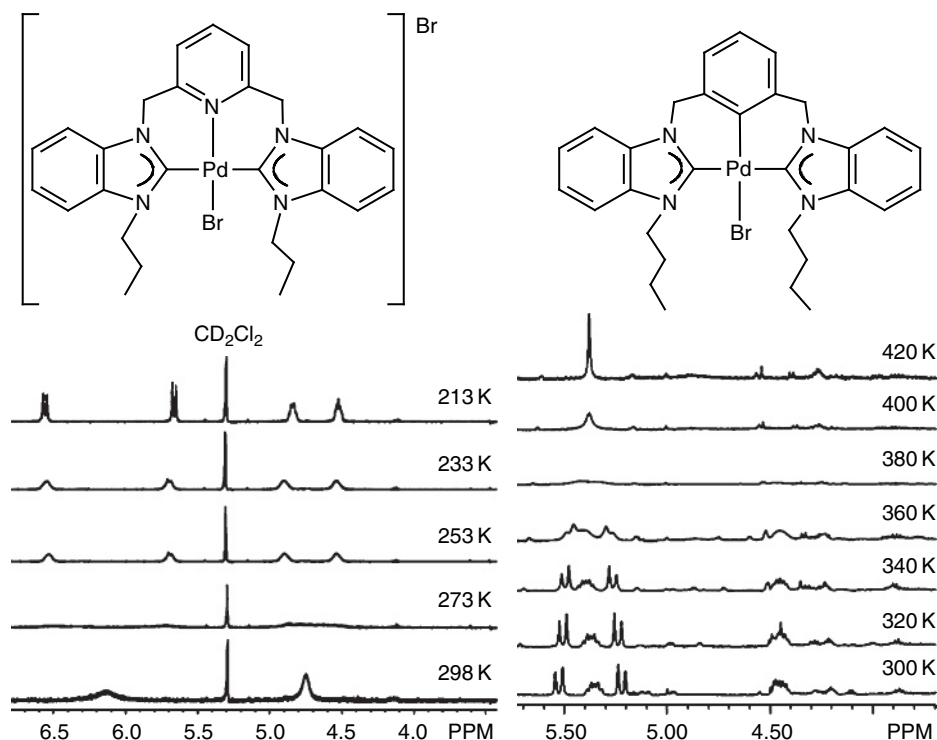
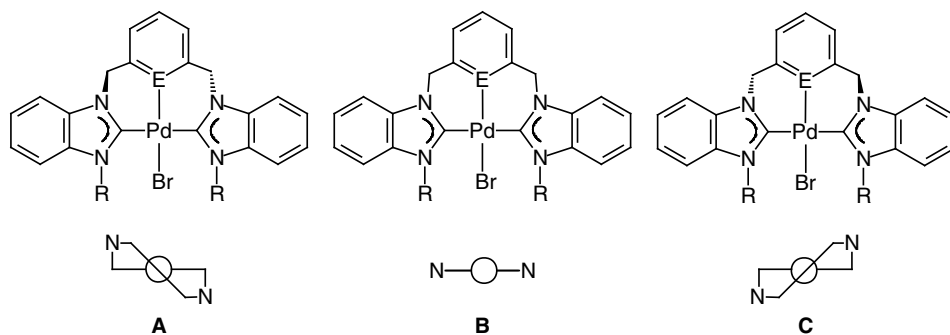


Fig. 7.8. Variable temperature ^1H NMR spectra of complex [12c] $^+$ Br $^-$ (in CD_2Cl_2 , left) and complex [14d] $^+$ (in $\text{DMSO}-d_6$, right).



Scheme 7.7 The twisted conformations **A** and **C** and the average structure **B** of the pincer-type dicarbene palladium complexes.

NMR experiments at different temperatures using a dichloromethane solution of **[12c]Br** show decoalescence of the broad singlet at 273 K (Fig. 7.8, left). At 213 K the interconversion process is stopped and two sharp doublets at $\delta = 6.58$ and 5.68 ppm were observed.

The neutral phenylene-bridged palladium complexes of type **[14]** gave different signals for the bridging methylene groups in the ^1H NMR spectra. Already at room temperature two doublets are observed for these protons (Fig. 7.8, right). This difference can be explained with a hinderance of the interconversion process. The rotation barrier for the change between the conformers is too high at room temperature. Thus the interconversion is slow and cannot be detected on the NMR time scale. In the variable temperature NMR spectra coalescence was observed at 380 K and above 420 K a broad singlet appeared for the methylene protons indicating rapid interconversion of the conformers (Fig. 7.8, right).

In summary, the interconversion of the conformers for the lutidine-bridged complex is fast, while it is hindered in the phenylene-bridged complexes at room temperature. Line shape analyses of the variable temperature NMR spectra allowed the determination of the thermodynamic parameters for the atropisomerization process. As described previously [16a, 16g], $\Delta S^\ddagger$ is close to zero because interconversion is an intramolecular process. Based on the decoalescence temperature and the values of the geminal coupling constants between the nonequivalent methylene protons in the twisted conformers, it is possible to calculate $\Delta H^\ddagger$, which has been determined to 50.5 kJ/mol for the lutidine-bridged dicarbene palladium complexes **[12c]Br**. As expected, a significantly larger value of $\Delta H^\ddagger = 73.8$ kJ/mol was found for the phenylene-bridged palladium complex **[14d]**.

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Pincer complexes of N-heterocyclic carbenes. Potential uses as pharmaceuticals

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8.1 INTRODUCTION

The purpose of this chapter is to present synthetic routes for the formation of metal complexes of pincer *N*-heterocyclic carbenes (NHCs) and to investigate their potential use as pharmaceuticals. In particular, the discussion will focus on NHC-pincer complexes of silver and rhodium. Silver complexes will be explored for their antimicrobial efficacy and rhodium complexes as models for ^{105}Rh -based anticancer agents.

8.1.1 *N*-heterocyclic Carbenes

The past decade has been marked by continually growing interest in NHC metal complexes. Although the first transition metal complexes of NHCs were synthesized by Öfele [1] and Wanzlick [2] in 1968, it was Arduengo's discovery of the first isolable free NHC in 1991 that began a resurgence into this area of chemistry [3]. Several reviews have been published on the subject [4–10], and NHCs and their metal complexes remain actively studied in the area in catalytic chemistry.

NHCs are most typically obtained by the deprotonation of imidazolium salt precursors. Their enhanced stability is derived from the $p\pi$ – $p\pi$ donation of the two nitrogen atoms adjacent to the carbene carbon. This synergistic effect gives rise to a stabilization energy of approximately 70 kcal/mol [5]. An additional 25 kcal/mol of stabilization is gained from aromaticity. The various resonance forms of NHCs are shown in Fig. 8.1. Fig. 8.1B and C shows the multiple bond character of the nitrogen to carbene carbon bond and is summarized by D. The overall aromatic structure is depicted by E.

The high stability of NHC complexes makes them very attractive for use as metal-based therapeutic agents. Current observations show that NHCs will bind more tightly to metals than other common organic ligands. This stability is extremely important, especially when using NHC ligands for therapeutic radiopharmaceuticals. One of the

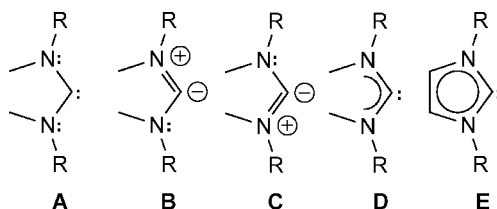


Fig. 8.1. Resonance structures for NHCs, adapted from [4].

most frequent problems of potential radiopharmaceuticals is dissociation of the radioisotope from the chelating ligand. This results in an increased probability of accumulating radioactive materials in healthy tissues causing the patient increased physical and potentially fatal harm. Because NHCs bind so tightly to metals, this major problem may be significantly reduced.

8.2 SILVER NHC-PINCER COMPLEXES

NHCs have been used to bind nearly every transition metal and have also been shown to complex a variety of main group and lanthanide metals [1–13]. The first characterized silver NHC was synthesized by the reaction of a free NHC with a silver salt [14]. It has since been shown that such complexes can be easily generated *in situ* from the reaction of an imidazolium salt with a silver base. Examples of such reactions are well documented using AgOAc, Ag₂O and Ag₂CO₃ [15–17]. The ability to make silver NHC complexes without first generating the free carbene is a major synthetic advantage over many other transition metals. This enables reactions to be carried out in aqueous solvents and avoids the need for inert atmospheres.

8.2.1 Silver Antimicrobials

The effective use of silver in various forms for its antimicrobial properties has been well known throughout history [18]. It was most likely first used to maintain water purity by the Greeks and Romans, a practice which is still employed today by NASA on space shuttles. Silver nitrate was first employed in medicine prior to the 1800s. In recent history, the application of 1% silver nitrate solution to a newborn's eyes was used as an effective treatment for the prevention of gonorrheal ophthalmia [19]. In the 1960s, silver sulphadiazine was developed. Marketed as Silvadene® Cream 1%, this silver complex still remains one of the most successful and widely used antimicrobial treatments for burn wounds.

In studies, strips of metallic silver have been shown to cause zones of inhibition on lawns of bacteria. If the tarnish is removed from the surface of the strips, no inhibition is observed. Molten silver cooled in the presence of air also shows activity in contrast to being cooled in an inert atmosphere which displays no antimicrobial activity. These facts point towards the necessity of the silver metal having surface oxidation for efficacy and that silver cations are responsible for the antimicrobial activity [20].

8.2.2 Synthesis of Pyridine-Based Silver NHC-Pincer Complexes

A variety of NHC-pincer precursors can be generated from imidazole and pyridine starting materials. A large selection of alkyl imidazoles is commercially available, making them convenient reagents for one-step synthesis of imidazolium salt precursors. Alternatively, precursors with the N3 positions of the imidazoles unsubstituted can also be made. This enables the synthesis of imidazolium salts functionalized with substituents currently unavailable commercially.

A general synthesis for pyridine-based bis-NHC-pincer complexes is depicted in Fig. 8.2. Precursor **4** can be synthesized by the reaction of 2 equiv. of potassium imidazole **2** with 2,6-bis(bromomethyl)pyridine **3** in dry THF [21].

The condensation of **4** with either 2-iodoethanol or 3-bromopropanol gives imidazolium salts **5a** and **5b** with corresponding halide anions [22]. The halide salts can be reacted with an equivalent of Ag_2O to afford polymeric biscarbenes **6a** and **6b**. The alcohol functional groups give these complexes exceptionally good water solubility. **6a** and **6b** decompose slowly in water gradually releasing silver cations. A thermal ellipsoid plot of **6a** is shown in Fig. 8.3 with atoms shown isotropically.

Pyridine-based NHC-pincer complexes containing only one NHC unit are also attainable, Fig. 8.4. The reaction of potassium imidazole **2** with 2 equiv. of (6-bromomethylpyridin-2-yl)-methanol **7** affords imidazolium precursor **8** as the bromide salt [23]. The nitrate salt **9** is readily generated by the addition of an equimolar amount of AgNO_3 to **8** in water. When nitrate salt **9** is combined with 0.6 equiv. of Ag_2O in methanol, a trinuclear silver NHC-pincer complex **10** is formed. This complex gains stability not only from the NHC units but also from the six coordinating pyridines. A thermal ellipsoid plot of **10**, with the pyridine carbons removed, is shown in Fig. 8.5.

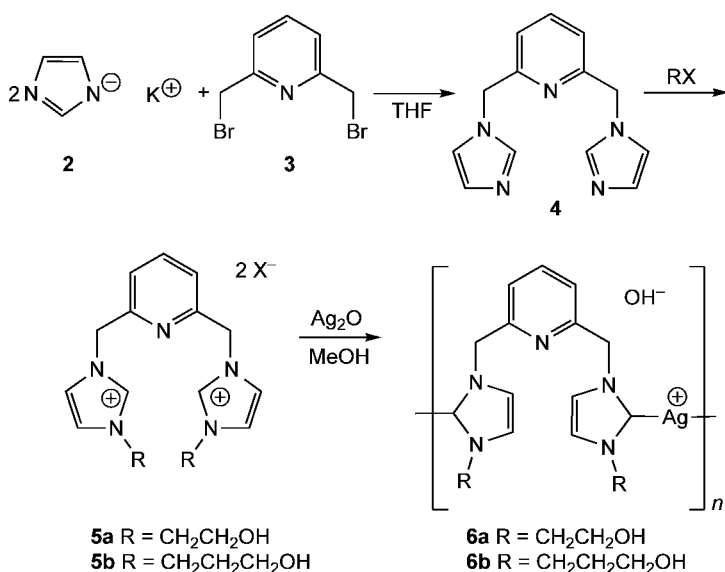


Fig. 8.2. General synthesis for pyridine-based NHC-pincer complexes.

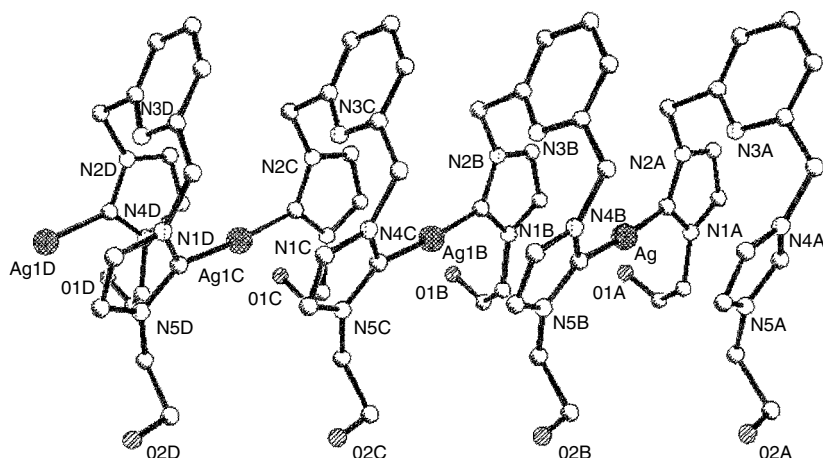


Fig. 8.3. Solid state structure of polymeric **6a**.

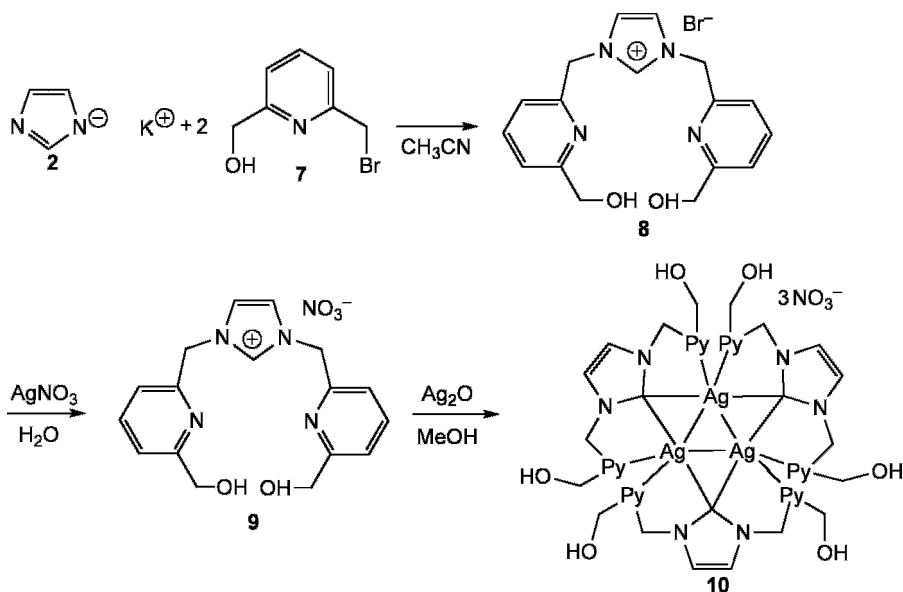


Fig. 8.4. Synthetic route for the formation of trinuclear silver NHC-pincer complex, adapted from [23].

8.2.3 Antimicrobial Activity of Silver NHC-Pincer Complexes

Silver NHC-pincer complexes **6a** and **6b** have been tested for their antimicrobial efficacy against several strains of bacteria [17]. Laboratory strains of *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa* were chosen because of their common association with chronic wound infections. Both compounds were tested for their ability to inhibit growth of the organisms (results shown in Table 8.1) and for their minimum inhibitory concentrations (MICs) (results shown in Table 8.2). In all tests,

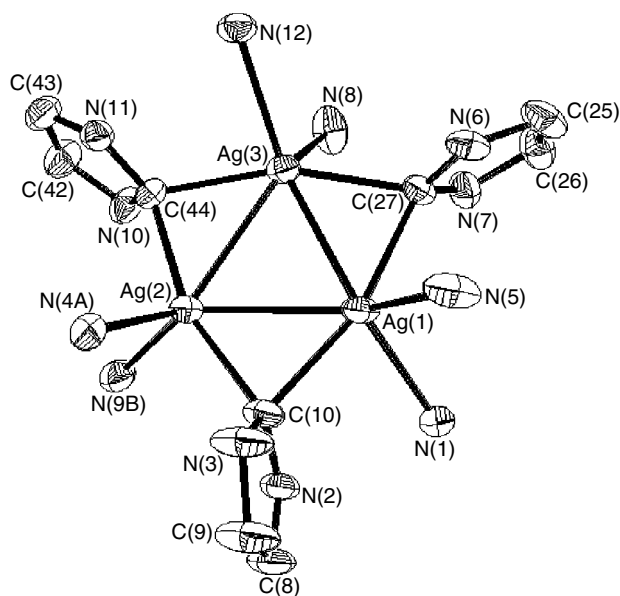


Fig. 8.5. Thermal ellipsoid plot of trinuclear silver complex **10** with the pyridine carbons removed.

Table 8.1. Efficacy of silver complexes for inhibiting bacterial growth, adapted from [22]

Tested compounds (w/v)	Ag ($\mu\text{g/ml}$) ^a	Diameter of the zone of inhibition (mm)		
		<i>E. coli</i>	<i>S. aureus</i>	<i>P. aeruginosa</i>
AgNO ₃ (0.50%)	3176	11.38	10.88	11.00
6a (1.31%)	3130	11.50	11.00	12.00
6b (1.42%)	3195	11.58	10.67	10.25
6a (0.50%)	1195	10.13	10.00	11.13
6b (0.50%)	1125	10.00	9.00	12.00
5a (0.50%)		6.00	6.00	6.00
5b (0.50%)		6.00	6.00	6.00

^a The amount of silver $\mu\text{g/ml}$ for each complex was calculated as (molecular mass of Ag/formula weight of the compound) $\times$ weight %.

silver nitrate was used for comparison and the imidazolium salt precursors were used as controls.

A constant volume of the bacteria was spread over a nutrient-rich agar plate and a lawn of bacteria was established. Filter paper disks measuring 6 mm were bathed in 20 μl of

Table 8.2. MIC results for silver complexes (AgCl removed)^a, adapted from [22]

Test compounds	Ag (mg/ml)	<i>E. coli</i>		<i>S. aureus</i>		<i>P. aeruginosa</i>	
		Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
3a	1186	—	—	—	—	—	—
1DF		—	+	—	+	—	—
2DF		—	+	+		—	+
3DF		+		+		+	
4DF		+		+		+	
3b	1125	—	—	—	—	—	—
1DF		—	+	—	+	—	+
2DF		—	+	—		—	+
3DF		+		+		+	
4DF		+		+		+	
AgNO ₃	3176	—	+	+		—	+
1DF		+		+		+	
2DF		+		+		+	
3DF		+		+		+	
4DF		+		+		+	

^a 0.5% w/v each of the silver complexes was used. DF is the dilution factor (1 ml).

+, growth; —, no growth.

the silver complexes at known concentrations. The plates were incubated overnight with the filter disks, and the activity of the silver compounds was determined by measuring the diameter of the clear zone of growth inhibition around the disks, Fig. 8.6. The zone of inhibition for the imidazolium salt precursors remained constant throughout the study. The 6-mm diameter observed during testing coincides with the diameter of the filter paper disks and shows that the ligands have no antimicrobial activity by themselves.

The MIC values were determined using the same three types of bacteria; however, the MICs were based on the amount of silver available instead of the concentration of silver ions [24]. On adding silver compounds to the growth medium (LB broth), AgCl began to precipitate in all samples. The AgCl was removed and a dilution series of the Ag complexes in LB broth was prepared. Freshly grown organisms (20 µl)

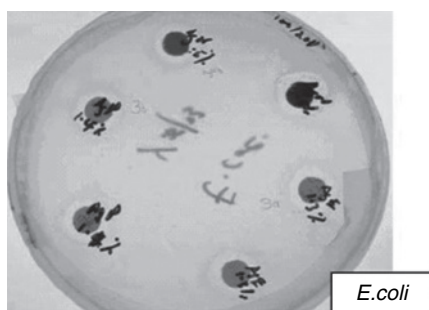


Fig. 8.6. Kirby-Bauer diffusion method compared on *E. coli* for **6a** compared to AgNO₃.

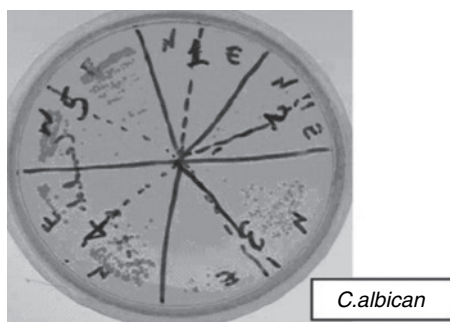


Fig. 8.7. Agar plate showing **N** (AgNO_3) compared to **E** (**6a**) from high (1) to low (5) concentration.

were added daily. MIC values were determined by visual inspection of the solution's turbidity [17].

Both compounds **6a** and **6b** showed greatly enhanced activity over silver nitrate even at lower initial concentrations. This is most likely due to the added stability that the NHC-pincer ligand gives to the complexes against the formation of AgCl . The higher stability of these complexes was likely responsible for a greater concentration of silver ions remaining in solution.

Similar tests were also conducted on yeast and fungi (*Candida albicans*, *Aspergillus niger*, *Mucor*, *Saccharomyce cerevisiae*) using complexes **6a** and **6b**. For each organism, a solution of LB broth containing the MIC for each silver compound was used to inoculate agar plates with active fungal colonies. The absence of viable organisms was observed for **6a** versus silver nitrate at various concentrations. **6a** appears to outperform silver nitrate until very low concentrations of silver complex are used (Fig. 8.7).

8.3 RHODIUM NHC-PINCER MODEL COMPLEXES

The use of radionuclides for cancer therapy is by no means a new concept in medicine. The specific use of a radionuclide is based on its main mode of radioactive decay. $^{99\text{m}}\text{Tc}$ radiotracers were first synthesized in 1964 [25], and $^{99\text{m}}\text{Tc}$ still remains the most widely used radionuclide for diagnostic imaging. ^{131}I administered in the form of NaI is a common and exceptionally effective treatment for differentiated thyroid carcinoma [26].

^{105}Rh -like ^{131}I decays through the emission of β radiation. ^{105}Rh emits β particles in a ratio of 70% 0.560 MeV and 30% 0.250 MeV that are suitable for radiation therapy as well as a 319 keV gamma particle that is suitable for imaging. Its $t_{1/2}$ of 36.4 h is advantageous, in that it should provide sufficient time to kill large tumours, when appropriately targeted, but it is also short enough to avoid prolonged accumulation of radioactive material in the body [27].

8.3.1 Synthesis of Rhodium NHC-Pincer Complexes

The only radioactive ^{105}Rh starting material available for synthesis is $^{105}\text{RhCl}_3 \cdot x\text{H}_2\text{O}$. This presents the challenge of making a robust, chelating rhodium NHC-pincer complex

starting with $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$. The synthetic preparation also needs to be relatively simple and be able to be performed well within the 36.4-h half-life of the radioisotope. There are several ways to approach these challenges. The first involves rapid transformation of the $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ into a form that had been previously used to form rhodium carbene complexes [28]. The second would be direct synthesis of rhodium NHC-pincer complexes from $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$.

When investigating potential radiopharmaceuticals, it is always preferable to start with non-radioactive model complexes. $^{103}\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ was used in the synthesis of rhodium NHC-pincer model complexes. Initial attempts to make rhodium NHC-pincer complexes from $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ involved a conversion to $(\text{Rh}(\text{OAc})_2)_2 \cdot 2\text{MeOH}$ [29]. The reaction of NHC-pincer precursor **11a** with $(\text{Rh}(\text{OAc})_2)_2 \cdot 2\text{MeOH}$, KI and sodium acetate in acetonitrile afforded rhodium complex **13** (Fig. 8.8) [30]. Although the complex is a suitable model, its synthetic preparation raises some major problems. Acetonitrile is toxic and not acceptable for medical use, and the reaction requires several steps that would later involve radioactive materials. These problems all but exclude this approach for practical use.

Because of the obstacles associated with the first approach, a synthetic route for the formation of a rhodium NHC-pincer complex directly from $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ was pursued. Silver complexes **12a** and **12b** were obtained by the reaction of Ag_2O with the appropriate imidazolium salt precursors [31]. Following isolation of the silver complex, an aqueous solution was prepared, and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was added. A red solid could be

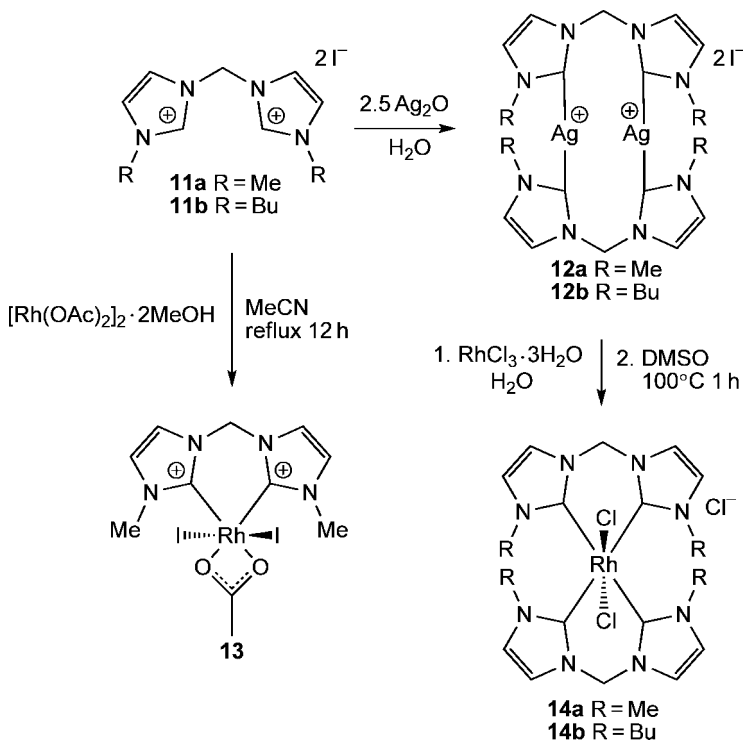


Fig. 8.8. Synthetic route to rhodium NHC-pincer complexes, adapted from [32].

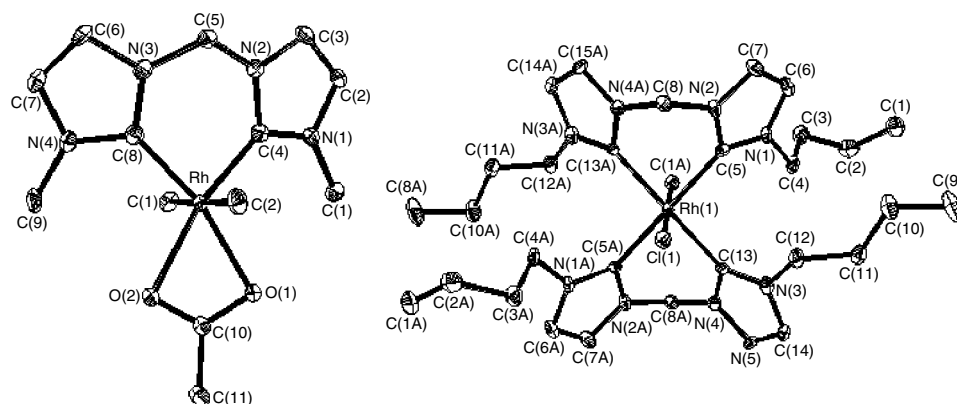


Fig. 8.9. Thermal ellipsoid plots of rhodium NHC-pincer complexes **13** and **14b**, adapted from [32].

isolated from the reaction which was subsequently heated in DMSO at 100°C for 1 h to give rhodium complexes **14a** or **14b** [32]. Both rhodium complexes are exceptionally stable in physiological sodium chloride solutions. This synthetic procedure appears to avoid the use of medically unacceptable solvents, DMSO is biologically benign [33], and only introduces what will be the eventual radioactive material at the final stage of preparation (Fig. 8.9).

8.3.2 Ligand Modification for Targeting

Although successful self-targeting radiological agents exist for the treatment of cancer, their range of use is very specific. As mentioned previously, ^{131}I in the form of NaI is an effective treatment for differentiated thyroid carcinoma [21]; however, this treatment relies on the body's natural affinity to accumulate iodine in the thyroid. Another approach involves the use of targeting moieties to localize a radioactive source at the site of a tumour.

The typical assembly for a targeted bioinorganic radiopharmaceutical is depicted in Fig. 8.10. The desired radioisotope is contained by a strongly chelating ligand which through a linker of desired length is attached to a specific targeting group. This group could be a large monoclonal antibody, a smaller peptide or a non-peptide targeting molecule which would bind to over-expressed receptor sites on tumours. In recent years, peptides have become a much more attractive choice because of the advent of peptide synthesizers [34].

A general route for the formation of targeted pyridine-based NHC-pincer complexes is shown in Fig. 8.11. The condensation of (6-bromomethyl-pyridin-2-yl)-methanol **7** with an equivalent of substituted imidazole **15** would yield a monocationic imidazolium

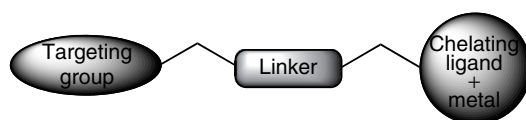


Fig. 8.10. Targeted radiopharmaceutical assembly, adapted from [23].

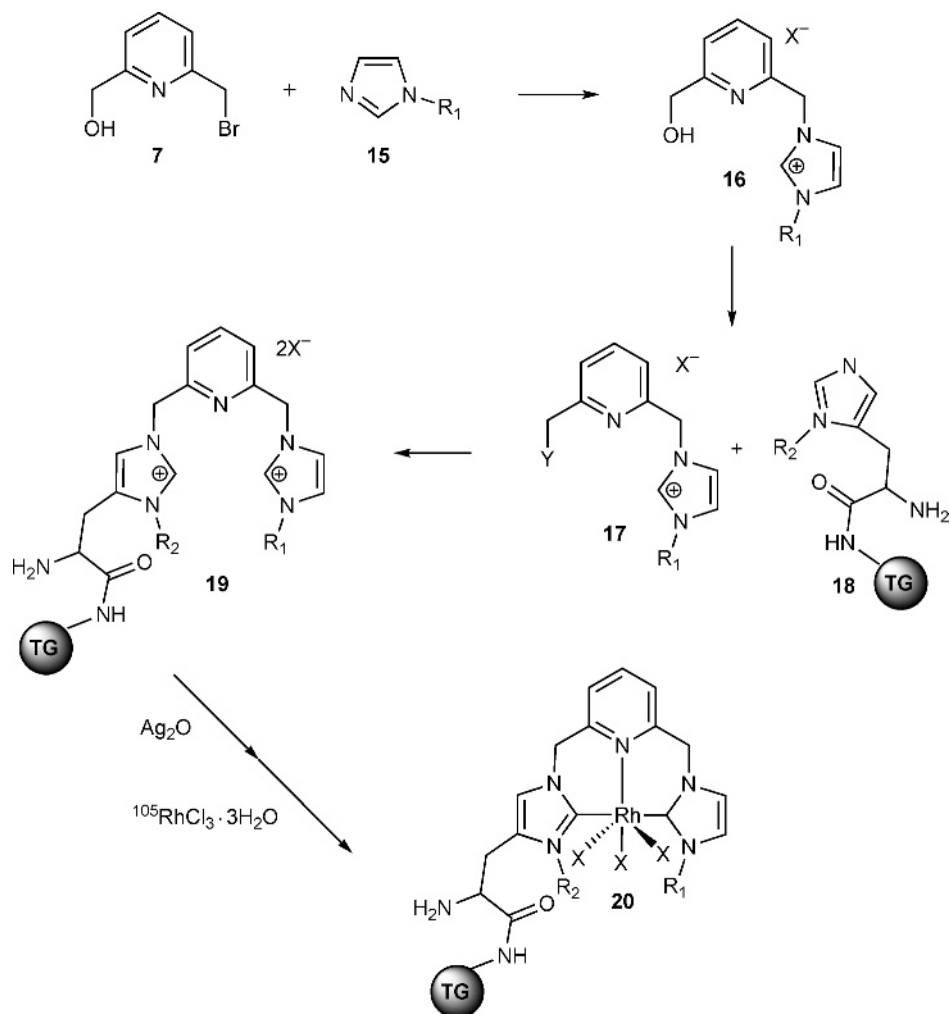


Fig. 8.11. General synthesis for the formation of targeted pyridine-based NHC-pincer complexes, adapted from [23].

salt **16**. Conversion of the alcohol group to a more readily displaced leaving group **17** followed by reaction with a targeting peptide terminated by a histidine derivative **18** would yield a targeted NHC-pincer precursor **19** [18]. In the final step, this precursor could be used to form a silver complex used for transmetalation to form the ^{105}Rh pharmaceutical.

An alternative precursor could be synthesized starting with 1,1'-methylene bis(imidazole) **20**, Fig. 8.12. The condensation of **20** with bromoester **21** forms the ester-functionalized bisimidazolium salt **22**. Hydrolysis of the ester would give the carboxylic acid-functionalized salt. This compound could be potentially used for condensations, with small peptides known to have binding affinities to over-expressed receptor site-specific tumour cells.

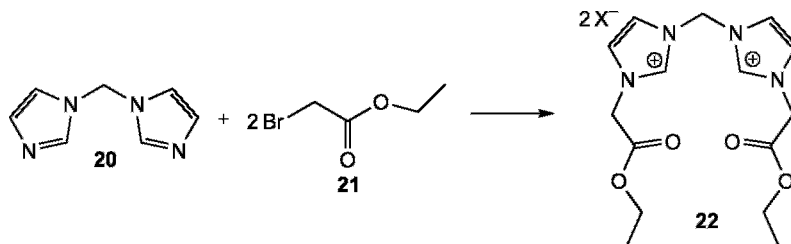


Fig. 8.12. Bisimidazole precursor for targeting.

8.4 CONCLUSIONS

NHC-pincer complexes show a great deal of promise for use in various medicinal applications. The fact that NHCs form such strong metal complexes should give them a major advantage over current organic ligands. Initial studies of silver NHC-pincer complexes show that they have properties important for use as effective antimicrobials. These complexes have better MIC results and bacterial growth inhibitions than silver nitrate against a variety of infectious bacteria and fungi. Also, silver NHC-pincer complexes can be easily generated in biologically friendly solvents such as water and alcohols.

Alternatively, the synthesis of rhodium complexes in water has not yet been achieved. The use of silver NHC-pincer complexes for transmetallation reactions to give rhodium complexes is a major step forward towards this goal. Currently, this route requires the use of DMSO as a solvent which, although not ideal, is a medically acceptable solvent. Studies will continue for improving this synthesis as well as incorporating targeting moieties to form fully functional pharmaceuticals.

ACKNOWLEDGEMENTS

We thank the National Institute of Cancer, National Institute of Health (grant number 1R15 CA096739-01), The University of Akron and the Ohio Board of Regents for Financial Support. We also thank the National Science Foundation (CHE-0116041) for funds used to purchase the CCD Single Crystal X-ray diffractometer used in this work.

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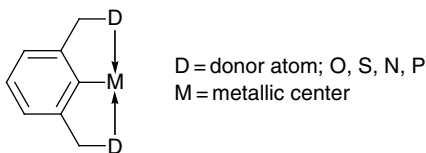
The chemistry of PCP pincer phosphinite transition metal complexes

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9.1 INTRODUCTION

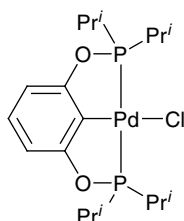
The last decade has witnessed the continuous growing on the development of the chemistry and applications of pincer complexes. Thus, since the seminal report by Moulton and Shaw in 1976 [1] regarding the synthesis of what will become the first pincer complex, these species have passed from being mere curiosity compounds to chemical chameleons able to perform a wide variety of applications, from chemical sensors [2] to extremely efficient catalyst for the activation of strong chemicals bonds [3] and from their use as syntons for the synthesis of dendrimeric and nanomaterials [4] to complexes with potential pharmaceutical applications [5]. Hence, the very basic and apparently simple backbone first attained for the first pincer complex has been proved to be extremely versatile having now a days a very rich variety of pincer motifs including in their structures NHCs heterocyclic carbenes, phosphines, thioethers, oxazolines, etc.



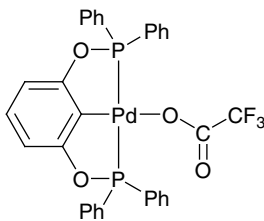
In general these compounds have been first synthesized for their potential applications in some organic transformations, fact that has served as motivation for the chemical community to include stereochemical centers in their structures and thus making available today a rich variety of chiral pincer species able to perform efficiently enantioselective processes.

Thus, the facility to modify and tune the properties of these ligands and their complexes has been reflected in the profuse employment of these species in different areas of chemistry this being particularly true in the case of catalysis [6].

However, one of the caveats on the use of these complexes has been the sometimes difficult or tedious synthesis of the pincer ligands and complexes. An answer to this problem was given by Morales-Morales and Jensen [7] and by Bedford [8] almost simultaneously in the year 2000, where they reported independently the synthesis of the first PCP phosphinite palladium pincer complexes.



Morales-Morales
and
Jensen



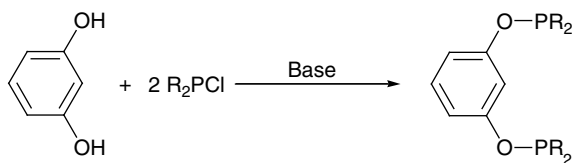
Bedford

Since then, these ligands and their complexes have become more and more important due to the fact that they exhibit the same characteristics of robustness and thermal stability and, as will be shown in further sections of this chapter, enhanced reactivity compared with their phosphine counterparts.

Thus, the scope of this chapter is to present the evolution and recent advances on the chemistry of phosphinite PCP pincer-type ligands, their complexes and the applications that these species have had in different relevant organic transformations and catalysis. For completeness, we will also present and discuss some reactions of these ligands with transition metals that not necessarily lead to the formation of pincer complexes but to the formation of P-coordinated complexes that in some cases people have been able to use as intermediates for the further formation of the genuine PCP pincer derivatives.

9.2 SYNTHESIS OF THE LIGANDS

In general, the synthesis of the ligands can be attained in a very facile manner from the corresponding chlorophosphine and resorcinol (for the most commonly known version of the PCP phosphinite ligands) in the presence of a base.



This procedure has been used successfully for the synthesis of a variety of PCP phosphinite ligands (*vide infra*) and the same method has been probed adequate for the synthesis of other pincer ligands containing in their structures at least one phosphinite functionality [9].

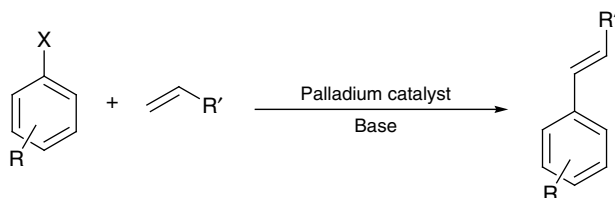
9.3 SYNTHESIS AND REACTIVITY OF TRANSITION METAL PHOSPHINITE PCP PINCER COMPLEXES

Due to the fact that these ligands and their complexes were initially synthesized to be used in C–C coupling reactions, most of the chemistry of these compounds has been dominated by the synthesis of several palladium derivatives and their application as catalysts in C–C coupling reactions. Most recently, and due the importance that their phosphine counterparts have had in the catalytic dehydrogenation of alkanes [10], attention has been placed in the synthesis of the corresponding iridium derivatives and it has not been but in the last couple of years that the platinum, nickel, rhodium and ruthenium derivatives have been successfully synthesized and their chemistry, in many cases radically different from the phosphine counterparts, explored.

9.3.1 Palladium Complexes

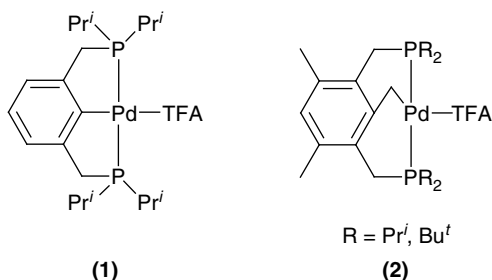
9.3.1.1 Heck reaction

Since its discovery in the 1960s, the Heck reaction has turned into a real power tool in organic synthesis, now a days reaching the status of angular stone in the modern organic synthesis [11]. In general the Heck reaction consists of the coupling of an α -olefin with a bromo or iodo derivative. Most of the processes involving the Heck reaction are catalyzed by Pd(II) or Pd(0) derivatives in the presence of PPh_3 in excess.



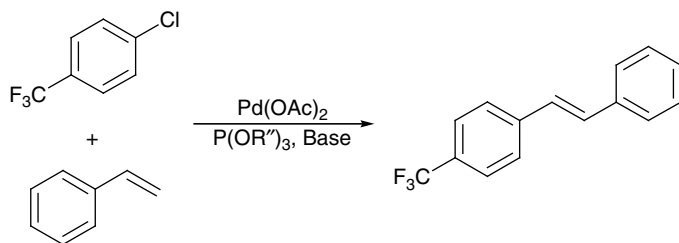
General scheme of the Heck reaction

Unfortunately, the reaction intermediates formed during the catalytic reaction are sensitive to oxygen or thermally unstable, hampering the coupling process. In recent years several research groups have done important advances with the aim of getting the ideal catalyst with the proper characteristics of reactivity and stability to carry out this process, the results of these experiments have led the researchers to the use of orthometallated complexes, among which the pincer-type ligands represent one of the most important examples. Milstein and co-workers were the first to employ Pd(II)-PCP pincer complexes (**1**, **2**) in the Heck coupling reaction [12].



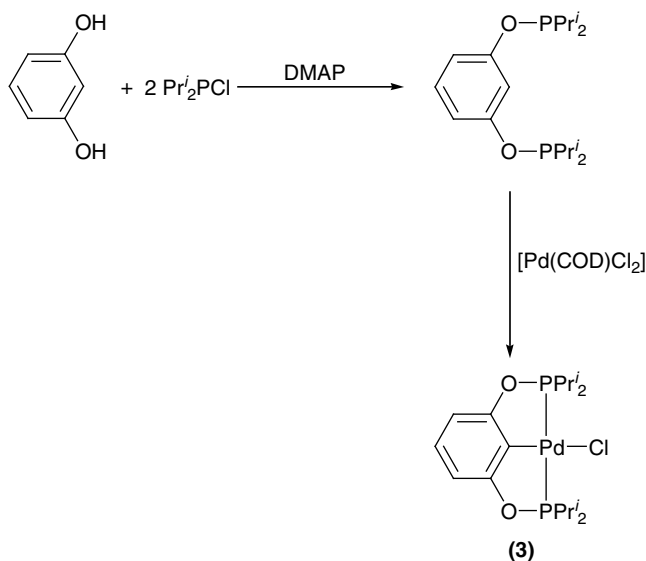
Milstein found that these complexes were active without decomposition at reaction temperatures as high as 140°C, over reaction periods of 300 h or higher. By using these catalysts (**1**, **2**) Milstein achieved full conversion in the couplings of iodobenzene with methylacrylate, using *N*-methylpyrrolidine (NMP) as solvent and sodium carbonate as base with a maximum of 500 000 turnover numbers (TON) for iodobenzene and up to 132 900 for bromobenzene.

By the same time, Beller and Zapf [13] reported the use of electro-attractor phosphite ligands for the Heck couplings of activated chlorobenzenes.

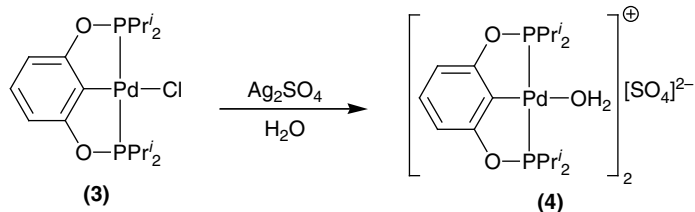


Inspired on these results Morales-Morales and Jensen [7] synthesized an analogous PCP pincer-type ligand based on phosphinito fragments as *P* donors. The palladium derivatives of this ligand (**3**) were shown to be efficient in the coupling of chlorobenzenes, being one of the few examples then known to activate, deactivated or sterically hindered chlorobenzenes [14].

Complex **3** showed to be as reactive as the PCP phosphine derivative reported previously by Milstein [12].



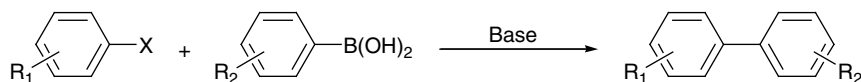
Most recently Ogo et al. have reported the synthesis of water-soluble phosphinite PCP pincer Pd(II) complexes [15]. These compounds were obtained by the reaction of compound **3** with Ag_2SO_4 in water to afford complex **4**.



However, this compound resulted inactive in the C–C Heck coupling reactions in water at a pH of 10.5 of 3-iodo and 3-bromo benzoic acids with 4-vinylbenzoic acid.

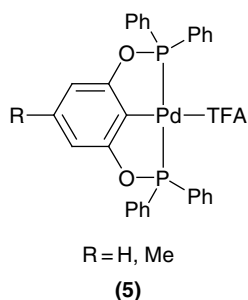
9.3.1.2 Suzuki–Miyaura coupling reaction

The Suzuki or Suzuki–Miyaura C–C couplings [16] consist of the reaction of a halobenzene with arylboronic acids in the presence of a base. This reaction proceeds by a similar reaction mechanism as that of the Heck reaction, thus most of the catalysts usually employed in the Heck coupling reactions have been successfully employed in the Suzuki reaction.



General scheme for the Suzuki type couplings

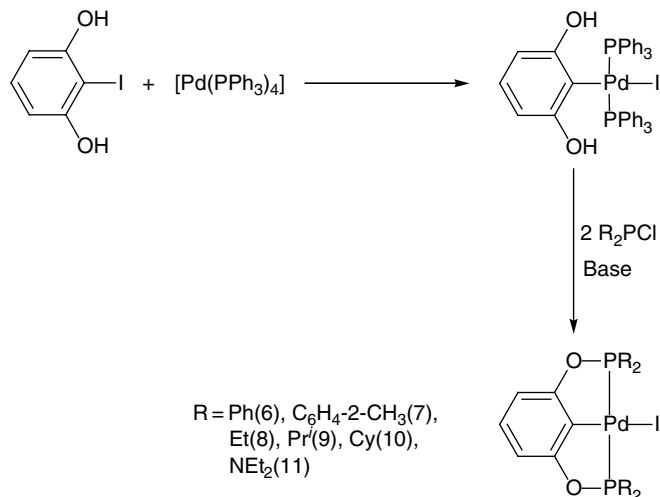
Thus, Pd(II) complexes having phosphinito PCP pincer ligands (**5**) have been successfully used by Bedford et al. [8] in the couplings of aryl halides with phenyl boronic acid, exhibiting quantitative yields and TON in the order of 92 000. These complexes are also efficient in the couplings of deactivated and sterically hindered aryl bromides.



Complex **4** (vide supra) was also evaluated by Ogo et al. in the Suzuki coupling of Ph₄BNA and 3-iodo and 3-bromo benzoic acids in water at a pH of 10.5, attaining TON as high as 123 000 for the case of the 3-iodobenzoic acid [15]. These results are very important as they clearly reflect that the phosphinite ligand and their complexes are not sensitive to water and that they can withstand considerably basic reaction media.

Recent advances in the use of phosphinite PCP pincer complexes in Suzuki couplings have been reported by Kimura and Uozumi providing additionally a novel method for the synthesis of pincer complexes denominated as the ‘ligand introduction route’ this method being particularly useful for the synthesis of pincer complexes having bulky and/or chemically unstable ligand units [17]. This procedure consists of the oxidative addition reaction of 2-iodoresorcinol to a Pd(0) complex [Pd(PPh₃)₄]. Hence, once the insertion of the 2-iodoresorcinol on the metal center has taken place the procedure

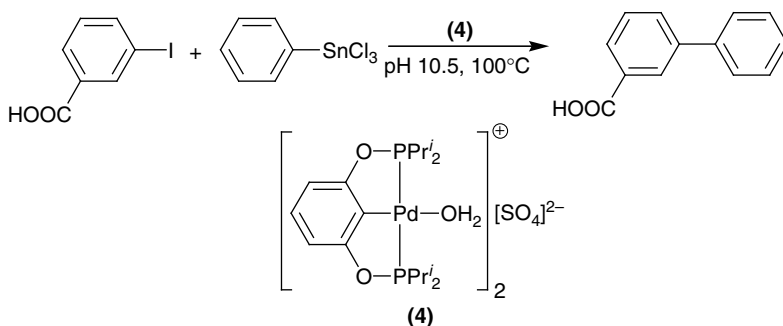
that follows resembles very much the traditional method described above. Thus the oxidative addition product is then reacted in a 1:2 molar ratio with the corresponding chlorophosphine in the presence of a base, to afford directly the PCP pincer complex.



The series of complexes (**6–11**) synthesized by the ligand introduction method were tested in the Suzuki couplings of 4-bromoacetophenone and phenylboronic acid, exhibiting TON from 603 to 5790 being the lower and higher values attained with complexes **11** and **6**, respectively.

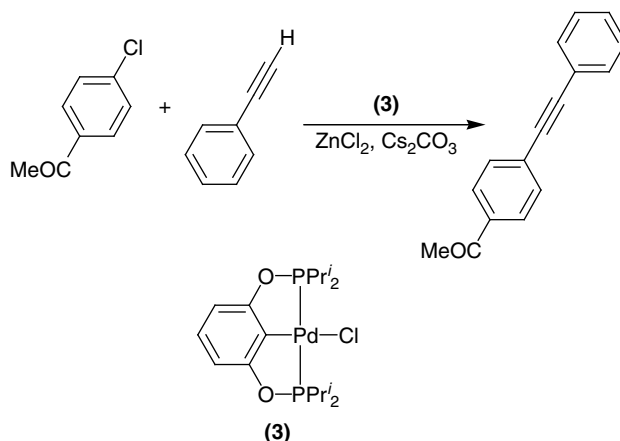
9.3.1.3 Stille coupling reaction

The Stille coupling [18] is a versatile C–C bond-forming reaction between stannanes and halides or pseudohalides, with very few limitations on the R-groups. Well-elaborated methods allow the preparation of different products from all the combinations of halides and stannanes. The main drawback is the toxicity of the tin compounds used and their low polarity, which makes them poorly soluble in water. Stannanes are stable, but boronic acids and their derivatives undergo much the same chemistry. Thus, in general the Suzuki coupling reactions are preferred to the Stille couplings thus avoiding the drawbacks of using tin compounds. In fact, the only report of Stille coupling using pincer complexes of any type is provided by Ogo et al. [15], using complex **4** (vide supra) for the coupling of PhSnCl_3 with 3-iodobenzoic acid in water at a pH of 10.5, achieving modest yields (42%) and TON of 2100 at 100°C.

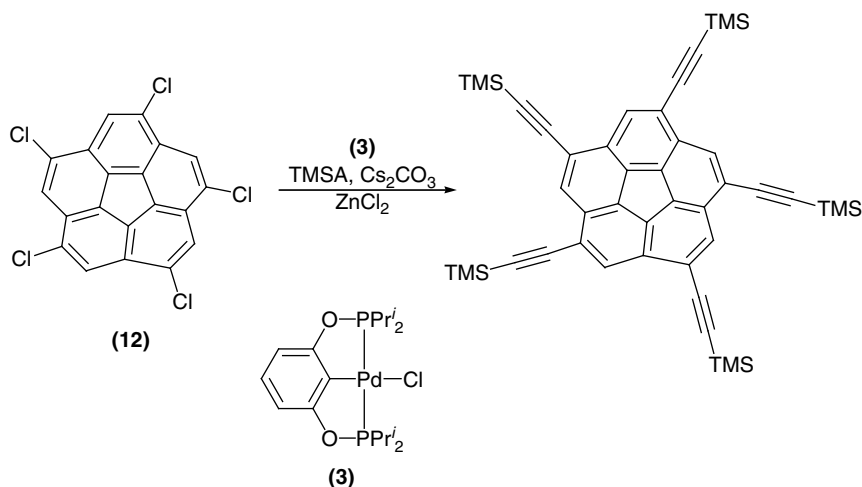


9.3.1.4 Negishi coupling reaction

In 2002 Jensen and co-workers [19], reported a modified Negishi coupling reaction protocol for the one-pot coupling of a wide array of aryl chlorides with phenylacetylene in the presence of ZnCl_2 using complex **3** as catalyst, achieving yields as high as 91% for the reaction of 4-chloroacetophenone with phenylacetylene at 160°C for 24 h reaction time.

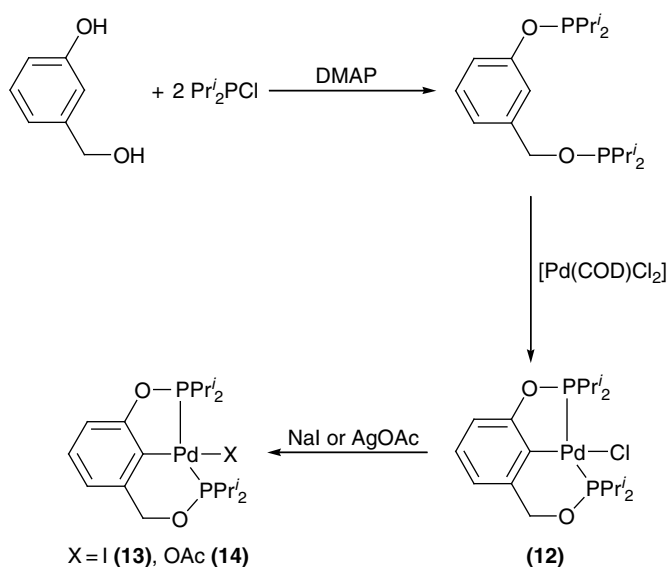


In fact based on this report Siegel and co-workers [20] have achieved what they have denominated a *milestone* of converting compound **12** into pentasubstituted corannulenes with carbon substituents of sp , sp^2 and sp^3 hybridizations.

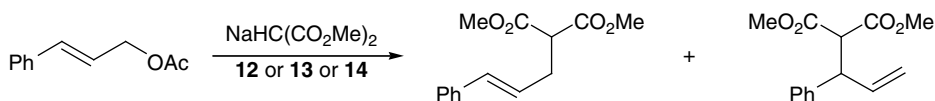


9.3.1.5 Allylic alkylation

Further efforts by Jensen's group led them to the synthesis of a new class of unsymmetric PCP phosphinite pincer ligand and its palladium derivatives [21], according to the following scheme.

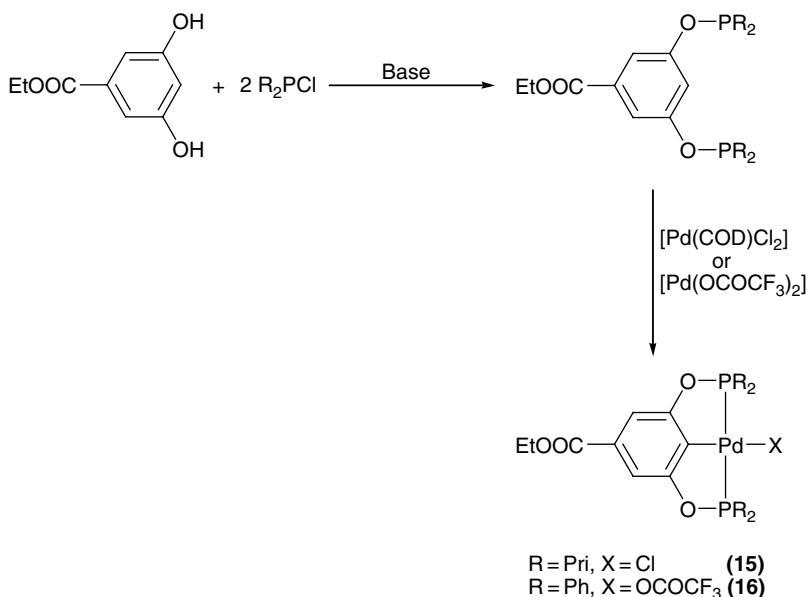


These compounds (**12–14**) were found to be active in the allylic alkylation of cinnamyl acetate with sodium dimethyl malonate, showing little isomerization activity affording exclusively the linear product. The authors have explained that the enhancement on the reactivity of complexes **12–14** as compared with compound **3** is due to the introduction of a six-membered metallacycle into the pincer complex structure, thus making these species more flexible and increasing the P–M–P bite angle. Moreover, the catalytic activity resulted to be strongly dependent on the anion coordinated to the palladium center, hence the activity of the complexes increases when the metal is more easily available, the more active specie being that having the less coordinating ligand (OAc^-) complex **14**.

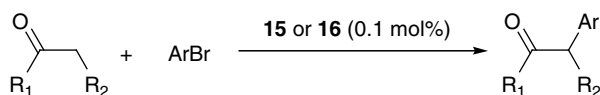


9.3.1.6 α -Arylation of ketones

SanMartín and co-workers have recently reported on the use of *p*-alkoxycarbonylated PCP-Pd(II) phosphinite pincer-type complexes (**15** and **16**) for the α -arylation of ketones [22].

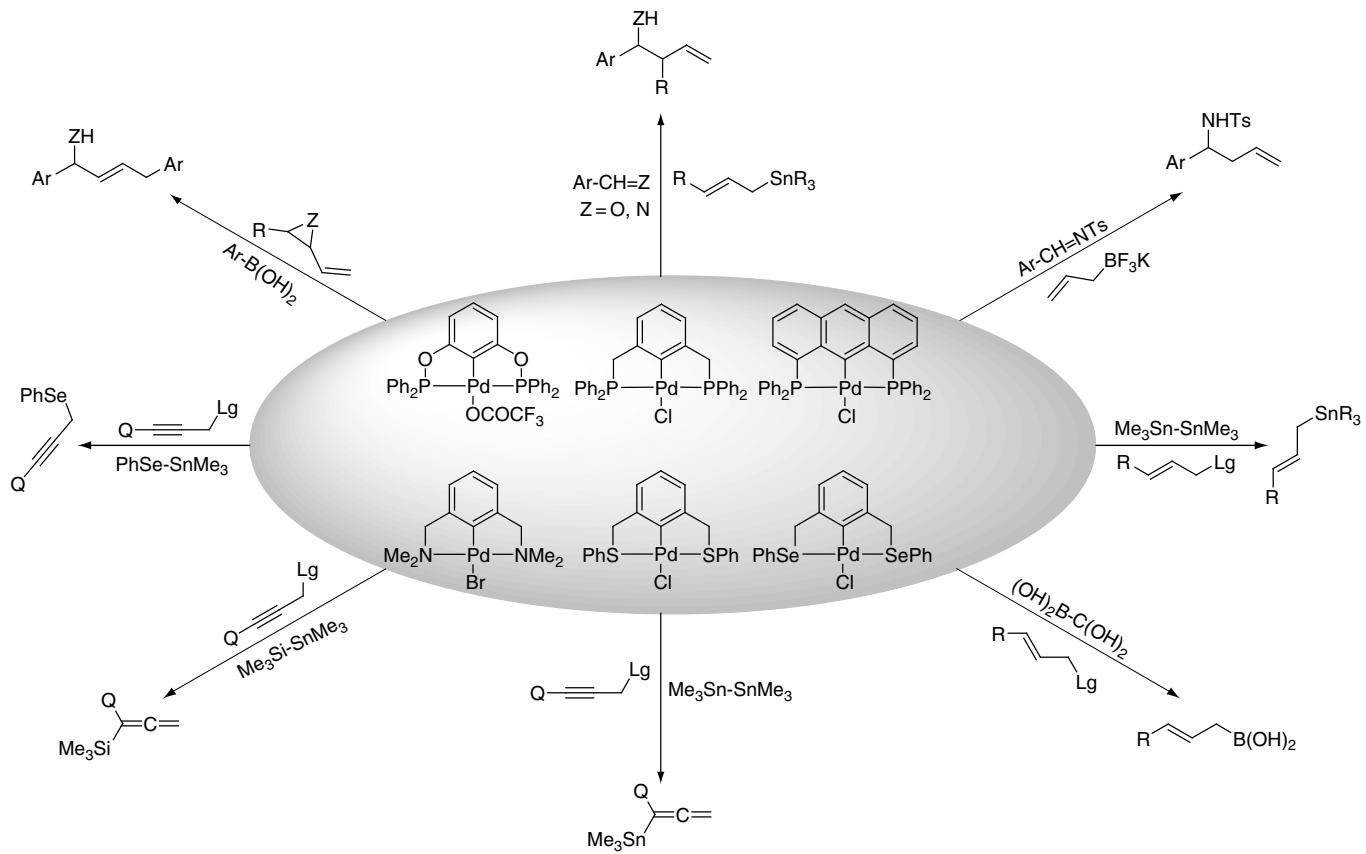


The experimental procedures developed allow both the regioselective monoarylation and diarylation of hindered and unhindered ketone enolates with a wide variety of aryl bromides without formation of phenyl-aryl exchange by-products, using significantly low catalysts loadings, thus yields up to 99% can be achieved using compound **15** as catalyst.

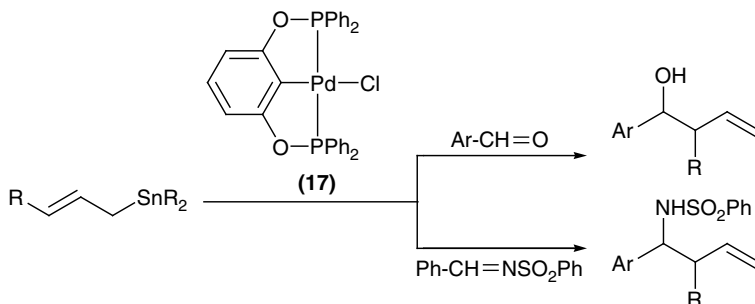


9.3.1.7 Allylation of electrophiles

In the last lustrum, Szabó and co-workers have directed their attention to the investigation of reactions involving the palladium-catalyzed allylation of electrophiles. Through several recent publications [23] they have shown that palladium pincer complexes can efficiently catalyze the electrophilic allylation of aldehyde and imine substrates and the allylation of sulfonimines with potassium trifluoro(allyl)borate. Moreover, the fact that some pincer complexes react very slowly, if at all, with allylstannanes and allylboranes and the possibility for an efficient and fine tuning of the substituents in the donor atoms and therefore the potential reactivity of these pincer complexes, makes them ideal catalysts for the synthesis of reactive organometallic compounds with allyl, allenyl and propargyl functionalities. Thus the use of various dimetallic compounds comprising Sn–Sn, Sn–Si, Sn–Se and B–B bonds allows the synthesis under mild conditions of allylstannanes, allylboronates, allenylstannanes, allenylsilanes and to perform in an efficient manner the phenylselenation of organohalides.



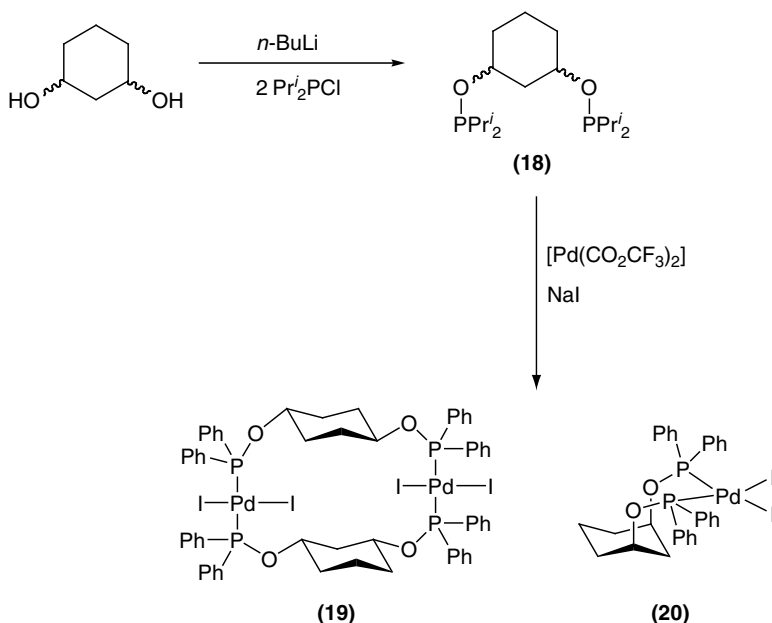
From this set of reactions, palladium phosphinite PCP pincer complexes have been employed successfully in the electrophilic allylation of aldehyde and imine [24] substrates and in the allylation of sulfonimines with potassium trifluoro(allyl)borate [25].



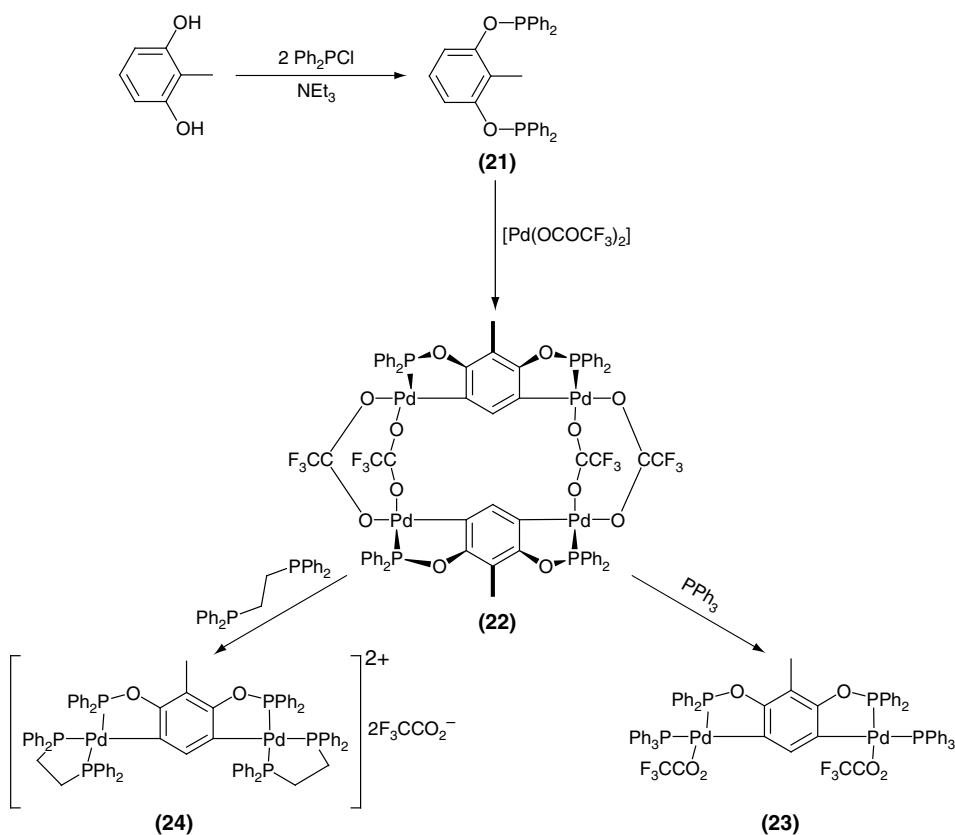
These chemistry has been motif of a recent review [26] and it is presented and discussed in full detail in Chapter 2 of the present book.

9.3.1.8 Palladium curiosities

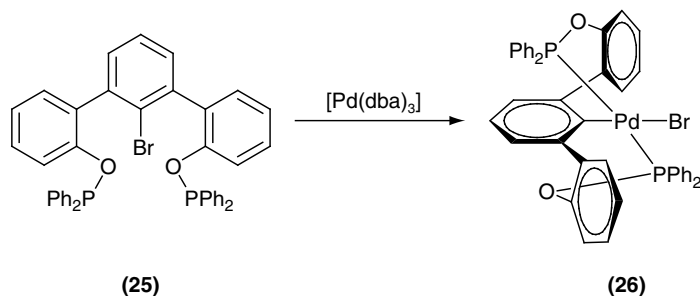
As we have shown above the evolution of the chemistry of palladium PCP-phosphinite pincer-type ligands has had its advances and as any other evolution some curiosity species have emerged from the continuous design and synthesis of new compounds. For instance, in 2001 Wendt and co-workers [27] synthesized the $\text{PC}_{\text{sp}^3}\text{P}$ phosphinite ligand (18); however, after reacting this ligand with $[\text{Pd}(\text{CO}_2\text{CF}_3)_2]$ in the presence of NaI , no cyclometallated product was obtained, instead two products were isolated and crystallographically characterized: a dimeric species (19) where two units of ligand 18 act as bridges between two palladium centers and a monomeric species where ligand 18 behaves as chelating diphosphine (20). The reactivity of these two species was not explored further, nor their potential catalytic activity.



A similar phenomenon occurred when Bedford et al. [28] reacted compound **21** with $[\text{Pd}(\text{CO}_2\text{CF}_3)_2]$ in a 2:1 molar ratio affording complex **22** as the major product. In individual experiments, complex **22** was further reacted with PPh_3 and dppe to afford compounds **23** and **24** as unique products, presumably these reactions proceeded through the breaking action of the phosphines over the trifluoroacetate bridges. The crystal structure of complex **22** was determined. Once again the reactivity of these complexes was not explored further.



Most recently, Protasiewicz and co-workers reported [29] on the synthesis of new pincer ligands based on *m*-terphenyl scaffolds and their complexes. Among these, a phosphinite pincer-type ligand (**25**) with the largest 'twist' angle so far observed was reported. Ligand **25** reacts with $[\text{Pd}(\text{dba})_3]$ to yield the pincer complex **26**. Analysis by X-ray diffraction studies of **26** revealed a PCP pincer structure with a twist angle of 73.8° . This new pincer complex is robust and displays great air and heat stabilities and can be easily purified by flash chromatography on silica gel under ambient conditions. The reactivity of this complex was not explored further either, although the authors have already recognized the potential of these species particularly in catalysis.



9.3.2 Iridium complexes

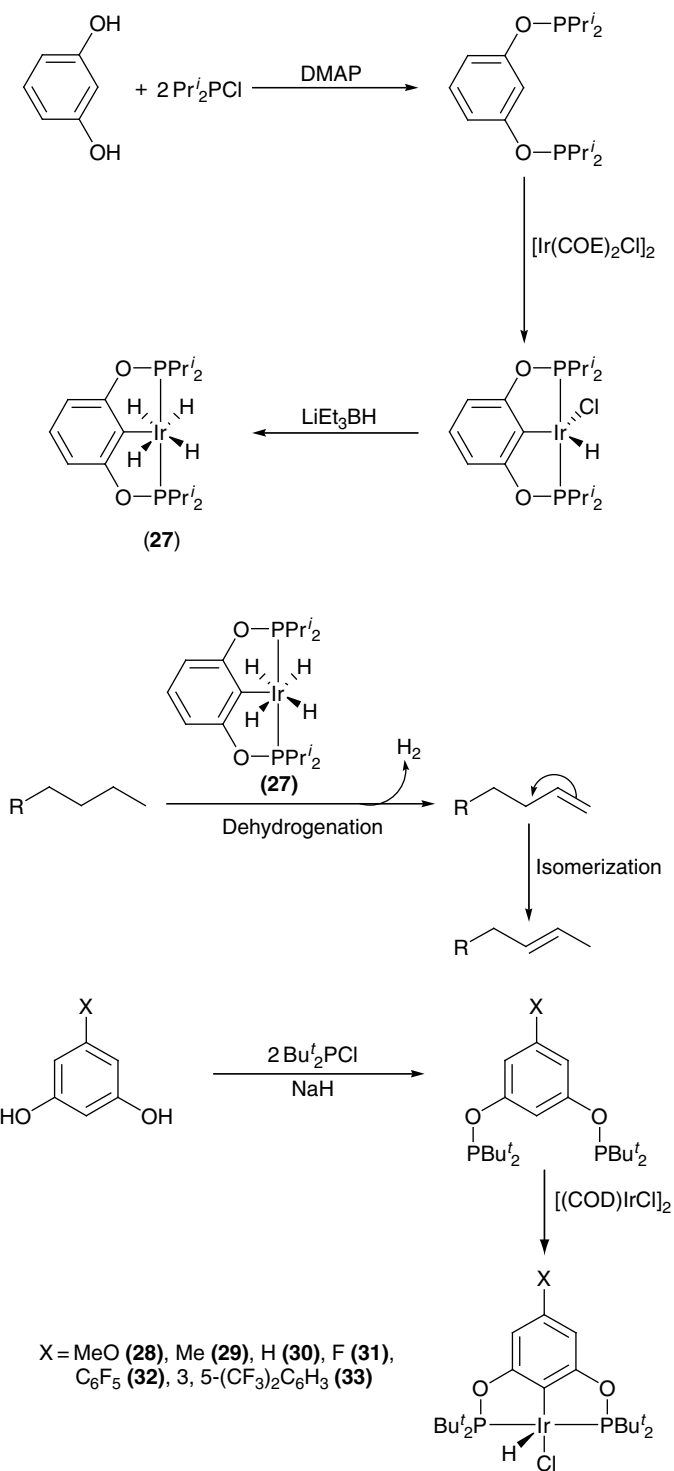
As it has been mentioned above, most of the motivation for the synthesis of these relatively new phosphinite PCP pincer complexes has been the relatively facile way of synthesis and most importantly the fact that these species also exhibit an extraordinary air and thermal stabilities as that shown for their phosphine counterparts. Hence, another important area where phosphinite PCP pincer complexes have been employed intensely has been in processes and catalytic reactions involving the activation of aliphatic C–H bonds [10]. The selective functionalization of aliphatic groups is one of the great unsolved problems of organic chemistry. The quest for methods to effect this type of transformation continues to entice chemical researchers through economic incentives and intellectual challenge. One of the most commercially tantalizing possibilities is the production of major organic feedstocks such as terminal alkenes (α -olefins) through regioselective aliphatic dehydrogenation reactions [3a]. Thus, due to the successful results attained in these reactions several research groups have recently explored the possibility of activation of other similar X–H bonds particularly N–H and B–H.

9.3.2.1 Dehydrogenation of aliphatic C–H bonds

The first reports regarding transfer dehydrogenation of alkanes using iridium phosphinite PCP pincer complexes were published by Morales-Morales and Jensen [30] and Brookhart and co-workers [31] in 2004. Morales-Morales & Jensen only reported on the use of iridium phosphinite PCP pincer complex (27) for both the transfer dehydrogenation of cyclooctane (COA) in the presence of *tert*-butylethylene (TBE) and the acceptorless dehydrogenation of *n*-undecane finding the reactivity of these complexes to be slightly superior to that found for the analogous phosphine derivative $[\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^t\text{Bu}'_2)_2\}_2]$ with similar yields and TON, exhibiting the same product inhibition and isomerization problems.

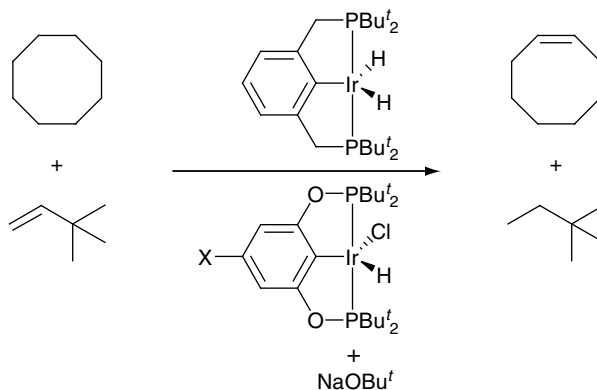
Brookhart and co-workers [31], on the other hand, synthesized a series of new phosphinite *p*-XPCPIrHCl pincer complexes.

Interestingly, in this case, in comparison with their phosphine counterparts, the air and moisture sensitive hydrido-chloride compound has to be converted into the even more sensitive dihydride species by treatment with LiBHET_3 . In this case, the generation



of the catalytically active species is made in situ by reacting complexes **28–33** with NaOBu^t in the reaction mixture.

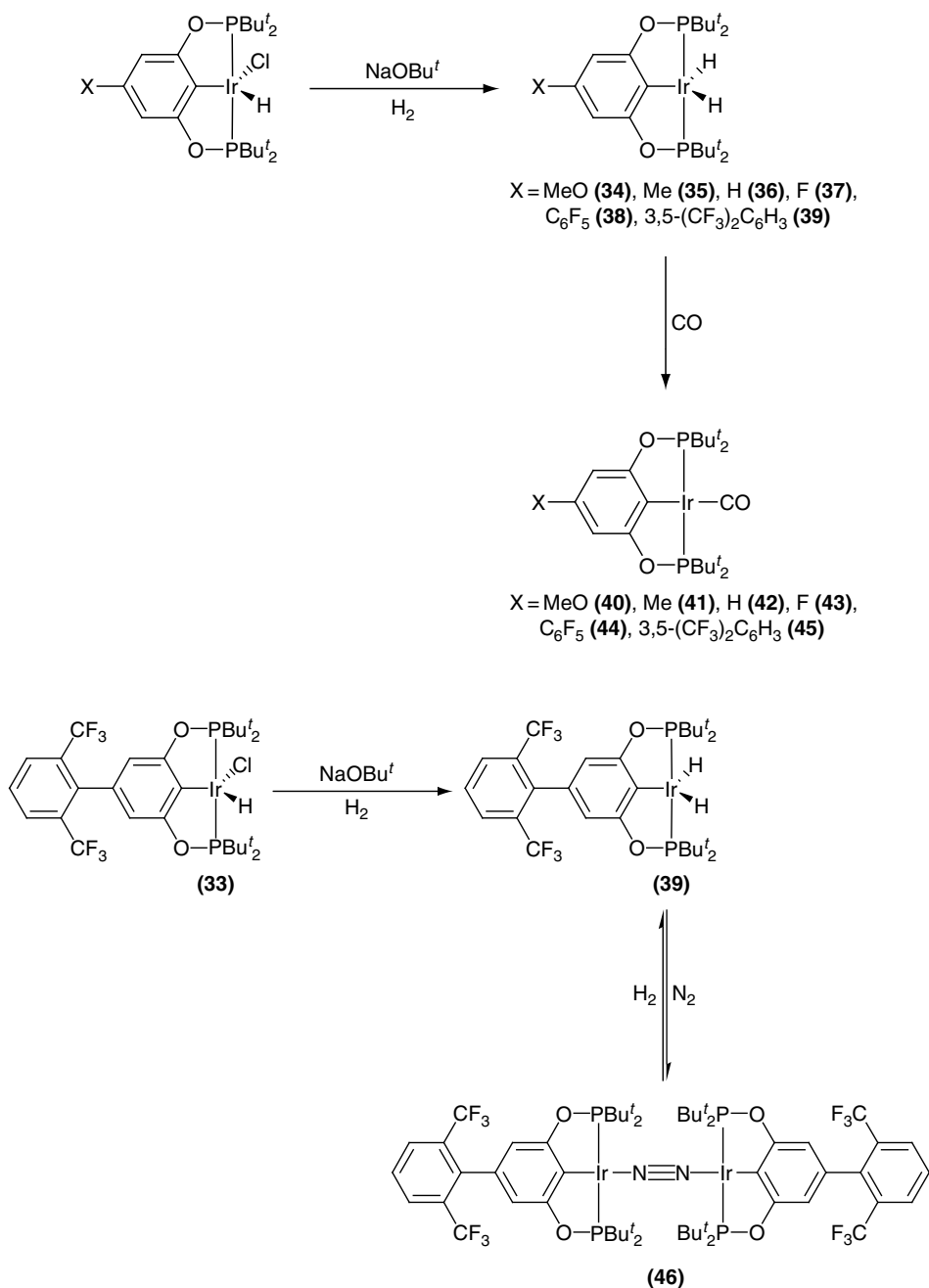
Thus, the transfer dehydrogenation of COA with TBE to form cyclooctene (COE) and *tert*-butylethane (TBA) was easily accomplished. Under comparable conditions, these new catalysts (**28–33**) are about one order of magnitude more active in terms of TOF, TON and substrate conversion than the benchmark catalyst [IrH₂{C₆H₃-2,6-(CH₂PBu^t₂)₂]₂. A further dehydrogenation of COE to form 1,3-COD was accomplished by transfer dehydrogenation in the presence of TBE at high COE concentration. Moreover, in the absence of another hydrogen acceptor, COE itself serves as hydrogen acceptor giving rise to disproportionation of COE into COA and 1,3-COD, which is further transformed into *o*-xylene and ethylbenzene at temperatures as low as 200°C. However, disproportionation of COE into 1,3-COD and COA at 200°C is only operative at relatively low COE to catalyst ratios (*ca.* 450:1).



Further studies with these compounds (**28–33**) led to the formation of the corresponding dihydride species (**34–39**) [32]. These compounds were then reacted with CO in order to evaluate the electronic effect of the *para* substituents in the catalyst by measuring the ν_{CO} values of their respective (CO) complexes (**40–45**), finding that except for the F derivative, the increasing electron deficiency varies in the following order: 3,5-(CF₃)₂C₆H₃ $\approx$ C₆F₅, F > H > Me > MeO. Thus, based on these information and data obtained from measurements of the initial TOFs in the transfer dehydrogenation of COA with TBE catalyzed by the dihydride species (**34–39**) correlate with the more electron-deficient systems being more active.

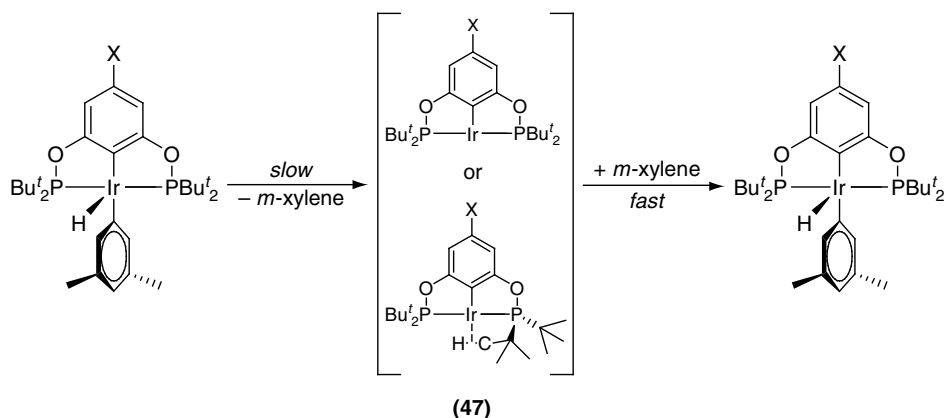
Moreover, treatment of a solution of compound **33** with NaOBu^t in toluene under a saturated N₂ atmosphere affords the dinitrogen complex **46**; it is noteworthy that the formation of the analogous phosphine derivative has been previously reported [33] and, similar to compound **46**, once it is exposed to a stream of hydrogen the dissociation of the dimer is observed giving place to the quantitative formation of mixtures of the corresponding di and tetrahydride compounds [34].

Mechanistic [35] as well as DFT studies [36] concerning the transfer dehydrogenation of COA catalyzed by iridium phosphinite *p*-XPCP pincer complexes (**28–33**) have also



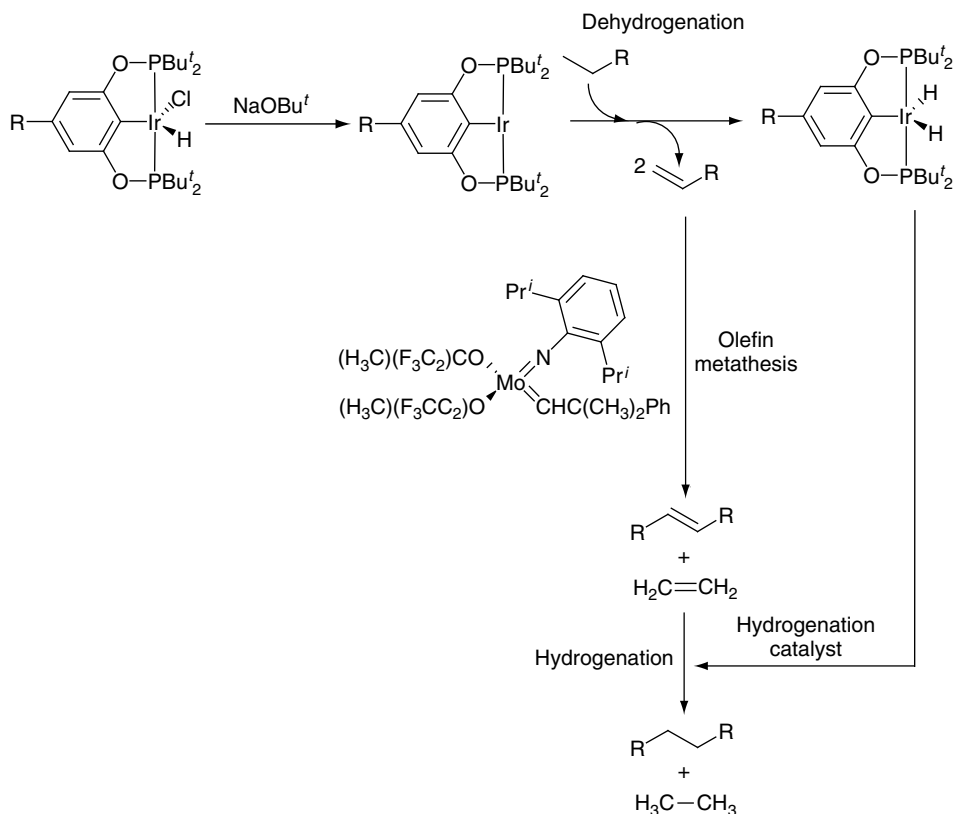
been reported recently. It is noteworthy that when the reaction between complexes **28–33** and NaOBu^t is carried out in aromatic solvents like benzene the originally formed 14e species (**47**) slowly reacts with the solvent to form the hydrido-phenyl derivative which is quickly eliminated to regenerate the reactive 14e species (**47**). Further studies

carried out with *m*-xylene allowed to conclude that the reductive elimination process is significantly enhanced for the more electron-deficient complexes **32** and **33**, while π -donation by the MeO and F substituents in compounds **28** and **31** results in the lower rates of reductive elimination [32].



A couple of the great problems of the systems presented above have always been the product inhibition of the catalyst and the isomerization processes once a certain yield of α -olefin is attained. Thus, it would be desirable to have a catalyst or a combination of catalysts able to use or drain the new double bonds formed in such a way that the olefin would not cause any of the mentioned problems. This would be even more interesting if it could be possible to carry out this tandem process in the dehydrogenation of linear alkanes for the formation of α -olefins and from there to other high-value products. An answer to this problem has been given recently by the joint work of Goldman and Brookhart where they report the combined application of an iridium phosphinite PCP pincer complex with a Schrock-type metathesis catalyst [37]. The idea resulted very simple, to have a catalyst able to acceptorless dehydrogenate linear alkanes for the production of the corresponding α -olefin and once the α -olefin is formed to undergo olefin metathesis catalyzed by the Schrock-type metathesis catalyst. Thus, the consumption of the recently formed α -olefin would lead the dehydrogenation catalyst to keep performing its function while the metathesis catalyst will consume any of the α -olefin produced thus creating a synergic system. However, in this particular case the phosphine analog resulted to be more effective than the phosphinite derivative, due to faster isomerization reactions to internal olefin using the late catalyst. The present system is completely selective for the linear product (*n*-alkane).

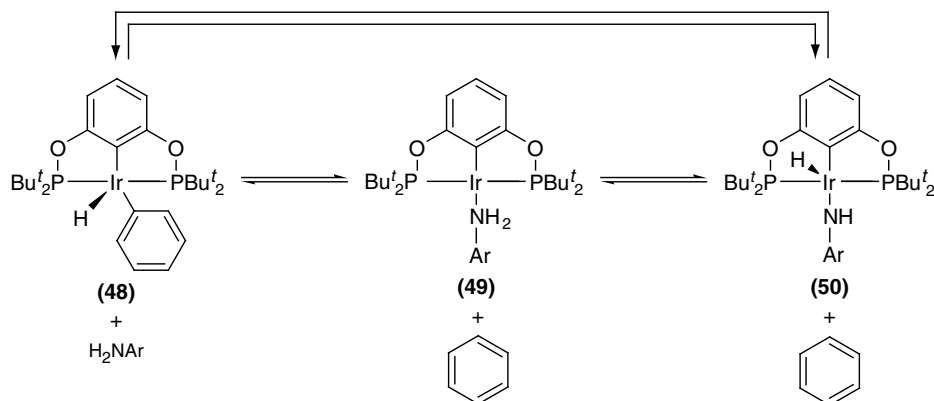
Although the exposed process is promising, the decomposition of the olefin metathesis catalyst appears to limit the conversion, so it is expected that more robust and compatible olefin metathesis catalysts will yield higher TON.



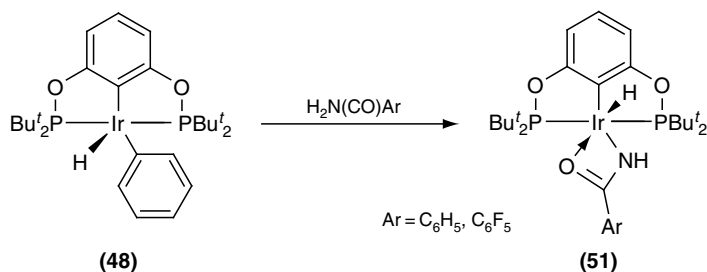
9.3.2.2 Reactivity with N–H bonds

Although N–H and C–H bonds exhibit similar homolytic bond strength, much fewer investigations of late transition-metal activation of N–H bonds have been carried out. The comprehension of these processes can have a great impact on the rapidly growing number of metal-catalyzed transformations of amines and related compounds, such as hydroamination of alkenes, styrenes, dienes and alkynes as some of these transformations may involve the oxidative addition of N–H bonds.

In this sense, Brookhart and co-workers have extended the scope and applications of the iridium phosphinite PCP pincer complexes presented in Section 9.3.2.1 to study now the reactivity of complex **48** toward a series of anilines [38]. Thus, by treatment of the hydrido-chloride complex (**36**) with NaOBu^t and a set of anilines in benzene at room temperature, they found that the phenyl hydride complex (**48**) reacts with the corresponding aniline to form either the σ -complex (**49**) or the oxidative addition adduct (**50**). The three species (**48–50**) are all found in equilibrium in solution at 25°C. Kinetic studies carried out for the different anilines allowed to conclude that as the substituent in the aniline becomes more electron-withdrawing, the Ir(III) oxidative addition adduct becomes increasingly favored. While for instance, for the electron-rich *p*-methoxyaniline, only the σ -adduct can be observed. The increased stability of the oxidative addition adducts bearing electron-withdrawing aryl groups was attributed to decreased repulsion between filled d_π and N_p orbitals.

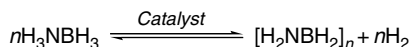


Additionally, the reaction of compound **48** with benzamides was tested observing the quantitative formation of the Ir(III) oxidative addition adducts (**51**).



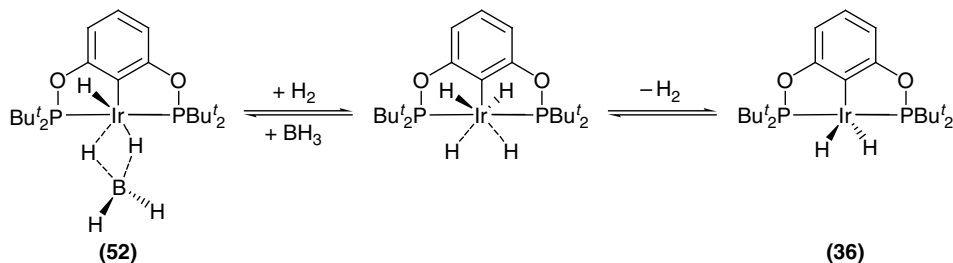
9.3.2.3 Reactivity with B–H bonds

Chemical hydrogen storage, where hydrogen is stored in a chemical compound and released via a reversible chemical reaction, is a promising strategy [39]. Ammonia borane (H₃NBH₃) and related aminoborane compounds have emerged as particularly attractive candidates for hydrogen-storage materials due to their high percentage by weight of available hydrogen and the potential reversibility of hydrogen-released reactions. However, catalysts are needed to affect the release of hydrogen from aminoborane compounds at efficient rates.



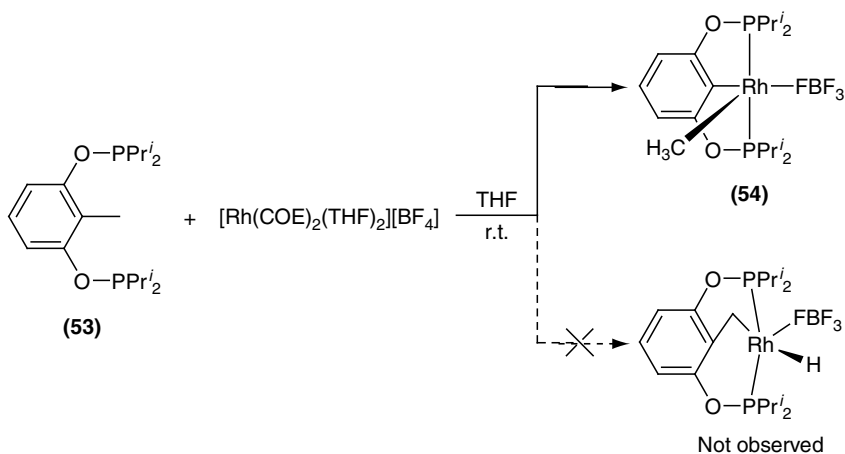
Given the excellent reactivity that the iridium phosphinite PCP pincer complexes have previously shown, compound **36** was employed in the dehydrogenation reaction of H₃NBH₃ showing to be an exceptionally active catalyst [40]. Thus, when catalyst **36** was added to a THF solution of ammonia borane, under an argon atmosphere, vigorous evolution of gas was observed. Accompanied by this the initially red-colored solution of **36** faded to pale yellow and a white solid precipitate. After complete consumption of the substrate, gas evolution was immediately renewed upon addition of more ammonia borane. This compound (**36**) is reported to be the best catalyst so far for the dehydrogenation ammonia borane. The catalytic system was tested in the presence and the

absence of elemental mercury exhibiting the same rate in both cases, thus suggesting the iridium catalyst to remain homogeneous along the whole dehydrogenation process. Control reactions to investigate the fate of the catalyst with $\text{H}_3\text{B} \cdot \text{THF}$ led to the isolation of complex **52**, a BH_3 adduct of **36**. The crystal structure of this adduct was determined and suggested to be the dormant form of the iridium PCP pincer phosphinite catalyst (**36**).

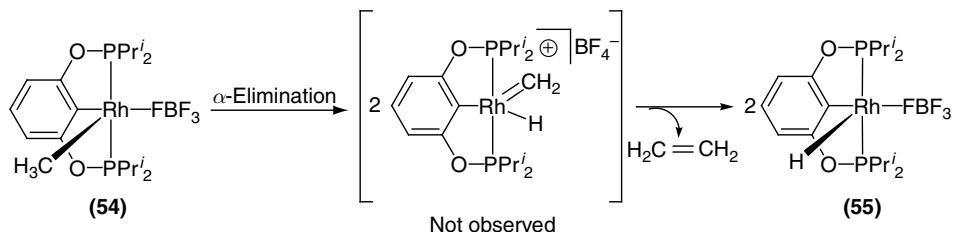


9.3.3 Rhodium Complexes

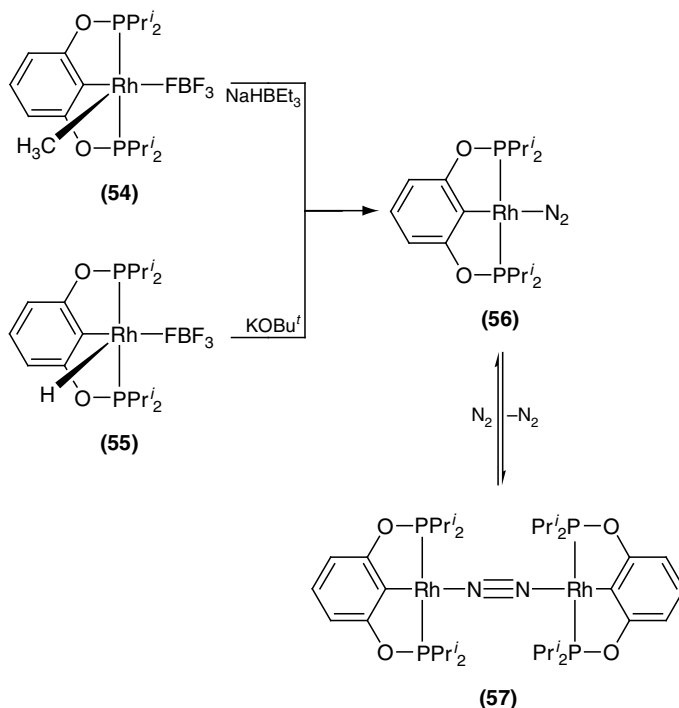
It was not until 2006 due to the success on different catalytic processes of the palladium and the iridium PCP phosphinite pincer catalysts, that chemists around the world started to explore the possibilities to synthesize and apply other transition metal derivatives of PCP phosphinite ligands into organic transformations and catalysis or just simply to compare the potential reactivity of these new complexes with the analogous phosphine derivatives. Thus, the first rhodium phosphinite PCP pincer complexes were just recently synthesized by Milstein and co-workers and their chemistry explored [41]. The ligand **53** was synthesized in an analogous manner as that of ligand $[\text{C}_6\text{H}_4\text{-1,3-(OPPr}^i)_2]_2$ by diphosphination of 2-methyl resorcinol with diisopropylchlorophosphine using 4-(dimethylamino)pyridine as base. Further reaction of this ligand with $[\text{Rh}(\text{COE})_2(\text{Cl})_2]_2$ resulted in a mixture of compounds. However, the reaction of ligand **53** with the cationic starting material $[\text{Rh}(\text{COE})_2(\text{THF})_2]\text{BF}_4$ at room temperature led to the immediate formation of the C–C activation product (**54**) as the main product. Noteworthy the fact that no Rh–H complex was formed. This being probably due to the better orientation of the metal vis-à-vis the C–C bond.



Complex **54** was further reacted with dihydrogen affording methane and the Rh–H product **55**. Moreover, heating of complex **54** in the solid state under argon atmosphere led to the formation of complex **55** and ethylene via an apparent α -H elimination process, followed by a binuclear carbene coupling yielding ethylene.



Deprotonation of complex **54** with NaHBET₃ or complex **55** with KOBu^{*t*} under a nitrogen atmosphere led to the formation of the mono- and dinuclear Rh(I) dinitrogen complexes (**56**) and (**57**). And as it has been the case for other PCP pincer Rh and Ir dinitrogen complexes, the dinitrogen ligand in these compounds is readily displaced by 1 equivalent of ethylene or CO.

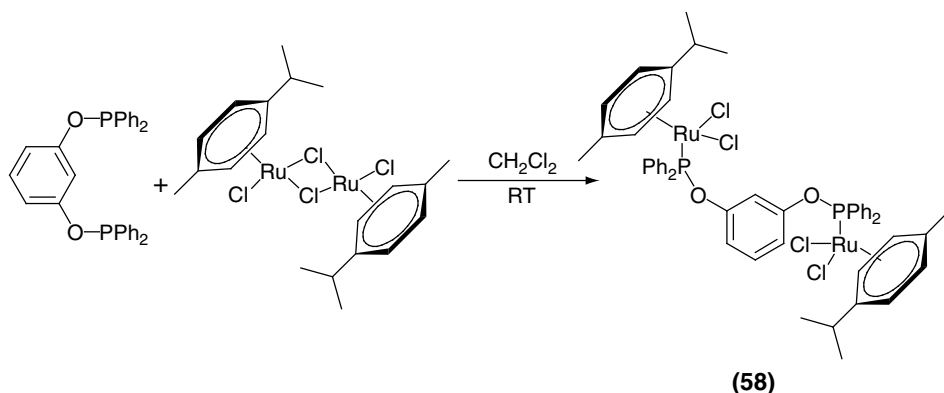


9.3.4 Ruthenium Complexes

The first attempts to explore the chemistry of ruthenium phosphinite PCP pincer complexes did not start until very recently. Thus, independently Morales-Morales [42] and

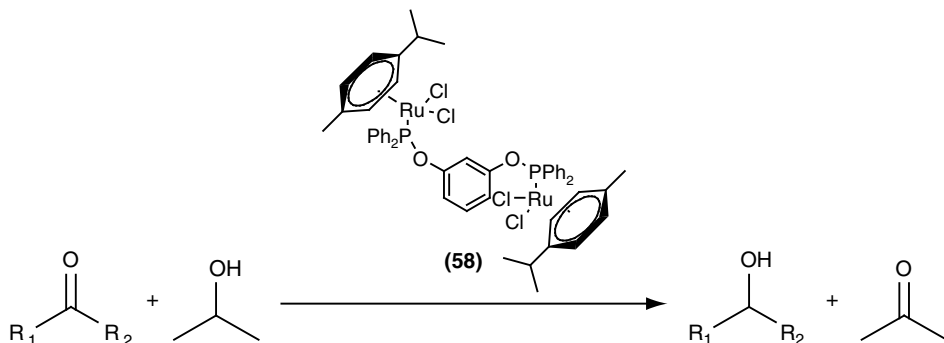
Bedford [43] reported the first reactions of ruthenium starting materials with phosphinite PCP pincer ligands.

Reactions of different ruthenium starting materials with the ligand $[\text{C}_6\text{H}_4\text{-1,3-(OPPh}_2)_2]$ led Morales-Morales and co-workers [42] to the formation of intractable mixtures of compounds. However, the compound $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$ reacts smoothly with the PCP phosphinite ligand at room temperature in CH_2Cl_2 to afford the dinuclear complex **58** without the formation of the orthometallated compound.

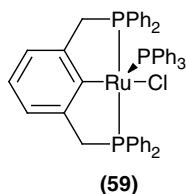


The structure of complex **58** was confirmed by X-ray structure determination and shows the geometry around the two ruthenium centers to be as slightly distorted pseudotetrahedrons, exhibiting the typical ‘piano-stool’ geometry around the ruthenium, having two chloride ligands and one diphenylphosphino group coordinated and completing the coordination sphere of the *p*-cymene group occupying the three coordination sites.

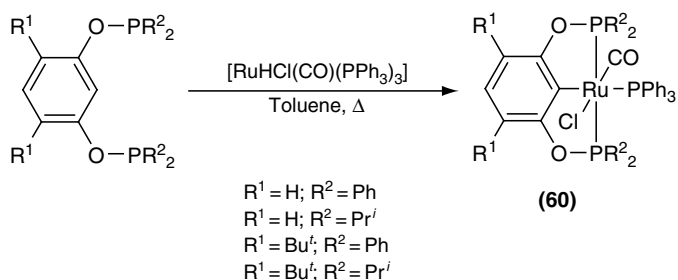
Although compound **58** is not necessarily a pincer complex this specie was tested in the hydrogen transfer of ketones showing similar results as to those reported by van Koten with the PCP pincer complex $[(\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PPh}_2)_2\text{RuCl(PPh}_3)]$ (**59**) for benzophenone and acetophenone [44].



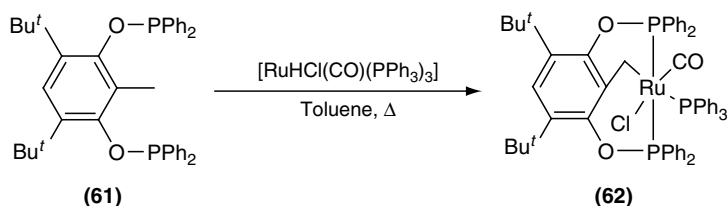
Interestingly, complex **58** resulted as a considerably faster catalyst, at least in the case of benzophenone, thus yields up to 84% were attained in only 10 h whereas van Koten's system affords 98% but only after 108 h of reaction [44]. Other ketones like the propiophenone and 3-heptanone were also tested; however, the yields under the same reaction conditions and reaction times were only of 34 and 58%, respectively. An interesting result occurred when the transfer hydrogenation of chalcone was attempted, affording the hydrogenation of the alkene C=C bond without any detectable (GC-MS) amount of alcohol as hydrogenated products, which in fact may favor the use of this catalyst in the regioselective hydrogenation of conjugated enones. It is noteworthy that extension of the reaction times up to 40 h afforded quantitative yields in all cases.



Independently, Bedford et al. [43], reached similar results as those exposed above; however, careful election of the ruthenium starting material and reaction conditions led them to the orthometallated PCP pincer complexes (**60**) by reacting $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ with the PCP phosphinite ligand $[\text{C}_6\text{H}_4\text{-1,3-(OPPh}_2)_2]$ under reflux conditions in toluene albeit in low yields.

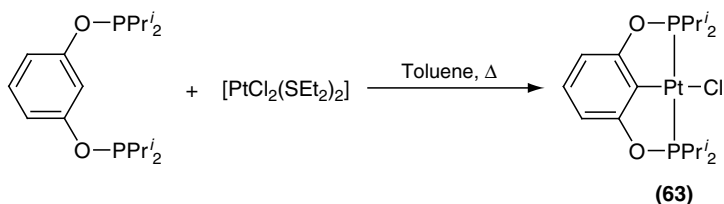


Phosphinite PCP pincer complexes can also be synthesized in a straightforward manner via alkyl activation of the ligand **61** with the same ruthenium starting material to produce complex **62**. These results indicate that ruthenium PCP phosphinite pincer complexes can be readily synthesized particularly when steric bulk is introduced onto the resorcinol backbone, in which case the C–H activation rate is significantly accelerated.

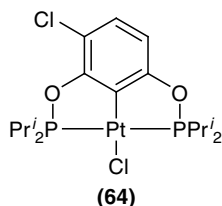


9.3.5 Platinum Complexes

The chemistry of platinum phosphinite PCP pincer complexes has only been reported recently and is limited to a single report by Morales-Morales and Jensen [45]. Thus, the novel phosphinite PCP pincer Pt(II) complex, $[\text{PtCl}\{\text{C}_6\text{H}_3\text{-2,6-(OPPr}^i_2)_2\}]$ (**63**) was prepared from the reaction of the ligand $[\text{C}_6\text{H}_4\text{-1,3-(OPPr}^i_2)_2]$ and $[\text{PtCl}_2(\text{SEt}_2)_2]$ in good yields and the molecular structure of **63** determined through a single crystal X-ray diffraction study. The pincer-ligated platinum complex (**63**) was tested as catalysts for the hydroxylation of 1-propanol to 1,3-propanediol under mild conditions, attaining product ratios and TON comparable to those obtained with $[\text{PtCl}_4]^{2-}$. However, the pincer complex **63** catalyzes this transformation even upon replacement of PtCl_4 by the more economical CuCl_2 as the requisite stoichiometric oxidant.

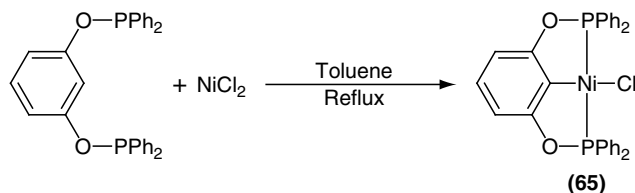


Further, analysis of the reaction mixtures by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy following the hydroxylation of 1-propanol by **63** in the presence of CuCl_2 revealed that **63** is partially converted to the ring-substituted complex, $[\text{PtCl}\{3\text{-Cl-C}_6\text{H}_2\text{-2,6-(OPPr}^i_2)_2\}]$ (**64**). The molecular structure of **64** was also determined through a single crystal X-ray diffraction study.

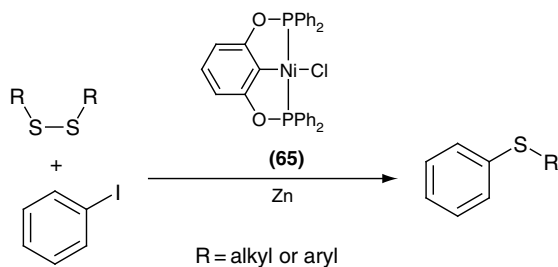


9.3.6 Nickel Complexes

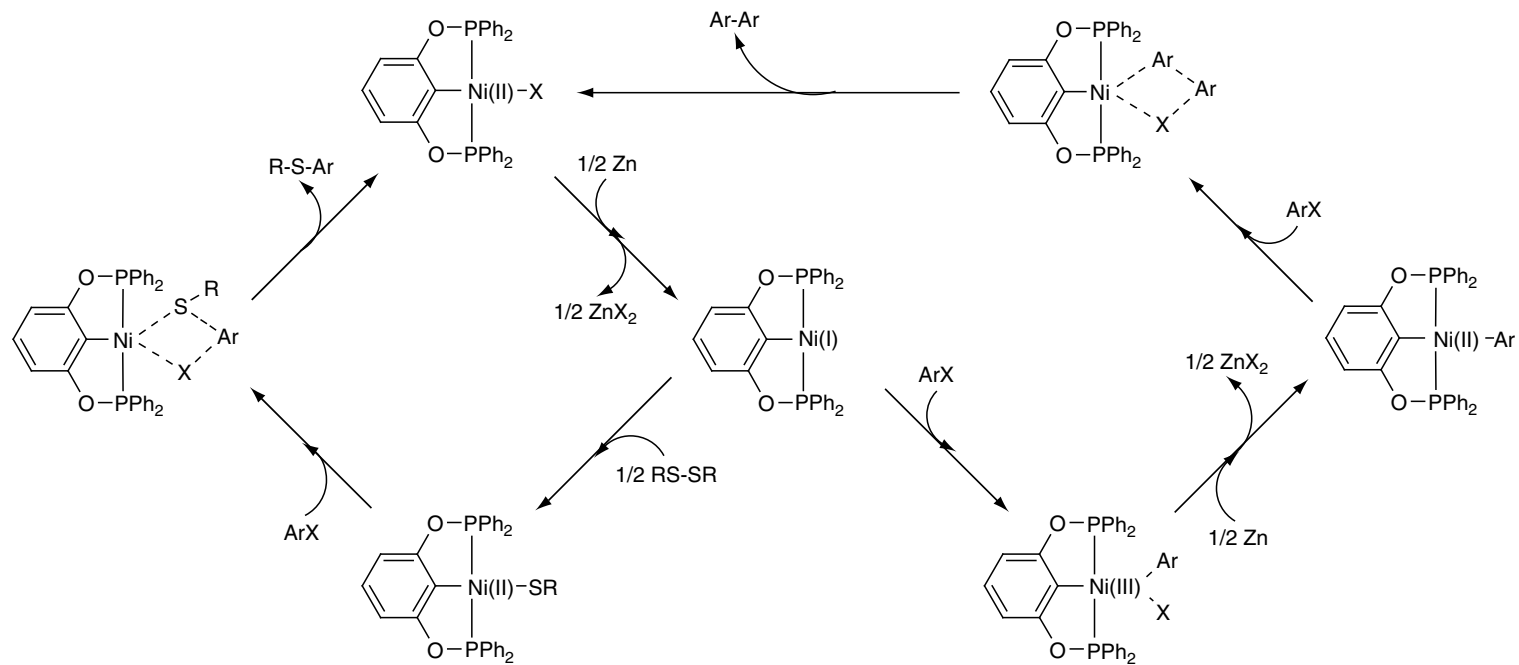
Finally, Morales-Morales and co-workers have recently reported the synthesis and applications in the catalysis of the nickel(II) phosphinite PCP pincer complex (**65**) [46]. This compound was obtained in a very facile manner from the reaction of the ligand [C_6H_4 -1,3-(OPPh_2) $_2$] with NiCl_2 under reflux conditions in toluene in good yields. The green compound is stable both in air and moisture.



Thus, given the increasing interest in the use and applications of diarylthioethers and alkylarylthioethers the design of efficient and high-yield methods for their synthesis is necessary [47]. Moreover, the scope and application of organosulfur chemistry in organic synthetic reactions has increased tremendously because sulfur-containing groups serve as an important auxiliary function in synthetic sequences [48], for instance, in the reversing of the polarity (Umpolung), the enhancement of the acidity of C–H bonds and the transfer of chirality from sulfur to carbon [49]. Additionally, arylsulfides are a common functionality found in a number of drugs commonly used for the treatment of diabetes, Alzheimer's and Parkinson's diseases [50]. Based on these antecedents, compound **65** was tested in the thiolation reactions of iodobenzene. It was observed that the nickel phosphinite PCP pincer complex [$\text{NiCl}\{\text{C}_6\text{H}_3\text{-2,6-(OPPh}_2)_2\}$] (**65**) catalyzes the high-yield C–S cross-coupling (thiolation reaction) of a broad scope of disulfides using zinc as necessary reducing agent. The reactivities of a variety of disulfides were examined under optimized conditions and uniformly showed >99% selectivity for the corresponding asymmetric sulfide, except for the cases of di-*tert*-butyldisulfide and diphenyldisulfide where the yields for the desired product were reduced by the formation of biphenyl, product of the C–C homo-coupling of iodobenzene. This fact was explained to be probably because of steric effects due to the larger size of the substituents in these disulfides.



A mechanistic proposal for the formation of the products was also formulated.



9.4 CONCLUSIONS

It looks clear that given the facility with which phosphinito PCP pincer ligands are synthesized and due to the physical properties that their transition metal complexes exhibit, these complexes will become more popular and thus unravel some new and exciting chemistry.

ACKNOWLEDGEMENTS

I gratefully acknowledge the support and enthusiasm of former and current group members and colleagues. The research from our group described in this chapter is supported by CONACYT (J41206-Q), DGAPA-UNAM (IN114605) and UC-MEXUS (Grant CN-03-100).

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Nitrogen-based pincers: a versatile platform for organometallic chemistry

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10.1 INTRODUCTION

Ligand design is one of the most important aspects of organometallic chemistry. The ability to simply and independently vary the steric and electronic impact of a given ligand provides a wealth of opportunities to influence reactivity, stability, catalysis, and other important properties at the metal center. Only certain classes of ligands can fulfill these synthetic requirements and also generate interesting metal complexes. The so-called pincer ligands are a prime example of a simple design that has enabled the development of a broad and diverse research portfolio with complexes containing this motif [1–11]. The basic structure incorporates a central ligating atom that carries a formal negative charge which forms a strong σ bond to a given metal center. This is flanked by two *ortho*-situated chains or rings containing neutral donor groups that datively bind to the metal, effectively forming a claw which ‘pinches’ the metal between its ‘arms’, see Fig. 10.1. With what are generally termed pincer ligands, the central ligating atom is typically carbon and the donors are generally N, P, O, and/or S atoms. As such, the typical designation of a pincer, for example ‘NCN’, stems from the presence of two amine or other nitrogen-based donors flanking the central aryl or alkyl C–M bond.

Transition metal complexes of pincer ligands containing a central aryl ring flanked by nitrogen-based donors, that is, NCN-type pincers, are the focus of this chapter.

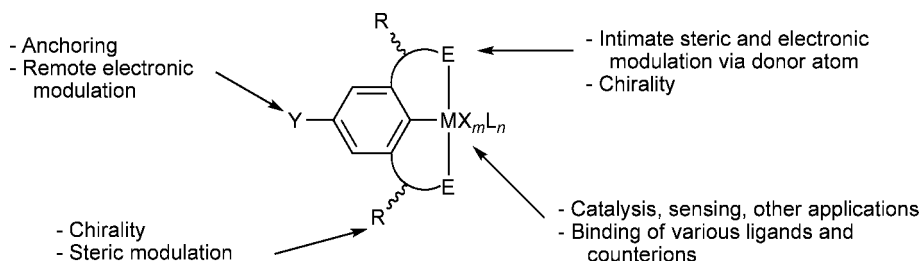


Fig. 10.1. The basic aryl-based metallopincer complex.

Compounds with this motif contain metals spanning the periodic table from titanium to mercury, due, in part, to the ready availability of versatile organolithium synthons [1, 2, 12]. Historically, pincer ligands are most commonly associated with transition metal organometallic chemistry, but chronologically, the first NCN-type metal complexes, reported by van Koten in 1978, were main group systems incorporating Sn and Li(NCN) species [13]. The prototypical Pt(NCN) species was disclosed soon thereafter [14]. In addition to the well-developed organometallic chemistry, there is also a relatively rich and diverse variety of main group complexes that have been studied [2, 15].

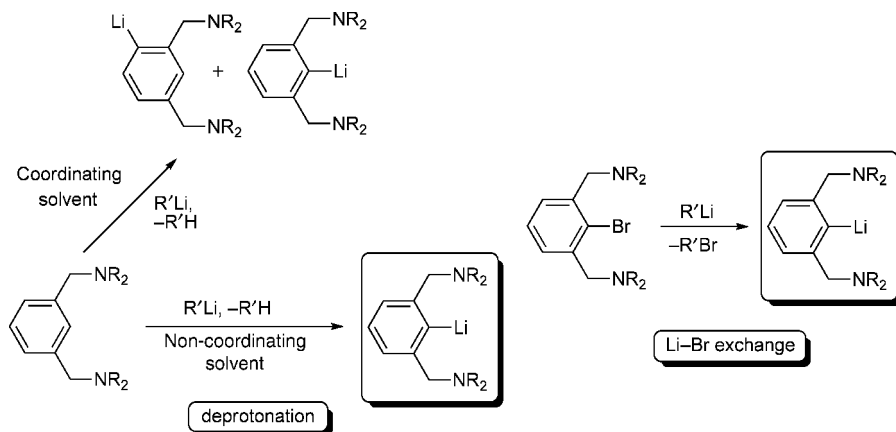
In terms of impact on organometallic and main group chemistry, complexes containing the NCN motif represent a rather large number of chemical 'firsts.' For example, the first well-characterized organometallic dendrimer applied to catalysis contained Ni(NCN) groups as the active sites [16, 17]. Dendritic effects in these systems were also thoroughly explained, a fairly rare occurrence in dendrimer chemistry [18, 19]. They have stabilized a number of unique complexes including the first κ^2 O,O-bound triflate anion with Ti [20], novel Pt-bound arenium cations [14, 21–23], and an octa-coordinate Si complex [24]. As well, the first chemical evidence for a germyne ($\text{RGe}\equiv\text{CR}'$) [25] along with the isolation of stable monomeric main group hydrides of Ga [26] and the first example of quantitative gas diffusion kinetics in a solid (Pt) [27] were furnished employing NCN-type ligands. Clearly, the NCN-pincer ligand is a well-utilized and extremely useful platform for the stabilization and isolation of unique complexes and exploring their utility in a variety of applications.

This chapter is organized by metal type, starting with early transition metals in group 4 (Ti–Hf) and working right across the periodic table to the late systems of group 12 (Zn–Hg). Preceding this is a short discussion on lithiated NCN complexes with special emphasis on their solution and solid-state structural chemistry in relation to synthetic utility. A number of excellent reviews [1–11] have been published in the pincer arena since the seminal reports of PCP-type pincer complexes by Shaw [28]. As such, we will avoid topics already completely covered in these reports. Also, due to the breadth of metallocpincers incorporating Pd and Pt, only a select number of specialized topics will be covered, but it must be noted that, irrespective of the treatment here, this is by far the most active area of current research.

10.2 LITHIUM COMPLEXES

Organometallic complexes of the alkali and alkaline earth metals, such as organolithium or organomagnesium species, constitute an extremely important class of synthetic reagents [29, 30]. This is also the case in pincer chemistry utilizing the NCN ligand. Indeed, one of the primary reasons for the quantity and variety of NCN complexes reported to date stems from the availability and well-understood chemistry of a variety of [Li(NCN)] species. These are truly the workhorse reagents for synthetic methods to generate other transition metal and main group complexes via transmetalation. Yet to be studied are the heavier congeners of Li and Na [31], and some other issues are associated with Grignard-type Mg reagents which may limit their usefulness as ligand transfer reagents [32]. While we cannot do justice to all the complexities in this chemistry here [2, 8], a small selection of the most important chemistry of Li(NCN) and potential pitfalls in the synthetic utility of these is presented.

Synthesis of $\text{Li}(\text{NCN})$ species is typically achieved by two related methods: Li –halogen exchange or selective deprotonation, which is effectively Li – H exchange. For the deprotonation route, the choice of solvent is critical as use of coordinating solvents, such as Et_2O or THF, results in competitive extra-annular lithiation outside the pincer arms [3, 8]. The employ of non-coordinating solvents, such as pentane, hexane, or toluene, generally gives the desired product. The typical syntheses are shown in Scheme 10.1. In addition, there was one report of a lithiated 1,8-bis(dimethylamino)anthracenyl-based NCN species, which was only accessible from the 9-bromo derivative [33].



Scheme 10.1 Synthesis of $\text{Li}[\text{NCN}]$ pincers via deprotonation or Li – Br exchange.

Besides the obvious synthetic utility of these species, a number of aspects of solution chemistry and solid-state structures have been investigated [12, 13, 34]. In both solution and solid state, the $\text{Li}(\text{NCN})$ species existed as dimers, see Fig. 10.2. Remarkably, the dimeric structure and strong Li – N coordination were retained even in strongly polar and coordinating solvents, such as THF. The core was comprised of an Li_2C_2 rhombus

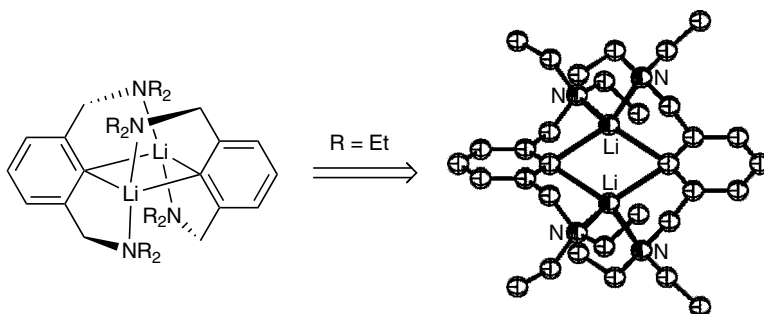
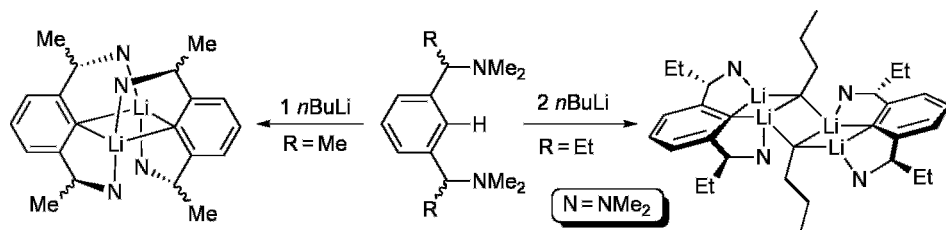


Fig. 10.2. Typical structure of an $[\text{Li}(\text{NCN})]_2$ dimer. Structure of diethylamino NCN pincer taken from ref. [34].

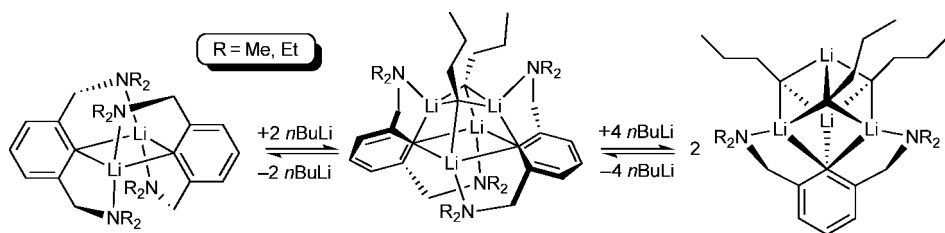
exhibiting formal 3-center, 2-electron Li–C–Li bonds. The coordination sphere at Li was completed by complexation of the N-donors of the pincer. Notably, each Li coordinated to amino donors from separate NCN arenes. In this sense, the amine (or oxazoline) arms acted as an intramolecular analog to the well-known Lewis base tetramethylethylenediamine (TMEDA), which will also typically break higher-order organolithium aggregates into dimeric species.

However, sterics at nitrogen played a large role in the kinetics of lithiation or with the nature of the product obtained. In some cases, such as with 1,3-bis(oxazoliny)benzene (Phebox), the deprotonation route was not successful, and the more reactive bromo species must be employed [35]. Another issue stemmed from the formation of heteroaggregates, mixed organolithium species containing multiple carbanionic organic fragments [8]. This is a noted characteristic of NCN pincer complexes and can directly interfere with subsequent synthetic procedures. For example, attempts to directly lithiate an NCN pincer substituted at the benzylic position with Et groups using 1 equiv. of *n*BuLi resulted in only 50% lithiation; a full 2 equiv. was needed to completely react with the NCN arene, see Scheme 10.2 [36, 37]. Conversely, the methyl-substituted analog lithiated in the expected fashion, highlighting the subtle differences in stability for these types of species. The resulting product for the ethyl benzyl system, a stable 2:2 mixed heteroaggregate of base formula $[\text{Li}_4(\text{NCN})_2(n\text{Bu})_2]$, was spontaneously generated, even in the presence of free NC(H)N. The crystal structure revealed a ladderane-type structure with an *n*BuLi dimer connecting the outer Li(NCN) rungs. Furthermore, the sequestered *n*BuLi was unreactive toward deprotonation of additional NC(H)N pincer arenes.



Scheme 10.2 Difference in Li(NCN) aggregate structure based on sterics.

These types of 2:2 mixed aggregates can also be purposely generated by reaction of a preformed $[\text{Li}(\text{NCN})]_2$ dimer with *n*BuLi [38]. In the crystal, both the dimethylamino- and diethylamino-substituted $[\text{Li}_4(\text{NCN})_2(n\text{Bu})_2]$ heteroaggregates were found, but the situation was much more complex in solution. Dissolution of these crystals or addition of 2 equiv. of *n*BuLi to an $[\text{Li}(\text{NCN})]_2$ dimer in toluene resulted in a multicomponent equilibrium containing the homoaggregate dimer $[\text{Li}(\text{NCN})]_2$, the 2:2 heteroaggregate $[\text{Li}_4(\text{NCN})_2(n\text{Bu})_2]$, and a new mixed 1:3 $[\text{Li}_4(\text{NCN})(n\text{Bu})_3]$ aggregate, see Scheme 10.3. The X-ray crystal structures of the 2:2 aggregates, unlike the ethyl benzyl-substituted complex, exhibited cubic Li_4R_4 cores, a more typical organolithium structural motif. With a view toward synthetic utility, the additional alkyl lithium was trapped and cannot be removed by crystallization or filtration, and thus, the initial stoichiometry of lithiating reagents should be strictly controlled when generating these species.



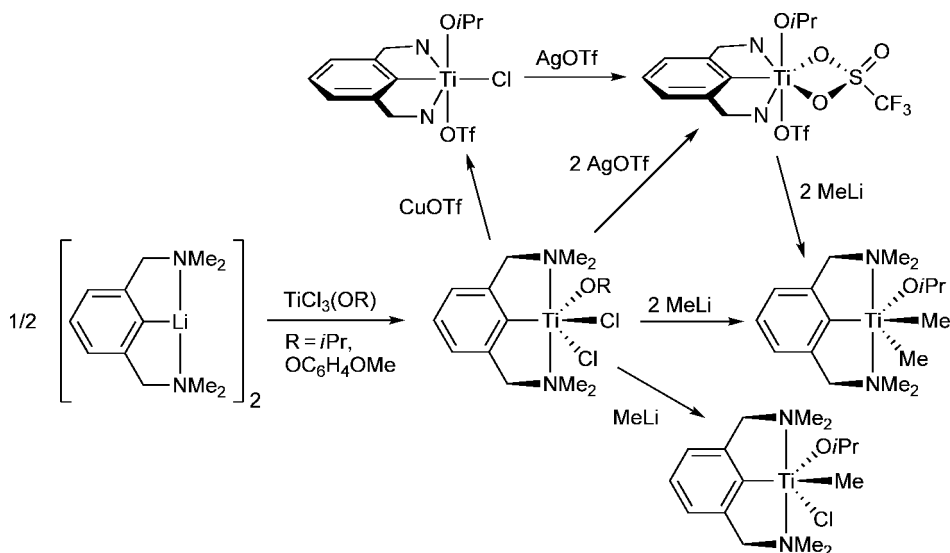
Scheme 10.3 Heteroaggregates involved in equilibrium with $\text{Li}(\text{NCN})$ and $n\text{BuLi}$.

10.3 EARLY TRANSITION METALS

The full details of the chemistry of the early transition metals, especially Ta, and the lanthanides (La and Lu) have been reviewed previously [2] and are not treated here. As such, only a limited number of Ti, Mo, and W complexes will be described in this section.

10.3.1 Titanium

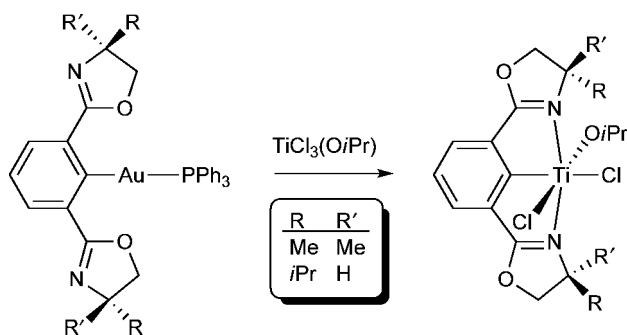
Only a small selection of NCN pincer complexes with Ti has been reported to date. These incorporated an additional alkoxide ligand, and synthesis of chloride, alkyl, and mixed species has been accomplished [20]. Reaction of 0.5 equiv. of $[\text{Li}(\text{NCN})]_2$ with TiCl_3OR ($\text{R} = i\text{Pr}$, $\text{OC}_6\text{H}_4\text{OMe}$) gave the expected $\text{Ti}(\text{NCN})\text{Cl}_2(\text{OR})$ complexes in good yields, see Scheme 10.4. The chlorides can be sequentially replaced with Me groups by reaction with the appropriate amounts of LiMe . In addition, triflates can be



Scheme 10.4 Synthesis and reactivity of $\text{Ti}(\text{NCN})\text{Cl}_2(\text{OR})$.

incorporated by reaction with AgOTf or CuOTf. NMR spectra for the chloride and alkyl complexes were indicative of *fac*-bound NCN ligand, a somewhat rare situation. This was confirmed in the X-ray crystal structure of $\text{Ti}(\text{NCN})\text{Cl}_2(\text{OiPr})$, where the metal-based geometry was best described as trigonal prismatic. The fluxional processes observed were ascribed to Ti–N dissociation. A lower energy process was also observed for $\text{Ti}(\text{NCN})\text{Cl}_2(\text{OiPr})$ involving non-dissociative exchange, possibly through a *mer*-bound pincer. Unlike $\text{Ti}(\text{NCN})\text{Cl}_2(\text{OiPr})$, the mono OTf complex was a distorted octahedron where the NCN group was bound in a *mer* fashion with the triflate *trans* to the OiPr. The bis(OTf) species contained the first structurally characterized example of a κ^2 -bound triflate ligand and is a relatively rare example of a seven-coordinate Ti center. In terms of reactivity, these species did not interact with common Lewis bases, such as THF, MeCN, DMF, or bipy. However, they are catalysts for the 1,2-addition of ZnEt_2 with benzaldehyde. While the Ti(IV) complexes were inactive for olefin polymerization, reduction to Ti(III) with Mg/Hg generated competent species for ethylene and propene polymerization. The structure of a bridging oxide $[\text{Ti}(\text{NCN})\text{Cl}(\text{O})]_2$ has also been reported [39].

An aryl transfer reaction with $\text{Au}(\text{NCN})\text{PPh}_3$ (see Section 10.4.5) can also be utilized to generate $\text{Ti}(\text{NCN})\text{Cl}_2(\text{OiPr})$ [40] as well as Phebox-type complexes, see Scheme 10.5 [41]. Separation of the *i*Pr,H-Phebox complex was hampered by its similar solubility characteristics to the $\text{AuCl}(\text{PPh}_3)$ by-product. Based on both crystallographic and NMR data of the Me,Me derivative, the OiPr ligand was *trans* to a chloride, and this arrangement was retained in solution. Unlike the amine NCN ligand, Phebox coordinated in a *mer* fashion with essentially coplanar aryl and oxazoline rings and the geometry is best described as octahedral. The Me,Me complex does display limited activity in the polymerization of ethylene with MMAO as a cocatalyst, but deactivation occurs after approximately 10 min.

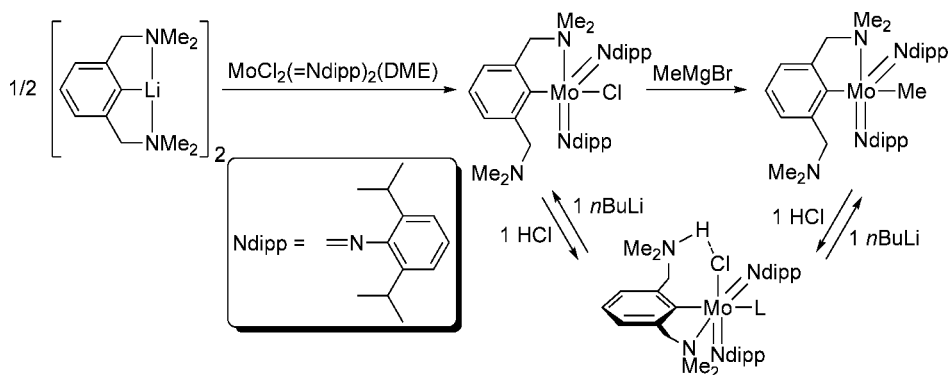


Scheme 10.5 Synthesis of Phebox-derived $\text{Ti}(\text{NCN})\text{Cl}_2(\text{OiPr})$.

10.3.2 Molybdenum

A set of related (imido)aryl NCN pincer complexes of type $\text{Mo}(\text{NCN})(=\text{NR})_2\text{L}$ have been reported in the search for Mo-alkylidene species [42]. Reaction of

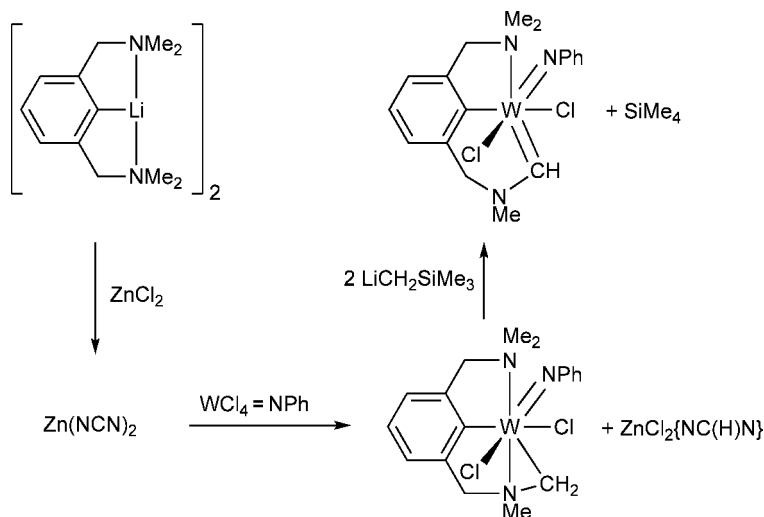
$\text{MoCl}_2(=\text{Ndipp})_2(\text{DME})$ ($\text{DME} = 1,2\text{-dimethoxyethane}$, $\text{dipp} = 2,6\text{-(}i\text{Pr)}_2\text{C}_6\text{H}_3$) with 0.5 equiv. of $[\text{Li}(\text{NCN})]_2$ cleanly generated $\text{Mo}(\text{NCN})(=\text{Ndipp})_2\text{Cl}$, which could be methylated with MeMgBr , see Scheme 10.6. Attempts to use the $=\text{N}t\text{Bu}$ analog were not successful. NMR and X-ray crystallographic analysis for the Cl and Me complexes revealed that the pincer ligand was only bound in a bidentate fashion; one of the amine arms was not associated with the Mo center and the intact Mo–N bond was fluxional in solution. The solid-state structure exhibited distorted square pyramidal geometry about the Mo center. Reaction with 1 equiv. of anhydrous HCl did not proceed via protonation of the aryl imine but rather by quaternization of the free amine and formation of an octahedral chloro ammonium molybdate. With $\text{Mo}(\text{NCN})(=\text{Ndipp})_2\text{Me}$, no reaction with the Mo–Me was noted, but on addition of excess HCl, multiple products were obtained. These ammonium species were air and moisture stable and could be quantitatively reverted to the acid-free species by reaction with 1 equiv. of $n\text{BuLi}$.



Scheme 10.6 Synthesis and reactivity of $\text{Mo}(\text{NCN})(=\text{NAr})_2\text{L}$ ($\text{L} = \text{Cl}, \text{Me}$).

10.3.3 Tungsten

One example of a tungsten-containing NCN complex with a direct W–aryl bond is known [43]. Somewhat surprisingly, direct reaction of 0.5 equiv. of $[\text{Li}(\text{NCN})]_2$ with either WOCl_4 or $\text{WCl}_4(=\text{NPh})$ in Et_2O only gave insoluble products, likely the result of formation of coordination polymers. Conversely, reaction of in situ-prepared $\text{Zn}(\text{NCN})_2$ (see Section 10.4.6) with $\text{WCl}_4(=\text{NPh})$ gave a clean reaction from which 1 equiv. of the arene $\text{NC}(\text{H})\text{N}$ ligated to ZnCl_2 could be isolated. In the W-containing species $\text{W}(\text{NCN})\text{Cl}_2(=\text{NPh})$, C–H activation of one of the NMe groups has occurred, see Scheme 10.7. The crystal structure has the modified NCN ligand in a *mer* configuration, with the imido group *cis* to the pincer aryl group. The complex can be alkylated with $\text{LiCH}_2\text{SiMe}_3$, resulting in an additional abstraction of a C–H from the W– CH_2N to give an alkylidene. The mechanism for this reaction is unclear and may proceed by direct deprotonation or via σ -bond metathesis from the dialkyl complex.



Scheme 10.7 Synthesis and reactivity of $\text{W}(\text{NCN})\text{Cl}_2=\text{NPh}$.

10.4 MID-TRANSITION METALS

10.4.1 Group 7 (Mn–Re)

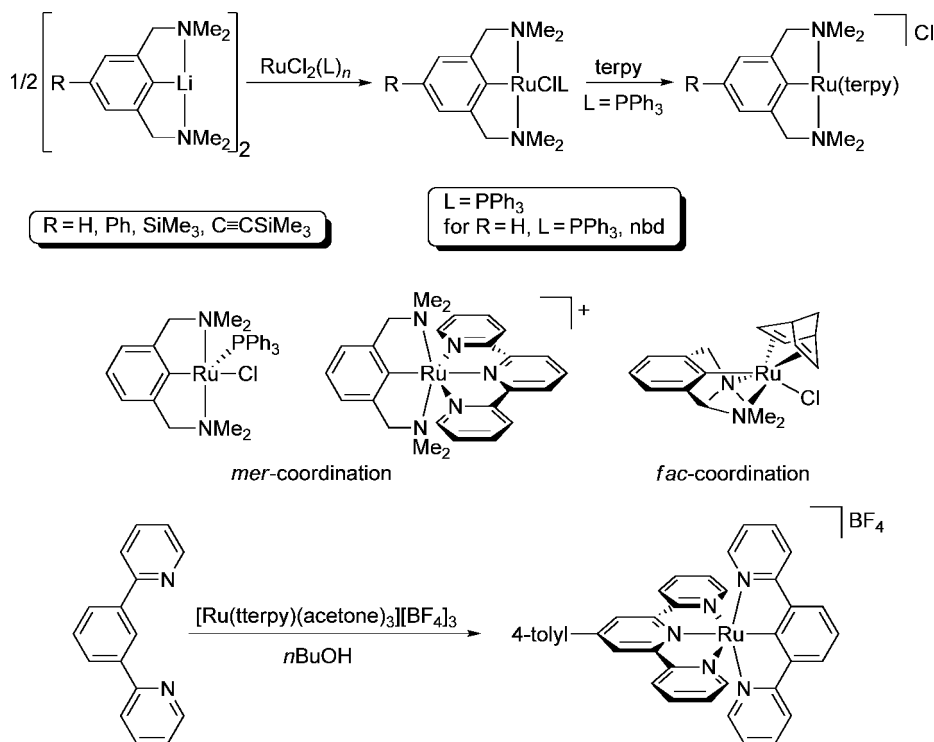
A single report of a monometallic $\text{Mn}(\text{NCN})$ complex disclosed its synthesis and reactivity in C–C bond-forming reactions [44]. Reaction of $[\text{Li}(\text{NCN})]_2$ with MnCl_2 gave a paramagnetic complex which best correlates with an empirical formula of $\text{LiMn}(\text{NCN})\text{Cl}_2$. This can be alkylated by reaction with a variety of organolithium salts (LiR ; $\text{R} = \text{Me}$, $n\text{Bu}$, Ph) to give LiCl -free heteroleptic $\text{Mn}(\text{NCN})\text{R}$ complexes in good yields. All of these were tested as catalysts for the cross-coupling of Grignard reagents with organyl bromides and in 1,4-addition reactions with α,β -unsaturated ketones. Under the reaction conditions, $\text{LiMn}(\text{NCN})\text{Cl}_2$ would be converted to the alkyl species, and no difference in catalytic activity was noted when different $\text{Mn}(\text{NCN})$ complexes were utilized. Mixtures of $\text{LiMn}(\text{NCN})\text{Cl}_2$ and CuCl formed the active catalyst, with yields of cross-coupled products reaching 92%, see Scheme 10.8. The reaction showed good chemoselectivity and functional group tolerance as well as enhanced reactivity with secondary Grignard reagents. Notably, catalytic amounts of Mn can be employed; co-solvents, such as NMP, which prevent β -elimination from the in situ-formed organomanganese complexes were avoided, and reactions times were much shorter than with classical Mn/Cu systems. The cooperative nature of the $\text{Mn}(\text{NCN})\text{Cl}/\text{CuCl}$ blend was demonstrated by the absence of reaction when only the individual components were used. In addition, $[\text{Cu}_2(\text{NCN})\text{Br}]_2$ did not catalyze the reaction, pointing to an intact $\text{Mn}(\text{NCN})$ motif during catalysis and not simply transmetalation with the CuCl . In addition, chiral ligands induced enantioselectivity to these C–C coupling reactions.

A single example of an $\text{Re}(\text{NCN})(=\text{O})_3$ complex has been reported [47]. Both the NMe_2 groups bind to the Re center, and in the crystal, the geometry about Re was a bicapped tetrahedron, with the amines coordinating to the triangular faces and the NCN ligand in a *fac* orientation. The complex was not catalytically active for epoxidation of alkenes.

10.4.2 Group 8 (Fe–Os)

Only one example of an $\text{Fe}(\text{NCN})$ complex has been disclosed. $\text{Fe}(\text{NCN})\text{Cl}_2$ can be successfully generated by transmetalation with either Li [48] or Au [40] reagents, and the crystal structure showed that both amine arms were coordinated to the Fe center, which was in a distorted square pyramidal environment. As well, only a limited number of $\text{Os}(\text{NCN})$ complexes are known to date [49, 50].

Conversely, the chemistry of $\text{Ru}(\text{NCN})$ species is very rich and is still a very active area today. The synthesis of simple monomeric $\text{Ru}(\text{II})(\text{NCN})$ species was achieved either by reaction of 0.5 equiv. $[\text{Li}(\text{NCN})]_2$ with $\text{RuCl}_2(\text{L})_n$ ($\text{L} = \text{PPh}_3$, $n = 4$; $\text{L} = \text{norbornadiene (nbd)}$, $n = 2$) [51, 52] or via C–H activation with cationic $\text{Ru}(\text{III})$ derivatives in the presence of a sacrificial reductant, typically the alcoholic solvent [53], see Scheme 10.10. The relatively air-sensitive $\text{Ru}(\text{NCN})\text{Cl}(\text{PPh}_3)$ can be stabilized by reaction with terpyridine (terpy) to give the ion-separated complex $[\text{Ru}(\text{NCN})(\text{terpy})][\text{Cl}]$. The flexibility of the NCN ligand to accommodate a variety of



Scheme 10.10 Synthesis and structures of various $\text{Ru}(\text{NCN})$ complexes.

configurations and coordination geometries was demonstrated in a series of Ru species. In the crystal, $\text{Ru}(\text{NCN})\text{Cl}(\text{PPh}_3)$ was square pyramidal, with a *mer*-terdentate NCN and the chloride in the basal plane and the PPh_3 occupying the apical position. Similarly, the octahedral complex $[\text{Ru}(\text{NCN})(\text{terpy})]^+$ also incorporated a *mer*-oriented NCN pincer. Conversely, $\text{Ru}(\text{NCN})\text{Cl}(\text{nbd})$ exhibited a *fac*-coordinating NCN moiety in a bicapped tetrahedral arrangement where the two NMe_2 groups were situated on adjacent triangular faces of the tetrahedron. Pyridyl-based $\text{Ru}(\text{NCN})$ complexes have also been synthesized using C–H activation routes [50, 54].

Results on electronic communication through extended ligand frameworks involved the study of bimetallic amine [55, 56] and pyridyl [50, 54] donor-based NCN Ru (and Os) complexes, see Fig. 10.3. Electrochemical studies clearly showed that the metal centers are in intimate electronic contact as oxidation of one Ru center markedly increased the potential of the second oxidation step. Both systems exhibited quite high levels of electronic communication, with rates of comproportionation (K_c) up to 900 [57]. Notably, these values were similar to that of 1,4-pyrimidine-bridged $\text{Ru}-\text{NC}_4\text{H}_4-\text{N}-\text{Ru}$ systems, even though the distance between the centers was much less. For the pyridyl systems, the analogous Os complex exhibited a lowered K_c value ($K_c = 100$). In addition, bimetallic pyridyl $\text{Ru}(\text{NCN})$ complexes incorporating phenylene spacers also had high degrees of electronic communication [49, 53]. For the NMe_2 NCN system, reversible chemical oxidation and reduction allowed for isolation of both $\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}$ and $\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$ complexes [55].

The synthesis of these bimetallic systems was also fairly unique. Here, the *metalated* ligands were used in oxidative coupling reactions between the *para* positions of the individual arenes. In the typical synthesis of organometallic compounds, the organic framework of the ligand is assembled and metalation is performed in the final step. Both Ag- [49, 50, 54] and Cu-based [55, 56] coupling routes were employed to give the C–C-coupled products, see Scheme 10.11. In addition, the metal-free pyridyl $(\text{NCN})_2$ dimers can be obtained via Pd-catalyzed couplings [53]. The non-transferability of the pincer ligand, due to the covalent $\text{Ru}-\text{C}$ bond, and the stabilizing influence of the pendant donor arms allowed for these types of complexes to be used in this organic transformation. In the Cu case, a small amount of oxidized $\text{Ru}(\text{III})$ product incorporating a 4-chloro-substituted NCN pincer was also isolated in limited yield.

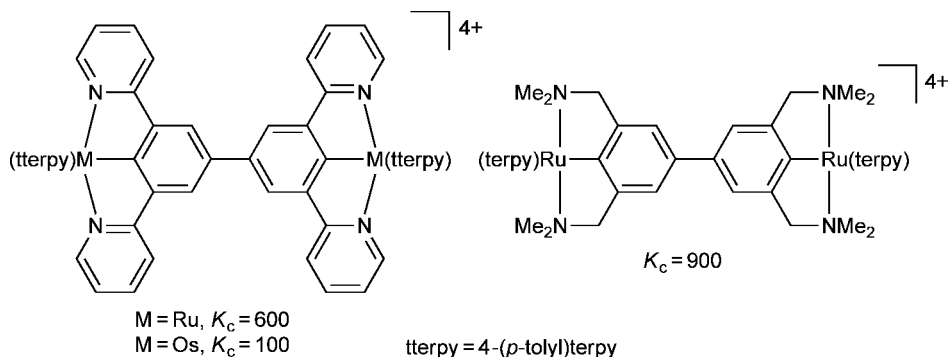
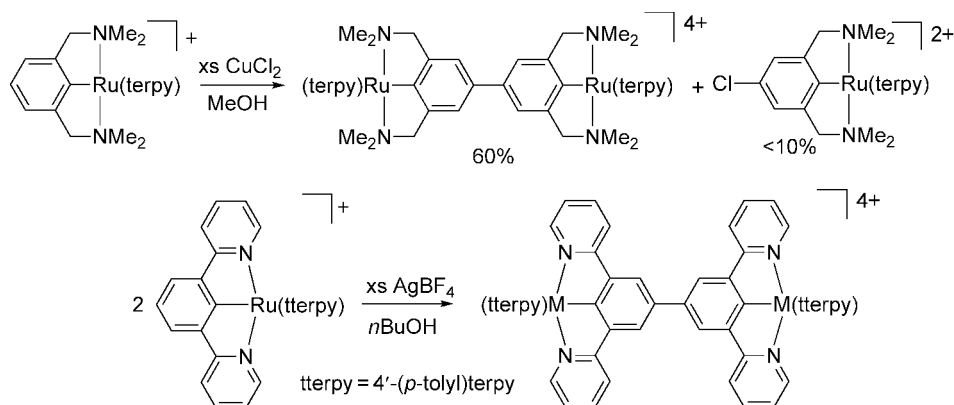
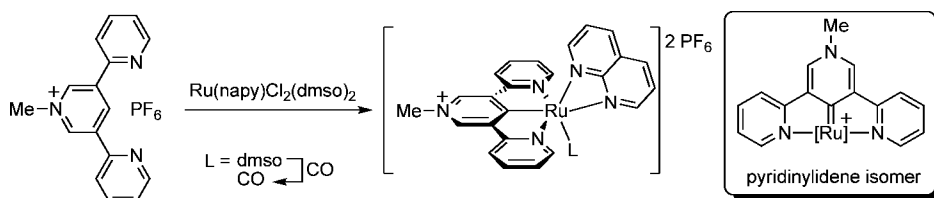


Fig. 10.3. Electronic communication in bimetallic $\text{Ru}(\text{NCN})$ complexes.



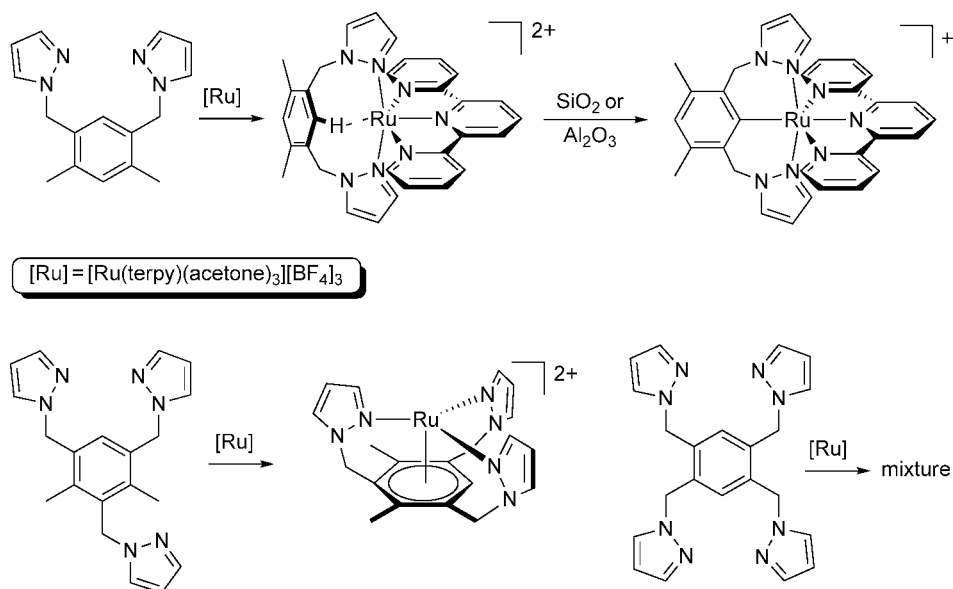
Scheme 10.11 Oxidative coupling of Ru(NCN)(terpy) derivatives.



Scheme 10.12 Synthesis of Ru(NC(4-NMe)N)(napy)L complexes.

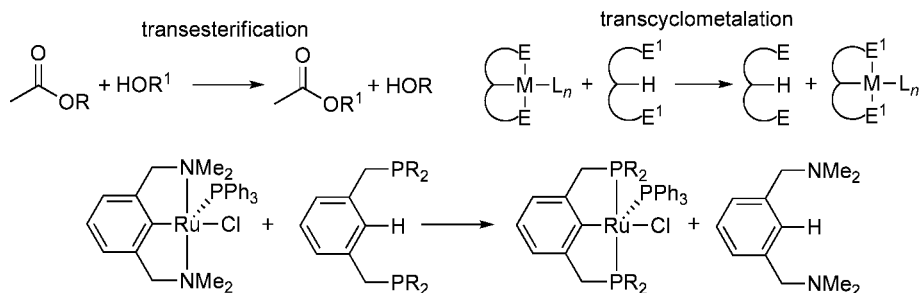
Recently, a new NCN ligand incorporating the metalation at the *para* position of a pyridine has been reported, see Scheme 10.12 [58]. The central pyridine was quaternized by reaction with MeI and C–H activation with Ru(napy)Cl₂(dmsO)₂ gave the desired complex (napy = 1,8-diazonaphylene). The more common arene Ru(NCN)(napy)Cl₂(dmsO) compound was also synthesized. The weakly bound dmsO was replaced by CO, and electrochemical studies showed that the new ligand is significantly more electron-withdrawing than arene-based NCN. Also, NMR studies and X-ray crystallography pointed to marked contribution of the Ru=C pyridinylidene resonance structure. Dynamic NMR experiments and reaction with additional donors indicated that the napy ligand was labile.

A modified NCN pincer ligand incorporating a pyrazolyl (Pz) donor has also been utilized to generate a number of Ru(PzNCN) complexes [59]. The synthesis of the metal complexes followed the C–H activation route, see Scheme 10.13. However, after reaction of PzNC(H)N with [Ru(terpy)(acetone)₃]³⁺, only the non-cyclometalated adduct was observed. The cyclometalated product was obtained after chromatography with either silica or alumina; the solid phase appeared to initiate cyclometalation. The X-ray crystal structure showed a typical octahedron with an almost ideal 175.4(1)° N–Ru–N angle for the *trans* pyrazolyl groups, due to incorporation of an extra atom in the NCN chelate rings. Efforts to cyclometalate with ligands containing more than two Pz groups were unsuccessful. A Ru–arene complex was generated with three Pz donors, while only mixtures of products were observed when attempting to obtain a bimetallic compound.



Scheme 10.13 Synthesis of Ru(^{Pz}NCN) complexes.

Ru(NCN)Cl(PPh₃) is a useful synthetic reagent in the selective ruthenation of other pincer-type ligands, a process coined the transcyclometalation reaction in analogy to transesterification in organic chemistry, see Scheme 10.14 [60, 61]. The driving force for the reaction is supplanting the Ru–N interactions with stronger bonds, such as Ru–P. This has allowed for the synthesis of a variety of Ru(PCP) species, which, in some instances, have proven difficult or impossible to obtain via conventional methods due to the mild conditions employed. Examples with chiral [62, 63] and highly fluorinated PCP ligands [64] as well as the full metalation of multi-PCP species have been reported [65–67]. Mechanistic studies indicated that the C–H activation step is quite facile and that the rate-determining step may be the exchange of bound PC(H)P for PPh₃ [60, 61, 63].

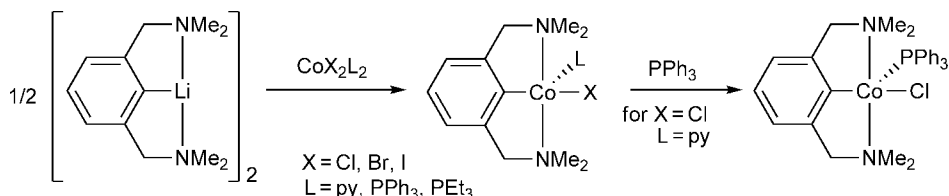


Scheme 10.14 The transcyclometalation reaction.

10.5 LATE TRANSITION METALS

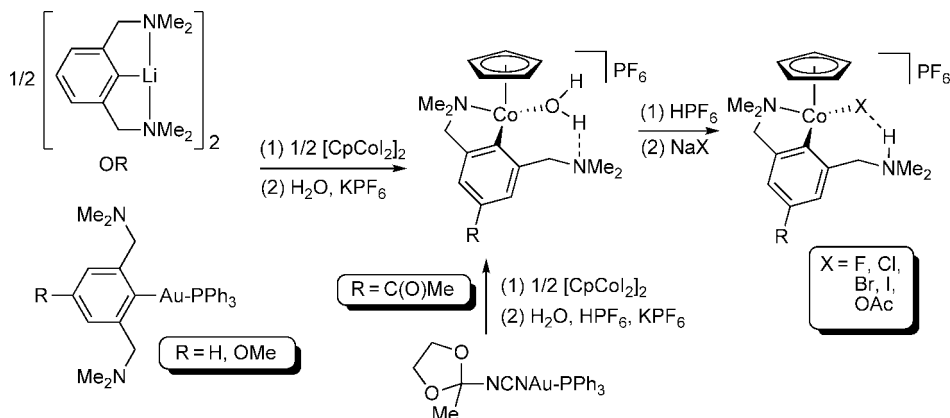
10.5.1 Cobalt

The first $\text{Co}(\text{NCN})$ complex was reported in 1986 and consisted of a paramagnetic $\text{Co}(\text{II})$ center supported by one NCN ligand [68]. Reaction of $[\text{Li}(\text{NCN})]_2$ with CoCl_2py_2 (py = pyridine) furnished $\text{Co}(\text{NCN})\text{Cl}(\text{py})$ in good yield (70%), with the molecular formula supported by analytical data. Other derivatives incorporating a variety of halides (Br , I) and Lewis bases (PPh_3 , PEt_3) were also reported, see Scheme 10.15. All complexes were highly colored, orange with py and blue-green with phosphine, and rapidly reacted with air to give blue solutions and the free $\text{NC}(\text{H})\text{N}$ arene. ESR spectra suggested a low-spin d^7 spin state ($S = 1/2$) and that the SOMO was mainly metal based. In frozen solutions, hyperfine coupling to Co (^{59}Co , $I = 7/2$) as well as N and P in the respective py and PR_3 complexes was observed. However, coupling to the pincer NMe_2 groups was not apparent. As the ESR spectra were strongly reminiscent of the isoelectronic $\text{Ni}(\text{III})$ pincer complexes, it was reasonable to suggest that the $\text{Co}(\text{II})$ complex also exhibits a similar square pyramidal geometry, with the Lewis basic donor ligand in the apical position. Chemical oxidation with a variety of reagents was unsuccessful, but ligand exchange of py for PPh_3 proceeded smoothly over the course of several days.



Scheme 10.15 Synthesis and reactivity of $\text{Co}(\text{NCN})\text{XL}$ complexes.

Further work has focused on the use of $[\text{CpCo}(\text{NCN})(\text{H}_2\text{O})][\text{PF}_6]$ complexes as selective anion sensors [69, 70]. Synthesis was initiated by either transmetalation with $[\text{Li}(\text{NCN})]_2$ or via a novel aryl transfer route utilizing $\text{Au}(\text{NCN})\text{PPh}_3$, see Scheme 10.16. Based on NMR data, X-ray crystallography, and complex reactivity, only one of the amine arms was bound to the Co center, and the dangling group served as a base and reacted swiftly with protons. These protonated species preferentially bound oxyanions over halides in water. For example, the *p*-methoxy-substituted system exhibits a selectivity of 40:1 for AcO vs. Cl , an unprecedented result in aqueous solution. The parent complex was 15:1, showing that rational ligand modifications can greatly impact the specificity of anion binding. However, attempts to increase the steric bulk of the pincer amines were not fruitful as the corresponding Co complex was quite unstable. The free protonated amine was essential for strong binding of the anion, as shown by relatively short anion–HN distances in the crystal structures, and the specificity in relation to the anion-binding pocket has been compared to allosteric or ‘lock and key’ phenomenon in biological systems.

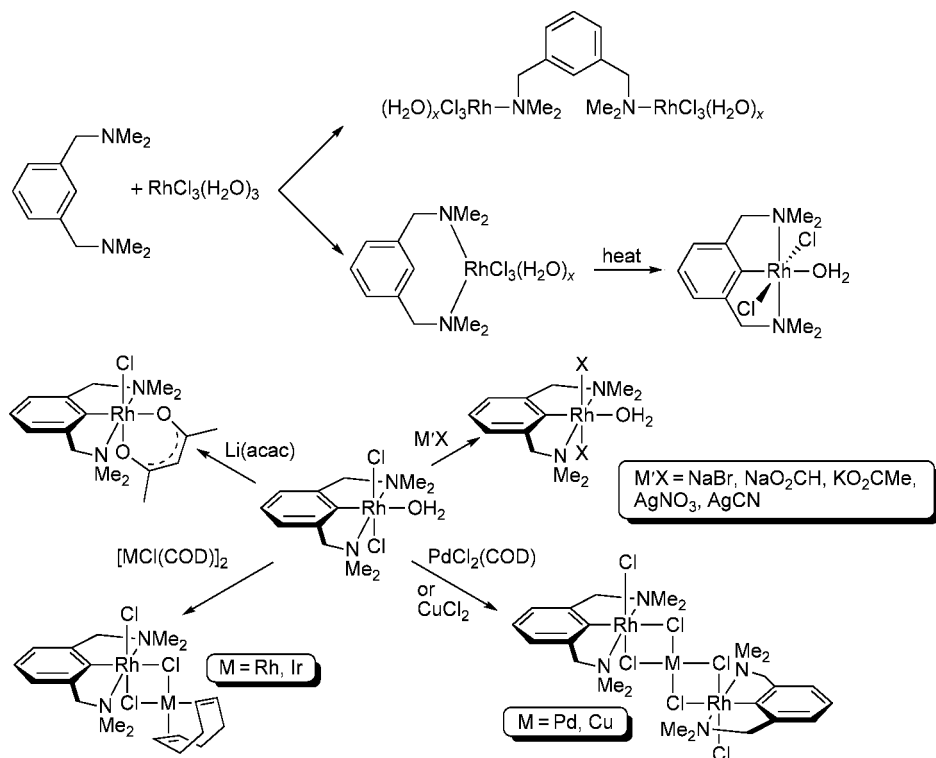


Scheme 10.16 Synthesis of cobaltoreceptors $[\text{CpCo}(\text{NCN})\text{H}_2\text{O}][\text{PF}_6]$.

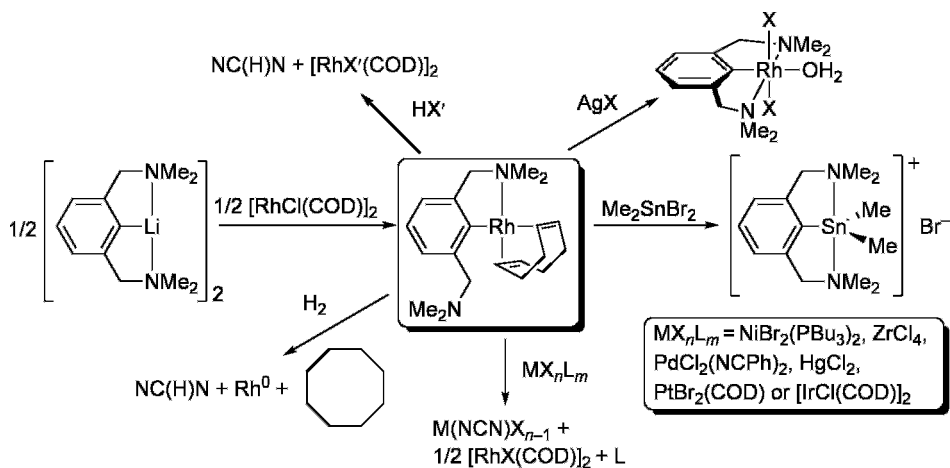
10.5.2 Rhodium

The chemistry of NCN containing Rh complexes has also been well studied. In the first report of a complex incorporating the $\text{Rh}(\text{NCN})$ motif [71], typical transmetalation with RhCl_3 and 0.5 equiv. $[\text{Li}(\text{NCN})]_2$ did not give the expected $\text{Rh}(\text{NCN})\text{Cl}_2$. Instead, coupling of two NCN molecules resulted. Also, attempts at the oxidative addition reaction of $\text{NC}(\text{Br})\text{N}$ or $\text{NC}(\text{H})\text{N}$ with various $\text{Rh}(\text{I})$ salts gave no coordination of the amine bonds and thus no reaction. Alternately, a rare example of C–H activation in NCN chemistry allowed for the synthesis of $\text{Rh}(\text{NCN})\text{Cl}_2(\text{H}_2\text{O})_2$, albeit in only moderate yields (45%), see Scheme 10.17. Mixing of $\text{RhCl}_3(\text{H}_2\text{O})_3$ with $\text{NC}(\text{H})\text{N}$ in ethanol at room temperature afforded an insoluble red solid, which on heating resulted in the formation of soluble, golden yellow $\text{Rh}(\text{NCN})\text{Cl}_2(\text{H}_2\text{O})$ and a gray solid, presumably the result of metalation outside the pincer pocket. Both X-ray crystal structural and NMR data revealed that both amines were firmly coordinated to the Rh center and that the Cl groups were mutually *trans*. The chlorides can be quantitatively exchanged for other anionic ligands, such as Br, O_2CH , O_2CMe , NO_3 , and CN. Conversely, the neutral water ligand was substituted by addition of some metal salts, such as $[\text{MCl}(\text{COD})]_2$ ($\text{M} = \text{Rh, Ir}$), and resulted in the formation of chloride-bridged bimetallic complexes, while $\text{PdCl}_2(\text{COD})$, Li_2PdCl_4 , or CuCl_2 gave trimetallic Rh_2Pd or Rh_2Cu species. Introduction of an acetylacetonate (acac) ligand, formally incorporating both a neutral and an anionic donor, substituted one chloride and a single bound water.

The closely related $\text{Rh}(\text{I})$ species, in contrast to $\text{Rh}(\text{III})$, was successfully generated with the $[\text{Li}(\text{NCN})]_2$ synthon, see Scheme 10.18 [72]. Reaction of $[\text{RhCl}(\text{COD})]_2$ afforded the expected monomeric $\text{Rh}(\text{NCN})(\text{COD})$ complex, where both NMR and X-ray crystallographic data showed that only one of the NMe_2 groups was ligated to Rh while the COD was acting as a bidentate ligand. The norbornadiene analog was similarly formed. Unlike the equivalent Ir complex (see below), the $\text{Rh}(\text{I})$ species were quite thermally stable. Fluxionality in the NCN and COD ligand was attributed to dissociation of the N–Rh bond, rotation about the Rh–aryl bond, and reformation of the Rh–N interaction as well as rigid complexation of the COD. In terms of simple reactivity, the coordinated amine can be displaced by π -accepting ligands CO, PPh_3 , or $\text{PhC}\equiv\text{CPh}$.



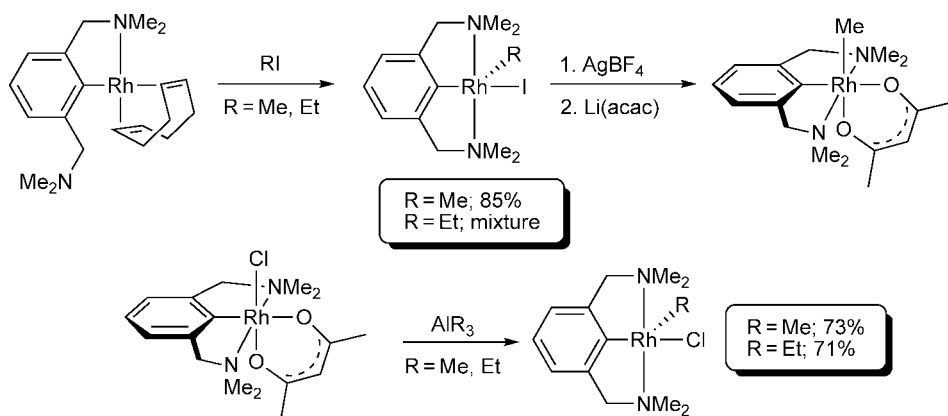
Scheme 10.17 Synthesis and reactivity of $\text{Rh}(\text{NCN})\text{Cl}_2(\text{H}_2\text{O})$.



Scheme 10.18 Synthesis and reactivity of $\text{Rh}(\text{NCN})(\text{COD})$.

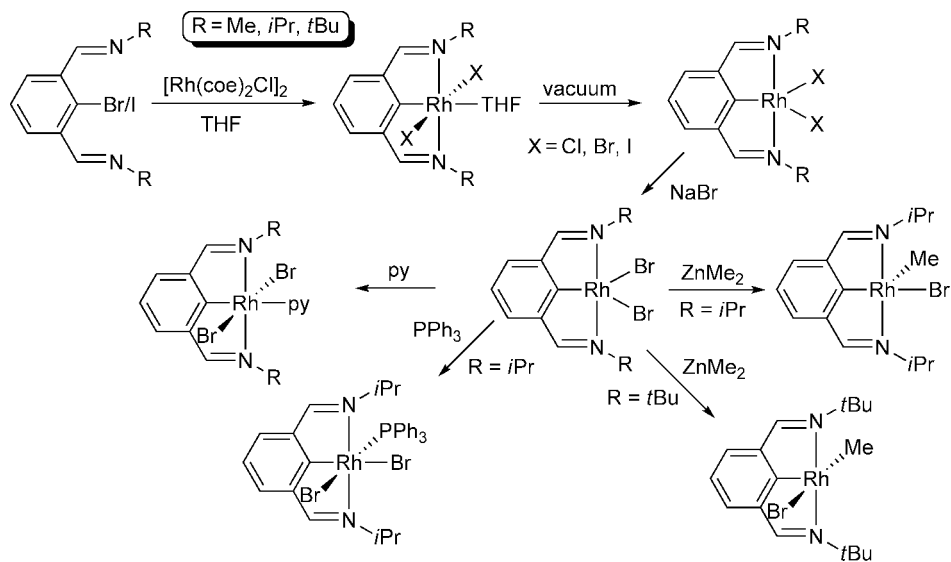
Proton sources, such as methanol or HCl, cleave the Rh–C bond, while reaction with metal salts Me_2SnBr_2 , $\text{NiBr}_2(\text{PBU}_3)_2$, ZrCl_4 , $\text{PdCl}_2(\text{NCPh})_2$, HgCl_2 , $\text{PtBr}_2(\text{COD})$, or $[\text{IrCl}(\text{COD})]_2$ resulted in transmetalation to give $\text{M}(\text{NCN})$ complexes with formation of $[\text{RhX}(\text{COD})]_2$. Attempts to abstract the chloride ligand with silver salts AgX ($\text{X} = \text{NO}_3$, OAc) instead produced a redox reaction with formation of metallic Ag and the previously synthesized Rh(III) complexes $\text{Rh}(\text{NCN})\text{X}_2(\text{H}_2\text{O})$. Introduction of dihydrogen resulted in ejection of the $\text{NC}(\text{H})\text{N}$ arene, cycloalkanes from hydrogenation of the bound diene, and metallic Rh.

Oxidative addition of MeI cleanly gave the Rh(III) species $\text{Rh}(\text{NCN})\text{MeI}$ which exhibited square pyramidal geometry, with the methyl group in the apical position and both amines complexed to the Rh center, see Scheme 10.19 [73]. However, bulkier EtI only reacted to a minor extent. The related chloro complexes with both Me and Et alkyl groups were selectively generated by reaction of the $\text{Rh}(\text{NCN})\text{Cl}(\text{acac})$ complex with AlR_3 . Here, NMR data indicated retention of the square pyramidal geometry at Rh and apical positioning of the alkyl group. The presumably open sixth coordination site did not react with coordinating ligands, likely due to the strong *trans* influence of the apical alkyl group and steric protection of the site by the NCN ligand. The halide in these complexes can also be abstracted with Ag salts, resulting in a viable synthesis of $\text{Rh}(\text{NCN})\text{Me}(\text{acac})$.



Scheme 10.19 Formation of diorgano $\text{Rh}(\text{NCN})\text{RX}$ species.

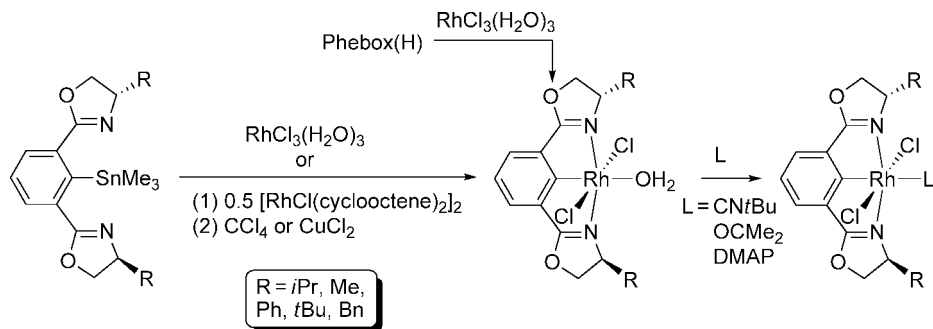
Some examples of imine-based halide and methyl Rh(III)(NCN) complexes have recently been reported by Elsevier and coworkers [74]. Unlike the amine NCN systems above, oxidative addition of Rh(I) precursors with $\text{NC}(\text{Br})\text{N}$ successfully generated the Rh(III) species where halide scrambling was observed, see Scheme 10.20. These mixed species can be converted to Br- or I-only species via treatment with excess NaBr or NaI. Large differences in the chemistry of these complexes were observed based on the steric size of the imino alkyl group. For example, the $=\text{NMe}$ and $=\text{N}i\text{Pr}$ $\text{Rh}(\text{NCN})\text{X}_2\text{L}$ compounds incorporated an Rh-bound water or THF ligand *trans* to the pincer arene while $=\text{N}t\text{Bu}$ prevented additional ligation. Crystal structures revealed an octahedral geometry about Rh. These ligands can also be removed under high vacuum. In the



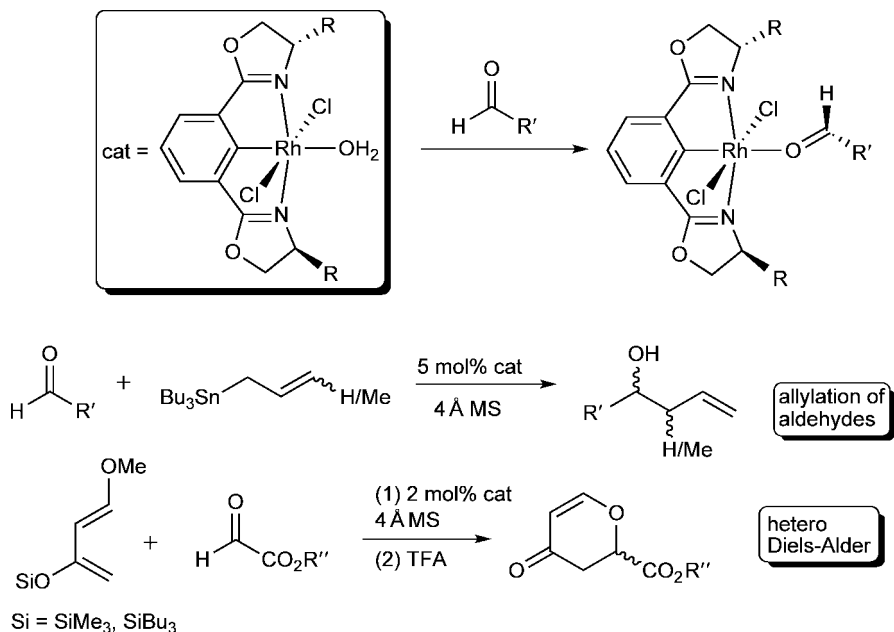
coordinatively unsaturated $\text{Rh}(\text{NCN})\text{Br}_2$ complexes, pyridine ligated *trans* to the pincer arene, but in the case of the $=\text{N}i\text{Pr}$ adduct, PPh_3 complexes *cis* and one of the bromides migrated to the *trans* position due to sterics and possibly π - π interactions. These species were also selectively methylated by reaction with 0.5 equiv. ZnMe_2 to generate $\text{Rh}(\text{NCN})\text{MeX}$. Here, the X-ray crystal structure of the $=\text{N}t\text{Bu}$ compound exhibits an unusual square pyramidal geometry where the pincer arene atom is situated in the apical position. However, the $=\text{N}i\text{Pr}$ analog retained the more common arrangement with three atoms of the pincer and the halide in the basal plane and an apical Me group.

A number of Phebox Rh complexes have been synthesized and utilized in a variety of enantioselective reactions, such as Michael additions, Diels-Alder, and allylation of aldehydes. Typically, the catalysts can be prepared by transmetalation with $\text{Sn}(\text{Phebox})\text{Me}_3$ and either $\text{RhCl}_3(\text{H}_2\text{O})_3$ or $[\text{RhCl}(\text{cyclooctene})_2]_2$ followed by treatment with CCl_4 , see Scheme 10.21 [75, 76]. C-H activation routes were also applicable but typically lower yielding. The water ligand can be replaced by other basic donors but not π -acids, such as CO or ethylene, showing that the Rh center behaved as a simple Lewis acid. The X-ray crystal structures revealed that the Rh was in a distorted octahedral environment, with *trans*-disposed chlorides and the water or other neutral ligands occupying the position *trans* to the aryl C_{ipso} of the pincer.

In the initial reports by Nishiyama, the allylstannation of aldehydes could be effected in good yields and up to 80% ees, although most substrates ranged from 40 to 60% ee, see Scheme 10.22 [76, 77]. The mechanism followed the typical course for a Lewis acid-catalyzed addition with initial σ -coordination of the aldehyde oxygen to the chiral Rh center, activating the carbonyl to nucleophilic attack. A Wang resin solid-supported



Scheme 10.21 Synthesis and reactivity of $\text{Rh}(\text{Phebox})\text{Cl}_2(\text{H}_2\text{O})$.

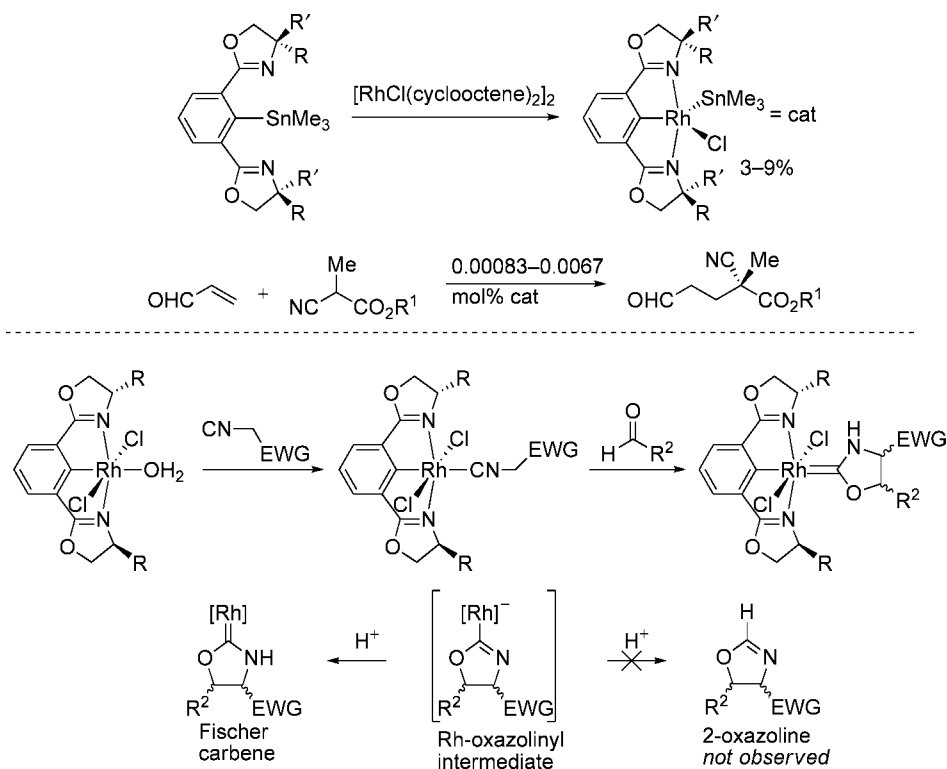


Scheme 10.22 General reactions catalyzed by $\text{Rh}(\text{Phebox})\text{Cl}_2(\text{H}_2\text{O})$.

version of $\text{Rh}(\text{Phebox})\text{Cl}_2(\text{H}_2\text{O})$ was also examined for this reaction. While the catalyst could be efficiently recycled, the ee dropped significantly [78]. Asymmetric hetero-Diels-Alder reactions between Danishefsky's diene and glyoxylates proceeded via a concerted $[4+2]$ cycloaddition mechanism in high yields and up to 80% ee [79].

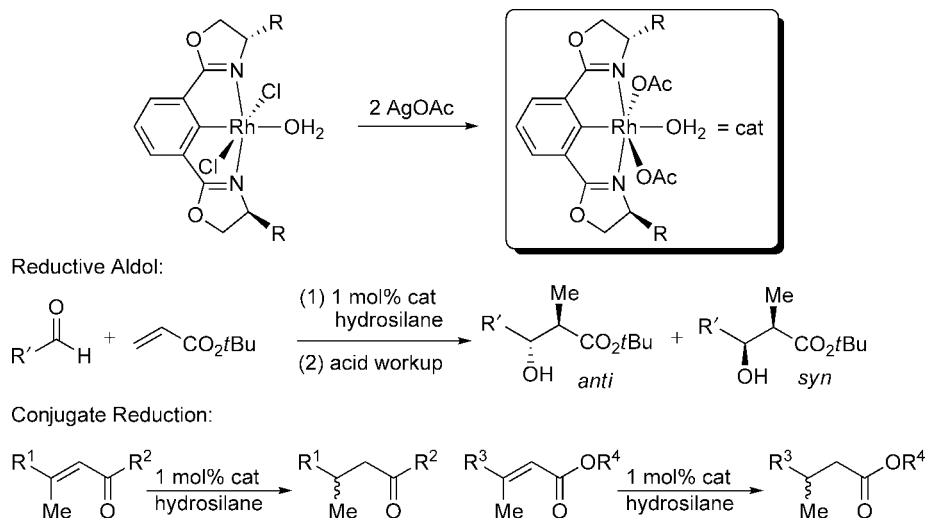
However, there were some interesting twists to the chemistry of $\text{Rh}(\text{Phebox})$ complexes. In the asymmetric Michael addition of cyanopropionates with α,β -unsaturated aldehydes, the catalyst was prepared in situ by reaction of $\text{Sn}(\text{Phebox})\text{Me}_3$ with $[\text{RhCl}(\text{cyclooctene})_2]_2$ [80]. It was found that 3–9% of the oxidative addition product

$\text{Rh}(\text{Phebox})\text{Cl}(\text{SnMe}_3)$ was generated and that this complex was an exceedingly active catalyst ($\text{TON} > 10\,000$) that also induced good enantioselectivity. $\text{Rh}(\text{Phebox})\text{Cl}_2$ alone was found to be inactive. The aldol-type condensation of isocyanides with aldehydes selectively generates chiral Rh-bound Fischer carbenes [81]. This resulted from the selective protonation of the nitrogen of the metalated oxazolinyl-Rh instead of at the more usual 2-position, which would liberate oxazoline and released the Rh back into the catalytic cycle, see Scheme 10.23.



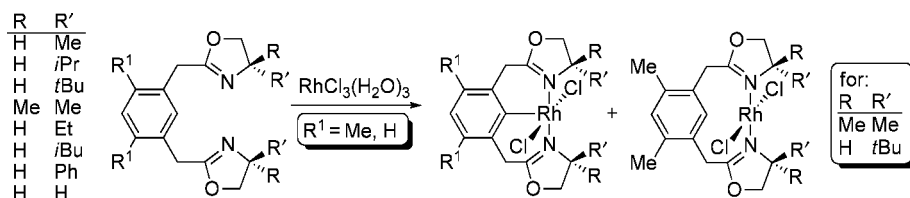
Scheme 10.23 (Top) Asymmetric Michael addition catalyzed by $\text{Rh}(\text{Phebox})\text{Cl}(\text{SnMe}_3)$. (Bottom) Synthesis and mechanism for generation of Fischer carbene complexes.

A number of $\text{Rh}(\text{Phebox})(\text{OAc})_2(\text{H}_2\text{O})$ complexes, generated by reaction of the corresponding dichlorides with AgOAc , were found to be active catalysts in the asymmetric reductive aldol reaction [82] and in conjugate reductions of α,β -unsaturated ketones and esters, see Scheme 10.24 [83]. In the reductive aldol reaction, high anti-selectivities (typically 95:5) were noted with concomitantly excellent ee in the *anti* products. Under optimized conditions, the conjugate reductions of ketones exhibited exclusive selectivity for the 1,4-reduction product with good ee (51–98%). Similarly, reduction of esters also gave exclusive 1,4-reduced products in high ee.

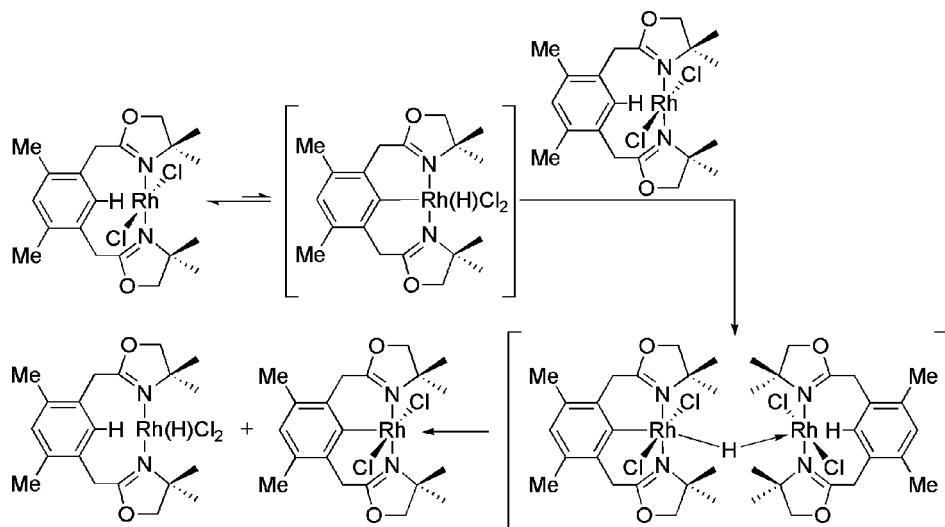


Scheme 10.24 Reductive aldol and conjugate reduction reactions catalyzed by Rh(Phebox)(OAc)₂(H₂O).

Modified Phebox ligands incorporating an additional methylene spacer between the oxazolines and the phenyl ring, dubbed the 'benbox' ligand, have been utilized in the isolation of a relatively rare Rh(II) species [84, 85]. This ligand was originally designed to provide a more defined steric pocket for enantioselective reactions by increasing the ligand's bite angle. During the synthesis, performed by C–H activation with Rh(III)Cl₃(H₂O)₃, the Me/Me and *t*Bu/H benbox systems, see Scheme 10.25, also gave appreciable amounts of Rh(II){benbox(H)}Cl₂. Significantly, all complexes were air and water stable and could be purified by column chromatography. Magnetic measurements and EPR spectroscopy confirmed the paramagnetic nature of the Rh(II) complex and were consistent with a *S* = 1/2 ground state. X-ray crystallography revealed a square planar geometry about the Rh center with mutually *trans* chlorides and oxazoline nitrogens and also contained a C–H agostic interaction with the pincer aryl group. However, these Rh(II) complexes were thermally unstable and disproportionate via initial oxidative addition of the Ar–H followed by rapid transfer of the hydride to another molecule of Rh(II){benbox(H)}Cl₂ giving the two Rh(III) species depicted in Scheme 10.26 [85].



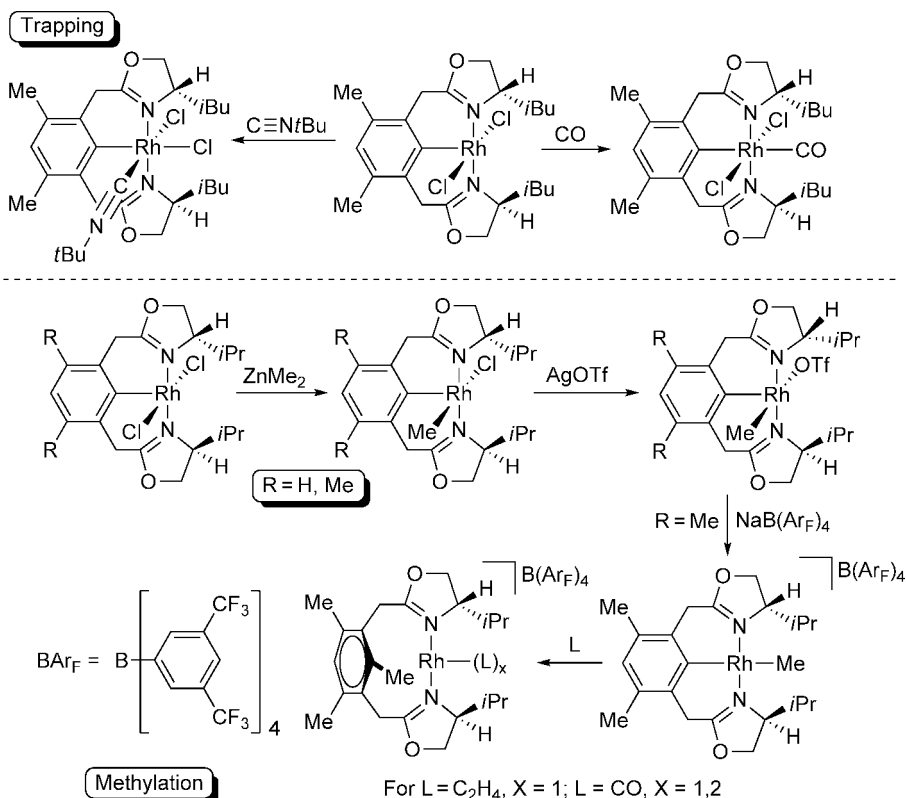
Scheme 10.25 Synthesis of Rh(benbox)Cl₂ complexes.



Scheme 10.26 Proposed decomposition pathway for Rh(II)(benbox)Cl₂.

Further derivatization and study of both the Rh(II) and the Rh(III) complexes have been performed. Homologs in which the 4,6-positioned methyl group has been removed can also be synthesized, see Scheme 10.27; however, only Rh(III) species were obtained [85]. Based on X-ray crystallography and NMR spectroscopy of the *i*Pr/H benbox derivative, the geometry at Rh was square pyramidal, with the pincer aryl in the apical position. In the solid-state structure, a CH–Rh agostic interaction from one oxazoline *i*Pr was present in the sixth coordination site. Accordingly, reaction with co-ligands, such as CO or CN*t*Bu, gave the electronically saturated six-coordinate complexes, see Scheme 10.27. Differences in the site of coordination, CO *trans* to the pincer aryl and CN*t*Bu *cis*, were ascribed to steric interactions between the groups on the oxazolines and the co-ligands. Methylation and chloride abstraction chemistry was also investigated. For example, Rh(*i*Pr/H-benbox)Cl₂ can be monomethylated with ZnMe₂, and the chloride in the resulting complex was replaced by reaction with AgOTf to give Rh(*i*Pr/H-benbox)Cl(OTf). The cationic monomethyl Rh species was obtained by subsequent reaction with NaB(Ar_F)₄ (Ar_F = 3,5-(CF₃)₂C₆H₃). When exposed to π -accepting ligands, such as ethylene or CO, methyl-aryl reductive elimination occurred to give Rh(I) cations. Unfortunately, these Rh(III) species were poor catalysts for hydrosilylation of alkenes or allylation of aldehydes. This lack of reactivity pointed to the greater effective steric shielding provided by the benbox ligand over its phebox analogs.

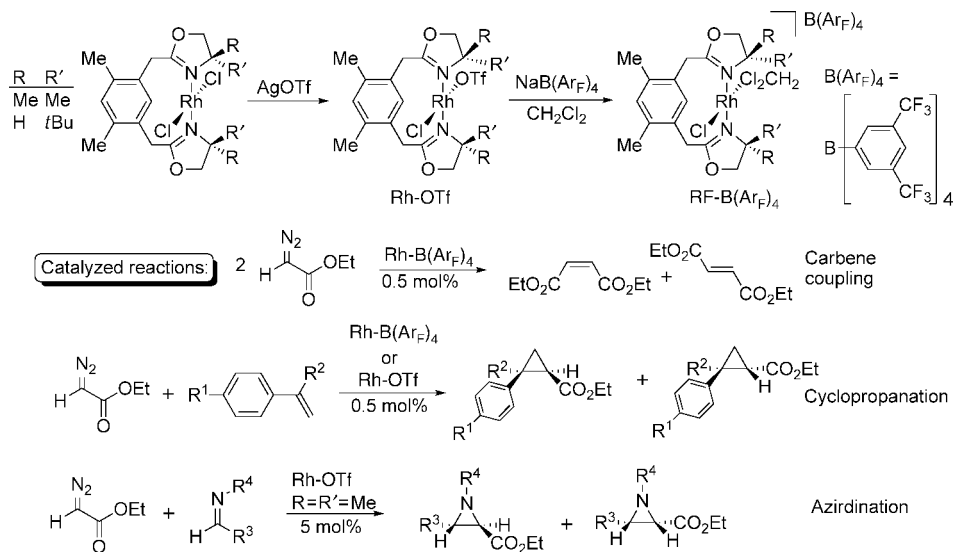
However, the Rh(II) complexes were effective catalysts for carbene transfer reactions, such as cyclopropanation of olefins and aziridination of imines [86]. Formation of the stable and monomeric active catalysts was achieved by replacement of one Cl ligand with either OTf or formation of CH₂Cl₂-stabilized cationic complexes [Rh(benboxH)Cl(CH₂Cl₂)]⁺[B(Ar_F)₄][−], see Scheme 10.28. The **Rh-B(Ar_F)₄** complexes were very active for the coupling of ethyl diazoacetate and were fairly selective (~80:20) for the *cis* alkene (maleate) at low catalyst loadings (0.5 mol%). Cyclopropanation of a variety of substituted styrenes was also catalyzed with both **Rh-B(Ar_F)₄** and **Rh-OTf**



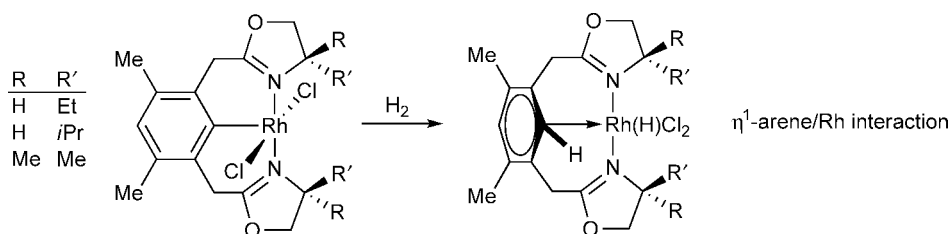
Scheme 10.27 Trapping and methylation reactions of $Rh(III)(benbox)Cl_2$.

complexes, although the OTf complex was much less active, indicating that a free coordination site on Rh needed to be accessible. The catalysts gave, in general, a slight preference for the thermodynamically less stable *cis*-cyclopropanes and ees were good (up to 80%). Notably, no reaction was observed when bulkier diazoalkanes were used. In the aziridination reaction, only the Me/Me-benbox **Rh-OTf** catalyst was active; the bulkier **Rh-OTf** species was inactive and the **Rh-B(Ar_F)₄** complexes gave only carbene coupling products. A variety of substituted imines were employed and again the *cis* isomers were preferred, here in approximately a 3:1 ratio. The reactions were accelerated in THF over CH_2Cl_2 , and ees were low (>11%). Significantly, this study showed that *monomeric* Rh(II) complexes can effect carbene transfer reactions.

Exposure of the Rh(III) complexes to H_2 results in scission of the C–Rh bond and formation of a hydrido Rh(III) complex with a neutral arene benbox ligand bound only through the oxazolines, see Scheme 10.29 [84, 87]. Interestingly, these complexes displayed significant Ar–H/Rh–H J_{HH} coupling of 2.5–3.3 Hz [87]. Also, the chemical shift of the Ar–H proton was significantly downfield ($\delta = 8.88$ –9.03) compared to normal arenes. Extensive NMR spectroscopy, X-ray crystallography, and computational methods showed that this coupling was not the result of agostic bonding, direct Ar–H/Rh–H interactions or Ar–H/Rh–Cl hydrogen bonding but rather due to the presence of a fairly rare η^1 -arene/Rh interaction.



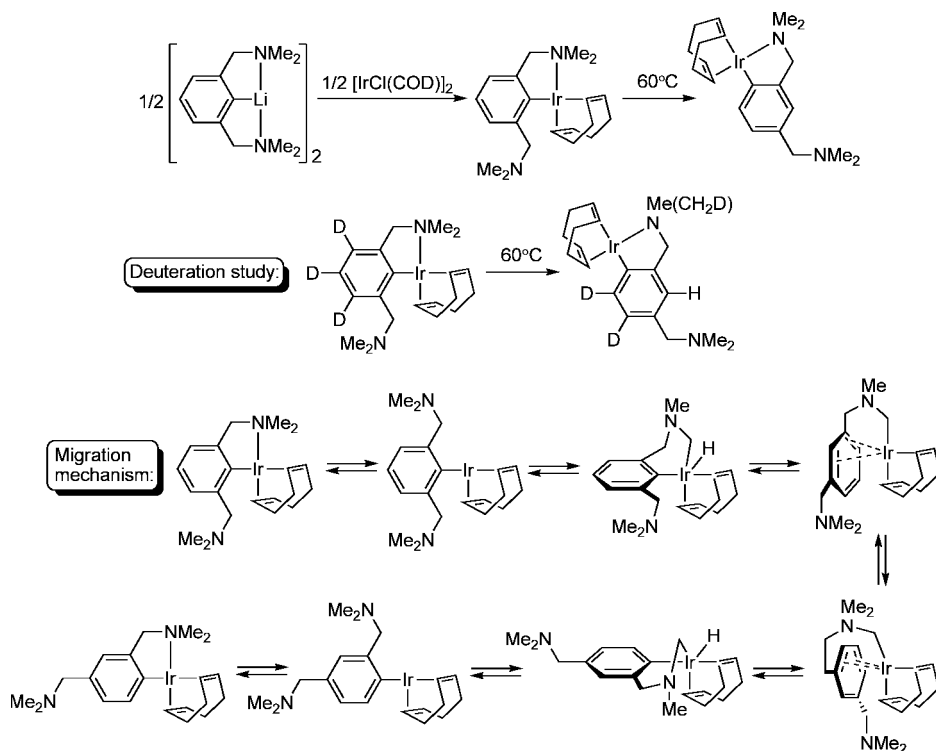
Scheme 10.28 Catalytic reactivity of Rh(II)(benbox) derivatives.



Scheme 10.29 Reactivity of Rh(III)(benbox)Cl₂, with H₂ resulting in an η^1 -arene/Rh interaction.

10.5.3 Iridium

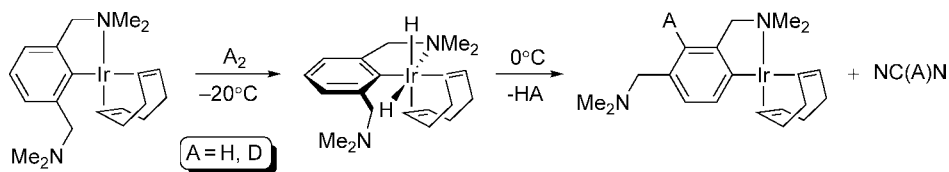
The small selection of iridium NCN pincer complexes reported to date has exhibited some interesting reactivity and potential applications. Similar to analogous Rh(NCN) complexes, synthesis of Ir(NCN)(COD) was effected by reaction of [Li(NCN)]₂ with [IrCl(COD)]₂ to give the expected species, see Scheme 10.30 [88]. Here, the COD was still bound to the Ir center in a bidentate fashion and one amine arm of the NCN pincer ligand was free, as shown by variable temperature NMR experiments. Heating induced a unique concerted C–H activation/Ir migration where the Ir atom underwent a formal 1,3-shift to the sterically less crowded position. Comparison of reactions of the two Ir species with CD₃OD showed the less crowded complex to be much more stable, in line with an Ir–C bond scission event in the 1,3-shift and a vacant site at Ir. Deuteration studies definitively showed the involvement of the N–Me groups and that an oxidative addition/reductive elimination pathway was likely. From this, a mechanism for the Ir-shift was deduced. Initial Ir–N bond dissociation was followed by rate-determining



Scheme 10.30 Synthesis of $\text{Ir}(\text{NCN})(\text{COD})$ and mechanism of 1,3-Ir migration involving four separate C–H bond activations in concert.

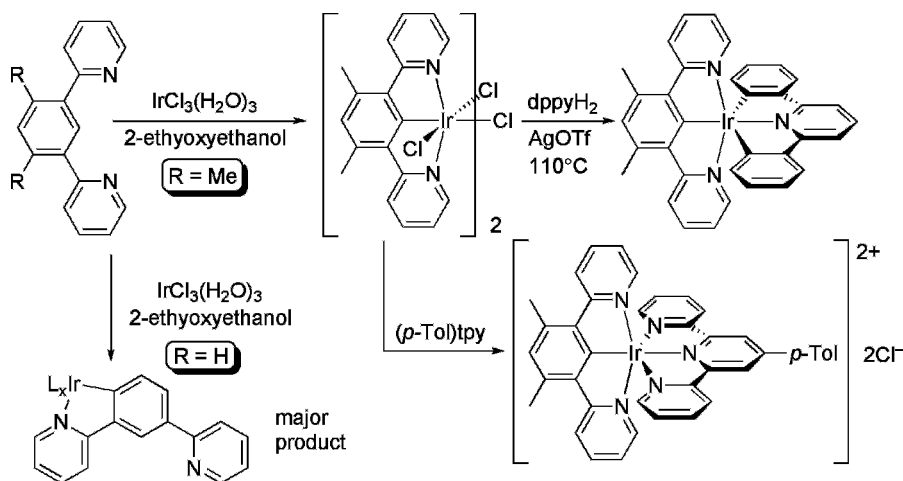
NMe C–H oxidative addition to the low-valent Ir center. Ar-H reductive elimination breaks the Ir-C aryl bond to give an arene-stabilized Ir center and a haptotropic aryl rearrangement positioned it for Ar-H oxidative addition with the less hindered position. C–H reductive elimination reformed the NMe_2 group and completed the exchange. Relief of steric pressure between the pendant CH_2NMe_2 and COD was driving force for the reaction. This whole process was exceptional as it involved regioselective bond formation and cleavage of four separate C–H bonds in concert.

This complex also reacted with dihydrogen to generate a fairly unique Ir(III) species in which oxidative addition of H_2 gave an Ir complex containing phenyl, hydride, and olefin ligands, see Scheme 10.31 [89]. This dihydride was characterized in solution by NMR at -20°C and had spectra consistent with *cis* orientation of the two Ir–H ligands with hydrides *trans* to NMe_2 and alkene groups, see Scheme 10.31. Upon warming to 0°C in the presence of H_2 (or D_2), the above-mentioned 1,3-Ir rearranged product was observed. As this reaction was only observed thermally above 60°C , H_2 was acting as a catalyst for this migration. This reduction in activation barrier can be attributed to more facile oxidative addition of H-H vs. C–H bonds. Some free arene ligand was also noted, in line with only a labile Ir–N bond anchoring the NC(H)N ligand to the complex vs. a strong Ir-CH_2 in the thermal process. Interestingly, no evidence for hydrogenation of the COD ligand was observed.



Scheme 10.31 Reaction of $\text{Ir}(\text{NCN})(\text{COD})$ with H_2 .

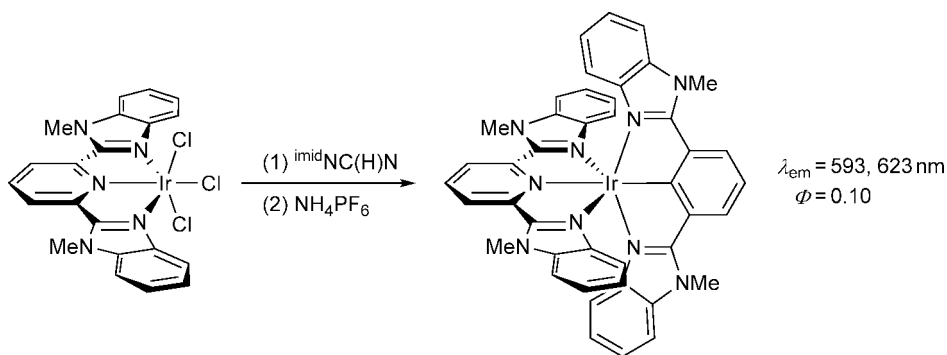
The chemistry of cyclometalated Ir(III) complexes has experienced a recent resurgence in activity due to the highly luminescent properties of this class of compounds and their potential use in electroluminescent devices [90–92]. In terms of NCN-type pincer systems that have been applied, reports with bis(pyridine) and bis(benzimidazole) donors have been shown to impart favorable properties to these complexes. For the pyridine-based donor systems, some synthetic difficulties were encountered and mainly ascribed to competitive 4,6-metallation [93]. This problem was elegantly solved by introduction of blocking methyl groups which forced the cyclometalation to the desired 2-position of the ligand, see Scheme 10.32. The resulting $[\text{Ir}(\text{NCN})\text{Cl}_2]_2$ dimer can be cleaved with DMSO. A second cyclometalated ligand, *meta*-diphenylpyridine (dppy), or a *p*-tolyl-substituted terpy can also be introduced. The *tris* cyclometalated $\text{Ir}(\text{NCN})(\text{dppy})$ complex was strongly luminescent with a fairly high quantum yield ($\lambda_{\text{em}} = 585 \text{ nm}$, $\Phi = 0.21$). Replacement of the cyclometalated dppy ligand with the substituted terpy resulted in drastic reduction in the quantum yield of emission ($\lambda_{\text{em}} = 560 \text{ nm}$, $\Phi < 10^{-3}$), highlighting the necessity of the strongly σ -donating aryls to boost $^3\text{MLCT}$ transitions. However, $\text{Ir}(\text{NCN})(\text{dppy})$ was not stable in solution under photolysis conditions, exhibiting one Ir–C bond scission of the dppy ligand.



Scheme 10.32 Synthesis of $\text{Ir}(\text{NCN})(\text{dppy})$ and $\text{Ir}(\text{NCN})\{(p\text{-Tol})\text{tpy}\}$ complexes.

A new set of NCN-type ligands has been reported where the pyridine donors were replaced with benzimidazoles [94]. Selective synthesis of the desired Ir-cyclometalated

product was not hampered by competitive 4,6-metalation. Here, the neutral NNN ligand, bis(benzimidazolyl)pyridine (bbimpy), was first complexed to IrCl_3 , followed by C–H activation of the bis(benzimidazolyl) arene, see Scheme 10.33. Compared to related all nitrogen-bound complexes, the oxidation potential of $\text{Ir}^{\text{(imidNCN)}}(\text{bbimpy})$ ($\text{imidNC(H)N} = \text{bis(benzimidazolyl) benzene}$) was substantially less positive, pointing to the stabilization of the Ir(IV) state by the phenyl group. Accordingly, the reduction potentials to both Ir(II) and Ir(I) were more negative. While the bbimpy ligand also incorporated benzimidazole groups, this $\text{Ir}^{\text{(imidNCN)}}(\text{bbimpy})$ complex was highly luminescent at 295 K ($\lambda_{\text{em}} = 593, 623 \text{ nm}$, $\Phi = 0.10$), despite incorporating only one Ir–C aryl bond.



Scheme 10.33 Synthesis of benzimidazole-based $\text{Ir}^{\text{(imidNCN)}}(\text{bbimpy})$.

10.5.4 Group 10 (Ni–Pt)

By far, the vast majority of metallopincer complexes, NCN-type systems included, incorporate group 10 metals. As such, a number of reviews that cover this area have been reported [1–11], which detail the interesting catalytic and material properties of these species in conjunction with studies in fundamental bond-making and bond-breaking processes. To a large extent, the viability of $\text{M}(\text{NCN})$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$) complexes for such varied and numerous studies stems from their relatively direct synthesis and high stability. Also, a number of metallo-dendritic complexes have been synthesized that incorporate pincer-ligated Ni, Pd, and Pt, a topic which has also been reviewed [3, 95]. For this section, it is convenient to group Pd and Pt complexes based on application rather than exclusively on metal as many Pd and Pt complexes have been employed in parallel studies. Here, a small selection of important recent results in the fields of catalysis and ligand design, supramolecular chemistry, chemical biology, and materials chemistry with Pd and Pt pincer complexes are presented.

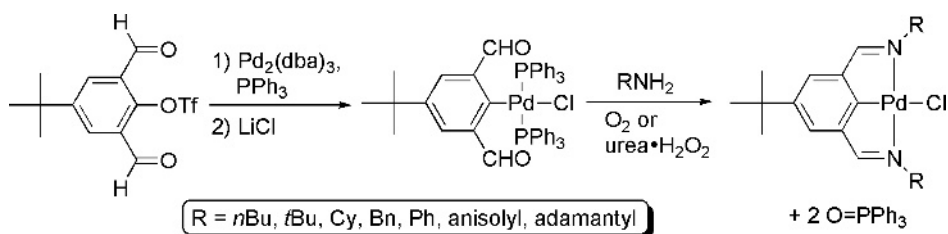
10.5.4.1 Nickel

For $\text{Ni}(\text{NCN})(\text{halide})$ species, the vast majority of its chemistry has been previously reviewed [2, 6]. The most important applications of these species are as an excellent catalyst for the Kharasch addition, an atom transfer radical addition (ATRA) reaction between an olefin and an alkyl halide, or similar radical polymerizations (ATRP) and

in the isolation of stable $\text{Ni(III)NCN(halide)}_2$ complexes. Furthermore, the first proof of direct correlation between catalytic activity at the Ni center and *para* substituents on the aryl ring was discovered [96]. These reactions have been extended to dendritic systems [16], from which one of the first rational explanations of a dendritic effect in catalysts was put forth [18, 19]. Recently, a phebox-based Ni(NCN)Cl complex has been reported and tested in the Michael addition [97].

10.5.4.2 Pd and Pt: selected new synthetic methods and ligand design

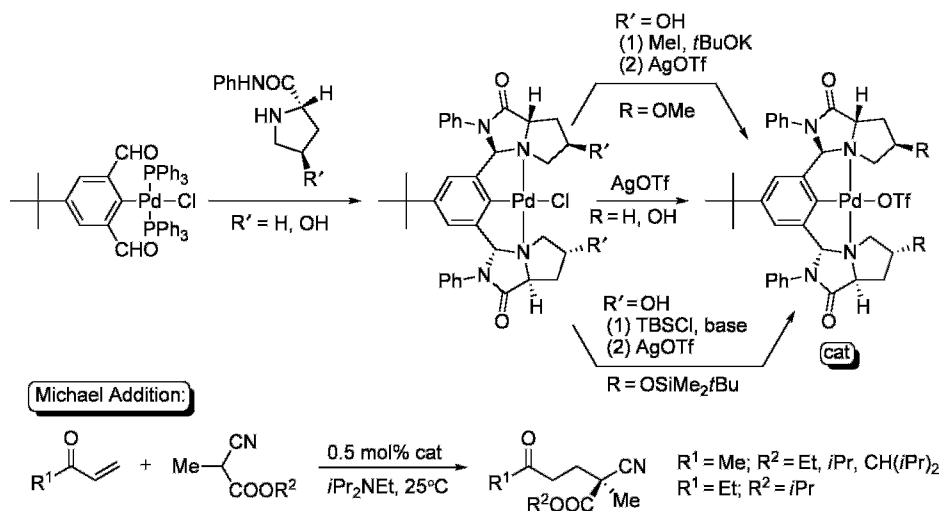
The design of an efficient chiral pincer ligand is an ongoing area of interest. A number of phebox-type species have been utilized, but with rather disappointing results as the chiral pocket developed for these is quite distant from the metal center. As both the site of reaction and approach of reagents are close to the nominal square plane, very bulky systems with chirality projected in a conical fashion out from the metal are predicted to be effective. However, metalation of very bulky pincer ligands is often plagued by low yields or competitive activations outside the pincer pocket. Work from Uozumi has provided a solution to the synthesis of bulky NCN complexes by the 'ligand introduction route' [98, 99], see Scheme 10.34, which has recently been extended to phosphite Pd(PCP) systems [100]. Here, a C–Pd bond was generated prior to incorporation of the amine or imine groups. Key was the oxygen stability of the 2,6-diformyl Pd starting material as oxidation of the PPh_3 ligands allowed for the isolation of the Pd(NCN)Cl complexes. The efficiency of this method was demonstrated by comparison with a typical oxidative addition reaction with the *tert*-butyl imino NCN pincer; ligand introduction furnished Pd(NCN)Cl in 96% yield, while the normal route gave only 48% product after prolonged reaction at high temperatures.



Scheme 10.34 The 'ligand introduction route' for synthesis of bulky Pd(NCN)Cl complexes.

Chiral and extremely bulky pyrroloimidazolone-based NCN complexes have also been synthesized with this approach, see Scheme 10.35 [98, 99]. They were found, along with the achiral imine Pd(NCN) complexes, to be exceedingly active pre-catalysts for Heck couplings with iodobenzenes and acrylates at ppm levels [98, 101]. In addition, the triflate complexes were quite reactive as stereoselective catalysts in the asymmetric Michael addition [98, 99]. With the hydroxy-substituted system, yields exceeding 80% were obtained for the coupling of vinyl ketones with 2-cyanopropionates, some of the best values for Pd pincer chemistry reported to date.

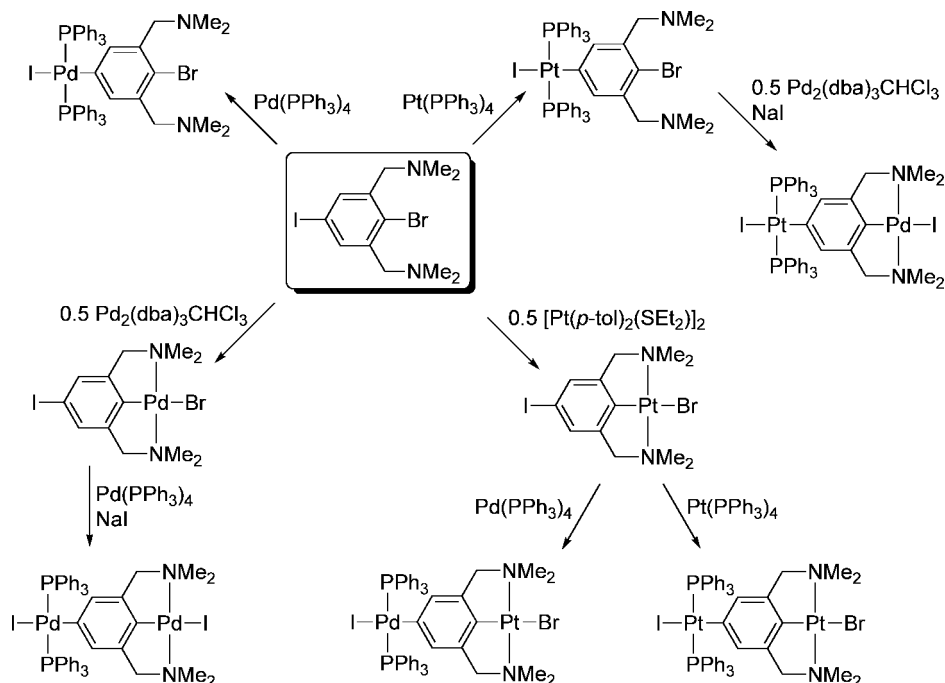
A number of studies have shown that variation of the *para*-position of the pincer arene allowed for remote control of the electronic situation at the metal center



Scheme 10.35 Synthesis of chiral Pd(NCN)Cl complexes and their use in the Michael addition.

which can affect catalysis (e.g., see [96, 102]) or other measurable attributes, such as determination of a Hammett σ_p relation for ^{195}Pt chemical shifts [103, 104]. A new functionalized NCN arene ligand, 4-bromo-1-iodo-3,5-bis[(dimethylamino)methyl]benzene (I–NC(Br)N) [105], has been utilized as a common synthon for a number of different *para*-substituted species. The most remarkable facet of this system was that either the I or the Br function can be chemoselectively metalated, potentially giving well-defined heterobimetallic complexes and that the metalated 4-iodo-substituted pincer complexes (M(I–NCN)X) can be used as substrates for organic reactions typical of iodobenzene. Scheme 10.36 details the selective metalation of either site with both Pd and Pt.

The iodine in the metal-free I–NC(Br)N ligand can also be selectively addressed by either lithiation routes or Pd-catalyzed cross-coupling reactions giving a diverse set of *para*-substituted ligands [103–105]. These reactions were also applicable to the Pd- and Pt-metalated pincers, but the Pd(NCN) moiety was somewhat less robust; for example, lithiation routes were only viable for the Pt systems. Scheme 10.37 details the substituents that can be introduced in this manner. Both Suzuki–Miyaura (see below) and Sonogashira couplings were also possible with the platinated system, although reaction with Ph–B(OH)₂ was unsuccessful [105]. Notably, the Hammett σ_p parameter for the ‘Pt(NCN)Br’ functionality was obtained by measurement of the acidity of the *p*-COOH complex. The platinum group was found to be strongly electron donating [$\sigma_p = -1.18$ (MeOH), -0.72 (1:1 H₂O/MeOH)], similar to NH₂ or NMe₂ [103, 104]. In addition, the stability offered by the binding pocket of the NCN pincer and the electron-donating characteristics of the Pt(NCN)Br group allowed for the direct electrophilic sulfonation of the *para* position of the simple aryl pincer, albeit in low yields [103, 104]. Also, the phenolic Pt(HO–NCN)Br can undergo typical condensation and addition reactions without impact on the Pt group [105].

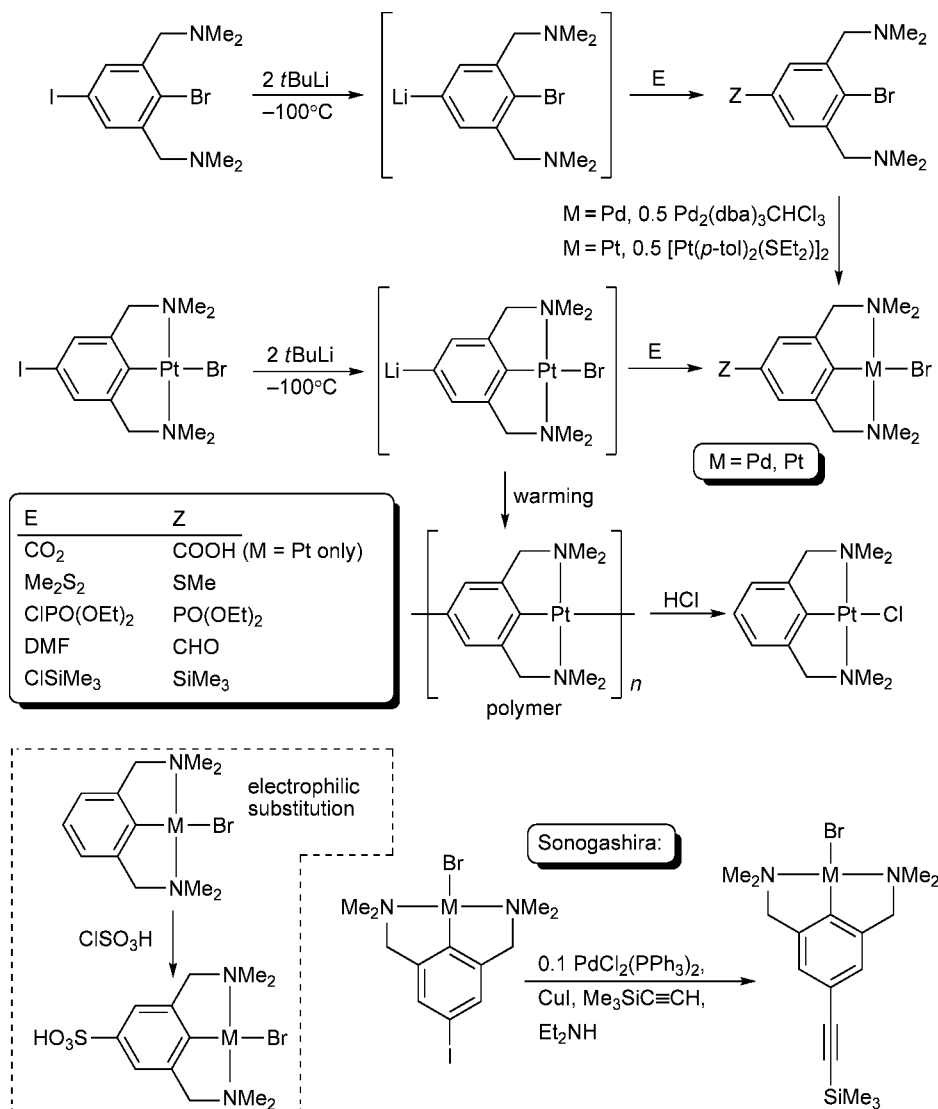


Scheme 10.36 Regioselective palladation and platination of I-NC(Br)N.

10.5.4.3 Pd and Pt: supramolecular architectures

Metallopincers have been employed in a variety of applications within the supramolecular arena. Reinhoudt has utilized $\text{Pd}(\text{SCS})$ –pyridine dative bonding motifs to generate a number of well-defined non-covalent dendritic or spherical systems, some of which were of sufficient size and stability to be detected as single molecules by atomic force microscopy [106–116]. Also, non-covalent $\text{H} \cdots \text{Cl}$ hydrogen bonding in crystalline $\text{Pt}(\text{NCN}-p\text{-OH})\text{Cl}$ organized the molecules into parallel infinite 1D polymeric chains. Remarkably, this crystalline solid efficiently absorbed SO_2 within the crystal lattice, expanding up to 25% in volume, with no loss of crystallinity, which allowed for the first quantitative measurement of gas diffusion kinetics in a crystal solid [3, 27]. The impressive stability of the crystal network can be attributed to this flexible network of H bonds.

Recent work from the Craig group has detailed the use of Pd and $\text{Pt}(\text{NCN})$ complexes in a supramolecular context utilizing dative M –pyridine interactions, similar to the work of Reinhoudt, to construct main-chain reversible polymers and to probe supramolecular cross-linking agents in networks. For both of these applications, subtle steric differences in the individual molecules played a large role in the observed properties. In the main-chain polymers [117], see Fig. 10.4, simple substitution of NMe_2 for NEt_2 groups resulted in a 100-fold decrease in the rate of dynamic exchange in DMSO, which was found to be a solvent-assisted associative process [118], while the equilibrium constants for complexation were essentially identical. Due to the similarity in K_{eq} , the polymers



Scheme 10.37 Lithiation of I-NC(Br)N and Pt(I-NCN)Br and reactivity of M(NCN)Br.

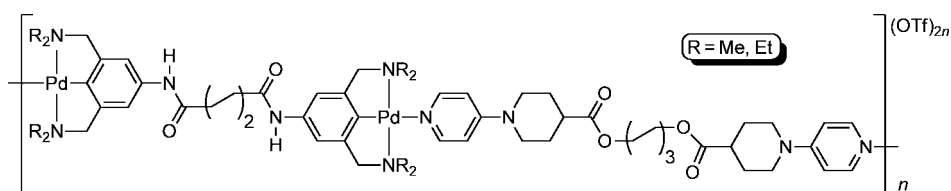


Fig. 10.4. Structure of repeating unit of Pd(NCN) containing main-chain reversible polymer.

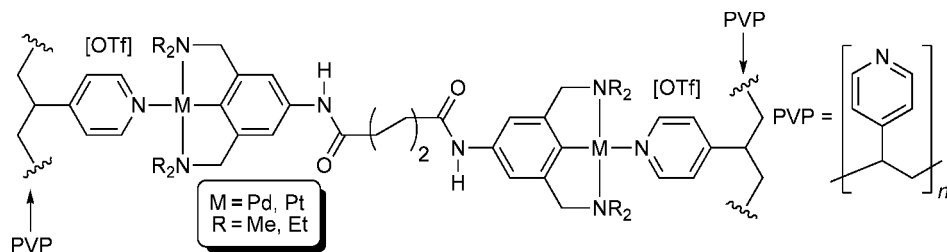


Fig. 10.5. Cross-linking unit in PVP/M(NCN) supramolecular networks.

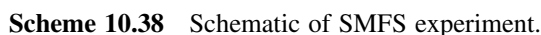
formed from either system were indistinguishable. This orthogonal control of dynamics may be useful in probing dynamic mechanical behavior in the polymers, such as self-repair.

A similar strategy has been employed to control and study dynamic cross-linking in poly(4-vinylpyridine) (PVP), but here, there was a large difference in the properties of the polymers, see Fig. 10.5 [118, 119]. Studies of the viscosity of the cross-linked solutions demonstrated that the impact of the *rate* of exchange (kinetics) far outweighs the strength of the M–py interaction (thermodynamics). For example, the Pd systems have essentially identical K_{eq} values, so the ground-state structures and degree of cross-linking should give isostructural polymers, but as above, the exchange rate was ~ 100 times faster for the NMe₂ complex. This difference had a dramatic effect. The viscosity of a 5% Pd(NCN)/PVP solution of the NMe₂ system was about 80 times less than the NEt₂ analog. In the case of Pt, the K_{eq} for the NMe₂ complex was double that of the NEt₂, with differences in exchange rates similar to the Pd systems, and again, the effect of the kinetics of exchange was paramount in the observed polymer properties. In addition, it was found that solvent-assisted rupture of the cross-links was most likely in operation.

The strength of the Pd–py interaction was probed mechanically by single molecule force microscopy (SMFS) [120]. Both the AMF tip and the silica surface were coated with PEG polymers incorporating terminal pyridines, see Scheme 10.38. When a bifunctional Pd(NCN) pincer was introduced in DMSO, individual bond rupture events can be observed. After a period of no appreciable load, there was a sharp increase in force at ~ 43 nm from the surface, consistent with the length of the two PEG tethers. Examination of the force vs. loading rate demonstrated that mechanical force accelerates the substitution reaction (py for DMSO) and implied that the mechanisms under stress-free and mechanically loaded conditions are very similar.

10.5.4.4 Coupling Pd and Pt(NCN) metallopincers to biological systems: synthesis of artificial metallo-bioconjugates

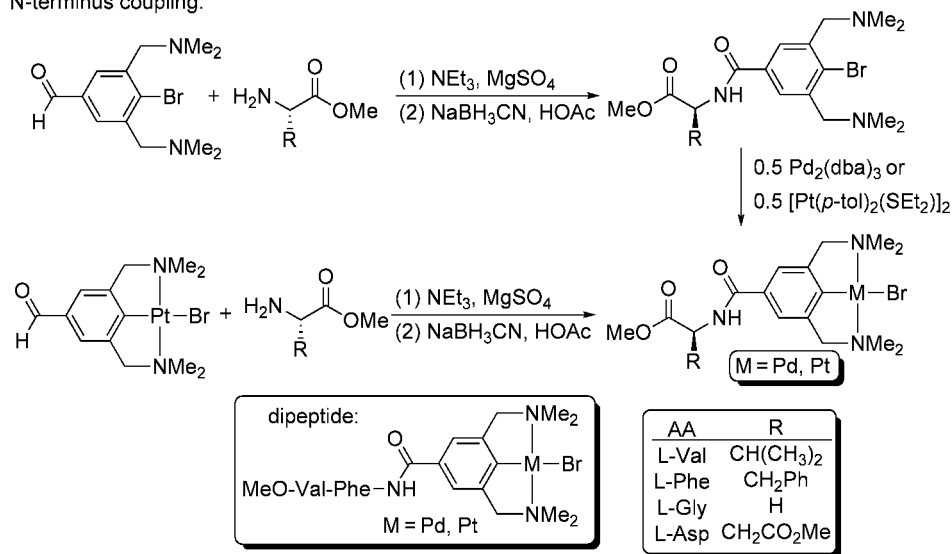
A Pt(NCN) moiety, along with Pd(SCS), has been utilized to generate metallopincer/enzyme hybrids [121]. The pincer complex was tethered to a potent inhibitor, *para*-nitrophenol phosphonate (PnP), which irreversibly binds to the active site of a variety of lipases. Here, the enzyme cutinase was coupled to the metallopincer fragments, see Scheme 10.39. Interestingly, half of the cutinase was rapidly inhibited in the 1:1 reaction, indicating that one PnP enantiomer of the racemic mixture was preferentially consumed



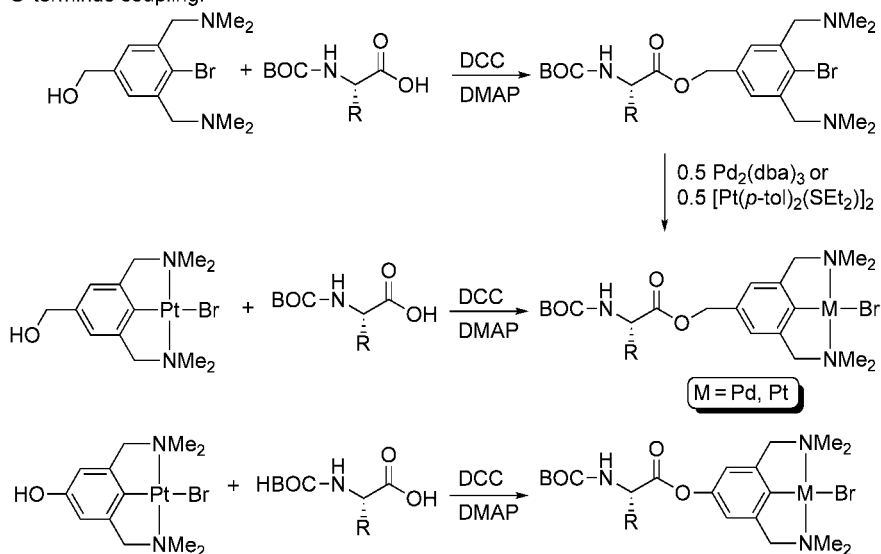
A number of methods have also been developed to couple Pd(NCN) and Pt(NCN) groups to amino acids (AAs) and to small peptides, see Scheme 10.40. Non-metalated NCN pincers could be linked to both the N- and C-termini of protected individual AAs and to dipeptides [122–124]. Linking the N-terminus was achieved by reaction of *para*-formyl NC(Br)N with C-Me-AAs followed by borohydride reduction of the resulting imine. C-terminus coupling was effected by DCC/DMAP-mediated condensation of N-BOC-AAs with *p*-(HOCH₂)–NC(Br)N. Palladation of the ligands with Pd₂(dba)₃CHCl₃ was clean and did not affect the peptide fragment. The Pd complexes were tested as aldol catalysts in the synthesis of oxazolines, but no chiral induction was observed.

Analogous chemistry can be performed to give Pt(AA-NCN)Br complexes, but here, the metal can be introduced either before or after coupling to the AA or peptide, see Scheme 10.41 [122, 123]. This flexibility in the synthesis can be beneficial as in some

N-terminus coupling:

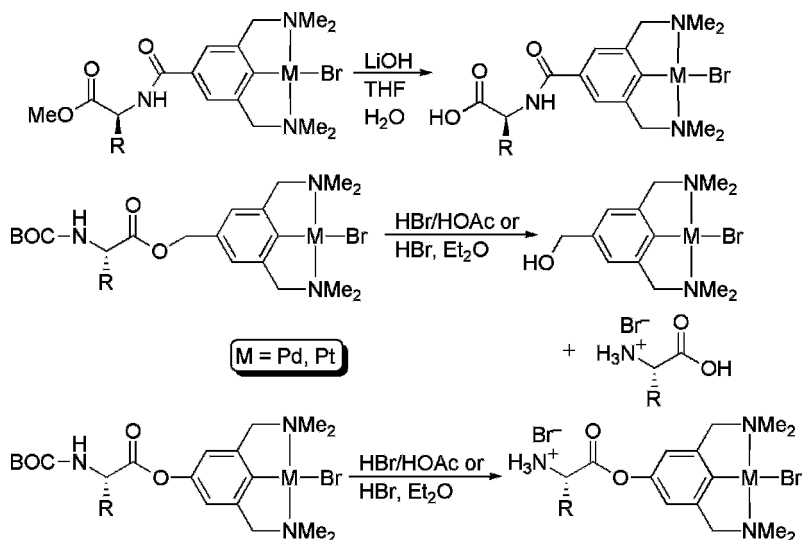


C-terminus coupling:



Scheme 10.40 Synthetic routes to N- and C-terminus-substituted AA-M(NCN)Br complexes.

instances the yield was much greater for one method over the other. For example, the synthesis of the C-terminus-labeled L-Val derivative proceeded in significantly greater yield utilizing the metalated starting material (42 vs. 6% over two steps). Attempts to deprotect the AAs met with mixed results. For the N-terminus-labeled metallopincers, the free carboxylate could be simply obtained by exposure to base (LiOH) in THF/H₂O. However, the commonly used TFA procedure for the BOC-protected (at the N-terminus) hybrids resulted in decomposition. Alternate acidic conditions with a

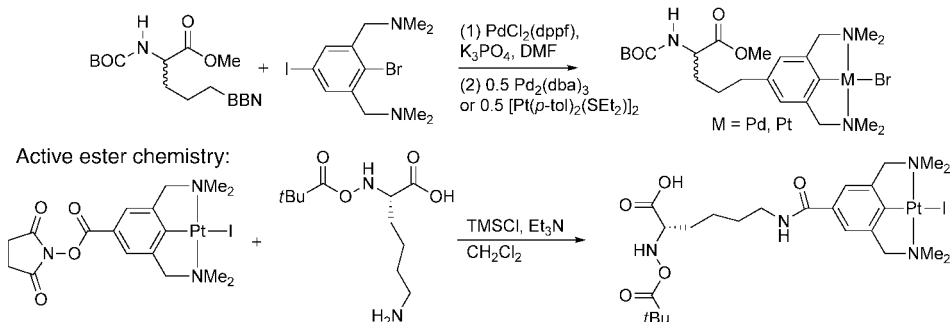


Scheme 10.41 Deprotection reactions for AA-M(NCN)Br complexes.

mixture of HBr/HOAc or HBr in Et₂O successfully removed the BOC group to give the protonated amide in the case where pincer aryl moiety was directly bound to the C-terminus carboxylate. The HBr/HOAc procedure gave only starting Pt(NCN) benzylic alcohol and the free AA.

Novel artificial AAs with Pd and Pt(NCN) groups incorporated at the α -carbon have also been generated. By far, these types of species have the most potential utility in incorporation of metallopincers into larger peptide arrays. A Pd-catalyzed Suzuki-Miyaura coupling was used to link the pincer to an AA residue, see Scheme 10.42 [123, 125]. The borylated AA was obtained by hydroboration of the vinyl compound. The deprotected free AAs were generated in a two-step procedure utilizing LiOH in THF to remove the C-terminus methoxy protecting group followed by treatment with HBr in Et₂O to detach the N-BOC functionality. Again, for the platinated derivative, the metal

Suzuki-Miyaura coupling:



Scheme 10.42 Synthetic methods for coupling M(NCN) groups to the α -carbon of AAs.

could be incorporated either before or after coupling with the AA residue. Alternately, the α -NH₂ of the BOC-protected natural AA L-lysine (as well as other primary amines) can be coupled to a Pt(NCN) pincer via an amide linkage using active ester chemistry [126]. The Pt(NCN) species are potential acid- and base-resistant biosensors, due to their reversible reaction with SO₂ gas which deeply colors the material and causes large shifts in the ¹⁹⁵Pt NMR spectrum, and biomarkers, due to the presence of the NMR active ¹⁹⁵Pt center [122]. Indeed, the Pt(NCN)I N-terminus-capped solid phase-supported peptides can be detected visually down to 6% capping by reaction with SO₂ (orange) and KI₃ (blue/black) [127].

Active ester chemistry has also been employed to attach a Pt(NCN)Cl group to a set of chemically modified mono- and di-saccharides, see Fig. 10.6, which can be used as biosensors for detection of carbohydrate-binding proteins [128]. Using surface plasmon resonance (SPR) techniques, support-bound proteins can be detected, but labeling

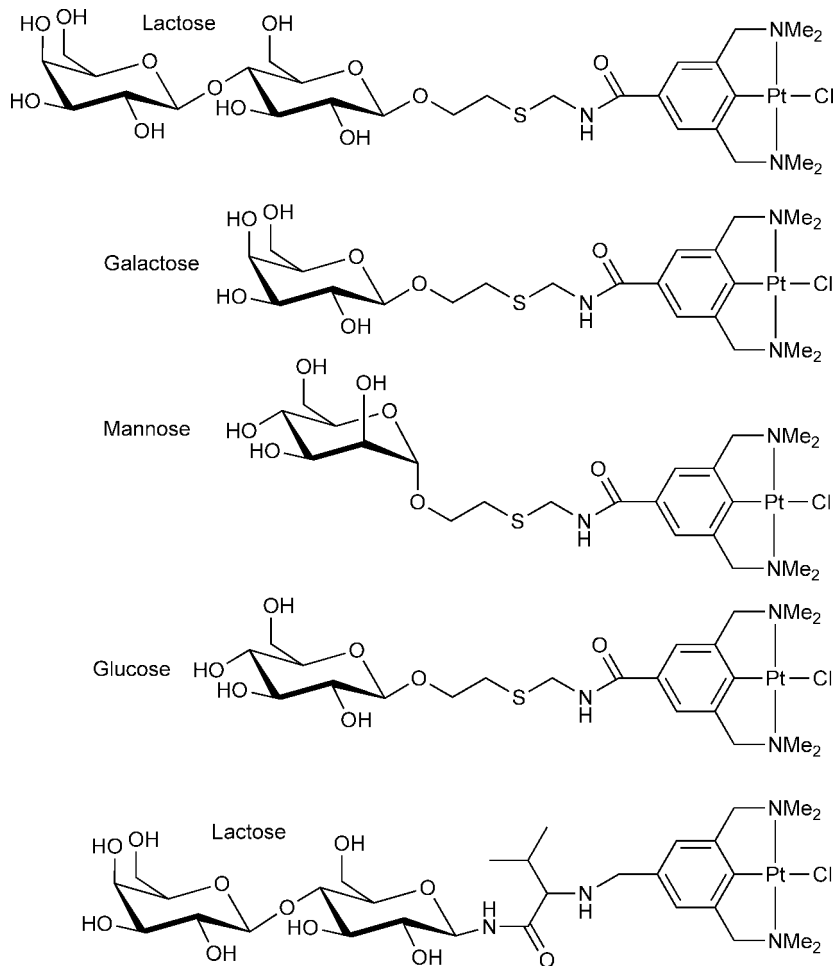


Fig. 10.6. Structures of saccharide-Pt(NCN) complexes.

procedures are usually required for low-molecular-weight oligosaccharides. Here, the incorporation of the Pt(NCN)Cl group spectacularly enhanced the SPR response, allowing for qualitative detection of surface-bound proteins RCA₁₂₀ (galactose/lactose specific) and Con A (mannose specific, weak affinity for glucose) down to saccharide–Pt pincer concentrations of 1.25 μ M. Reference experiments showed that both the saccharide and the Pt(NCN) group must be present and that there was no effect of tether length. While the enhancement effect prevented quantitative determination of concentrations and binding affinities, this method is potentially applicable to the rapid determination of binding specificities of unknown proteins, binding studies with synthetic saccharides or other small molecules and to screening of plant extracts or chemical libraries to provide bioactive hits for pharmaceutical research.

10.5.4.5 Pd and Pt: new photophysical and redox properties

The Connick group has investigated the chemistry of neutral and ionic piperidyl Pt(NCN)L (L = halide, imine, pyridyl, pyrazyl) complexes and found that they exhibited interesting luminescent attributes, see Fig. 10.7. [129–131]. The cationic complexes were generated by reaction of Ag(OTf) with Pt(NCN)(halide) in the presence of the appropriate ligand. This research demonstrated that the photophysical properties of the Pt(NCN)L group are strongly correlated to the nature of the ancillary ligand and not to the charge of the complex. The X-ray crystal structures and NMR data were typical of a terdentate NCN ligand, and for the pyridyl systems, approximately perpendicular arene and pyridyl rings are noted in the solid state. Electrochemical measurements of the pyridyl-based complexes showed primarily ligand-centered reduction processes in the available window and irreversible oxidations. In the UV–Vis spectra, MLCT bands at high energy along with low-intensity triplet MLCT and ligand field transitions dominated. For the pyridyl complexes, pyridine ligand-based π – π^* absorption bands were also present, in some cases dominating the UV portion of the spectrum. While no emission was observed in solution, all compounds were luminescent in the solid state or in glassy solutions (4:1 ethanol/methanol) at 77 K. The Cl, Br, I, imine, pyridine, 1,2-bis(4-pyridyl)ethene (bpe), and 1,2-bis(4-pyridyl)ethane (bpa) complexes all exhibited similar weak red-orange emissions, while the 4-phenylpyridine (4-ppy), 4,4'-bipyridine (bpy), and 1,4-pyrazine (pyz) complexes displayed intense yellow to yellow-green luminescence. The weak red emissions were found to originate from a spin-forbidden triplet ligand field excited state; the bpe complex also displayed a bpe $^3(\pi$ – $\pi^*)$ ligand-centered transition. By contrast, the bright yellow/yellow-green emissions were indicative of a significant change in the orbital character of the emissive state in these complexes. For the 4-ppy and bpy complexes, this was attributed to stabilization of the $^3(\pi$ – $\pi^*)$ state, whereas the pyz species exhibited emission characteristic of an MLCT transition from the dimer. Notably, the pyz complex also exhibited minor components in the absorption and emission spectra consistent with some dissociation of the ligand, likely due to steric crowding in the dimer. The absorption spectra of some Pd analogs showed a slight blue shift, in accord with replacement of the Pt [132].

Further enhancement of the luminescent properties of Pt(NCN) species was achieved by replacement of the piperidyl donors with pyridyl [133]. Here, the chloro complexes were highly luminescent (Φ = 0.58–0.68) with emission primarily from the $^3(\pi$ – $\pi^*)$ state. Also, small changes were noted in both absorption and emission maxima based

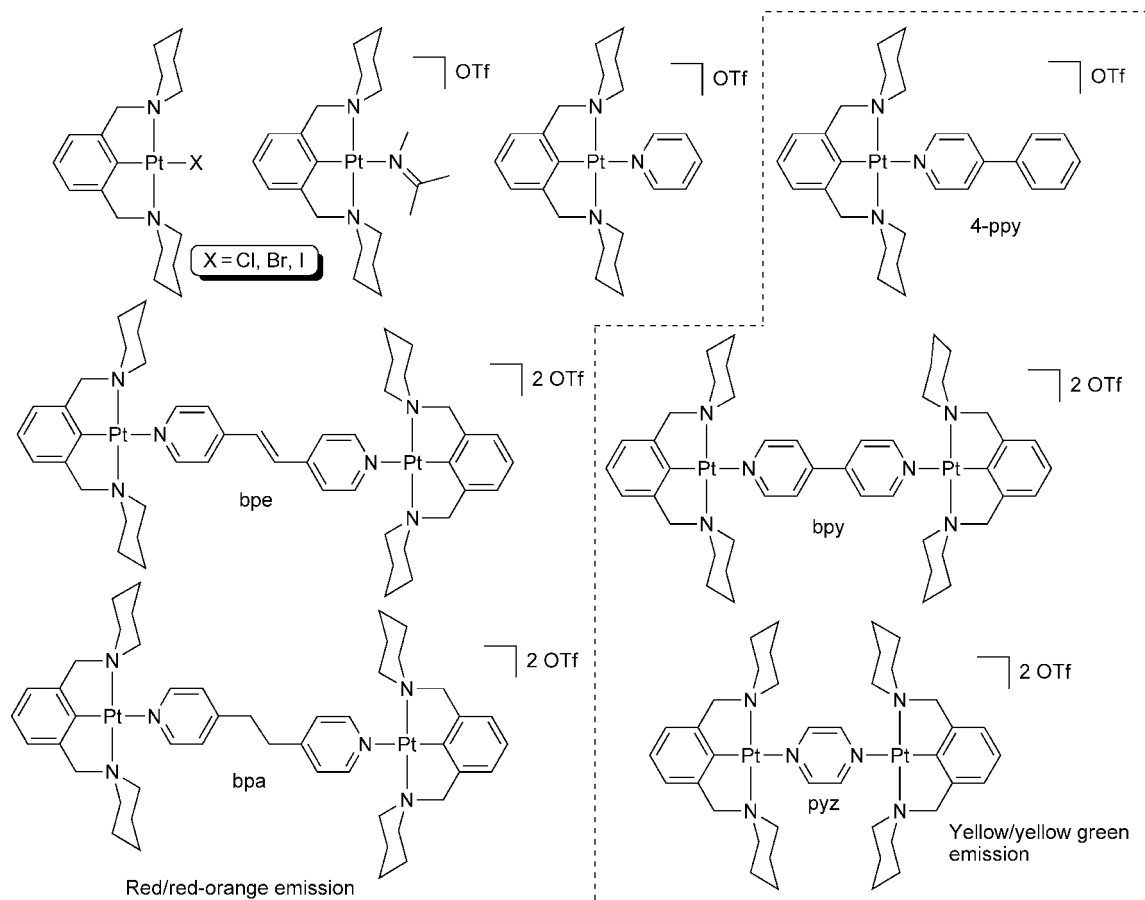
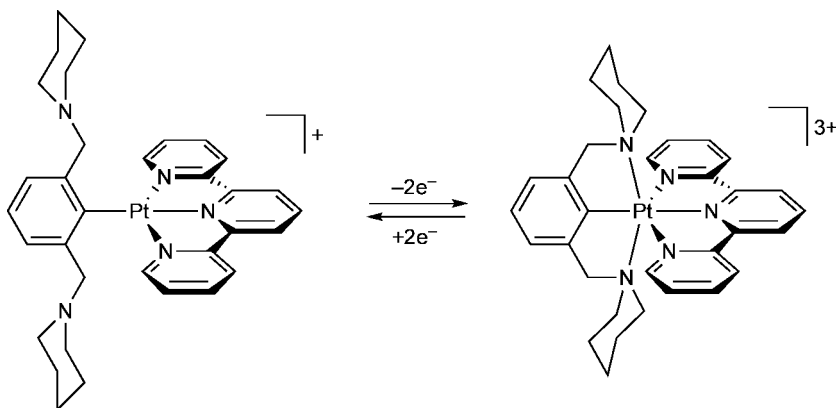


Fig. 10.7. Structures of luminescent $[\text{Pt}(\text{NCN})(\text{L})][\text{X}_n]$ complexes.

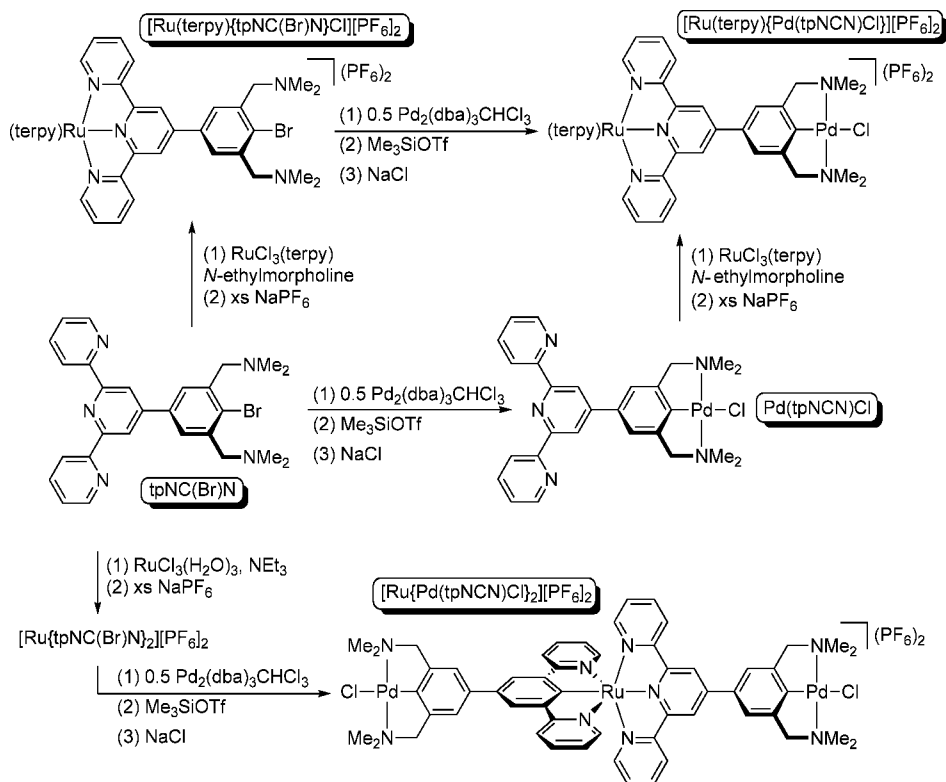


Scheme 10.43 Structural changes during redox reactions of $[\text{Pt}(\text{NCN})(\text{terpy})]^+$.

on the *para* substituents, H, Me, and CO_2Me . Also, the emissive properties of a bis(benzothiazole) $\text{Pt}(\text{NCN})$ complex have recently been reported [134].

In contrast to the typical electrochemical behavior of the $\text{Pt}^{\text{II}}(\text{NCN})(\text{pyridyl})$ monocations, the terpy analog exhibited a unique two-electron redox event [135]. In the synthesized $\text{Pt}(\text{II})(\text{NCN})(\text{terpy})$ cation, the pincer ligand was monodentate and bound only through the aryl group, see Scheme 10.43. Two separate one-electron terpy-based reversible reductions were found, but an additional two-electron oxidation wave was also found. For the oxidation reaction, there was a significant structural rearrangement in the complex, and the presence of the dangling amine arms was essential for the reversibility of the process. It also appeared that the oxidation was not concerted but rather that the second oxidation step was more favored by ligation of one or both of the amine arms during the first oxidation.

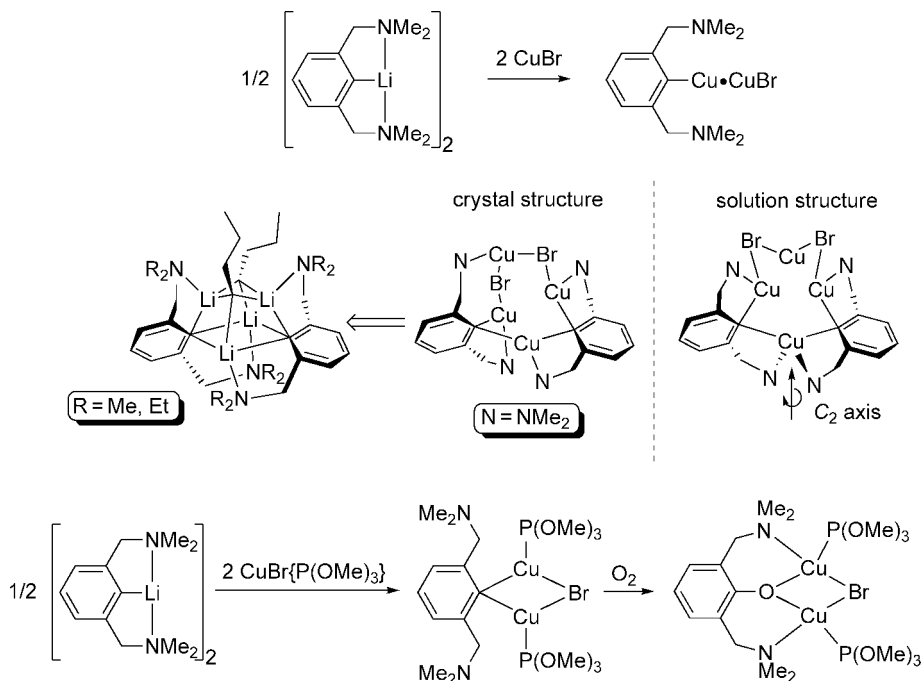
A photosensitizing $\text{Ru}(\text{terpy})_2$ moiety has been coupled to a $\text{Pd}(\text{NCN})\text{Cl}$ pincer (tpNCN), and the two metals weakly communicate electronically through the linked aryl system, despite the fairly large distance and dihedral angles between the aryl and terpy rings [136]. Again, the synthesis was modular, in that the individual metal species could be incorporated at different points in the synthetic design, see Scheme 10.44. The UV–Vis spectra were dominated by ligand-based $\pi\text{--}\pi^*$ transitions mixed with MLCT bands in the metal containing complexes. Electrochemistry showed that incorporation of the terpy pushed oxidation of the Pd center to higher potentials and that the $\text{Ru}^{\text{II}}\text{--}\text{Ru}^{\text{III}}$ redox couples were essentially invariant to the group between the pincer arms (Br or Pd). Luminescence studies from frozen matrix at 77 K showed bright red emission due to the $\text{Ru}(\text{terpy})_2$ moiety. Spectroelectrochemistry allowed for direct observation of the electronic communication between the metals by replacement of the Cl for an IR active SCN at Pd to give $[\text{Ru}(\text{terpy})\{\text{Pd}(\text{tpNCN})\text{SCN}\}]^{2+}$. Upon electrochemical reduction of the Ru center in a thin film, the $\text{C}\equiv\text{N}$ stretch shifted from 2080 to 2050 cm^{-1} , indicating higher electron density at Pd contributing to greater π -backbonding to the SCN ligand. The electronic properties, coupled with the modular synthesis and the possibility to incorporate a number of other metals, are potentially interesting for the construction of redox-active organometallic polymers.



Scheme 10.44 Synthesis of bimetallic Ru(terpy)/Pd(NCN) complexes.

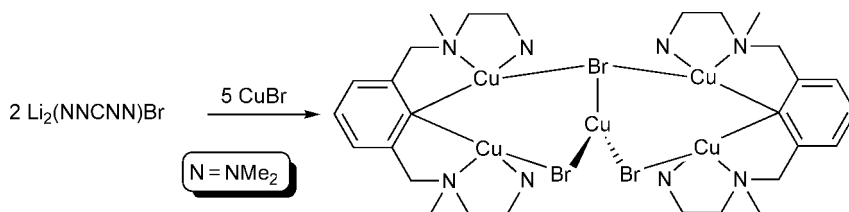
10.5.5 Group 11 (Cu–Au)

The limited number of Cu(NCN) compounds reported have been important in the determination of new bonding modes in organocopper chemistry. The reaction of 0.5 equiv. $[\text{Li}(\text{NCN})]_2$ with CuBr afforded a mixture of *ate* complexes containing both LiBr and CuBr [137]. Addition of extra CuBr gave a single product, see Scheme 10.45. Cryoscopic and crystallographic measurements revealed that this species is a dimer in both solution and solid state, see Scheme 10.45. In solution, a number of fluxional processes were present which exchange the CH_2 and NMe_2 groups, and these processes can be frozen out at 233 K to give NMR spectra that were consistent with a different connectivity and higher symmetry than what was determined in the crystal [138]. In the solid state, two 3-center 2-electron $\text{Cu}_2\text{--Ar}$ bonds were present and stabilized by Cu–N interactions. The four Cu centers formed a butterfly-type arrangement with edges associated with either Br or C_{ipso} of the pincer. This structure is closely related to that of the $[\text{Li}(\text{NCN})]_2[\text{Li}(n\text{Bu})]_2$ heteroaggregates [38], except that Cu is reluctant to participate in 4-centered 2-electron bonding. Formation of the Cu complex with base-stabilized $\text{CuBr}\{\text{P}(\text{OMe})_3\}$ gave monomeric $\text{Cu}_2(\text{NCN})\text{Br}\{\text{P}(\text{OMe})_3\}$; the ^1H NMR spectrum was consistent with dissociated NMe_2 groups. This reacted selectively with O_2 to give a unique phenoxycopper(I) complex [139].



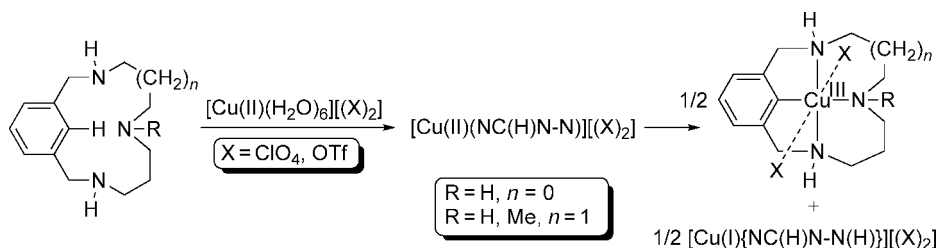
Scheme 10.45 Synthesis of $[\text{Cu}_4(\text{NCN})_2\text{Br}_2]$ and $\text{Cu}_2(\text{NCN})\text{Br}\{\text{P}(\text{Ome})_3\}$.

Incorporation of additional amine donors to give a potentially pentadentate NNCNN ligand allowed for the entrainment of additional equivalents of CuBr in the reaction with $\text{Li}_2(\text{NNCNN})\text{Br}$, which is also a rare example of a monomeric organolithium/lithium halide *ate* complex. The structure of dimeric $[\text{Cu}_5(\text{NNCNN})_2\text{Br}_3]$ formally contained two $[\text{Cu}_2(\text{NNCNN})]^+$ cations bridged by a $[\text{CuBr}_3]^{2-}$ dianion, see Scheme 10.46 [140]. Solution NMR measurements were also consistent with this formulation and that dynamic processes were operative.



Scheme 10.46 Formation of $[\text{Cu}_5(\text{NNCNN})_2\text{Br}_3]$.

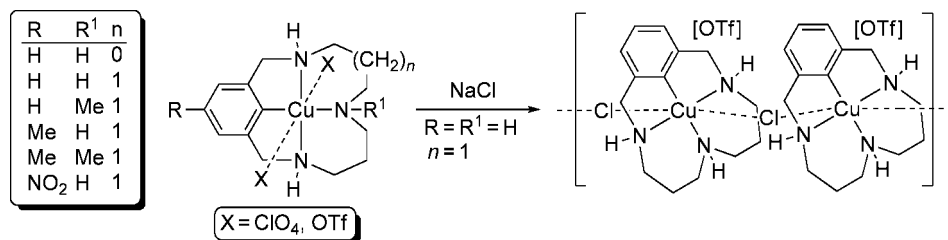
Copper complexes have also been synthesized that incorporate triazamacrocyclic pincer-type ligands $(\text{NC}(\text{H})\text{N}-\text{N})$ [141]. The ligand framework enabled C–H activation with $[\text{Cu}(\text{II})(\text{H}_2\text{O})_6][\text{X}]_2$ ($\text{X} = \text{ClO}_4$, OTf) via a disproportionation mechanism, see Scheme 10.47. Initial complexation gave the paramagnetic species $[\text{Cu}(\text{NC}(\text{H})\text{N}-\text{N})][\text{X}]_2$,



Scheme 10.47 Reaction of Cu(II)(NCN-N) complexes via C–H activation and valence disproportionation.

which then disproportionated to Cu(III)(NCN-N)X₂ and [Cu(I){NC(H)-N(H)}]₂[X]₂. The X-ray crystallography, NMR data and Cu K-edge X-ray absorption spectroscopy confirmed tetradentate bonding of NCN-N ligand and the Cu^{III} oxidation state. From the crystal structures of Cu(III)(NCN-N)(ClO₄)₂, the ligand encircled the Cu center in the equatorial plane of an octahedron; the axial sites were filled with weak Cu–O interactions to the ClO₄ counter anions. Mechanistically, fast electron transfer between the two Cu(II) centers was coupled with base-assisted deprotonation. The participation of the amine base was confirmed by rate acceleration in the presence of a slight excess of free NC(H)N-N ligand and the reaction was inhibited by excess Cu(II). Also, the larger, more flexible ligands reacted about 10× faster. The unique C–H activation step was rate determining as a large kinetic isotope effect (KIE) was noted with the NC(D)N-N isotopomer.

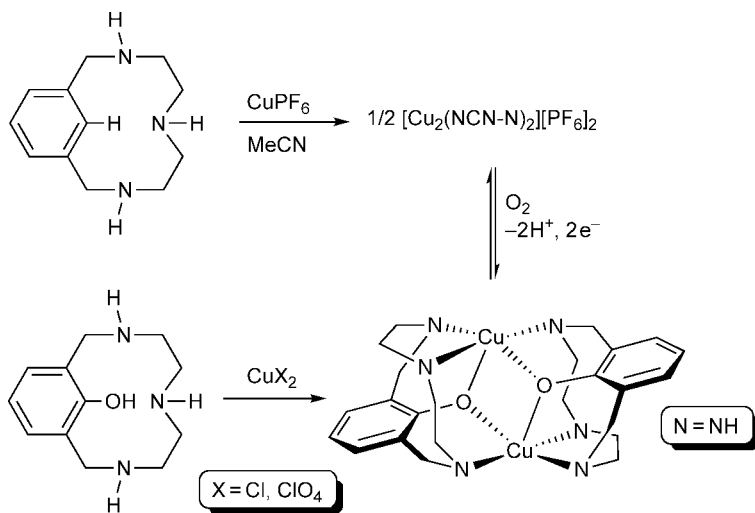
The range of Cu(III) NCN-N complexes was also expanded to include different groups in the position *para* to the Cu on the aromatic ring to investigate electronic and steric effects, see Scheme 10.48 [142]. The Cu(III) and Cu(I) complexes were efficiently separated by crystallization and the Cu(III)(NCN-N)X₂ species were all stable in acidic, pH 1–7, or protic solvents (MeOH) and in oxygenated MeCN or CH₂Cl₂ except for the NO₂-substituted system, which decomposed at room temperature. In the crystal, the Cu centers were in distorted octahedral environments with unequal Cu–O contacts; the long bond was always found on the side of the N–H or N–Me groups. Replacement of one OTf with Cl[–] gave a polymeric structure with bridging Cl[–] atoms and the same unequal Cu–Cl bond lengths. The effects of the substitution patterns on the UV–Vis and electrochemistry were studied. For the UV–Vis, a broad absorption between 370 and 520 nm was found, and both N-methylation and the nature of the *para*



Scheme 10.48 Structures of substituted [Cu(III)(NCN-N)][X]₂ complexes.

substituent affected the position and nature of the band. Time-dependent DFT (TD-DFT) calculations reveal that this was comprised of two LMCT $\pi-d_{x^2-y^2}$ transitions. As such, incorporating electron-withdrawing groups (NO_2) on the arene blue shifted the transition by stabilizing the occupied π orbitals, while electron releasing groups red-shift the absorption. N-methylation also red-shifted this band compared to the N-H complex due to stabilization of the LUMO. Similarly, the NO_2 group gave a cathodic shift of Cu(III)/Cu(II) redox potential due to destabilization of the Cu(III) oxidation state. Here, N-methylation also destabilized Cu(III) as tertiary amines are poorer donors than secondary.

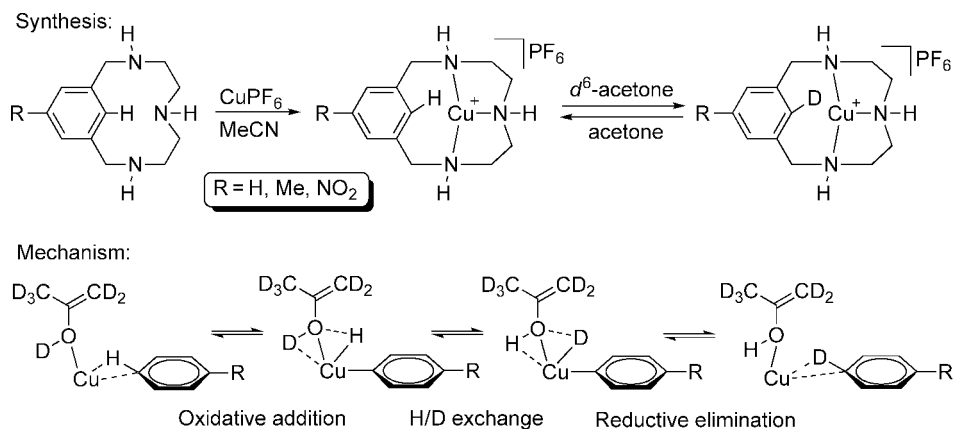
An interesting analogy to biological aromatic hydroxylation by Cu-containing enzymatic catalyst tyrosinase can be found in the reaction of Cu(III) complexes with OH^- or Cu(I) species with O_2 , see Scheme 10.49 [141, 143]. Both gave the same Cu(II) phenoxymacrocylic product and proceeded through the identical Cu(III) intermediates. Also, reaction of the pre-hydroxylated ligand with Cu(II) Cl_2 or Cu(II)(ClO_4) $_2$ directly generated this complex, and the Cu(I) dimer was obtained in one step by reaction of the NC(H)N-N arene with Cu(I)PF $_6$ [143]. The structure of the hydroxylated species was dimeric, with a Cu_2O_2 core bridging two of the macrocyclic ligands and each Cu was in a distorted square pyramidal arrangement. The necessary C-H activation step from the Cu(I) complex is contrary to the generally accepted mechanism of enzymatic action but no data preclude it, giving insight into a possible alternate pathway.



Scheme 10.49 Synthesis of $[\text{Cu}(\text{NC}(\text{O})\text{N}-\text{N})]_2$.

Para-functionalization of the arene ring also impacted the rate of reaction of a novel Cu(I)-mediated H/D exchange on the arene ring itself [144]. Reaction of the Cu(I) complexes in deuterated acetone selectively deuterated the intra-annular C-H bond. The proteo complex was regenerated by reaction with normal acetone. Notably, deuterated $\text{d}^3\text{-MeCN}$ or CD_2Cl_2 did not act as a viable deuterium source. Kinetically, the reaction

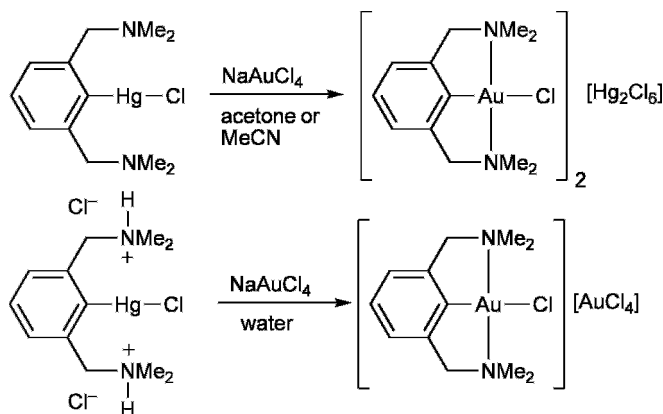
was first order in both acetone and Cu complex and the $-H-$ or $-Me-$ substituted systems reacted about $100\times$ faster than the $-NO_2$ complex. KIEs were also very different depending on the *para* substituent, large and primary for the NO_2 system ($KIE = 6.1$) and small and inverse for H and Me, ($KIE = 0.88$ and 0.81 , respectively), demonstrating a change in the rate-determining step (rds) dependant on the nature of the *para* group. The proposed mechanism is depicted in Scheme 10.50 and accounts for these observations. Initially, the enol form of acetone was coordinated to the Cu center, and oxidative addition of the arene to give a $Cu(III)-H$ took place. The calculated structure with acetone contained a pronounced arene $C-H$ agostic interaction with the Cu center, primed for oxidative addition. There was then H/D exchange in the enol and Cu followed by reductive elimination to give the deuterated product. To account for the KIEs, the strongly electron-withdrawing NO_2 group was proposed to destabilize the $Cu(III)$ oxidation state so that the rds for this complex was the oxidative addition of aryl $C-H(D)$ bond, consistent with the large primary KIE. As the $Cu(I)$ to $Cu(III)$ step was more facile for the H and Me substituted complexes, the rds is shifted to the H/D exchange in the coordinated enolate and was in line with a secondary inverse KIE. This was the first example of H/D exchange promoted by $Cu(I)$. Also, the orientation of the groups and nature of the N substituents were crucial for the observed reactivity.



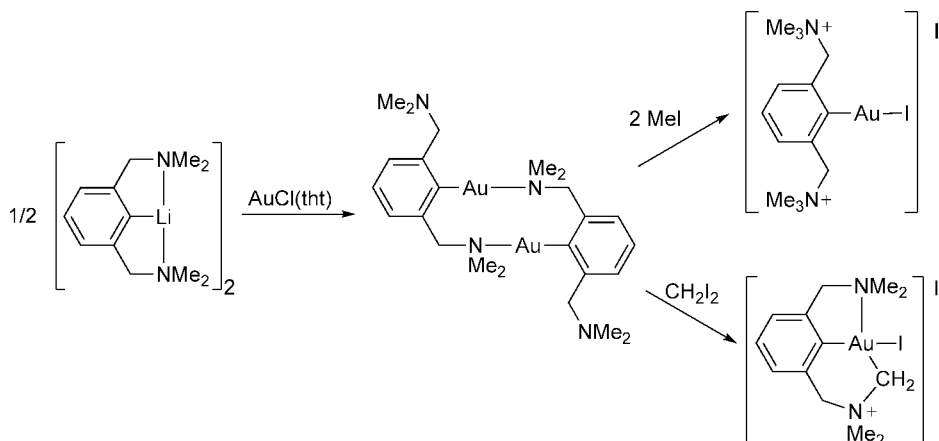
Scheme 10.50 Synthesis of $[Cu(NC(H)N-N)][PF_6]$ and mechanism of H/D exchange.

Parish and coworkers furnished the first example of a $Au(NCN)$ system [145]. The $[Au(III)(NCN)Cl]^+$ cation was synthesized as both its $[Hg_2Cl_6]^{2-}$ and $[AuCl_4]^-$ salts by transmetalation with $Hg(NCN)$ complexes, see Scheme 10.51. X-ray crystallographic analysis of the $[Hg_2Cl_6]^{2-}$ salt and NMR data showed terdentate binding of the NCN ligand and a square planar $Au(III)$ center.

A number of $Au(I)NCN$ species have also been prepared via reaction of 0.5 equiv. $[Li(NCN)]_2$ with $AuCl(L)$ ($L =$ tetrahydrothiophene (tht), PPh_3). In the case of tht, this weakly bound co-ligand was displaced to give the extremely light and thermally sensitive $[Au(NCN)]_2$ dimer exhibiting intermolecular $Au(I)-N$ bonding, deduced by LT NMR experiments, see Scheme 10.52 [146]. The dimer was shown to undergo



Scheme 10.51 Synthesis of $[\text{Au}(\text{NCN})\text{Cl}]^+$ cations.

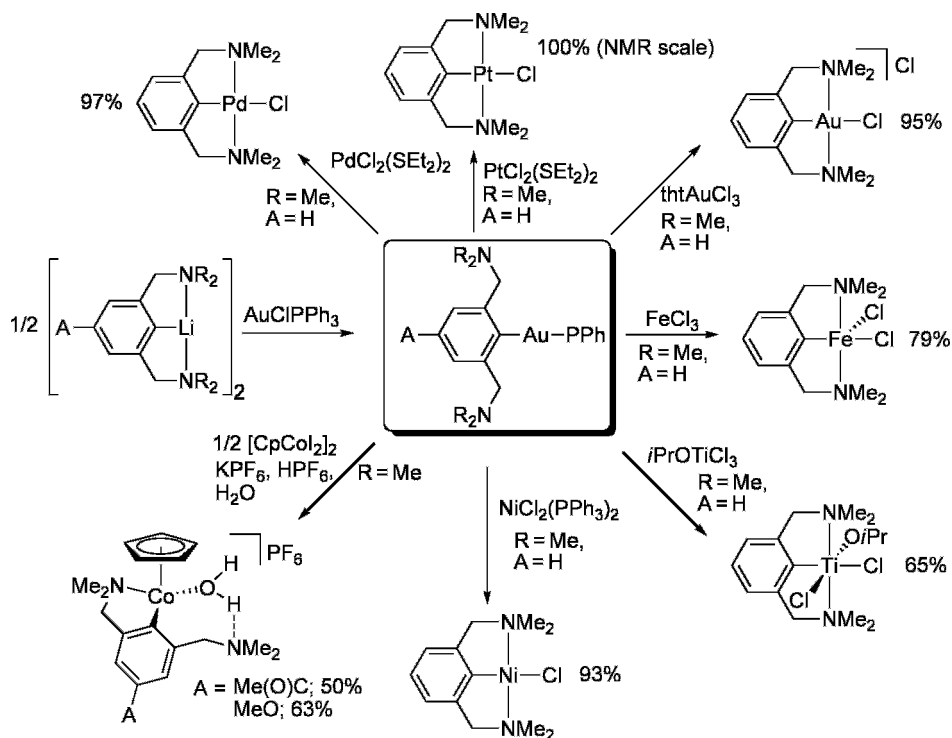


Scheme 10.52 Synthesis and reactivity of $[\text{Au}(\text{NCN})]_2$.

reactions with MeI and CH_2I_2 . In the case of MeI , a $[\text{Au}(\text{NCN})(\text{Me}_2)\text{I}][\text{I}]$ complex was obtained and both NMe_2 groups have been methylated. Conversely, the oxidative addition product with CH_2I_2 incorporated one five-membered ring with an $\text{Au}(\text{III})-\text{N}$ interaction and a six-membered ring in which the methylene was found bound to both Au and NMe_2 to give an $\text{Au}-\text{CH}_2-\text{N}^+\text{Me}_2$ link. For both species, oxidative addition of a $\text{C}-\text{I}$ bond was proposed to be the key for the formation of the observed species.

Monomeric air- and light-stable $\text{Au}(\text{I})$ species were obtained when AuClPPh_3 was utilized as the starting Au source [40]. The monomeric $\text{Au}(\text{NCN})\text{PPh}_3$ complexes exhibit no inter- or intramolecular $\text{Au}-\text{N}$ bonding and the $\text{C}_{\text{ipso}}-\text{Au}-\text{P}$ angle is essentially linear. Owing to the isolobal relation between $\text{Au}(\text{I})\text{L}$ and $\text{Li}(\text{I})$, these organogold complexes

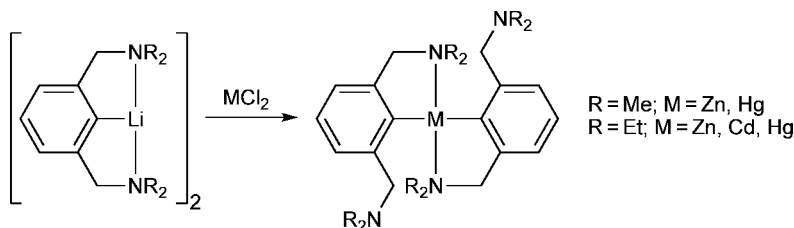
were found to be efficient-arylation reagents in the same vein as the organolithium species [40, 69]. Potential benefits are the air and moisture stability of $\text{Au}(\text{NCN})\text{PPh}_3$, allowing for small-scale synthesis, the stability of the Au(I) oxidation state which prevents unwanted redox reactions and that the $\text{AuCl}(\text{PR}_3)$ by-product can be recycled. Also, organogold(I) species are not especially toxic, as opposed to commonly employed alternative Hg, Tl, and Sn alkylation and arylation reagents. Scheme 10.53 shows that a large range of transition metal complexes (Ti, Fe, Co [69], Pd, Pt, Au(III)) can be efficiently synthesized, mirroring $[\text{Li}(\text{NCN})]_2$. The recycling of the $\text{AuCl}(\text{PR}_3)$ synthon can be enhanced by incorporation of multidentate phosphines, such as 1,4- $(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{C}_6\text{H}_4(\text{PPh}_2)\text{-4'}$ or 1,3,5- $(\text{Ph}_2\text{P})_3\text{C}_6\text{H}_3$ [41].



Scheme 10.53 Synthesis and arylation chemistry of $\text{Au}(\text{NCN})\text{PPh}_3$.

10.5.6 Group 12 (Zn–Hg)

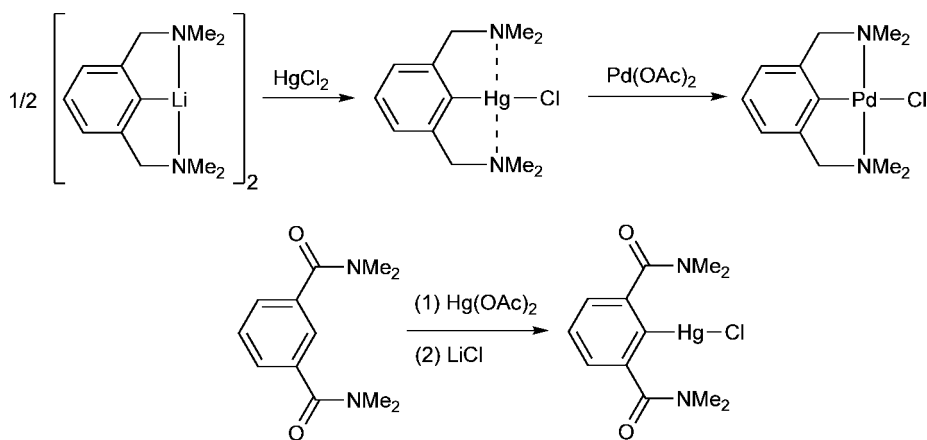
A series of diaryl Zn, Cd, and $\text{Hg}(\text{NCN})_2$ complexes have been synthesized and studied by NMR spectroscopy and mass spectrometry, see Scheme 10.54 [147]. Again, $[\text{Li}(\text{NCN})]_2$ was utilized in the synthesis of all of these species. Based on studies of NC-complexes, there should be two weak M–N bonds, but all of species exhibited room temperature NMR spectra where either no M–N interactions were



Scheme 10.54 Synthesis of $M(\text{NCN})_2$ ($M = \text{Zn}, \text{Cd}, \text{Hg}$) complexes.

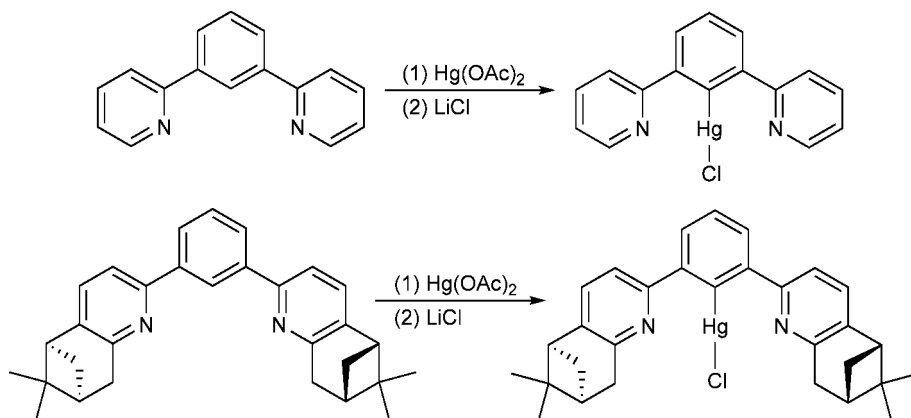
present or, more likely, the complexes were in the fast exchange regime. The $\text{Zn}(\text{NCN})_2$ compound was employed for synthesis of a tungsten species [43], see Section 10.3.3.

A monoaryl $\text{Hg}(\text{NCN})\text{Cl}$ species was also synthesized by reaction of $[\text{Li}(\text{NCN})]_2$ with HgCl_2 in a 1:2 stoichiometry, see Scheme 10.55 [148]. Transmetalation with $\text{Rh}(\text{NCN})(\text{COD})$ was also claimed to give the same product [72]. This reacted with $\text{Pd}(\text{OAc})_2$ to exchange the NCN ligand to Pd. Related amide-based NCN pincers have also been employed, and the Hg complex was directly obtained via C–H activation with $\text{Hg}(\text{OAc})_2$ [149]. Here, the NMR and IR data indicated that the Hg center was two-coordinate and there was no interaction with either the O or N donors.



Scheme 10.55 Synthesis and reactivity of various $\text{Hg}(\text{NCN})\text{Cl}$ complexes.

Only two well-characterized pyridyl-based $\text{Hg}(\text{NCN})$ complexes have been synthesized to date. An achiral [150] and a chiral [151] $\text{Hg}(\text{NCN})\text{Cl}$ complex were generated via C–H activation by reaction with $\text{Hg}(\text{OAc})_2$ followed by treatment with LiCl , see Scheme 10.56. The geometry about the Hg center in the X-ray crystal structures of the achiral species was linear with no Hg–N interactions. Like the amine systems, these mercury complexes were employed to selectively generate difficult-to-synthesize $\text{Pd}(\text{II})$ and $\text{Pt}(\text{II})(\text{NCN})$ species by transmetalation.



Scheme 10.56 Synthesis of $\text{Hg}(\text{NCN})\text{Cl}$.

10.6 CONCLUSIONS

Arguably, the NCN motif is the most versatile of the pincer ligands as complexes with almost all transition metals have been generated and also demonstrate the largest variety of binding modes and geometries. On this tour through the periodic table, it was shown that metalated NCN pincers have wide applications in catalysis and mechanistic studies, in the preparation of functional materials and sensors, and in the discovery of new reactivity. The stabilization of unusual metal oxidation states, geometries, and coordination numbers has also been observed. In addition to this expansive transition metal chemistry, NCN-ligated main group complexes have a rich history as well [2, 15]. Continued efforts in these areas utilizing NCN-type and other pincer ligands will surely add new and exciting facets to this already impressive array of complexes, reactions, and applications.

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S–P–S and S–C–S pincer ligands in coordination chemistry and catalysis

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11.1 INTRODUCTION

After seminal report by Shaw in the 1970s, the chemistry of pincer ligands has evolved to maturity. The structures that have been studied early on, $[2,6-(LCH_2)_2C_6H_3]^-$ (LCL), where L is a two-electron donor and C is an anionic aryl carbon atom, have allowed to uncover the peculiarities of these tridentate ligands. Of these, NCN, PCP and S–C–S have then found numerous uses. The first two types will be covered in other reviews whereas we will cover the literature related to the ligands which bear S atoms as pendant arms. These include both thioether (**C**), thioketone (**E**) derivatives and phosphino-sulfide (**F**) derivatives. The basic principles that make these ligands highly attractive have been applied lately to other anionic or dianionic ligands: S–C–S[−] (**G**) and S–C–S^{2−} (**H**), where C is an alkyl, and S–P–S (**B**) and S–P–S[−] (**A**). The chemistry pertaining to these species will also be presented here. Additionally, we have included a related Se~C~Se (**D**) pincer ligand because of its very recent and significant use in catalytic processes.

The structures that will be discussed are summarized in Chart 11.1.

For these pincer ligands, the syntheses of the complexes will be presented followed by the different areas they have been involved in (coordination chemistry, supramolecular chemistry, catalysis, etc.).

In a 2001 review dealing with pincer ligands, Albrecht and van Koten presented the chemistry pertaining to the monoanion bis-thioether (**C**) derivatives [1].

11.2 S–P–S PINCER LIGANDS

11.2.1 Bis(phosphinosulfide)phosphinines

11.2.1.1 Synthesis and electronic properties of ligands

The chemistry of bis(phosphinosulfides)phosphinines is based upon studies on the reactivity of λ^3 -phosphinines [2]. These heterocycles which are the phosphorus analogues of pyridines display unusual electronic properties which mainly result from the replacement

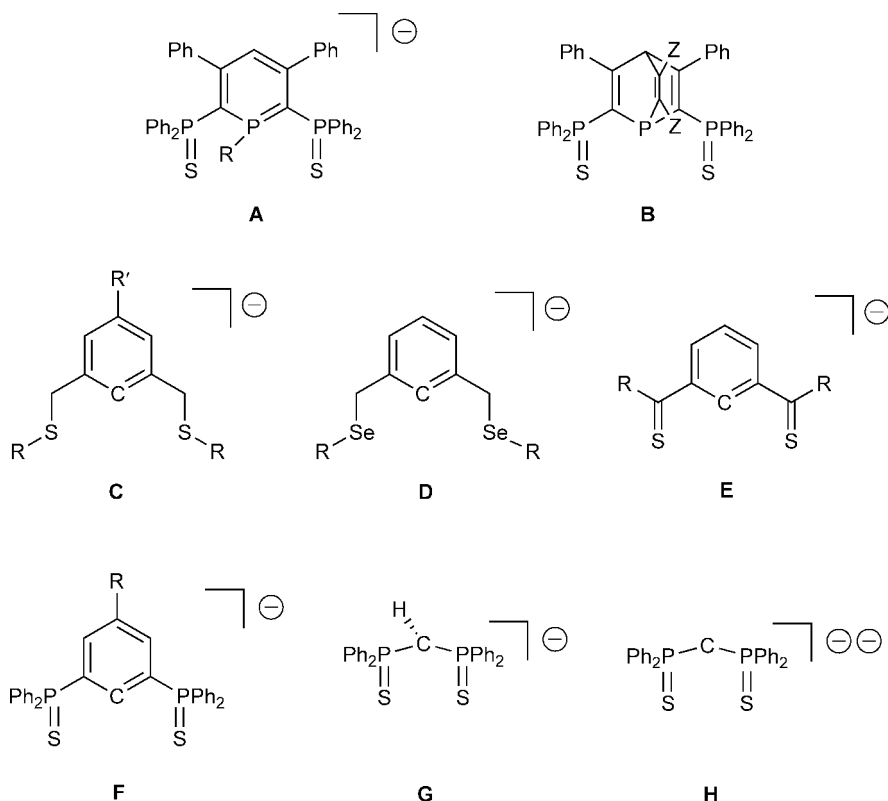
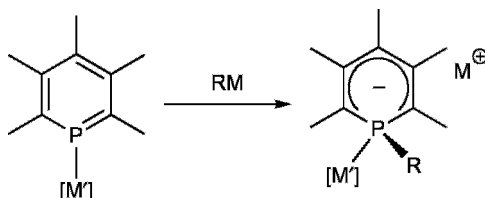


Chart 11.1

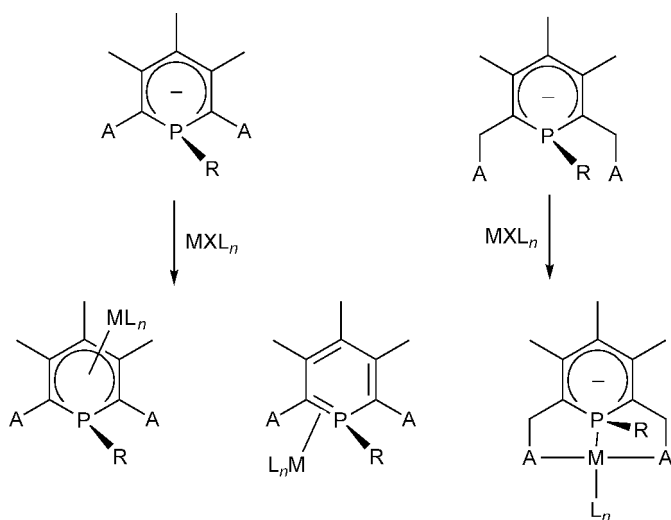
of nitrogen by phosphorus. Thus whereas pyridines show a significant negative charge at nitrogen, phosphinines exhibit the opposite charge distribution because of the lower electronegativity of phosphorus (2.1 for P versus 3.0 for N according to the Pauling scale). This unusual charge distribution and the presence of a low-lying π^* -system make these heterocycles particularly interesting for the stabilization of electron-rich or electron-excessive metal centers (poor σ -donor but strong π -acceptor ligands) contrary to pyridine ligands which behave as strong σ -donor but only moderate π -acceptor ligands [3–5]. These peculiar electronic properties have been widely exploited in the synthesis of low-valent transition metal complexes with early and late transition metals. Another important consequence of this particular electronic distribution concerns their reactivity toward nucleophiles. Whereas nucleophiles tend to react on the α -carbon atom in pyridines, they react at the electrophilic phosphorus atom of phosphinines to form λ^4 -phosphacyclohexadienyl anions which do not exhibit aromatic properties (Scheme 11.1). This nucleophilic attack occurs on free ligands as well as on their complexes with transition metals. This cumbersome reactivity has hampered the use of phosphinine as ligands in homogeneous catalysis as the aromatic character of the ring may be disrupted [6]. As a consequence, only a few applications of phosphinines in catalysis have been reported so far.

However, the reactivity of nucleophiles at the phosphorus atom furnishes a straightforward entry in the chemistry of λ^4 -phosphacyclohexadienyl anions which display an



Scheme 11.1

interesting coordination chemistry. Recent studies have shown that these ligands can behave either as two or six-electron donor ligands depending on the substitution scheme of the ring and the nature of the metal fragment MXL_n (Scheme 11.2). Thus, when no ancillary ligands are present at the alpha position to phosphorus, coordination through the ring is observed to form η^5 -phosphacyclohexadienyl complexes. Fe(II) [7] and Rh(I) complexes have been structurally characterized. Note that a neutral π -Rh(COD) complex featuring one of these phosphacyclohexadienyl ligands was shown to be a remarkable olefin hydroformylation catalyst [8]. When the metallic fragment cannot accommodate π -coordination, the formation of η^2 -coordinated complexes is observed. An example was provided with the synthesis of a $[PtCl(PPh_3)(\eta^1\text{-phosphacyclohexadienyl})]$ complex [9]. Finally, when ligating groups such as phosphinosulfides are present at the periphery of the ring, the ligand behaves as a 6e donor tridentate pincer ligand, σ coordination occurring through the phosphorus and the two sulfur atoms [10]. These six-electron ligands are thus relevant to this review.



Scheme 11.2

The preference for σ coordination has been rationalized by DFT calculations. In phosphacyclohexadienyl ligands, the HOMO describes the π -system of the ring and the lone pair at phosphorus lies lower in energy (HOMO-1). When ancillary ligands bearing

lone pairs are present at the periphery of the phosphorus atom lone pair, a through space 4e-destabilizing interaction occurs and the lone pair at phosphorus raises in energy. In such anionic tridentate ligand it has been showed that the HOMO results from the antibonding combination of the lone pair at phosphorus and two lone pairs at the sulfur atoms (Chart 11.2) [11].

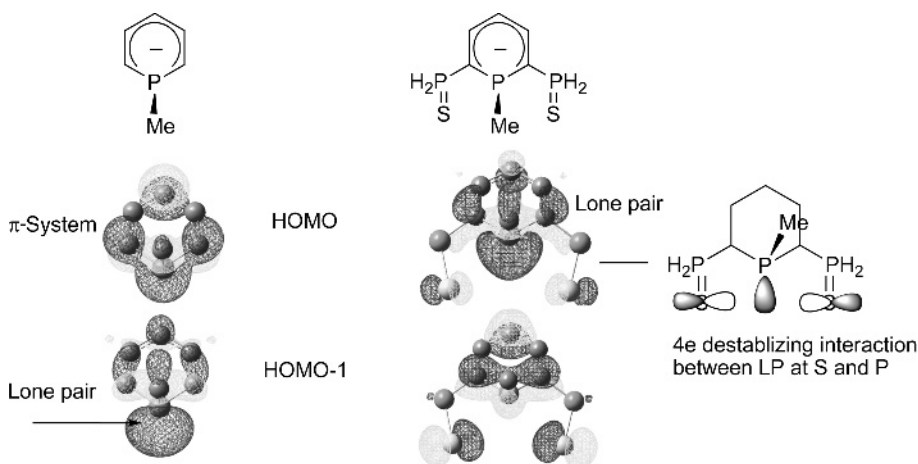
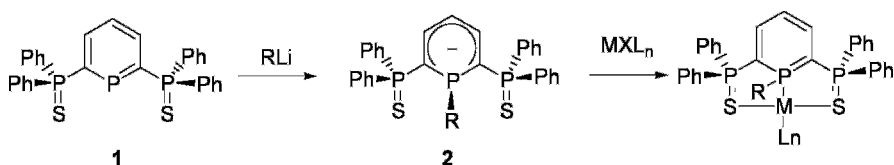


Chart 11.2

In practice, the synthesis of complexes with these tridentate-based ligands is easily achieved by the reaction of a lithium derivative with a 2,6-(diphenyl phosphino) phosphinine (**1**) to form anion (**2**) which can be subsequently trapped with a transition metal fragment (Scheme 11.3).



Scheme 11.3

Very different types of organometallic derivatives were used (Li, Na, K) and some of these anionic ligands were structurally characterized. Diverse R groups such as alkyl, aryl or benzyls groups, alcoxides, amides or alkynes were employed. Some of these anionic derivatives are presented in Chart 11.3 [12].

Apart from the above-mentioned method, other synthetic approaches were also developed especially in the synthesis of Pd(II) complexes. Thus it was shown that the reaction of the phosphinine ligand **1** with $[\text{Pd}(\text{COD})\text{Cl}_2]$ affords complex **4** which results from the attack of one chloride ligand on the phosphorus atom (Scheme 11.4). Dihydrophosphinine

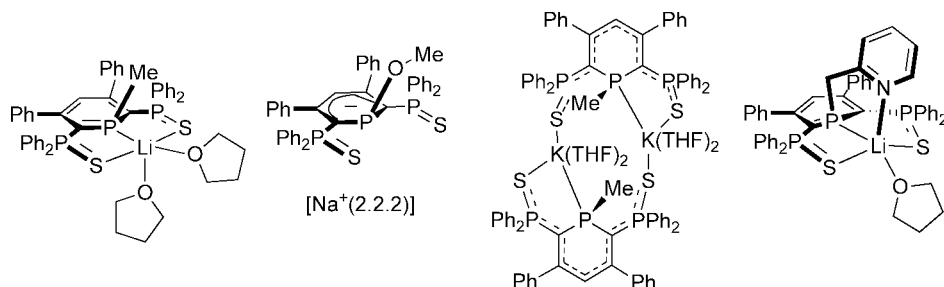
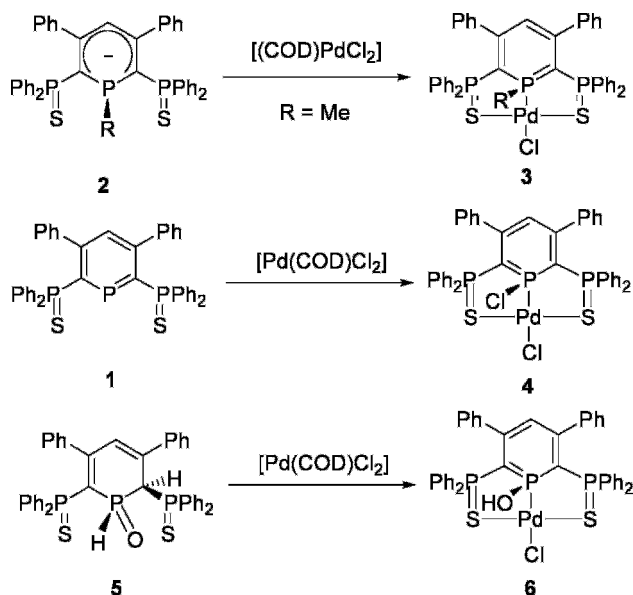


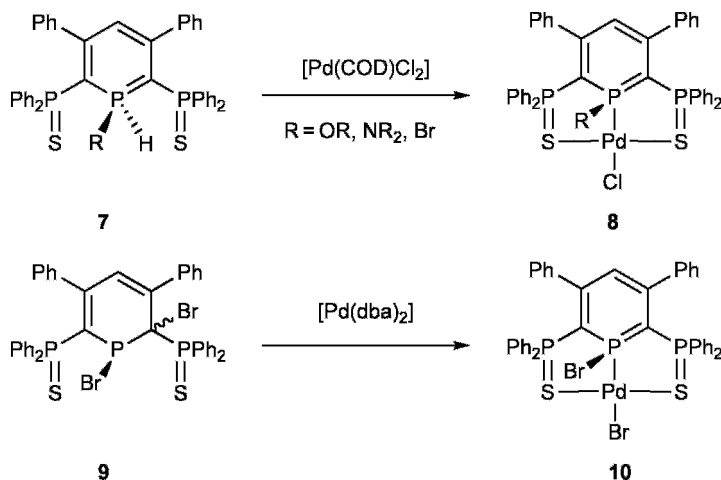
Chart 11.3

oxides such as **5** also behave as a convenient source of P–OH complexes (**6**). Though no mechanistic study were undertaken it is believed that this transformation is promoted by a $\text{P}(=\text{O})\text{H} \rightarrow \text{P}-\text{OH}$ isomerization. Tetracoordinated P–H λ^5 -phosphanines such as **7** were also used as precursors to yield complexes **8** (Scheme 11.5). These reactions very likely proceed through the insertion of the metallic fragment in the P–H bond. Finally, 1,2-dihydrophosphanines (**9**) featuring a P–Br functionality could also be used as a source of Pd–Br complexes (**10**) upon reaction with a source of zero-valent palladium ($[\text{Pd}(\text{dba})_2]$) [11].

The electronic structure of these palladium(II) complexes has been discussed on the basis of DFT calculations. Two forms for the ligand can be proposed (Chart 11.4). In the first form **2A**, the ligand behaves as an anionic L_2X ligand, four electrons being given by the two lone pairs at sulfur and two electrons by the phosphorus ring which is considered as an anionic λ^4 -phosphanine ligand. In the second form **2B**, the charge resides on the



Scheme 11.4



Scheme 11.5

carbocyclic part of the ring and the coordination occurs through the phosphorus atom lone pair. A charge decomposition analysis (CDA) and a NBO analysis were carried out on different model complexes. Though the charge analysis reveals a strong similarity between the charge distribution in complexes and λ^4 -phosphinine ligands, results of CDA calculations suggest that a dative bonding occurs between the phosphorus atom and palladium and therefore that form **2B** is probably preponderant.

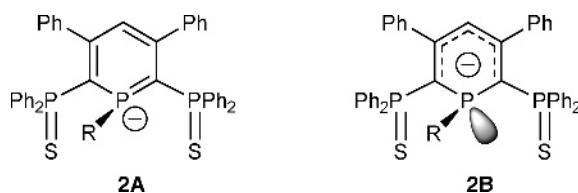
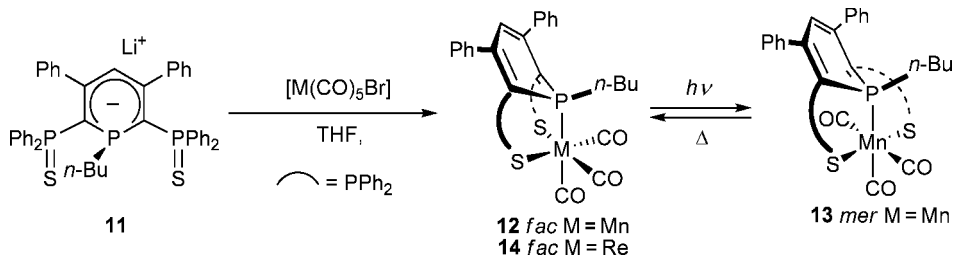


Chart 11.4

11.2.1.2 Coordination chemistry of bis(phosphinosulfide)phosphinines

Numerous complexes were synthesized. In this subchapter for the sake of clarity, only the most significant results and applications will be presented. So far no complexes of early transition metals have been prepared (groups 3–6). Manganese(I) and rhenium(I) carbonyl derivatives of the bis(phosphinosulfide)phosphinines were conventionally obtained by the reaction of the corresponding anions (**11**) with the pentacarbonyl complexes $\text{M}(\text{CO})_5\text{Br}$ ($\text{M} = \text{Mn}, \text{Re}$). In both cases, the *fac* complexes were obtained (**12** and **14**, respectively) (Scheme 11.6). The Mn complex exhibits interesting photochemical properties. Indeed, under irradiation a *fac* ($\lambda_{\text{max}} = 470 \text{ nm}$) to *mer* ($\lambda_{\text{max}} = 4500 \text{ nm}$) conversion is observed and complex **13** was found to be sufficiently thermally stable to be structurally characterized. Back conversion to **12** occurs in 8 h in the dark. The

lifetime of **13** proves to be remarkable with regards to *mer*-[MnX(CO)₃(α -diimine)] (X = halogen) complexes (a few seconds in most cases) [13].



Scheme 11.6

Interestingly, theoretical studies indicate that frontier orbitals of *fac* and *mer* complexes are localized on the S–P–S ligand. Electrochemical studies revealed that both oxidized ($E_{1/2} = +0.34$ V versus Fc/Fc⁺) and reduced forms ($E_{1/2} = -2.34$ V versus Fc/Fc⁺) of complex **12** are stable within the voltammetry time scale. The presence of the odd electron on the ligand in the reduced form of **12** has also been evidenced by EPR spectroscopy. On the contrary, the Re complex proved to be photochemically stable and the formation of the *mer* isomer was not observed upon irradiation.

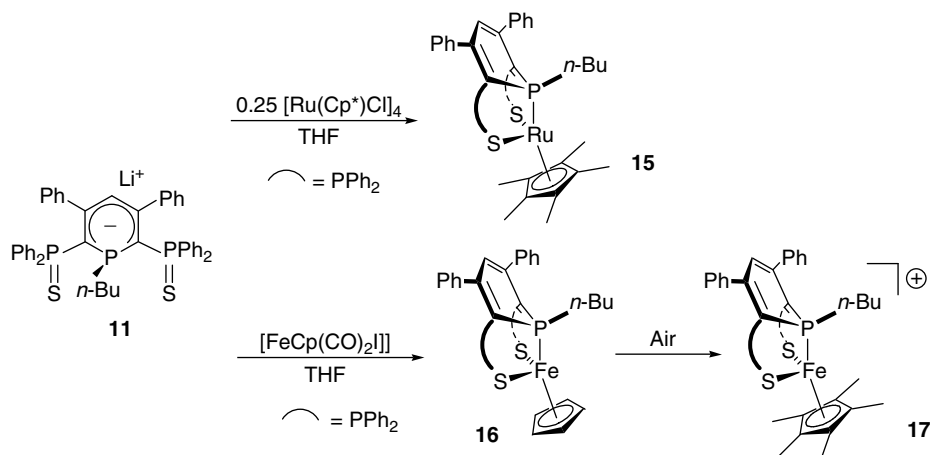
Only two complexes of group 8 metals were characterized so far, the RuCp* complex **15** and its CpFe analog **16**. Both complexes, which were structurally characterized, exhibit interesting electronic properties. Complex **15** exhibits one reversible oxidation wave at ($E_{1/2} = -0.01$ V versus SCE) and two reversible reduction waves at ($E_{1/2} = -1.10$ V and -1.4 V versus SCE). A comparison with the oxidation potential of [Ru(Cp*)₂] indicates that the S–P–S ligand is a better electron donor than the Cp* ligand. The X-ray crystal structure of the 17 VE complex **17**, which results from the air oxidation of complex **16**, has been recorded (Scheme 11.7) [14].

A lot of efforts were devoted to the synthesis and the study of group 9 complexes which appeared quite reactive. Rhodium(I) complexes of S–P–S ligands were conventionally prepared by reacting anions such as **2** with [Rh(COD)Cl]₂ to afford the stable 18 VE pentacoordinated complex **18** which was structurally characterized (Scheme 11.8, Fig. 11.1).

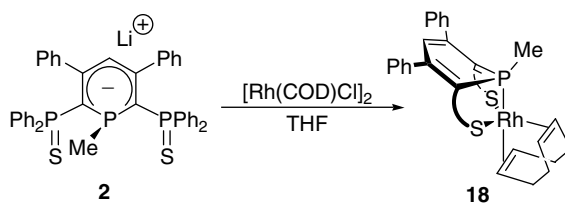
Importantly, complex **18** reacts with triphenylphosphine through a displacement reaction of the COD ligand to afford the highly reactive 16 VE square-planar complex **19** which was structurally characterized [15]. Complex **19** exhibits an interesting reactivity toward small molecules such as CO, CS₂, O₂, C₂Cl₆ and MeI to yield Rh(I) (**20–23**) or Rh(III) complexes (**24–26**) depending on the nature of the incoming substrate. The reactivity of **19** is presented in Scheme 11.9. A view of the peroxo complex **26** is presented in Fig. 11.2.

As can be seen in the scheme above, all reactions had taken place with a complete regioselectivity on the upper side of the complex (*syn* attack of the substrate) (Scheme 11.10) [16, 17].

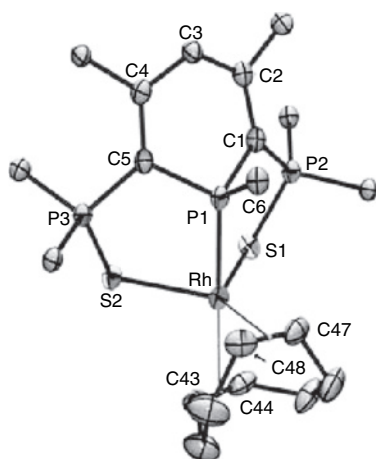
This result was rationalized through DFT calculations on a model reaction with H₂ [18]. All possible attacks were modeled assuming the formation of a dihydride complex

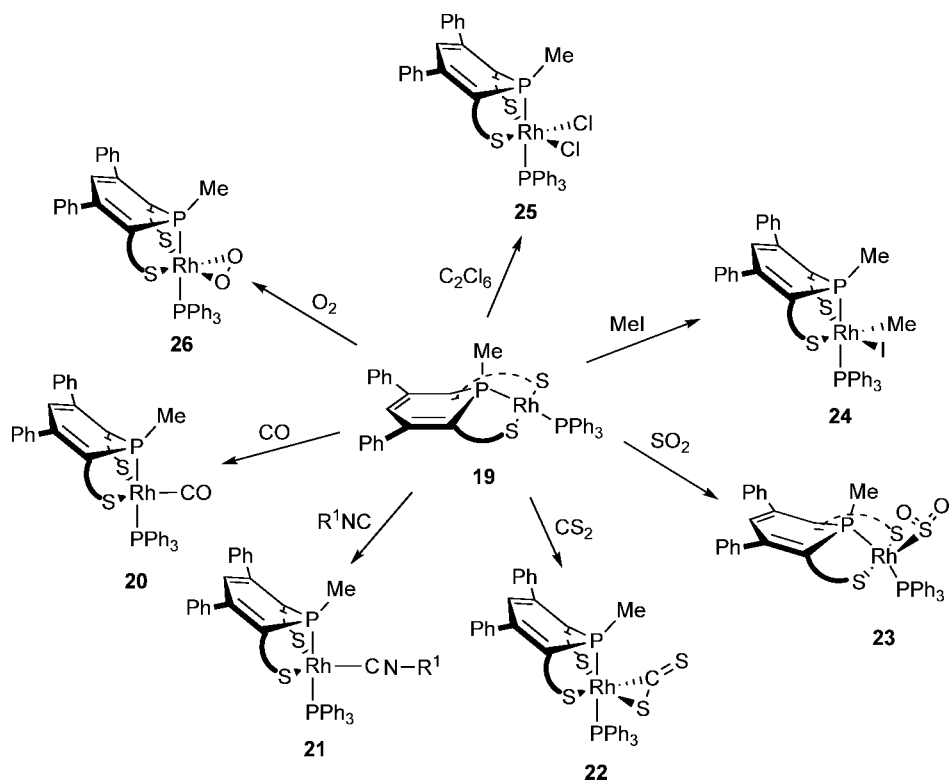


Scheme 11.7



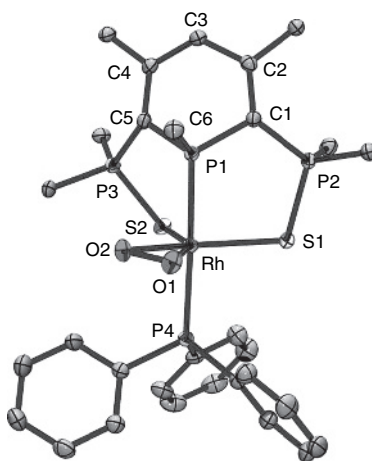
Scheme 11.8

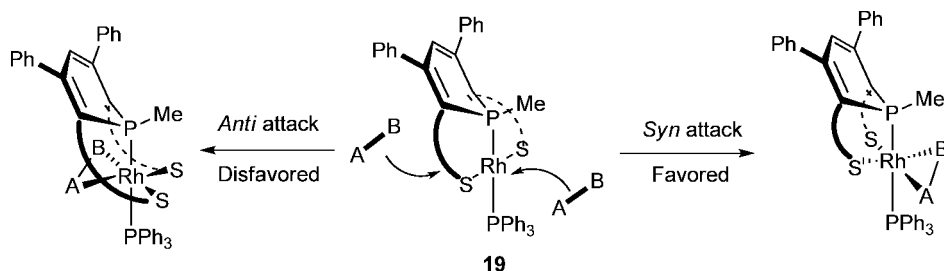




Scheme 11.9

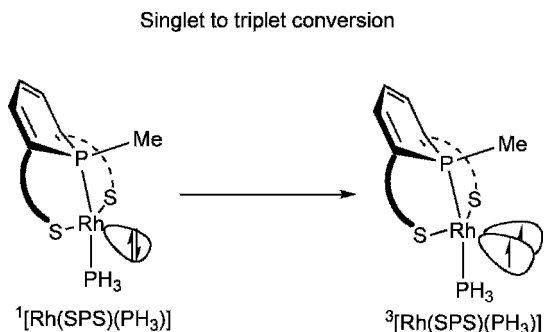
resulting from the attack of H₂. It was shown that energy associated to this oxidative addition process results from different factors such as the distortion of the metal fragment, a singlet to triplet conversion, the energy of the dissociation of H₂ and the energy

Fig. 11.2. ORTEP plot of complex **26**. Copyright American Chemical Society 2003.



Scheme 11.10

associated with the formation of two new Rh–H bonds. Using a thermodynamic cycle taking into account these different data, it was shown that preference for the *syn* attack essentially results from the ability of the $[\text{Rh}(\text{S}-\text{P}-\text{S})(\text{PPh}_3)]$ fragment to form a triplet state in the appropriate geometry to react with the incoming substrate (Scheme 11.11). A view of the calculated spin density in the model complex $[\text{Rh}(\text{S}-\text{P}-\text{S})(\text{PH}_3)]$ is presented in Fig. 11.3.



Scheme 11.11

An homoleptic Rh(III) complex featuring two S–P–S ligands has been synthesized by the reaction of two equivalents of the anionic ligand **2** with the $[\text{RhCl}_3(\text{THT})_3]$ precursor. The X-ray crystal structure of complex **27** was recorded. Interestingly, **27** can be electrochemically reduced to form the 19 VE Rh(II) complex **28**. Reduction of **27** can also be achieved in THF with Zn as reducing agent. Though complex **28** could not be characterized by X-ray techniques, complete EPR and DFT studies were performed. Combination of the calculations and the experimental data allowed to conclude that the odd electron is localized in a MO which results from the antibonding combination of the metal d_z^2 AO with two lone pairs at sulfur atoms of different ligands. A view of the SOMO of **28** is presented in Scheme 11.12 [19].

Analogous experiments were carried out with cobalt precursors. Thus reaction of two equivalents of anion **2** with $[\text{CoCl}_2]$ afforded the corresponding 19 VE complex $[\text{Co}(\text{S}-\text{P}-\text{S})_2]$ which proved to be highly sensitive toward air oxidation. Oxidation

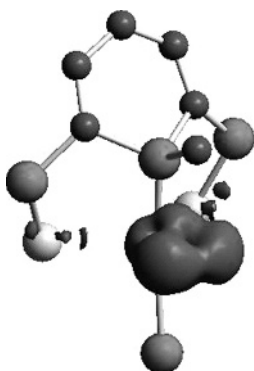
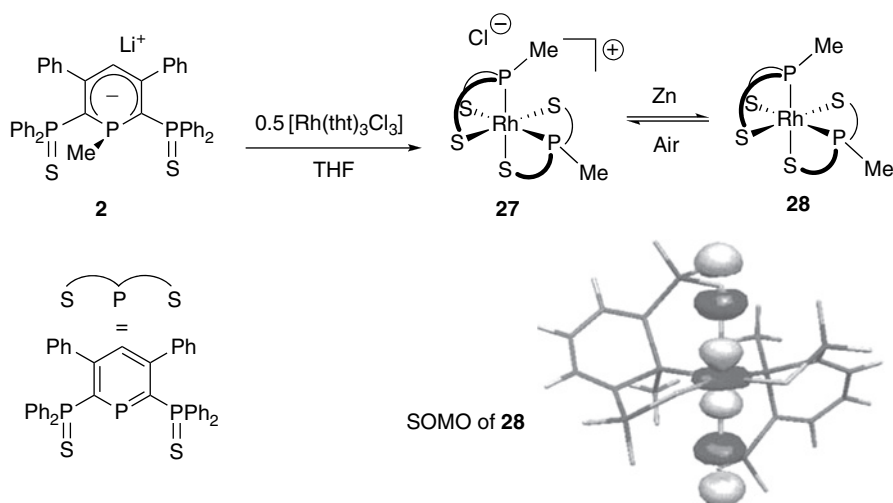


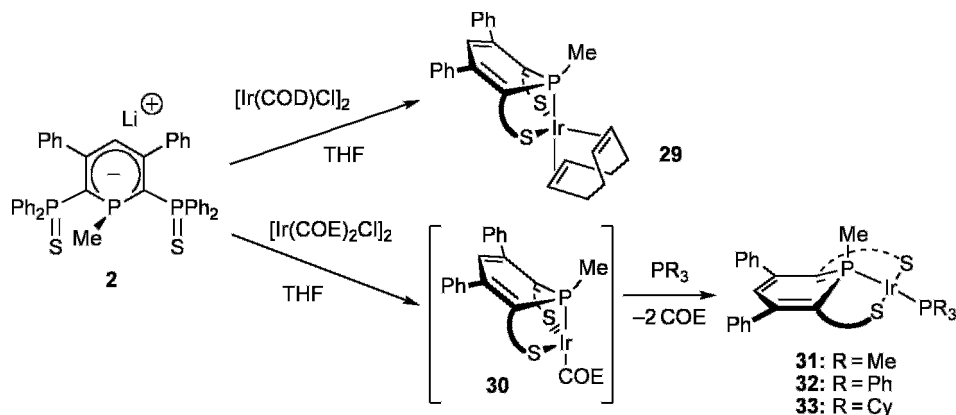
Fig. 11.3. Calculated spin density. Copyright American Chemical Society 2006.



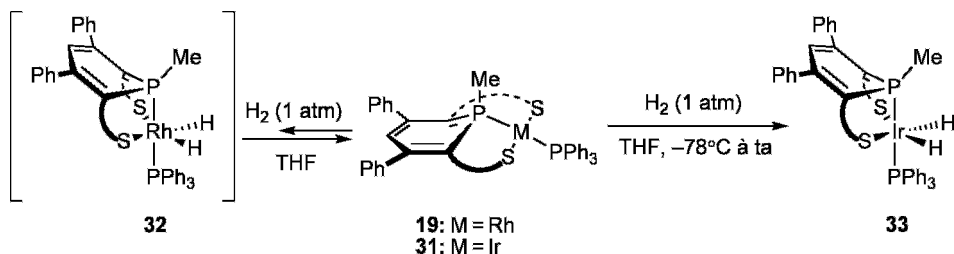
Scheme 11.12 Copyright American Chemical Society 2005.

with C_2Cl_6 afforded the very stable 18 VE $[\text{Co}(\text{S}-\text{P}-\text{S})_2]^+[\text{Cl}^-]$ complex which was structurally characterized [14].

The reactivity of anion **2** toward iridium(I) precursors was also investigated. Reaction of **2** with the $[\text{Ir}(\text{COD})\text{Cl}]_2$ dimer yielded the very stable complex **29** which proved to be reluctant toward displacement of the COD ligand. The cyclooctene 16 VE derivative **30**, which was prepared following the approach depicted in Scheme 11.13, proved to be moderately stable and readily reacted with PPh_3 , PMe_3 and PCy_3 at room temperature to afford complexes **31–33**. Complex **31** and **32** which are highly reactive toward oxygen were characterized by ^{31}P NMR only and complex **33** proved to be sufficiently stable to be fully characterized by ^1H , ^{13}C NMR spectroscopies. Reactivities of the rhodium complex **19** and its iridium counterpart **31** toward the oxidative addition of dihydrogen were compared (Scheme 11.14). Whereas the addition proved to be reversible in the case of rhodium at room temperature the stable Ir(III) dihydride complex **33** was isolated



Scheme 11.13



Scheme 11.14

and spectroscopically and structurally characterized. A DFT study has shown that the oxidative addition to the Ir derivative **31** is more exothermic ($\Delta G = -36.1$ kcal/mol) than the addition onto the Rh complex ($\Delta G = -14.9$ kcal/mol). Though the singlet-to-triplet conversion requires a weaker activation barrier in the case of the rhodium complex, the gain in stabilization energy provided by the formation of two strong Ir–H bonds (-171.2 kcal/mol) is the determinant factor (-145 kcal/mol for the Rh complex). A view of one molecule of the dihydride complex **33** is presented in Fig. 11.4 [18].

So far the reactivity tests have not been extended to cobalt complexes. However, a very recent DFT study suggests that although the Rh(I) and Ir(I) compounds were found to be diamagnetic with a square-planar geometry, the yet unknown Co(I) complex is predicted to be paramagnetic ($\Delta E_{S/T} = -22.4$ kcal/mol) with two unpaired electrons localized on the metal center.

Group 10 complexes of S–P–S anionic ligands were synthesized with the complete triad (Ni, Pd, Pt). Apart from the classical approach which relies on the reaction of anionic SP^RS ligands (R = alkyl) with metal halides (Scheme 11.2), group 10 complexes could also be prepared following the second route which involves in a first step the reaction of the bis(phosphinosulfide)phosphinine **1** with metal halides as in Scheme 11.4, followed by nucleophilic substitution of the Cl group at the P center. This route was somewhat

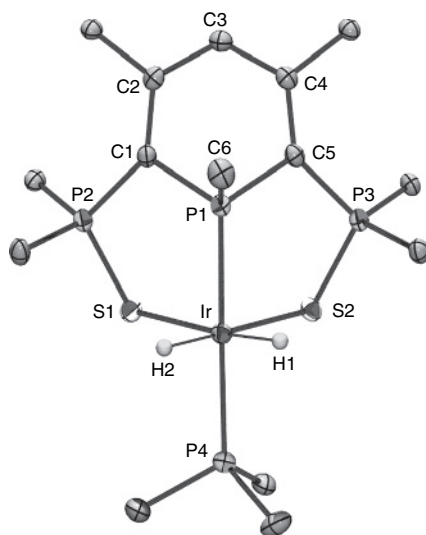
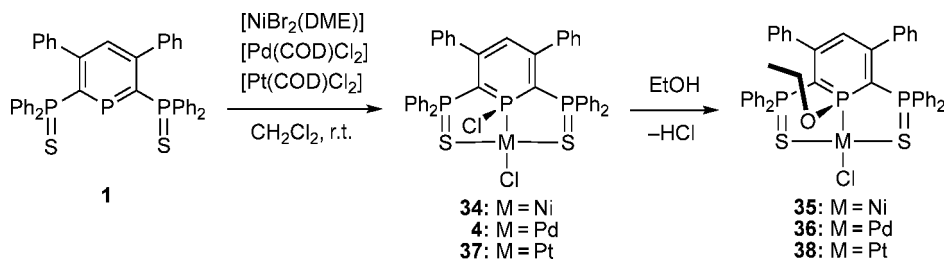


Fig. 11.4. View of one molecule of complex **32**. Copyright American Chemical Society 2006.

preferred for the synthesis of P-functionalized complexes (**4**, **34**, **37**). The following example illustrates the synthesis of P-alkoxy derivatives **35**, **36** and **38** (Scheme 11.15).

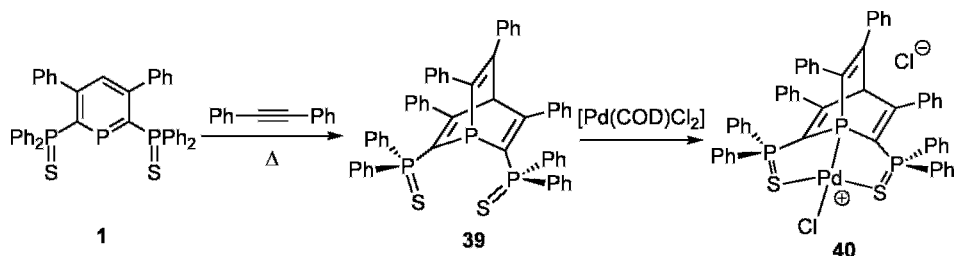


Scheme 11.15

These d^8 complexes proved to be less reactive than their group 9 analogs and no reaction takes place with H_2 , O_2 , CO_2 and MeI. DFT calculations suggest that the addition of H_2 onto square-planar $[\text{Pt}(\text{S}-\text{P}-\text{S})\text{Cl}]$ and cationic $[\text{Pt}(\text{S}-\text{P}-\text{S})(\text{PH}_3)]^+$ complexes to afford the corresponding Pt(IV) derivatives should require a weaker activation energy than for the corresponding palladium(II) complexes. However, these calculations indicate that the oxidative additions would still be highly endothermic for both metal centers.

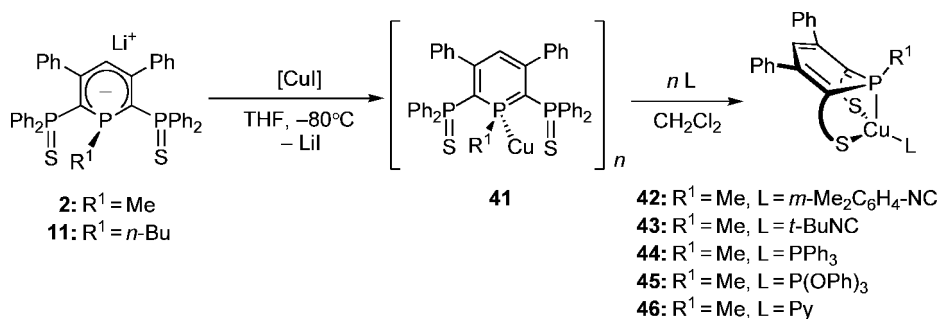
Recently, the bis(phosphinosulfide)phosphinine **1** has also been employed to devise a new type of pincer S–P–S ligand which features a 1-phosphabarrelene as central ligand. It was shown that **1** can react through a $[4+2]$ cycloaddition process with diphenylacetylene to afford ligand **39** which was fully characterized (Scheme 11.16). Theoretical

investigations through DFT have shown that the presence of the two strong electron-withdrawing phosphinosulfide substituents are crucial to activate the ring. Indeed, classical λ^3 -phosphanes are known not to react easily with unactivated alkynes. Reaction of ligand **39** with $[\text{Pd}(\text{COD})\text{Cl}_2]$ afforded the very stable cationic complex **40** which adopts the expected square-planar geometry [20].



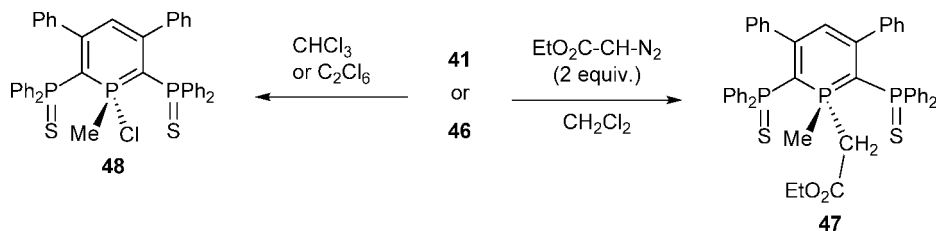
Scheme 11.16

Finally, a few group 11 metal complexes have been synthesized. Studies exclusively focused on the synthesis with Cu(I) and Au(I) complexes. It was shown that the reaction of anionic S–P–S ligands on CuI yields a polymeric structure $[\text{Cu}(\text{S}–\text{P}–\text{S})]_n$ **41** whose structure was not determined. However, reaction of this polymeric material in dichloromethane at room temperature with 2e donor ligands such as isonitriles, phosphines and pyridines affords 16 VE neutral complexes **42–46** with general formula $[\text{Cu}(\text{S}–\text{P}–\text{S})\text{L}]$. X-ray crystal structure studies have shown that all these complexes adopt a pseudo-tetrahedral geometry around copper as expected for complexes having the d^{10} electronic configuration (Scheme 11.17) [21].



Scheme 11.17

A series of experiments have shown that the P–metal bond is more reactive in the Cu complexes than in other S–P–S complexes (Rh, Ir, Pd, etc.). Thus, reaction of ethyldiazoacetate with the polymeric $[\text{Cu}(\text{S}–\text{P}–\text{S})]_n$ **41** or with the monomeric complex **46** yields the λ^4 -phosphanine **47** (see Scheme 11.18). Similarly, the P–Cu bond is cleaved by chloroform or C_2Cl_6 to afford the chloro derivative **48** (Scheme 11.18) [14].

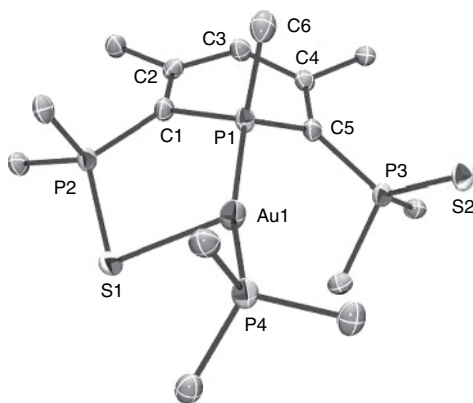


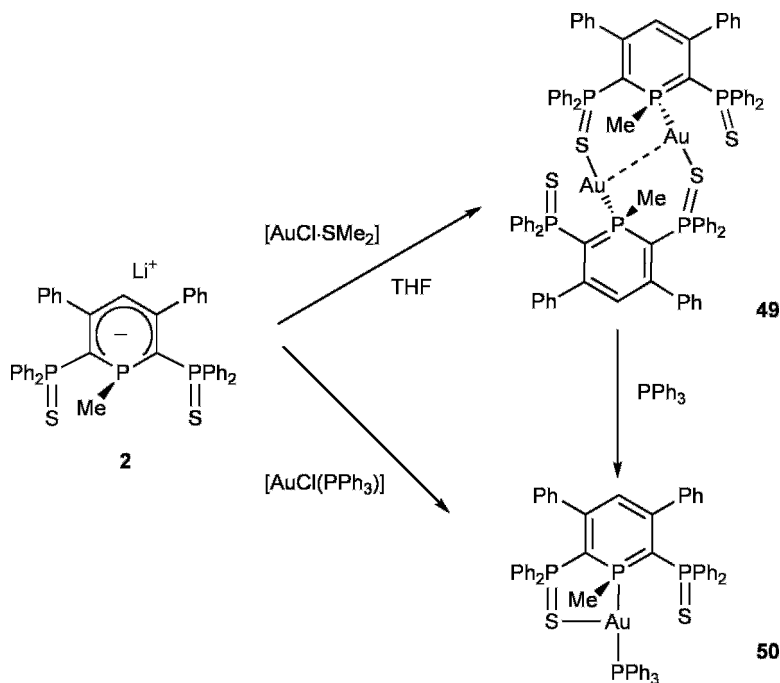
Scheme 11.18

Gold(I) complexes were conventionally prepared by the reaction of an anionic S–P–S ligand with cationic gold(I) precursors. It was shown that the outcome of the reactions depends on the presence of strongly coordinating ligand on the gold atom. Thus reaction of anion **2** with the $[\text{AuCl}(\text{SMe}_2)]$ complex yielded the dimeric structure **49** in which only one phosphinosulfide ligand of the tridentate ligand is coordinated to the gold center. On the other hand, examination of metric parameters suggest that the weak interaction which occurs between the two gold atoms forces a slightly bent geometry at Au. Reaction of this dimeric complex with triphenylphosphine afforded complex **50** which adopts a T-shape geometry. A view of one molecule of **50** is presented in Fig. 11.5. Note that complex **50** can also be prepared in a more straightforward way by reaction of anion **2** with the $[\text{AuCl}(\text{PPh}_3)]$ complex (Scheme 11.19).

11.2.1.3 S–P–S ligands in catalysis

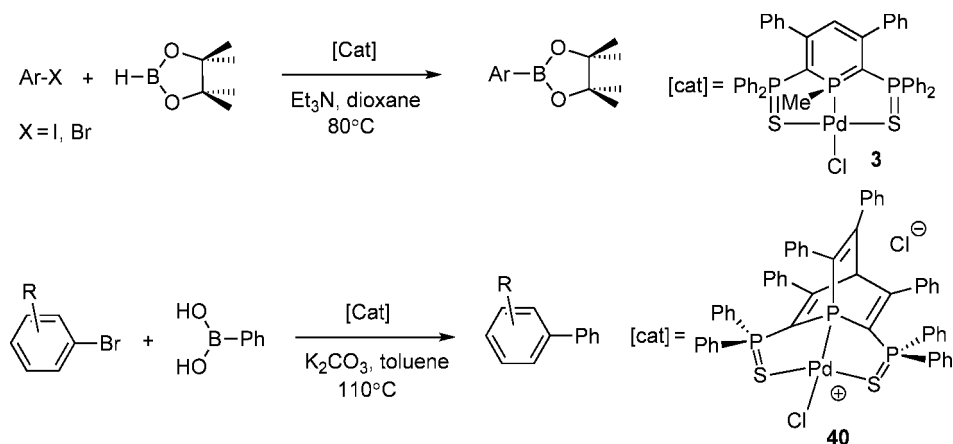
Bis(phosphinosulfide)phosphinine ligands have not been extensively employed in catalysis so far. Only two applications, which both rely on the use of palladium complexes, have been reported. The first result deals with the Miyaura cross-coupling process which allows the synthesis of boronic esters from halogenoarenes and pinacolborane. Complex **3** led to good conversion yields in the coupling of iodoarenes (TON between 5×10^3 and 10×10^3). Coupling of bromoarenes also occurred but with smaller TON (880) (Scheme 11.20). Although seemingly modest, these performances remain highly competitive with regards to classical catalysts. The second application was found in the classical Suzuki coupling between boronic acids and bromoarenes. The cationic complex **40** which features a barrelene-based pincer S–P–S ligand, catalyzed the coupling

Fig. 11.5. ORTEP plot of complex **50**. Copyright Royal Society of Chemistry 2004.



Scheme 11.19

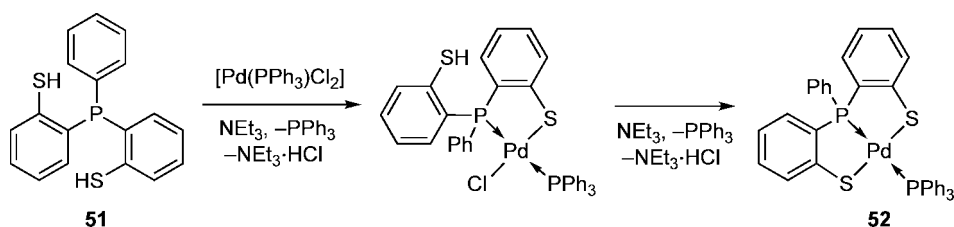
between bromobenzene and $\text{PhB}(\text{OH})_2$ with a TON of 9.5×10^4 ($\text{TOF} [\text{h}^{-1}] = 3958$) (Scheme 11.20). Note that bidentate palladium complexes featuring P–S ligands (combination of a phosphinosulfide with a phosphinine anion or a phosphabarrelene) [22] were also successfully employed in this coupling process (TON up to 7×10^6) and in the allylation of primary amines with allylic alcohols.



Scheme 11.20

11.2.2 Bis(thioether)phosphines

The coordination chemistry of bidentate S~P ligands of the type $R_2PCH_2CH_2SH$ and $R_2P(C_6H_4-SH)$ has been investigated in depth. Comparatively, the tridentate analogs $HS-P-SH$ have received little attention. Most recently, Morales-Morales and co-workers have reported the in situ double deprotonation–coordination sequence of ligand **51** to form a square-planar Pd(II) complex **52** (Scheme 11.21) [23].



Scheme 11.21

The use of this complex in catalysis has not been reported so far.

11.3 S–C–S (AND Se~C~Se) PINCER LIGANDS

11.3.1 Thioether (N1) and Related Selenoether (N2) Derivatives

11.3.1.1 Syntheses of palladium-metallated complexes

Up until 2002, the organometallic chemistry of derivatives of **C** (Chart 11.1) was limited to palladium complexes (except one platinum analogue reported in 1992) [24]. In fact, based on a 1980 report by Shaw et al. it was believed that cyclometallation was only possible with Pd(II). Historically, the direct cyclometallation of SC(H)S pincer ligand with a Pd(II) precursor was the first efficient method to form new carbon–Pd bonds. It appears that several factors influence the yield of the desired complex to a very large extent: nature of the R substituent of the sulfur center, nature of the substituent para to the CH moiety and last but not least the palladium precursor (Chart 11.5).

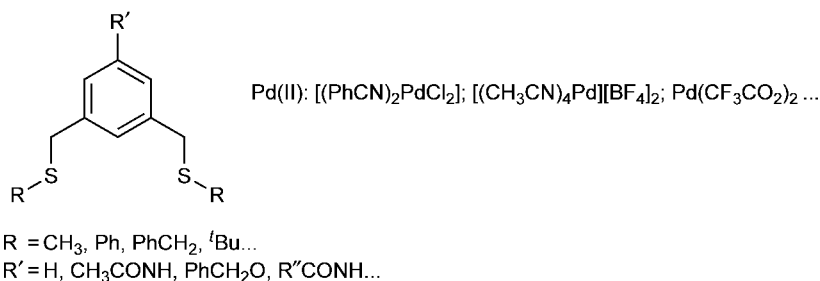
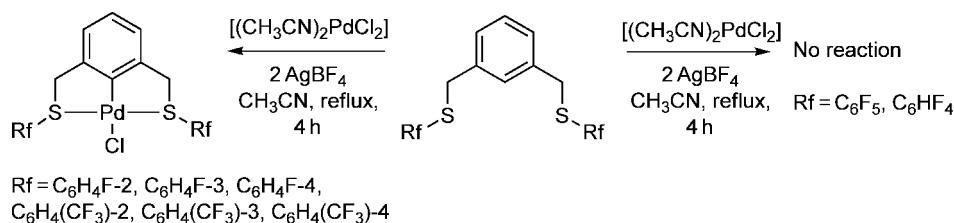


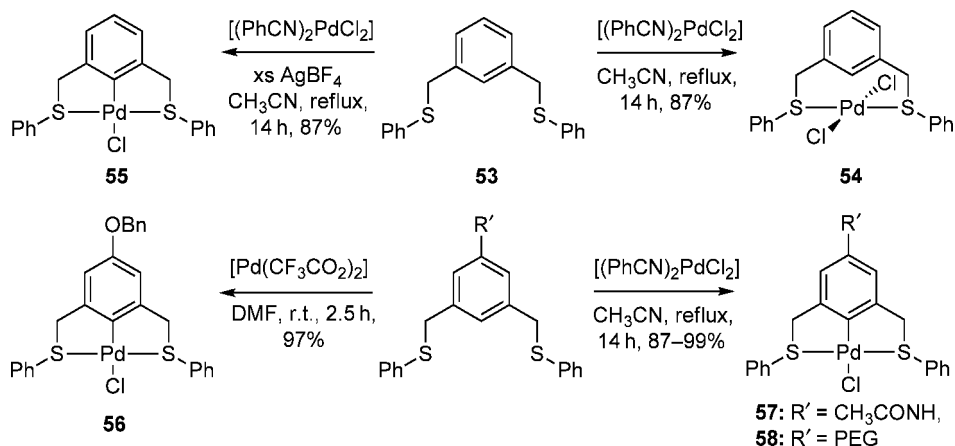
Chart 11.5

Indeed, for small alkyl groups, low yields of complexes were obtained, whereas for phenyl or benzyl groups the insertion was more efficient. For the ^tBu group the insertion required longer heating periods. In a very recent article, Torrens and co-workers have studied the influence of the number of fluorine substituents on the phenyl ring bound to the S center on the outcome of the insertion reaction [25]. They showed that the palladation could only be observed for the substituents with one F atom or one CF₃ moiety (Scheme 11.22).



Scheme 11.22

These results are consistent with earlier reports as for the derivative R=Ph, R'=H, insertion could not be achieved with [(PhCN)₂PdCl₂] even after prolonged heating in CH₃CN. Only the 'PdCl₂' adduct **54** was obtained. On the other hand, increasing the electrophilicity of the metal center by chloride abstraction led to the desired complex **55** after prolonged refluxing in acetonitrile (Scheme 11.23).

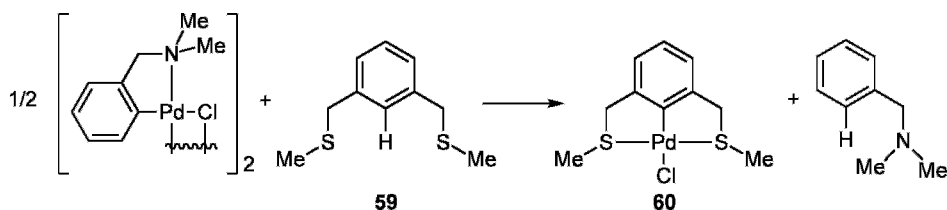


Scheme 11.23

Using more electron donating R' substituents, such as NHCOCH₃, O-benzyl or polyethylene glycol (PEG) moieties, this silver salt activation was not required to lead to the cyclometallated complexes **56–58** in excellent yields. Lastly, a milder, however seldom employed, method was devised involving [Pd(CF₃CO₂)₂]. With this precursor,

palladation occurs at room temperature in DMF within a couple of hours when refluxing acetonitrile overnight is required with other precursors [26]. Overall, it appears that increasing the electron density of the central ring does favor the insertion process.

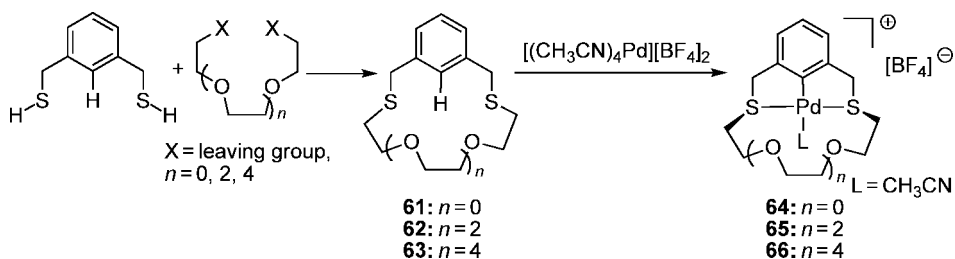
In 1999, van Koten and co-workers developed a novel method: the transcyclometallation [27, 28]. It is based on the substitution of one cyclometallated ligand by another. It allows the efficient synthesis of the otherwise difficult to obtain SMe derivative **60** as illustrated in Scheme 11.24.



Scheme 11.24

11.3.1.2 Applications: metalloreceptors

In the early 1990s, Loeb and co-workers synthesized a range of thiacyclophane ligands **61–63** in order for the corresponding cyclometallated palladium complexes **64–66** to act as metalloreceptors (Scheme 11.25). One of the major goals was to show that simultaneous first and second sphere coordination would allow a selective recognition of various substrates [29].



Scheme 11.25

Competition experiments between pyridine and *o*-aminopyridine or the DNA bases cytosine, guanine, adenine and thymine were performed [30]. They showed that the crown ether ligand **62** bearing three oxygen centers provided the best results in terms of recognition. The resulting complex **65** was selective for cytosine over the three other DNA nucleobases (Scheme 11.26, Fig. 11.6).

The solvent molecule (acetonitrile) was also quantitatively displaced by H_2O , NH_3 , hydrazine or hydrazinium cation. For these, H bonding with the ether oxygen center could be observed [31]. Later, the same group extended the scope of the substrates

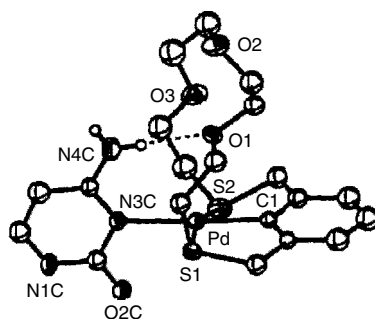
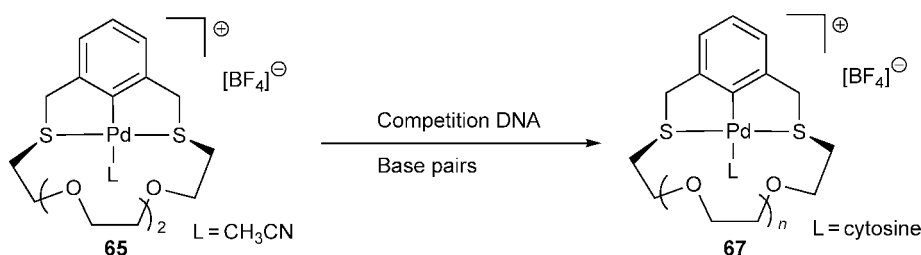


Fig. 11.6. ORTEP view of the cytosine–Pd metalloreceptor complex **67** of Ref. [30]. Copyright American Chemical Society 1993.



Scheme 11.26

that could be recognized by designing receptors in which the subunit for second sphere interaction was calix-[4]-arene units (ligand **68**, Fig. 11.7) [32].

11.3.1.3 Applications: supramolecular chemistry, metallodendrimers

The early on recognized high stability of the S–C–SPd complexes as well as the quantitative displacement of the ‘solvent’ molecule from the above-mentioned square-planar cationic complexes inspired several groups to design self-assembling structures and metallodendrimers.

Self-assembled structures required the development of ‘bis-pincer’-type ligands, the tetra-1,2,4,5-thioether derivatives **69** ($R = n\text{Bu}$ or Ph) which underwent double palladation efficiently [33]. The subsequent quantitative synthesis of Pd_6 hexagons **71** was achieved because of the reversible binding to 4,7-phenanthroline to the palladium center **70**. In this process, the thermodynamically favored species is formed (Scheme 11.27) [34].

van Veggel, Reinhoudt and co-workers have relied on non-covalent interactions between the S–C–SPd fragment and a two-electron donor to develop convergent and divergent synthesis of metallodendrimers. The species formed are highly functionalized on the surface. Their first studies focused on nitrile (**72**) or pyridine (**73**) functionalities such as shown in Chart 11.6 [35]. More recently, because of their stronger coordinating properties, phosphine derivatives (**75**) and thioureas (**76**) were used [36, 37]. A whole series of metallodendrimers were constructed using these building blocks (**72–76**) [38].

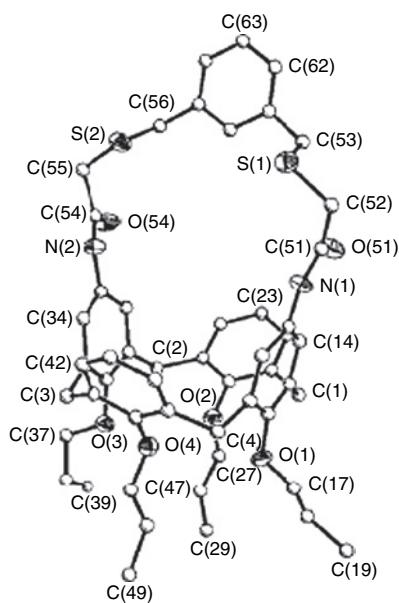
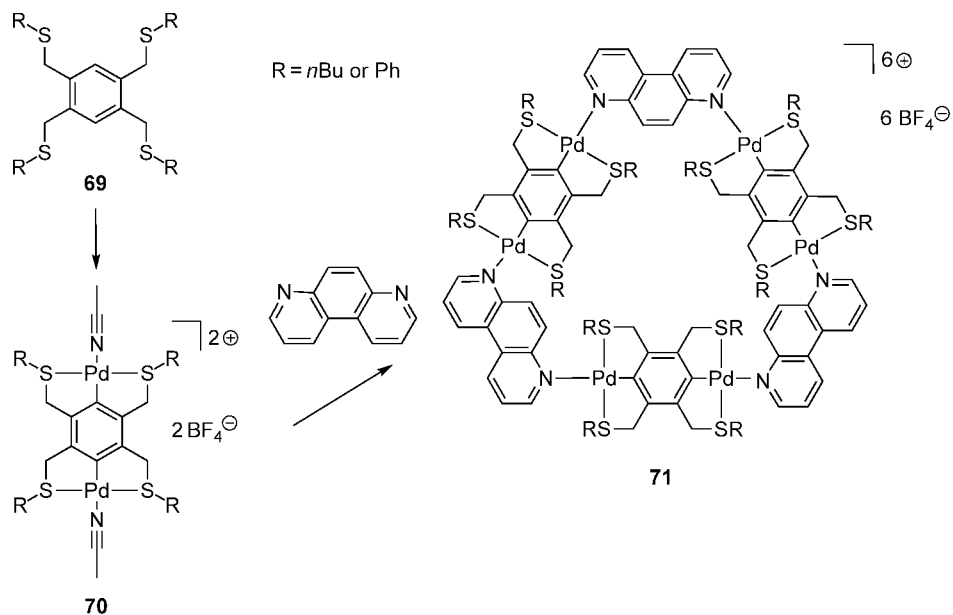


Fig. 11.7. ORTEP view of the calix-[4]-arene metalloreceptor **68**. Copyright American Chemical Society 1997.



Scheme 11.27

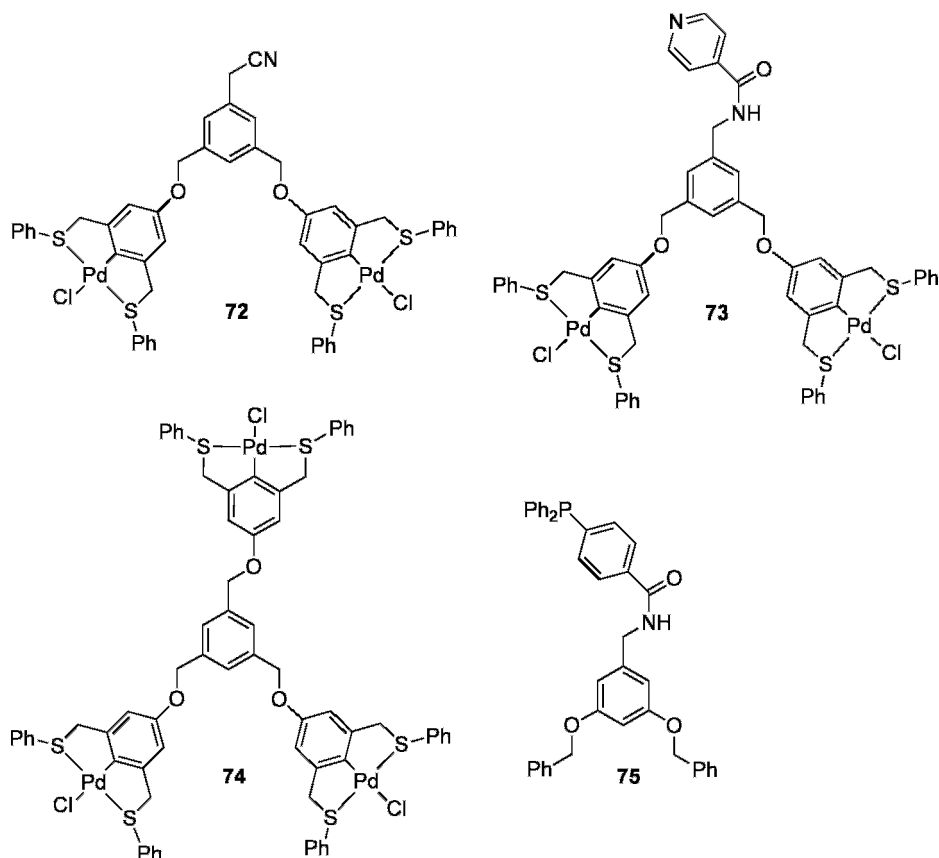


Chart 11.6

One may note that in only one instance, the thioether ligands of the pincer were displaced by an excess of incoming phosphine ligand.

11.3.1.4 Applications: metallodendrimers anchoring on Au surfaces

A further step toward applications was obtained by van Veggel, Reinhoudt and co-workers. One of the requirements in nanotechnology is to be able to control the position of the nanosize devices in order to address them selectively. In their work, they took advantage of both the self-assembly of sulfur-containing molecules on gold surfaces and the possibility to incorporate individual thiols into a preformed monolayer of thiols on a surface. From a dendrimer core containing a single Pd complex **77** (MG0), they built up two dendritic generations, compounds **78** (MG1) and **79** (MG2). Subsequently, the dendrimers could be incorporated into a thiol-coated Au surface. A surface coverage of roughly 1% was obtained by AFM counting the individual dendrimers (Chart 11.7 and Fig. 11.8) [39, 40].

In 2001, based on their above-mentioned work on dendrimers obtained by coordination of phosphines on the S-C-SPd fragments, the same authors reported the immobilization of Au nanoparticles stabilized by alkane thiols and phosphine-terminated alkane

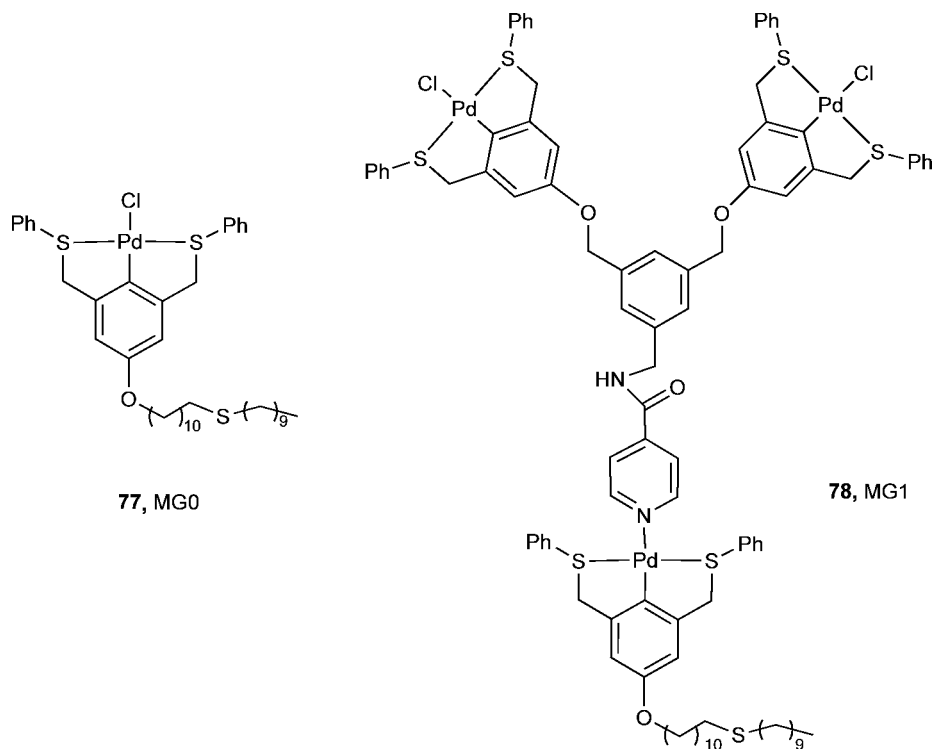


Chart 11.7

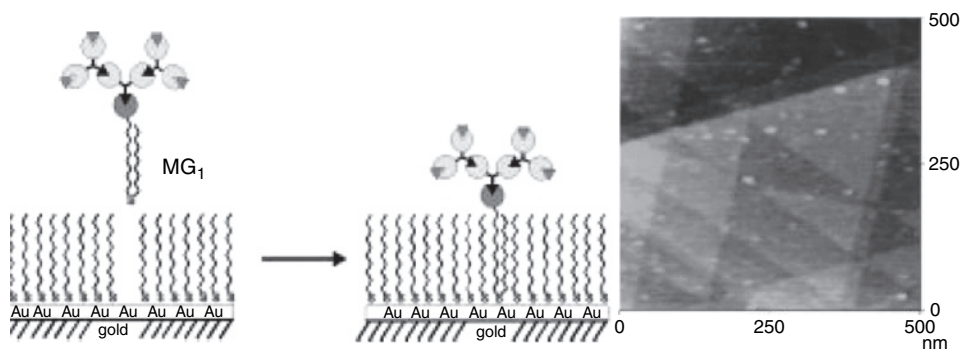


Fig. 11.8. Metallo dendrimer **79** (MG2) binds through its dialkyl sulfide group at a defect site in the alkanethiol monolayer; AFM height image of the monolayer after treatment with a metallo-dendrimer MG2 solution. Copyright Wiley 1999.

thiols (20 P moieties per 2.0 nm Au nanoparticle) on thiol monolayer-stabilized Au surfaces. The desired spatial confinement of Au nanoparticles was achieved as shown by AFM. A measured height average of 3.5 ± 0.7 nm (AFM) was correlated to the average nanoparticle size (2.0 ± 0.5 nm measured by TEM) added to the thickness of the alkyl chains measured by AFM (Fig. 11.9) [41].

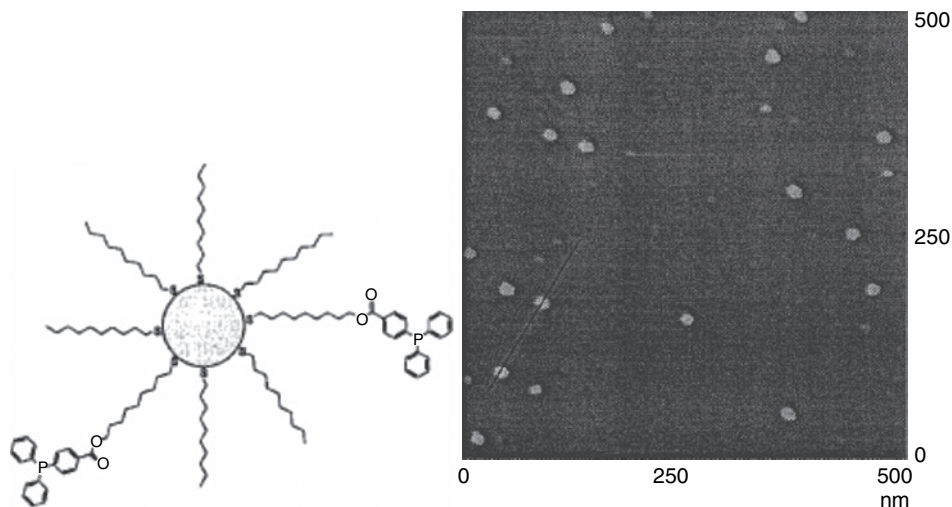


Fig. 11.9. Schematic representation of Au-stabilized nanoparticle. TM AFM height image of mixed monolayer of decanethiol and Pd pincer sulfide after exposure to a solution of Au nanoparticle. Copyright American Chemical Society 2001.

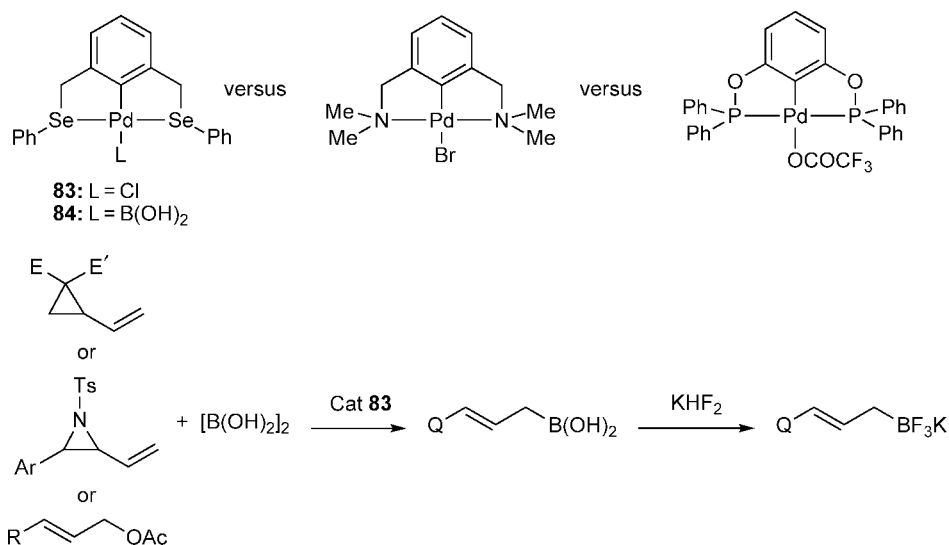
11.3.1.5 Applications: catalysis

The first studies aimed at developing the use of the S–C–SPd fragment in catalysis were conducted in 1999 by Bergbreiter et al. [26]. In order for the catalyst to be efficiently recycled, robust complexes were sought after. It was shown that *para*-acetamido substituent led to catalysts (**57**, Scheme 11.23) with long-term stability to thermal, oxidative, acidic/basic conditions or in the presence of water. Then simple organic transformations on the aryl central ring of the pincer ligand led to the immobilization of the pincer ligand in PEG-type polymer (complex **58**, Scheme 11.23). The immobilized complex (0.1% mol) showed an interesting activity in Heck-type couplings between aryl iodide and alkene moieties in air at 115°C. More interestingly, three catalytic cycles without loss or deactivation of the complex were carried out. From another standpoint, Dijkstra et al. envisioned the possibility of using nanomembrane filtration techniques in order to recycle a complex. For that purpose, they developed a hexameric highly rigid cartwheel molecule **80** from persubstituted benzene derivatives (Scheme 11.28) [42].

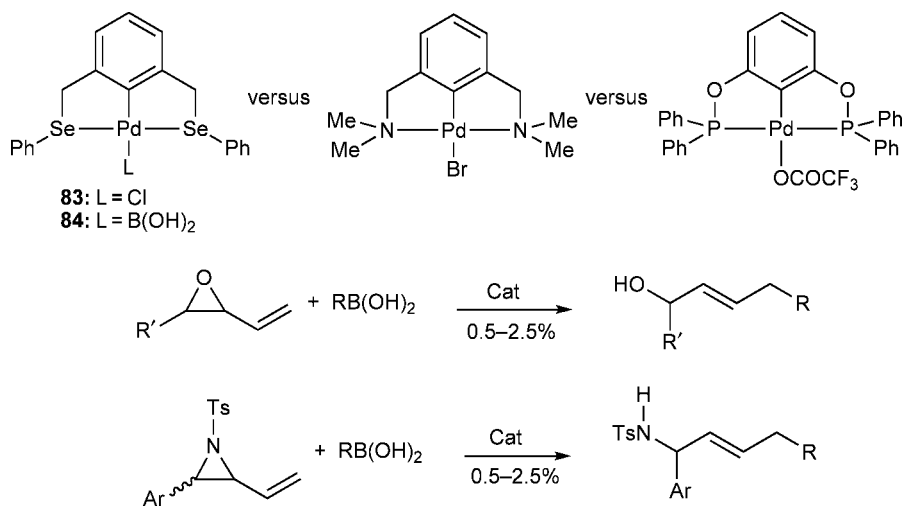
The nanoparticle size dimension for this hexameric Pd structure is sufficiently large for the desired nanomembrane filtration. However, the performance of the complex in catalysis has not been reported yet.

Following the early catalysis report, Dupont and co-workers showed that activated aryl bromides could also be used in the Heck reaction with a S–C–SPdCl complex **81** [43]. TON of about 45 000 for the aryl iodide could be obtained. Although interesting in terms of stability of the pincer complex, these results do not compare to analogous bidentate complexes **82** in terms of activity (same study, TON of 1 850 000) (Scheme 11.29).

Very promising results in terms of catalysis have appeared in the last 2 years. For palladium-catalyzed processes with allyl species, both the nucleophilic substitution and the electrophilic substitutions are possible. It was shown that the first type involved an η^3 -monoallyl palladium intermediate whereas the second usually involved a bisallyl



Scheme 11.30

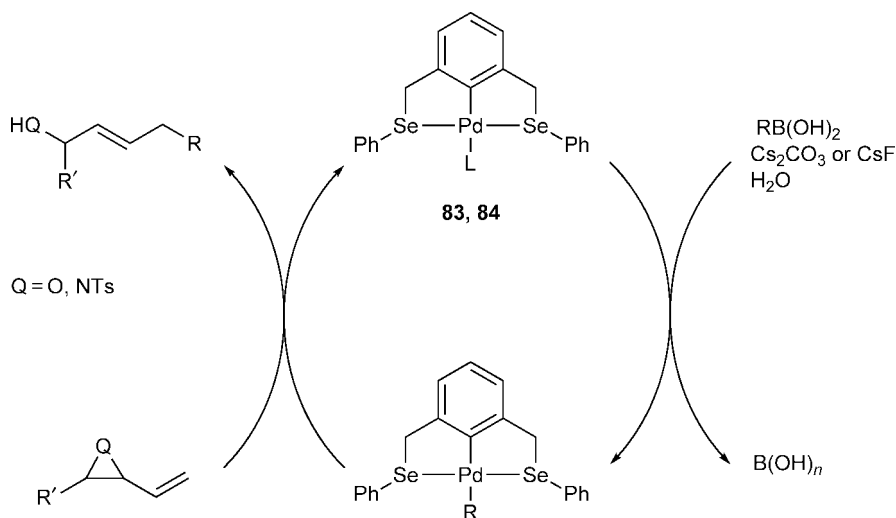


Scheme 11.31

that were tested and only efficient in the Suzuki–Miyaura coupling reaction with iodo derivatives (TON up to 96 000) [50].

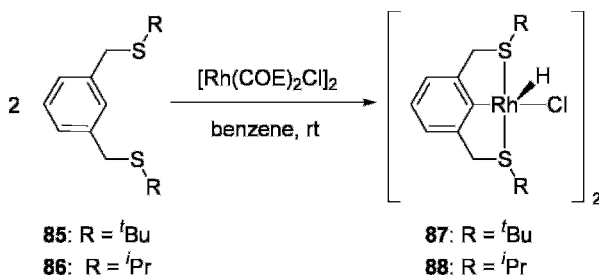
11.3.1.6 Synthesis of rhodium complexes

As mentioned above, there is only one complex of the ligand **C** (Chart 11.1) with a metal center other than palladium. In a very complete study, Evans et al. developed the insertion of a Rh(I) center into the C–H bond [51]. In fact, their synthesis led to



Scheme 11.32

the formation of a chloride-bridged dimers, which is highly unusual for pincer-type Rh complexes (Scheme 11.33).



Scheme 11.33

With the ligand **85** bearing S- ^tBu substituents, two hydride resonances were observed at about -20 ppm for complex **87**, typical for such hydrido-rhodium species. On the other hand, for the analogous ligand **86** with S- ^iPr substituents, no less than 11 hydride resonances were found for complex **88**. Variable temperature ^1H NMR experiments showed that these resonances coalesced to a single one at 88°C suggesting a dynamic process that is slow at room temperature. In fact, for this type of ligands, two processes can be operative, S inversion and $\text{Rh}-\text{C}_{\text{ipso}}$ bond rotation leading to diastereomeric species. In the first case (complex **87**), only the Rh–C rotation was observed and in the second case (complex **88**), the two dynamic processes were found to occur.

11.3.2 Thioamide (E) and Phosphine Sulfide (F) Derivatives

11.3.2.1 Syntheses of group 10-metallated complexes

Kanbara et al. have studied the luminescence of the palladium and platinum complexes of the two types of ligands (**E**, **F**, Chart 11.1), in part because of their long-term stability in air [52, 53]. These are obtained via the classical insertion route from the bis(benzonitrile) dichloride precursor under reflux (Chart 11.8).

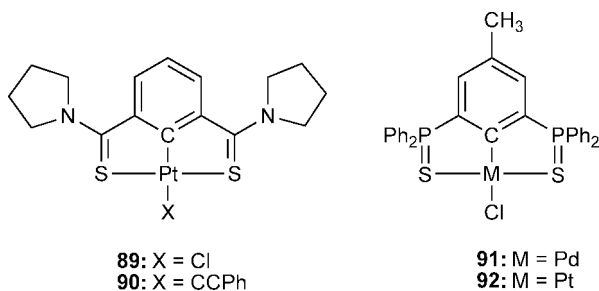


Chart 11.8

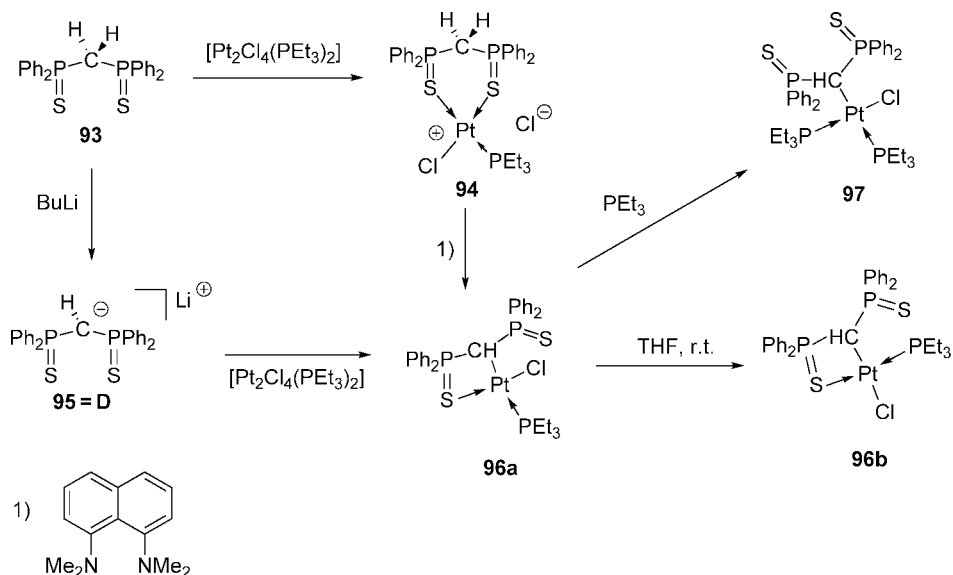
None of the complexes **89–92** showed light emission in solution at room temperature, but strong luminescence was observed in the solid state and in the glassy frozen state. They showed an emission at 630 nm for complex **89** and at 640 nm for complex **90** with fluorescence quantum yields of 0.11 and 0.24, respectively. Preliminary application of these two complexes as light emitting diodes (LEDs) was examined.

11.3.3 Anion (G) and Dianion (H) of the Bis-(diphenylphosphinosulfide)-methane

The first report of the coordination chemistry of the anion of dppmS₂ (**G**, Chart 11.1, **95**) dates back to 1983. Dixon and co-workers studied both the coordination of the neutral ligand (**93**) to a platinum precursor followed by deprotonation and the reverse order reactivity [54]. Interestingly, they showed that starting from the ‘neutral’ SS bidentate coordination (complex **94**), a rearrangement to the SC bidentate coordination (complex **96**) was observed upon deprotonation (Scheme 11.34). Addition of an excess of basic phosphine resulted in the displacement of the second phosphinosulfide moiety (complex **97**). However, the carbon–palladium bond was not cleaved.

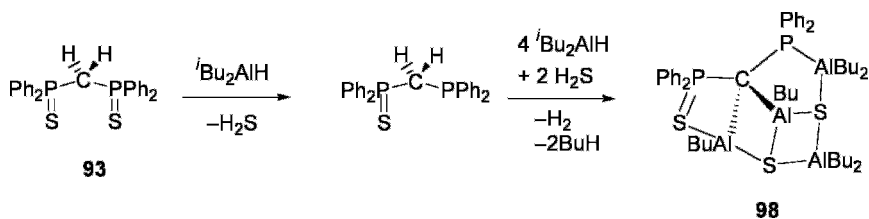
The tridentate coordination S–C–S was not observed starting from the anion **95**. A similar coordination–deprotonation sequence was later carried on with an iridium center. ³¹P and ¹³C NMR spectroscopies indicated that the SS bidentate coordination was preserved upon deprotonation with NaH in THF [55]. In the same article, it was shown that SS bidentate coordinated to a platinum center slowly evolved (2 days) to a dimeric species in which the carbon atom acts as the bridge.

With the aim of comparing the coordinating ability of the extensively studied dppm (bis-diphenylphosphinomethane) with the one of its bissulfide derivative, Robinson et al. investigated the organoaluminum chemistry of the latter ligands in 1988. The reaction



Scheme 11.34

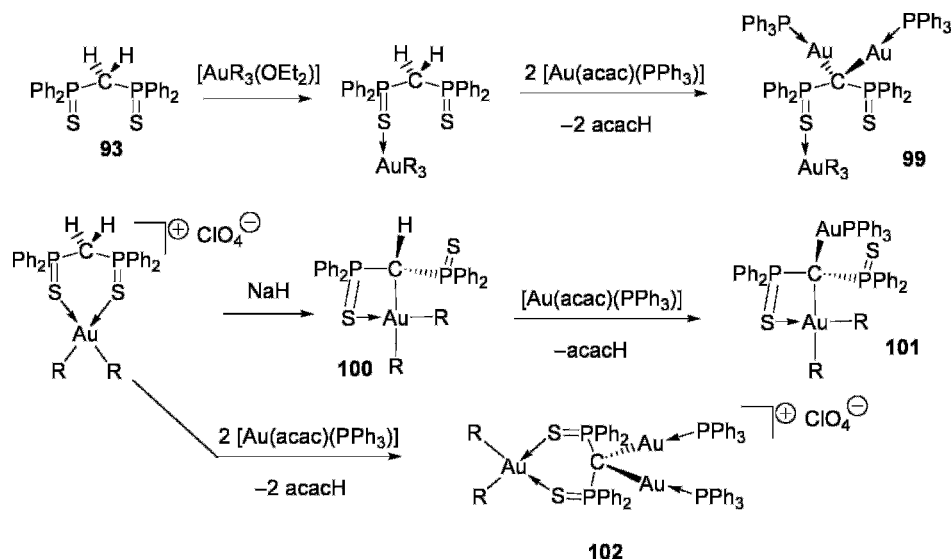
of the neutral ligand (**93**) with DIBAlH at 160°C led to the isolation of a complex (**98**) which had undergone a peculiar rearrangement. In fact, in the product which was probably obtained by a two-step sequence, two new carbon–aluminum bonds were formed (Scheme 11.35) [56].



Scheme 11.35

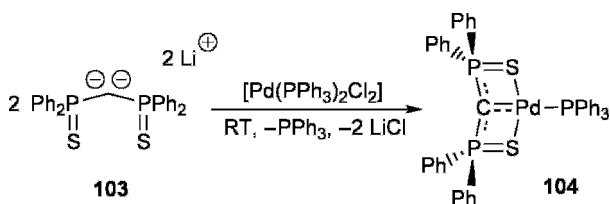
The first step involved a reduction of one P=S bond followed by a high temperature ‘double deprotonation’ by the aluminum hydride. This was in sharp contrast to the analogous reaction with dppm for which only the 2:1 AlMe₃:ligand adduct was obtained [57]. This clearly proved a significantly increased acidity of the protons of the methylene bridge upon sulfuration of the phosphine moieties. Laguna and co-workers studied, some 10 years later, the coordination of the neutral species **93** to gold(III) precursors followed by their deprotonation by a gold(I) precursor (Scheme 11.36). They obtained polymeric, mixed gold(I)–gold(III) complexes [58].

They observed both the mono-deprotonation to form a new C–Au bond (complex **100**) and the double deprotonation to form two bonds between the bridging carbon atom



Scheme 11.36

and two Au(I) centers, as in complexes **99**, **101** and **102**. Based on these early reports, Le Floch and co-workers synthesized and isolated in 2004 the dianion (**H**, Chart 11.1, **103**) in order to test its coordinating behavior. In a first publication, the coordination of this $\text{S}-\text{C}-\text{S}^{2-}$ ligand (**103**) to a Pd(II) center was studied (Scheme 11.37, Fig. 11.10) [59].



Scheme 11.37

As shown, the X-ray structure of complex **104** presents a central tricoordinate carbon atom as expected. However, unusual features were also found. First, a long Pd–C1 bond ($2.113(2) \text{ \AA}$) ruled out a ‘true’ double bond. The metal center seems to be located in a quasi-perpendicular plane to the carbene fragment (angle of 102.0°). This unprecedented geometry was rationalized by DFT calculations. The HOMO of the complex consists of a π -type antibonding interaction between the n_σ orbital of the carbene fragment with the d_{xz} orbital of the metal center. Overall, as both the π bonding and antibonding orbitals are filled, there is no π bonding character between the Pd and C centers (Fig. 11.11).

As expected from the shape of the HOMO, this complex possesses a nucleophilic character and reaction with the strong electrophile MeI, resulted in the quantitative formation of the corresponding cationic complex, in which a new C–C bond had been formed between the formal carbenic center and the Me^+ .

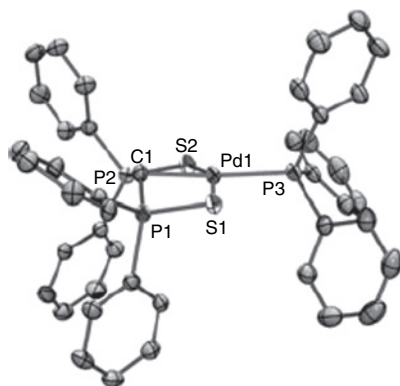


Fig. 11.10. ORTEP plot of complex **104**. Copyright Wiley 2004.

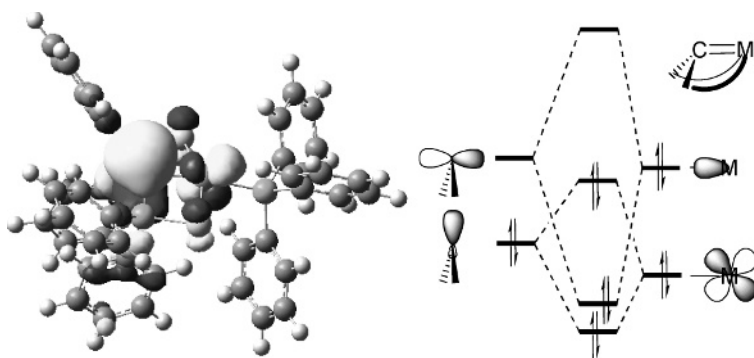


Fig. 11.11. HOMO of complex **104** and simplified OM diagram. Copyright Wiley 2004.

In a subsequent study, using a similar strategy these authors synthesized a ruthenium complex (**105**) (Scheme 11.38) [60]. The X-ray structure showed a more typical coordination of the carbene fragment with the metal center in the plane of the carbene (Fig. 11.12). However, the C–Ru bond length was also quite long (Ru–C of 2.053(2) Å) suggesting to a very weak double bond character. Again, it was rationalized by means of DFT calculations, which showed a Wiberg bond index of 0.67 for the Ru–C bond. Moreover, the LUMO of this complex is an antibonding π^* orbital between the n_σ orbital of the carbene fragment and the d_{xz} orbital of the metal center. In terms of reactivity, the ruthenium analog proved very robust, neither reacting with nucleophiles nor with electrophiles.

The use of dianion **103** was successfully extended to the synthesis of rare lanthanide alkylidene complexes ($\text{Ln} = \text{Sm}, \text{Tm}$) (Scheme 11.39) [61, 62].

The reactivity of these complexes with electrophiles such as benzophenone led to the formation of the expected alkene. As the reaction of **103** itself with the ketone did not lead to the same product, the alkylidene nature of the $\text{Ln}=\text{C}$ bond was clearly established. Additional pieces of evidence for the existence of multiple bonding between

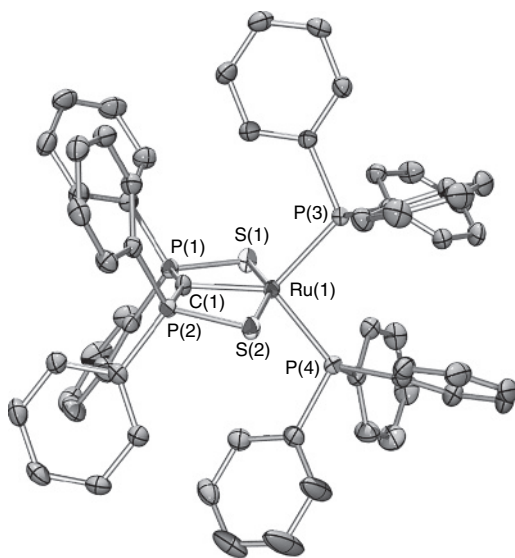
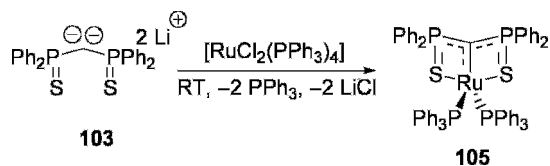


Fig. 11.12. ORTEP plot of complex **105**. Copyright ACS 2005.



Scheme 11.38

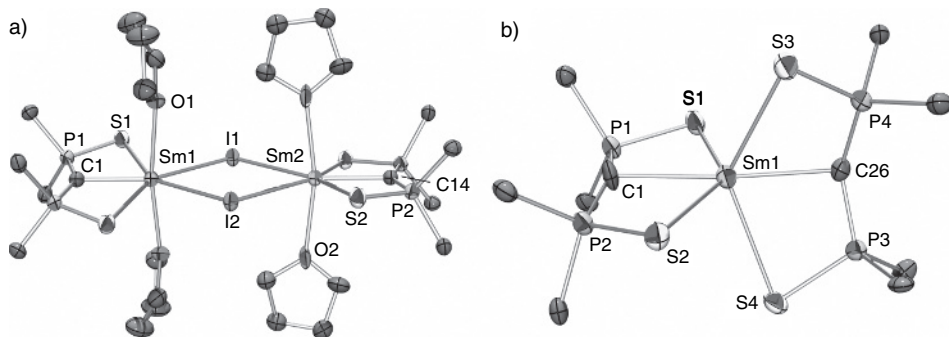
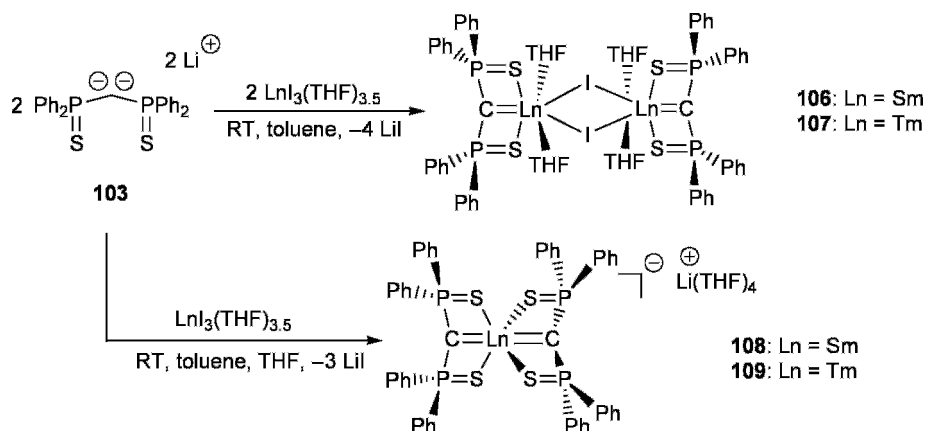


Fig. 11.13. ORTEP plots of complexes **106** and **108**. Copyright RSC 2005.

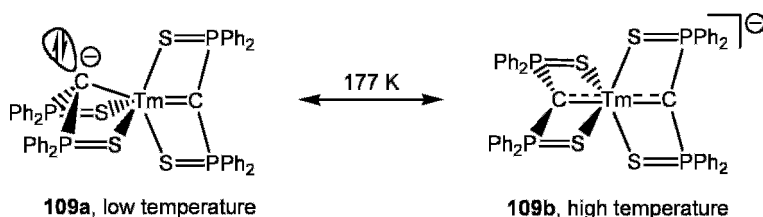
Ln centers and the carbon center were given by the X-ray structures obtained for these species (Fig. 11.13).

First, in the iodide-bridged dimers (complexes **106** and **107**), the geometry at carbon is planar (sum of the angles of 357.8–359.4°), showing the donation of both lone pairs of



Scheme 11.39

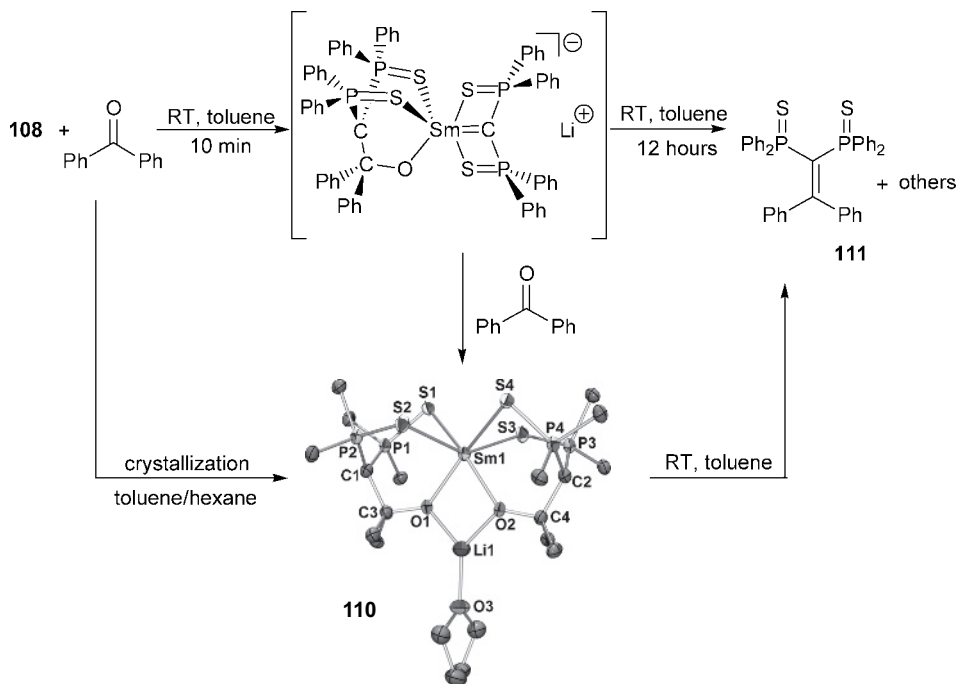
the dianionic fragment to the Ln center. Second, in the homoleptic anionic bisalkylidene complex of Tm (**109**), a low temperature (177 K) phase transition in the crystal was observed. Two significantly different structures were thus recorded (at 150 and 230 K). In the low-temperature form (**109a**), the two carbenic moieties are geometrically different. In one fragment, the carbon is tetrahedral ($\Sigma \text{angles} = 332^\circ$) and the bond distance of 2.42 Å falls in the range of single Tm–C bonds. In the other fragment, it is planar and the bond length is shorter. Therefore the overall charge is located on the first carbon atom which bears a significant sp^3 character whereas the second carbon center behaves as a four-electron donor. In the higher-temperature form (**109b**), the two fragments become identical, the bond distance averages between single and double bond length and the geometry at the carbon atoms is nearly planar. These data point to a delocalization of the anionic charge over the two carbon and the thulium centers, thereby indicating that a π interaction develops between these atoms (Scheme 11.40).



Scheme 11.40

In the course of the reaction between the homoleptic anionic alkylidene Sm complex with benzophenone **108**, several intermediates were observed by ^{31}P NMR spectroscopy. Metalla-oxetane has been proposed as intermediate in the reaction of early transition metal carbene complexes with carbonyl derivatives, but few related species have been isolated. In this reaction, one such reactive species **110** could be crystallized. In the

structure, new C–C and O–Sm bonds are formed while the Sm–alkylidene bond is cleaved. When redissolved in toluene, this complex evolved to the alkene **111** and samarium oxide derivatives, proving this open metalla-oxetane to be an intermediate in the transformation (Scheme 11.41).



Scheme 11.41

11.4 CONCLUSION

The early studies on palladium complexes with pincer ligands bearing thioether pendant arms (Ligand **C**, Chart 11.1) proved the robustness of the metal–ligand interaction. It results both from the tridentate coordination and the C–Pd bond strength. The complexes have been used with great success in many areas, ranging from supramolecular chemistry to catalysis. In particular, significant results have been obtained with the Se analog (ligand **D**) in catalysis. Changing thioether arms by phosphinosulfide ones (ligand **F**) or thioketone (ligand **E**) resulted in similar palladation of the central aromatic ring, although little attention has been paid to the chemistry of these species. The major drawback in the development of these S–C–S ligands is that it requires a C–H to C–M formation, which is limited to few metal centers. In fact, until 2002 it was believed that it could only be achieved with Pd. In the 1980s, the replacement of the central aromatic ring by an alkyl group (Ligand **G**) was envisaged, but the S–C–S tridentate coordination to the metal centers that were chosen was not observed. Nevertheless, the C(alkyl)–Pd bond was robust in these complexes similarly to the C(aryl)–Pd bond. Most

recently, the dianion (ligand **H**) obtained from the double deprotonation of dppmS2 (or the deprotonation of anion **G**) was shown to act as a tridentate ligand. It seems therefore that the tridentate coordination of **G** could be observed provided that the appropriate precursors are used. Importantly, the coordination of the dianion **H** was observed with very different metal centers: from lanthanides to palladium, which opens the way to various applications.

The other ligands (**A** and **B**, S–P–S type) whose chemistry is presented in this review bear resemblance to the above-mentioned S–C–S ligands. Indeed, the tridentate coordination and the robustness of the complexes was evidenced. Some applications in catalysis have appeared with palladium complexes, and rhodium complexes have shown interesting activation of ‘small’ molecules (H_2 , CS_2 , SO_2).

In conclusion, it makes no doubt that the easy handling and the various uses already reported, of the SXS–M pincer complexes ($X=C$ or P) will lead many more researchers to study this highly interesting family of organometallic complexes.

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Pincer ligand complexes with unusual atoms and molecular backbones

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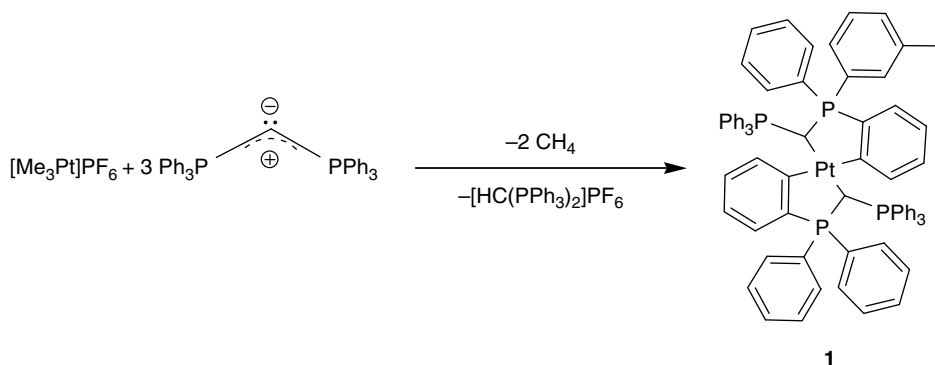
12.1 INTRODUCTION

12.1.1 From Ylides to Pincers

The word ligand which comes from the Latin ‘ligare’ [1, 2], to bind, was first introduced to chemistry by Stock in 1917 [3, 4]. This seems rather strange because Stock was more or less well known for his boron hydride and silicon research. Most likely, he sought to convey the similarities between boron, carbon and silicon chemistry. But in another context, perhaps Stock used the word as a conceptual unifying principle in chemistry because of the seminal work of Werner [5] and the theories of Lewis who laid the foundations for its use [6] in a much broader scope. This included the ideas of coordination chemistry [7, 8] in the sense of modifying the behaviour of metal ions in the gas phase and in solution. Chemists subsequently used the term to describe atoms or groups attached to a central atom in coordination. The term was also used in describing the structure of organometallic compounds [9–11]. This description fits the role of chelating organic bases with donor atoms of the main group elements of nitrogen, phosphorus or sulphur which have proved to be the *sine que non* of transition metal complex chemistry for the past 50 years [12, 13]. These ideas in turn led to ‘ligand tailoring’ [1, 2] of metal substrate reactivity which now forms the basis of modern organometallic chemistry, coordination chemistry and organic synthesis as well as nanochemistry.

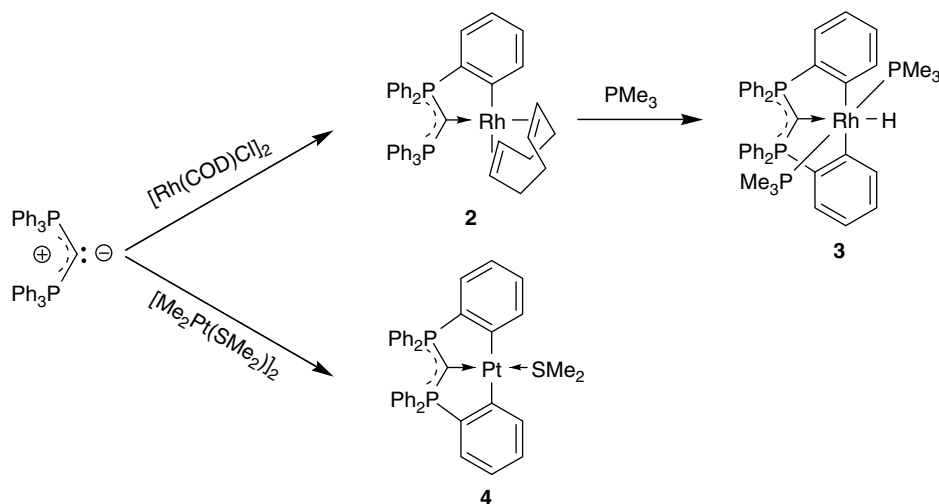
Cyclic coordination of transition metals with C_{2v} symmetric anionic meridional, tridentate ligands had been studied since first inceptions by Meek [14, 15], van Koten [16] and Shaw [17, 18]. The facile ability of these ligands to strongly coordinate a wide variety of transition and non-transition metals depends on the presence of at least two donor atoms and an *ipso*-C metal bond to complement the structure [19]. Molecular control of the bite angle, steric environment and frontier orbitals can thereby be affected [20, 21]. Together, these factors translate into materials with thermal stability, ease of

coordination and potential for interesting homogeneous catalysis [22–25]. Of particular importance is the presence of one metal–carbon bond to reinforce the structure. This prevents the dissociation of the metal from the ligand under a variety of thermal conditions. Our foray into the field of ‘pincer chemistry’ emerged by a circuitous route with the study of the interaction of hexaphenylcarbodiphosphorane ($\text{Ph}_3\text{P}=\text{C}=\text{PPh}_3$) with Me_3Pt^+ and the observation that *ortho* metalation of the phenyl groups of at least one Ph_3P fragment could occur until all the methyl groups on the platinum are eliminated (**1**) (Scheme 12.1) [26].



Scheme 12.1

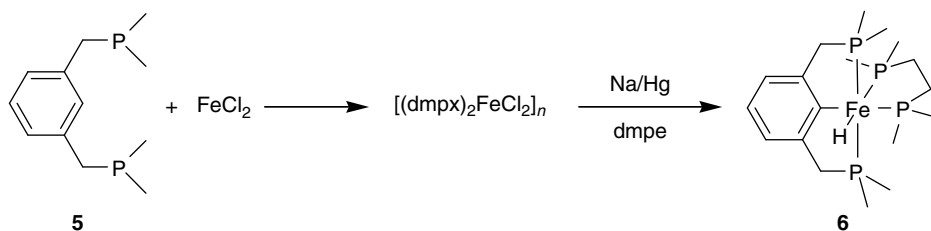
This gave a proposed structure **1** with some similarity to that reported more recently by Cavell [27], which illustrates a more obvious symmetrical meridional arrangement of the metalated central carbon atom and the metalated aromatic rings **3** and **4** (Scheme 12.2).



Scheme 12.2

Thus, pincer carbene complexes which are formed via double *ortho* metalation are obtained if coordinatively unsaturated precursors of late transition metals are employed. The generality of this behaviour is not always consistent as is shown by the metalation of a coordinated ligand after the treatment of hexaphenylcarbodiphosphorane with a corresponding iridium cation [28].

The extension of the carbodiphosphorane ligand research began with the synthesis of 1,3-bis(dimethylphosphinomethyl)benzene (dmpx) (**5**) from 1,3-dibromo-*m*-xylene and potassium dimethylphosphide [29]. Treatment of dmpx with ferrous chloride was studied to test the concept of internal metalation of the aromatic ring (Scheme 12.3). In accordance with ideas set forth by Shaw [17, 18] and later from ideas adapted from the work by Bruice [30], there was no metalation. Metalation was indeed achieved, however, by reduction of the iron to Fe(0) which then gave the Fe(II) hydride product **6**, presumably after oxidative addition [29].

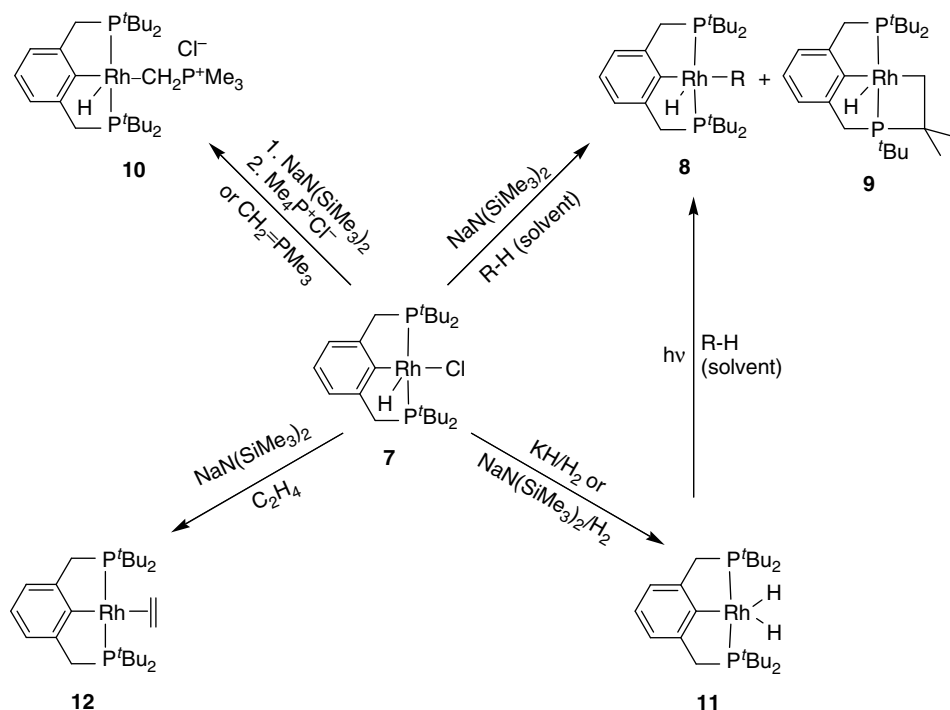


Scheme 12.3

12.2 INTRA- VS. INTERMOLECULAR C–H ACTIVATION

In the meantime, research was pursued with the corresponding *t*-butyl phosphine-based ligands to explore the then unreported dihydride complexes. In a paper first presented in the Biennial Inorganic Symposium in Guelph, Canada, the internal self-metalation and external activation of C–H bonds were reported [31].

Even though the work described in this paper was initiated in the 1970s, there were problems in identifying the nature of the products formed by treating the rhodium hydrochloro complex **7** with $\text{NaN}(\text{SiMe}_3)_2$ (Scheme 12.4), especially because none of the products would crystallize even after months of experimentation. The resort to using all the spectroscopic tools available led us to suspect that aliphatic C–H bonds were being attacked. Based on spectroscopic evidences, the inter- and intramolecular C–H oxidative addition products **8** and **9** were suggested (Scheme 12.4). Because no compounds could be isolated for X-ray studies, there always remained some skepticism about the results. Nevertheless, one direct experiment led us finally to conclude that a significant discovery had been made and that was the treatment of **7** with $\text{Me}_3\text{P}=\text{CH}_2$ and Me_4PCl which gave $[\text{Rh}](\text{H})\text{CH}_2\text{PMe}_3\text{Cl}$ (**10**) in two separate reactions. Thus, if **7** was dehydrochlorinated and then rapidly treated with Me_4PCl or if **7** was treated directly with $\text{Me}_3\text{P}=\text{CH}_2$, the result was the same. In both cases, the synthesis of the rhodium ylide adduct $[\text{Rh}](\text{H})\text{CH}_2\text{PMe}_3\text{Cl}$ (**10**) has been achieved. Moreover, treatment of the rhodium hydrochloro complex **7** with $(\text{CD}_3)_3\text{P}=\text{CD}_2$ and $[\text{Rh}](\text{D})\text{Cl}$ (**7**) showed



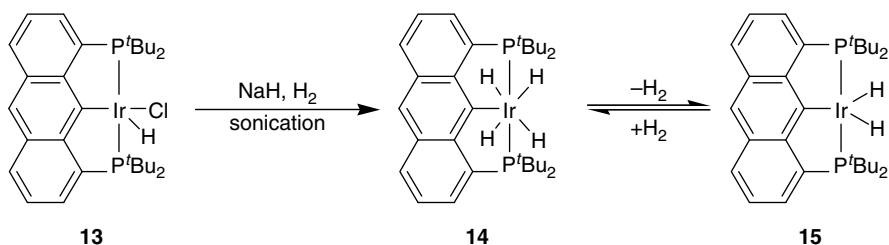
Scheme 12.4

no incorporation of H into the ylide adduct, presumably because the Rh atom was more reactive to the acidic trialkylphosphonium salt than the hydrocarbon solvent applied (benzene, hexane, cyclohexane and octane). When the trialkylphosphonium salt is absent from the reaction mixture, the hydrocarbon interaction products **8** and **9** are observed. Interestingly, compound **8** is also accessible by photolysis of the dihydride **11**, whereas the cyclometalation to **9** has not been observed (Scheme 12.4). Furthermore, treatment of **7** with $NaN(SiMe_3)_2$ in the presence of ethylene leads to the rhodium(I) olefin compound **12** (Scheme 12.4).

Thermal stability is a recurrent problem in homogeneous catalysis, especially for kinetically hindered or endothermic processes where high reaction temperatures are indispensable. Complexes with a higher thermostability are expected with more rigid backbone ligands than those known for the phenyl PCP pincer system. By replacing the phenyl ring with an anthracene system, the expected stability increase is observed. The determination of the melting point and the temperature of decomposition using differential scanning calorimetry resulted in m.p. $196^\circ C$ and dec. $308^\circ C$ [32].

The reduction of **13** in a hydrogen atmosphere gives the equilibrium mixture of the tetrahydride complex **14** and the dihydride compound **15** (Scheme 12.5). The equilibrium can be shifted by saturating the solution of the mixture with hydrogen towards the tetrahydride **14** or by evaporating the solvent under vacuum giving the dihydride **15**.

The possibility of using the anthracene dihydride PCP pincer complex **15** with temperatures up to $250^\circ C$ makes it a potent dehydrogenation catalyst. Transformations of



Scheme 12.5

cyclododecane to *cis/trans*-cyclododecene at 250°C are described with an initial turnover frequency of 40 h⁻¹ and a turnover number of 136 after 148 h, although the turnover frequency for the dehydrogenation of cyclooctane at 150°C is about one order lower than that for the analogous phenyl PCP Ir complex. Calculations about the transition states of associative, dissociative or interchange pathways came to the conclusion that the interchange mechanism could be favoured for the reaction conditions. But because of the similarity of the free activation enthalpies of the different transition states, the dynamics of the reaction most likely involves the entire range between associative, dissociative and interchange pathways.

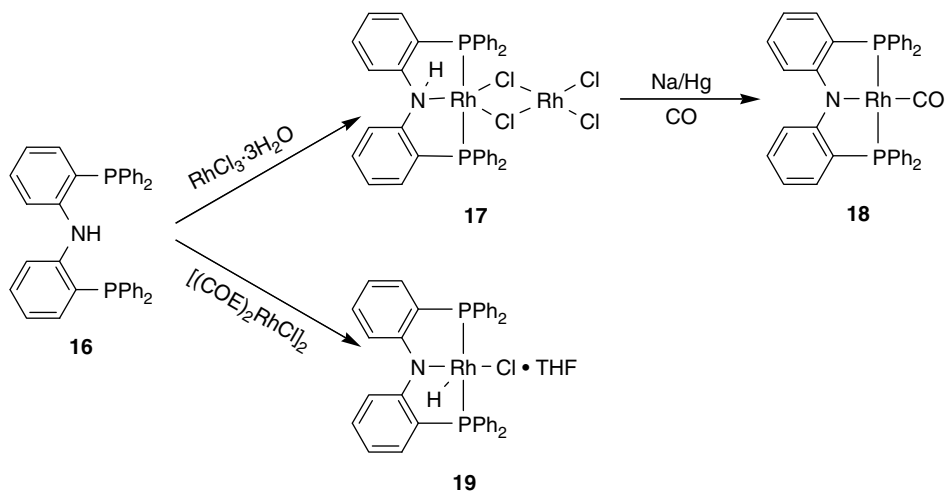
12.3 PNP Pincer Ligand Backbone

The general nature of pincer chemistry has allowed for the very facile synthesis of numerous analogs of tridentate bonding to the central metal atom. One of these arrangements involves the replacement of the sigma bond to the metal with nitrogen, silicon and phosphorus rather than carbon.

The obvious advantage of nitrogen as central atom is the possibility that the lone pair of non-bonded electrons on the nitrogen atom will interact with suitable symmetrical orbitals on the metal atom, thereby decreasing or increasing the electron density [33–35]. There are normally three bonding modes for metal-substituted amines [33, 36–38]. In one case, there is a pyramidal nitrogen atom sp³ hybridized, a localized lone pair, and secondly one with sp² hybridization where there is more or less interaction of the lone pair with the d orbitals on the metal.

The pincer complexes with nitrogen in the backbone that have been synthesized recently have more or less an almost planar form, which indicates some amount of π -electron interaction (Scheme 12.6) [39]. In the ligand system **16**, the amine is positioned between two diphenylphosphine groups. Thus, the strong metal-binding properties of the phosphines and the chelate effect prevent the dissociation of the highly electron-rich amide from the electron-rich low-valent rhodium(I) (**18**) and rhodium(III) (**19**) amide complexes.

The amide complexes **18** and **19** have been synthesized by two different routes. Upon refluxing of RhCl₃ trihydrate with **16** in methanol, the air-stable pale-yellow dinuclear complex **17** is formed, which can be converted to the rhodium(I) amide complex **18** by treatment with Na/Hg in the presence of CO in THF. The rhodium(III) amide **19** is obtained by direct reaction between the pincer ligand **16** and [(COE)₂RhCl]₂



Scheme 12.6

(COE = cyclooctene) in THF. Interestingly, the latter reaction is a rare instance where a chelate-assisted oxidative addition of N–H bond occurs with rhodium. Moreover, it has been demonstrated recently that the N–H bond of ammonia can be cleaved by intermolecular oxidative addition to a pentamethylenediphosphine pincer iridium(I) complex fragment [40].

There is no clear-cut evidence that there is an appreciable amount of $p\pi$ – $d\pi$ -bonding in these types of complexes [41]. The experimental Rh–N bond distance of 2.074(9) Å as well as the theoretically calculated values for **18** suggests that this is a single bond. Moreover, the planarity of the rhodium-amide bond does not necessarily confirm whether π -bonding occurs between these fragments. This agrees with calculations which also give no indication for an interaction between the Np orbital and the d orbital of the rhodium atom. According to a Mulliken population analysis (B3GGA-II), both nitrogen (–0.7 a.u.) and rhodium (–0.3 a.u.) carry a negative charge. This ambiguity is evident from a recent paper by Caulton [42], which describes a novel osmium pincer complex with an Os–N bond of 2.26 Å in one case and then in another paper by Ingleson [41] where the Os–N distance is 2.137 Å and it is still called an amide bond, with sp^3 hybridization.

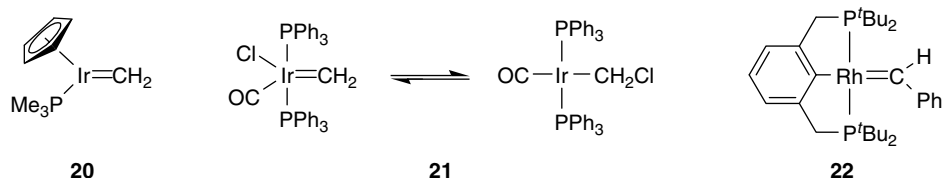
Liang [43–45] and Ozerov [46–50] who have recently studied nitrogen pincer complexes also found that most nitrogen atoms in the backbone of pincer complexes are more or less of the amido type with little π -bonding.

12.4 PINCER CARBENE COMPLEXES

12.4.1 Endocyclic Pincer Carbenes

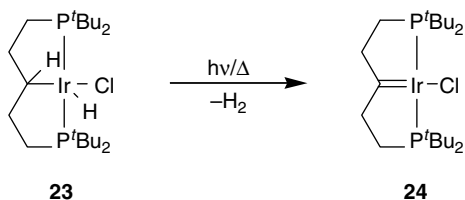
Many pincer ligand systems, especially examples with phosphorus donor atoms, can exist with exocyclic carbene fragments. An example of this is shown from the research of Fryzuk [51, 52] and Milstein. Wittig ylides can serve as functional group transfer agents

as demonstrated by Milstein [53]. Oftentimes, these exocyclic carbenes are thermally more stable than the exocyclic examples described by Bergman [54] and Roper [55] (Scheme 12.7).



Scheme 12.7

Another much less common form is the endocyclic carbene-alkylidene. An example of this was first prepared by Shaw [56] in less than 5% yield by thermally heating the corresponding hydrochloride (Scheme 12.8). We have subsequently observed that the compound can be prepared in good yield by continuous photolysis of the hydrochloride, with concomitant removal of hydrogen with a stream of argon followed by chromatography to remove unreacted hydrochloride [57].

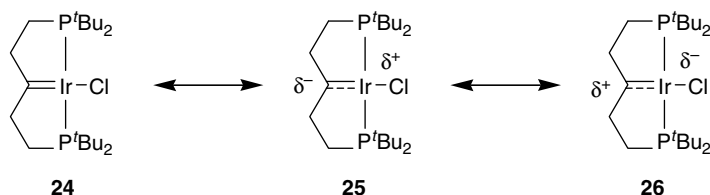


Scheme 12.8

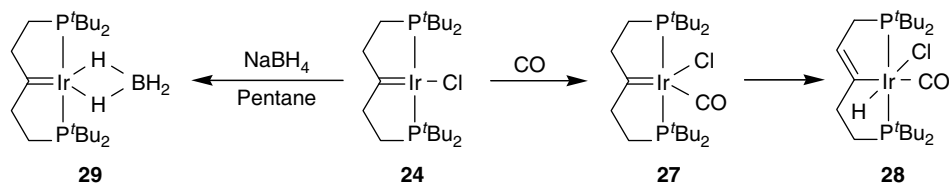
One of the major advantages of endocyclic or internalized carbon–metal double bonds is the flexibility of changing modes of electron density on the metal atom. For example, the metal atom can have more or less electron density depending on the polarity of the carbon–metal bond as illustrated in the resonance structures (Scheme 12.9). We chose chemical methods to probe the character of the carbon–metal bond by treating the carbene chloride with NaBH_4 and carbon monoxide.

When treated with carbon monoxide, we presume that an adduct is formed, followed by the isolated product shown in Scheme 12.10 which undergoes rearrangement.

On treatment with NaBH_4 , the Cl atom is replaced with a hydrogen atom. The released borane fragment is, however, subsequently complexed to the hydride of which there are other examples of bonding. The available chemical data at this juncture still do not give a clear understanding of the bonding in the endocyclic carbene chloride.



Scheme 12.9

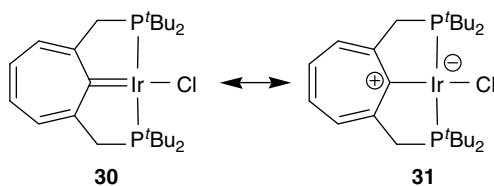


Scheme 12.10

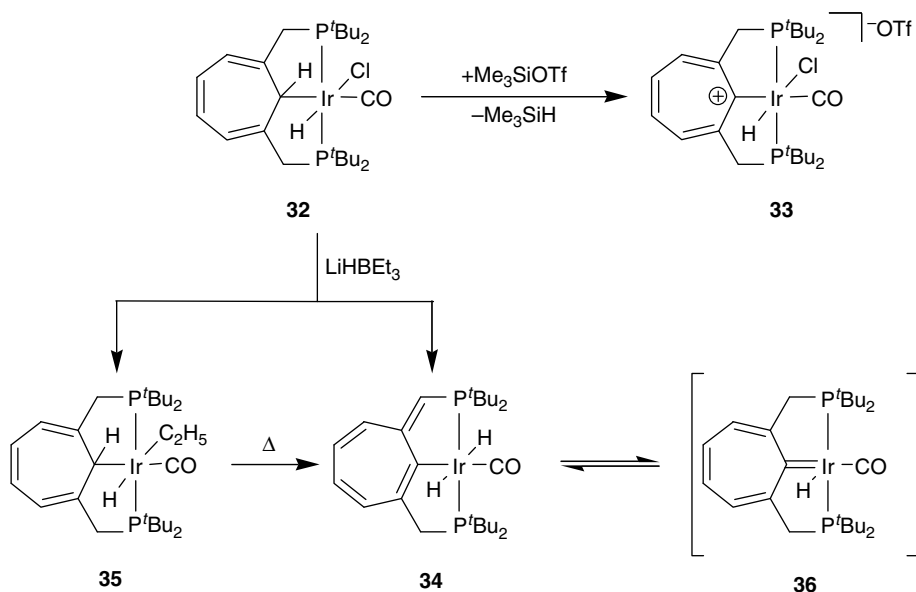
12.4.2 Cycloheptatriene as Ligand Backbone

The seven-membered monocyclic ring C_7H_6 has been an attractive synthetic motif for organic as well as organometallic chemists. From the two valence isomeric forms, the allene was found to represent the ground state, whereas the carbene may be either a transition state or an energy minimum on the isomerization pathway between enantiomeric allenes. In this context, the chemistry of transition metal complexes of C_7H_6 has been of special interest because of the various modes of bonding which could be expected [58]. Thus, cycloheptatriene metal complexes of early transition metals prefer the carbene (cycloheptatrienyldiene) structure. This configuration is supported by the aromaticity of the tropylium resonance form and the low-lying vacant orbitals on the metal. Late transition metals show a more differentiated behaviour. While platinum(0) favours the allene structure, a carbene could be established for a d^8 Pt(II) complex. This was explained with strong interactions between the cycloheptatrienyldiene HOMO and the metal LUMO [59]. Therefore, the cycloheptatriene moiety is believed to be an interesting and basic integral part of a pincer ligand system. Moreover, because of the positively charged character of the aromatic 6π electron system, the cycloheptatrienyl ring will impose a reversed polarity into the otherwise alkylidene carbon bond as compared to the pentamethylenediphosphine complexes **24** and **26** (Schemes 12.9 and 12.11).

The particular feature of most of the complexes described is their unsaturated but non-aromatic ligand backbone. Thus, it can be considered as intermediate between the phenyl- and alkane-based pincer ligands. The cycloheptatrienyl PCP complex **32** displays a rather unusual reactivity towards electrophiles as well as nucleophiles [60, 61]. Thus, when **32** is treated with trimethylsilyl trifluoromethanesulphonate (Me_3SiOTf), the yellow tropylium triflate complex **33** is obtained in a clean reaction in almost quantitative yield



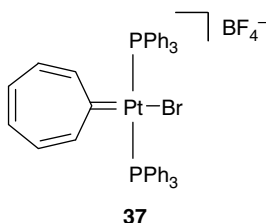
Scheme 12.11



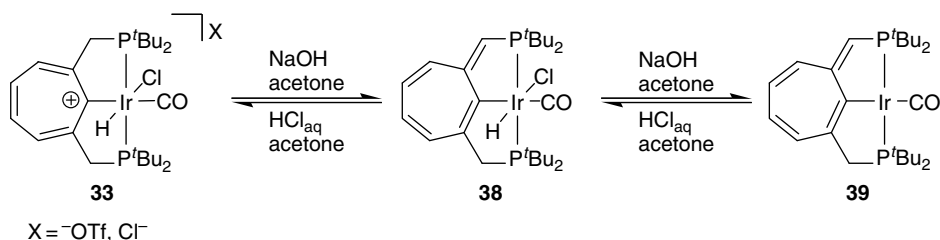
Scheme 12.12

(Scheme 12.12). The new tropylum system **33** is generated by abstraction of a hydride from the metal-bound ring carbon atom of **32** and the formation of trimethylsilane. This conversion is rather remarkable as the electrophile Me_3SiOTf is typically replacing a chlorine ligand by the less coordinating triflate anion in organometallic compounds.

On the other hand, the products which were isolated when compound **32** was treated with the powerful nucleophile LiHBEt_3 were unexpected as well (Scheme 12.12). The octahedral *trans*-dihydride complex **34** is of unusual stability and the result of a dehydrohalogenation followed by a prototropical rearrangement. Moreover, the *trans*-ethylhydride **35** must arise from an alkyl transfer, although the hydride transfer is expected to occur much faster in these systems. Complex **35** can be cleanly converted into compound **34** by careful sublimation. Interestingly, complex **34** is isomeric to the d^8 carbene **36** which has not been observed. The comparable d^8 carbene $[(1,2,4,6\text{-cycloheptatetraene})\text{Pt}(\text{PPh}_3)_2\text{Br}]\text{BF}_4$ (**37**) has been reported recently [59]. Obviously, the advantage of structure **34** in which the π -system is extended into one of the phosphine side arms is the reduced electron density at iridium despite the unfavourable arrangement of the metal hydrides which exert a strong *trans* influence on each other.



The cationic complex **33** undergoes a remarkable sequence of reversible reactions (Scheme 12.13) [61]. Due to the positively charged aromatic tropylium ring and the coordinated phosphine groups, the protons of the methylene bridges become acidic. Thus, in an aqueous solution of sodium hydroxide, one of the bridging methylene protons is removed, followed by a rearrangement of the π -system of the cycloheptatriene backbone in a way that it is extended into one of the five-membered rings. The neutral orange hydrochloro complex **38** is formed, which can be isolated and fully characterized if the sodium hydroxide is employed stoichiometrically. According to the spectroscopic data the π -acidity of the ligand backbone in **38** is strongly reduced compared to the one in **33**. This is especially nicely reflected in the ^{13}C resonances of the metal-bound ring carbon atoms which differ by 74.2 ppm, the one in **38** being shifted to higher field than the one in **33**.

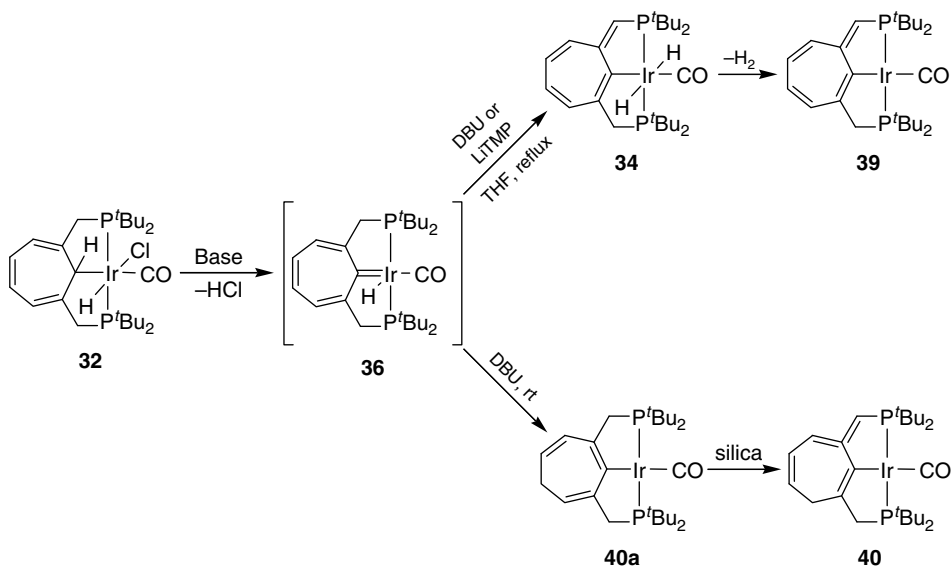


Scheme 12.13

The iridium(III) complex **38** continues to react with sodium hydroxide. In a rare case of a base-induced reduction, **38** loses HCl and gives the dark-red planar iridium(I) compound **39**. The reversibility of the reaction has been demonstrated by the treatment of solutions of **39** with hydrochloric acid as well as with gaseous hydrochloride. In both cases, the tropylium complex **33** could be isolated as the final product. If one succeeds in terminating the reactions, a mixture of **33** and **38** is obtained. All data suggest that the reaction of the tropylium complex **33** with a base yields **39** via **38**. Conversely, if **39** is treated with hydrochloric acid, the sequence is reversed, first giving **38** and in a second step forming the tropylium chloride **33**.

When **32** is treated with NaH, DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) and LiTMP (TMP = 2,2,6,6-tetramethylpiperidide) under various conditions, hydrogen chloride is removed from the starting compound (Scheme 12.14). Depending on the base used and the reaction conditions applied, three unexpected products were observed: the *trans*

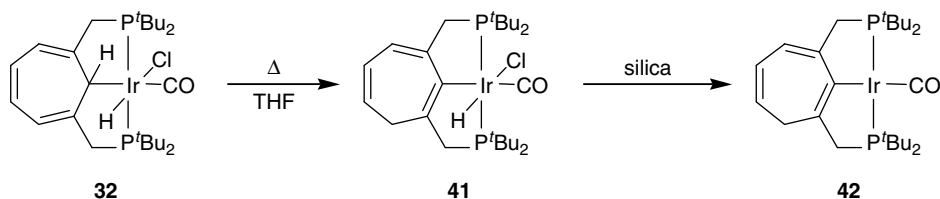
dihydrido iridium(III) complex **34** and the square planar iridium(I) carbonyls **39** and **40**. Interestingly, the different oxidation states of complexes **34** and **40** are only the result of the distinguished arrangement of two hydrogen atoms. Thus, in **34**, the two hydrogen atoms are bound to the metal resulting in the *trans* dihydride iridium(III) complex, whereas the shift of the two hydrides into the ligand backbone leads to a reduction of the metal center in **40**.



Scheme 12.14

A detailed analysis of the different reactions led to the conclusion that in the initial step in each reaction of the hydrochloro complex **34** with the bases NaH, DBU and LiTMP, the cycloheptatrienyl carbene complex **36** is formed by removal of hydrogen chloride from the metal–carbon bond [62]. As has been shown by experiments and by density functional calculations, the carbene complex **36** is rather unstable. Consequently, it cannot be observed but quickly rearranges in a sigmatropic shift to give a more stable product (**34** or **40a**). Only this second reaction step is determined by the conditions applied as well as the base used. The primary products **34** and **40a** can then rearrange on silica to **40** or loose hydrogen at elevated temperature to give **39** (Scheme 12.14).

Interestingly when **32** is heated in THF, the isomerization to the hydrochloro complex **41** is observed which loses hydrogen chloride upon chromatography on silica to form **42** (Scheme 12.15). Moreover, a perusal of the reactions described in this chapter reveals that the formation of a metal–carbon sp² bond is one of the driving forces of the reactions carried out starting from the tropylium PCP pincer complex **32**.



Scheme 12.15

12.5 CONCLUSION

Pincer ligation with transition metals has already shown a broad collage of structural and chemical reactivity. Almost all pincer complexes have unique properties of thermodynamic and kinetic stability along with electron density flexibility on the transition metal atoms. In the future, these types of complexes should be expected to show an unusual array of chemical reactivity, synthetic potential, spectroscopic details and an advance in new material research.

ACKNOWLEDGEMENTS

We thank those students, colleagues and the funding agencies DAAD, DFG, Fond der Chemischen Industrie, National Science Foundation, Petroleum Research Fund, Studienstiftung des Deutschen Volkes, who have supported this research.

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Rigid PNP pincer ligands and their transition metal complexes

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13.1 INTRODUCTION

Pincer ligands have been steadily gaining in popularity since their introduction by Shaw and co-workers in the mid-1970s [1]. The advantages of pincer ligands lie in the extreme stability of their transition metal complexes and in the frequent imposition of unusual reaction pathways. PCP ligands **A** (Fig. 13.1) and similar ligands represent the most widely used pincer structure [2]. PNP pincer ligands with a central amido donor are less common. Amido-PNP ligands were first constructed by Fryzuk et al. in the early 1980s (**B**, albeit they were not originally referred to as ‘pincers’) [3–5]. PNP ligands **C** with aliphatic backbones were first reported by Edwards and co-workers [6, 7]. The use of **C** has been limited to several early transition metal and actinide complexes [8–11].

Amido-PNP ligands may be viewed as a chelating analog of the ubiquitous *mer*-Cl(R₃P)₂ motif. Amido is probably a better mimic of Cl than the aryl donor in PCP. In contrast to the aryl C donor in PCP, amido is a much stronger π -donor and is a ligand of weaker *trans*-influence. These factors, inter alia, may lead to significant structural and reactivity differences between PCP- and PNP-supported chemistry. As well, PNP ligands provide a hybrid environment that combines soft phosphine donors and a hard amido donor. Thus, PNP ligands are capable (as originally envisioned by Fryzuk) of supporting both the hard early transition metal centers and the soft late transition metal ones.

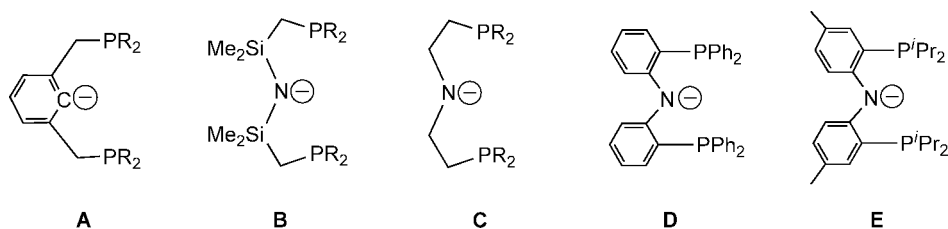


Fig. 13.1. Examples of pincer ligands.

The Fryzuk PNP ligands **B** have made possible a number of unusual transformations and structures [3–5], most recently through the work of Caulton and co-workers [12–16]. However, the presence of the oxophilic Si in the backbone of the Fryzuk ligands renders them susceptible to facile attack by oxygen-containing reagents, particularly water and alcohols [17, 18]. In addition, both **B** and **C** are quite flexible and do not have any intrinsic preference for meridional vs. facial binding to a metal center.

In 2003, Liang et al. [19] and Mayer, Kaska, and co-workers [20] reported the synthesis of a new PNP ligand wherein the PPh_2 donor arms were connected to the amido by *ortho*-phenylene linkers (**D**). Shortly thereafter, our group reported similar ligands bearing PPr^i_2 arms (**E**) [21]. The construction based on the diarylamido backbone offers increased rigidity (and therefore preference for meridional coordination) and is devoid of β -hydrogens (cf. **C**) and moisture-sensitive functionalities. In this chapter, we will cover the key aspects of the transition metal chemistry of these new rigid PNP ligands that have developed over the last few years. Reviews whose coverage includes certain aspects of the diarylamido-PNP chemistry have appeared recently [22, 23]. For convenience, from here on, the generic notation ‘PNP’ will be used to mean any PNP ligand based on the diarylamine backbone.

13.2 LIGAND SYNTHESIS

13.2.1 Approaches to C–P Bond Construction

The phosphine fragment is often the most expensive component in the synthesis of the PNP ligands. Therefore, it is prudent to install the phosphine functionality as late as possible in the synthesis. This strategy is also sensible because (a) at least the more basic phosphines (and thus PNP ligands) are air-sensitive and thus require special treatment and (b) transition metal-catalyzed procedures (such as Pd-catalyzed amination) are unlikely to work well with phosphine-containing reagents.

There are two apparent approaches to construct the C–P bond in the context of the PNP synthesis. The first approach calls for a C-electrophile and a P-nucleophile (Fig. 13.2) [19, 24]. While aromatic nucleophilic substitution is often difficult, it appears that the fluoride in fluorinated diarylamines can be displaced by dialkyl- or diaryl-phosphide anions (in the form of alkali metal salts). A similar approach was used to synthesize the anthraphos PCP pincer from difluoroanthracene [25]. The requisite alkali metal diorganylphosphides in these syntheses have been prepared by deprotonation of corresponding secondary phosphines.

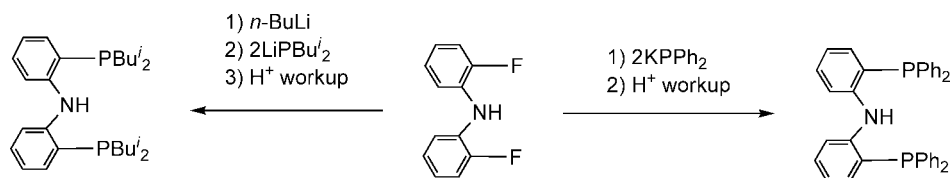


Fig. 13.2. Nucleophilic replacement of fluoride.

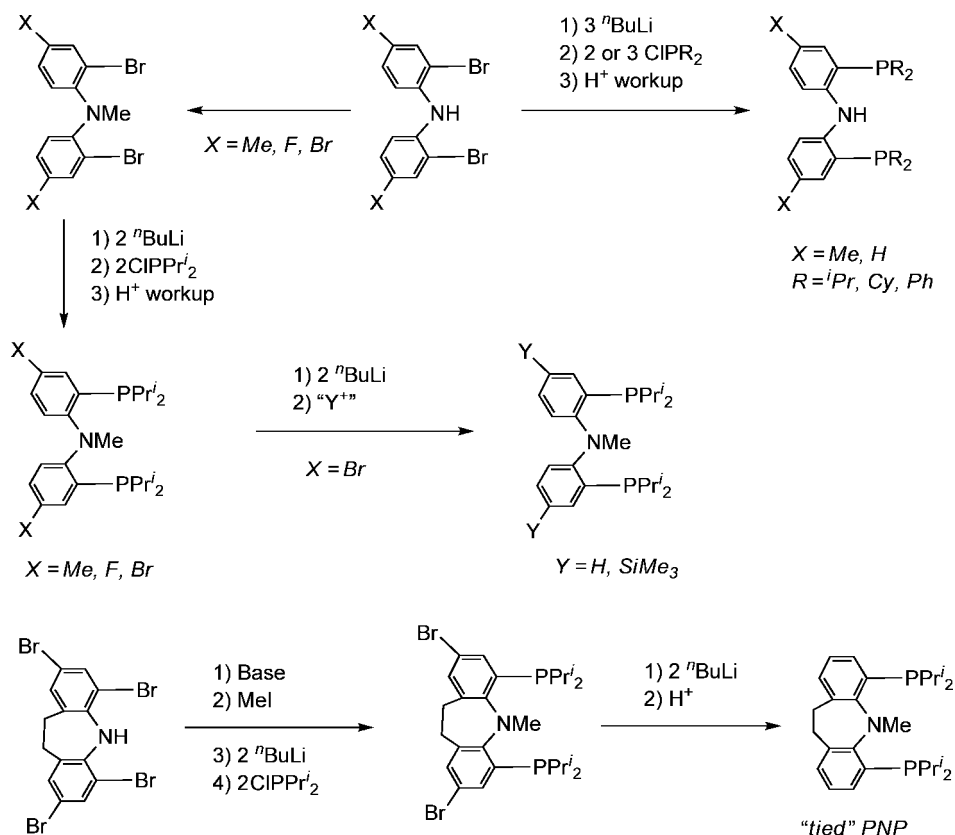


Fig. 13.3. PNP synthesis from brominated precursors.

The second approach calls for a P-electrophile and a C-nucleophile (Fig. 13.3). This can be realized through the use of a ClPR_2 reagent and the corresponding aryllithium derivative [20, 21]. Many ClPR_2 compounds are commercially available. The aryllithium derivatives are most conveniently accessed via Li/Br exchange of the corresponding aryl bromides with $n\text{-BuLi}$.

Several N-methylated PNP ligands have been prepared as well (Fig. 13.3) [26–28]. In several cases, group 9 and 10 metals have been shown to cleave the N–Me bond, thus making N-methylated PNP ligands viable precursors for the transition metal complexes of anionic PNP (vide infra).

13.2.2 Approaches to the Diarylamine Precursors

Both C–P bond construction approaches require diarylamine precursors with bis(*ortho*-halogen) substitution: either fluorines for the C-electrophile/P-nucleophile approach or bromines for the P-electrophile/C-nucleophile approach. Although other methods are conceivable (e.g., preparation of bis(*o*-bromophenyl)amine via the Chapman rearrangement by Kaska, Mayer, and co-workers) [20], the most expedient way to put together

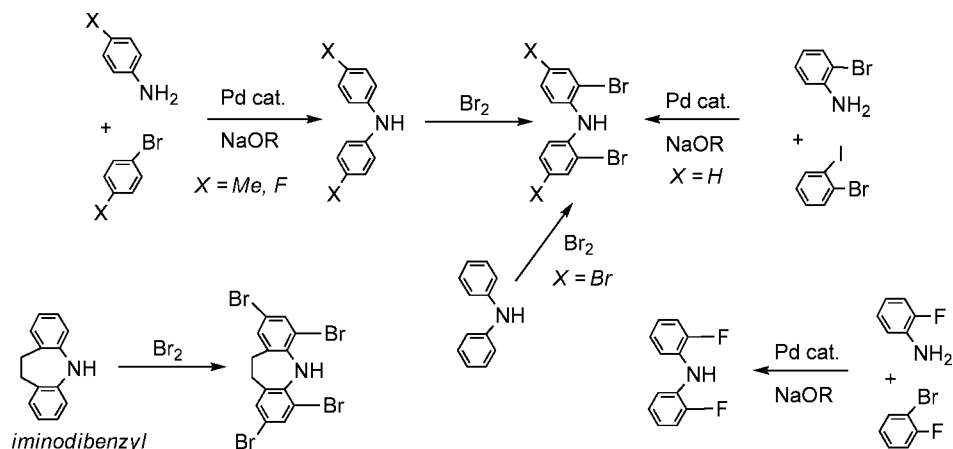


Fig. 13.4. Synthesis of brominated diarylamines.

the diarylamine core appears to be the Pd-catalyzed [29, 30] coupling of anilines with aryl halides (Fig. 13.4).

It is possible to construct the requisite halogenated diarylamines directly via Pd-catalyzed amination [31]. For the fluorinated derivatives, this is the only option [19, 24]. Alternatively, two *ortho*-bromines can be installed by bromination of a diarylamine [21, 26–28, 32]. The latter approach allows access to a greater variety of substituents on the aromatic rings.

Some of the simple diarylamines are commercially available; others can be conveniently synthesized by Buchwald–Hartwig amination [29, 30]. The so-called ‘tied’ PNP ligand [28] is a variation on the diarylamine theme and can be accessed from the cheap, commercially available iminodibenzyl.

13.3 GROUP 4 METALS: MULTIPLE METAL–CARBON BONDS

The rigid PNP ligands serve well as robust scaffolds that support unusual group 4 metal complexes with multiple metal–carbon bonds. Unlike for groups 5 and 6, the alkylidene compounds for group 4 are rather rare, particularly for the heavier congeners Zr and Hf. The PNP ligands of Fryzuk have been applied to the group 4 chemistry, but not in the context of alkylidene formation [3–5].

Early metal alkylidenes (Schrock carbenes) are most commonly formed via α -abstraction in polyalkyl metal complexes [33]. α -Abstraction is inherently favored by the larger size of the ligands and by the greater coordination number in the starting polyalkyl. Introduction of two neutral bulky phosphine donors while utilizing only one unit of valence makes the PNP ligand a prime candidate to induce α -abstraction reactions. The rigidity of the PNP ligand is important because it makes impossible the alleviation of steric congestion by simple phosphine dissociation (a path that is typical for the flexible Fryzuk PNP and P_2Cp ligands [3–5, 34–37]).

13.3.1 Synthesis of Zr Alkylidenes

The PNP ligand framework can be successfully installed on a Zr^{IV} center via reaction of (PNP)Li (**1**) with $\text{ZrCl}_4(\text{OEt}_2)_2$ (Fig. 13.5) [38]. The overall symmetry displayed by **2** in solution on the NMR timescale is C_2 or C_s with *trans*-disposed phosphine arms. The significant upfield shift of the ^{31}P NMR resonance in **2** compared with the free ligand is consistent with coordination of phosphines to Zr.

Alkylation of **2** with Me_2Mg cleanly affords (PNP)ZrMe₃ (**3**) upon workup. **3** is thermally stable (no NMR-detectable change after 5 h at 80°C in C_6D_6). The structure of **3** in the solid state was determined by X-ray diffraction methods. It revealed an unusual geometry about the 6-coordinate Zr center where each of the PNP and Me₃ sets of donors can be described as intermediate between facial and meridional. These distortions are likely a consequence of the rigidity of PNP and of the drive to avoid *trans*-placement of the Me ligands. Polyalkyl d^0 metal compounds often show related distortions [39–44].

Alkylation of **2** with dibenzylmagnesium leads to the formation of **4**. **4** was not isolated but NMR characterization in situ supports their assignment. Even at 22°C, **4** evolves into the alkylidene complex **5**. The definitive spectroscopic features of **5** are the presence of a downfield alkylidene signal in the ^{13}C NMR spectrum ($\delta = 231.0$) and the low value (92 Hz) of the alkylidene $^1J_{\text{CH}}$ coupling constant indicative of an α -agostic alkylidene [33]. The alkylidene H resonates at $\delta = 7.32$ in **5**. These data for **5** are similar to those reported for Fryzuk's $(\text{P}_2\text{Cp})\text{Zr}=\text{CHPh}(\text{Cl})$, the only other known Zr alkylidene type [34].

Kinetic studies on the conversion from **4** to **5** indicate the importance of entropic effects. The enforced dual phosphine coordination of the PNP phosphines in the ground state and throughout the reaction reduces the entropic barrier in the formation of **5** compared with the formation of $(\text{P}_2\text{Cp})\text{Zr}=\text{CHPh}(\text{Cl})$.

13.3.2 Synthesis of Ti Alkylidenes and Related Compounds

In collaboration with the Mindiola group, we initially attempted to approach Ti alkylidenes analogously to the successful Zr chemistry. While (PNP)TiCl₃ was easily prepared,

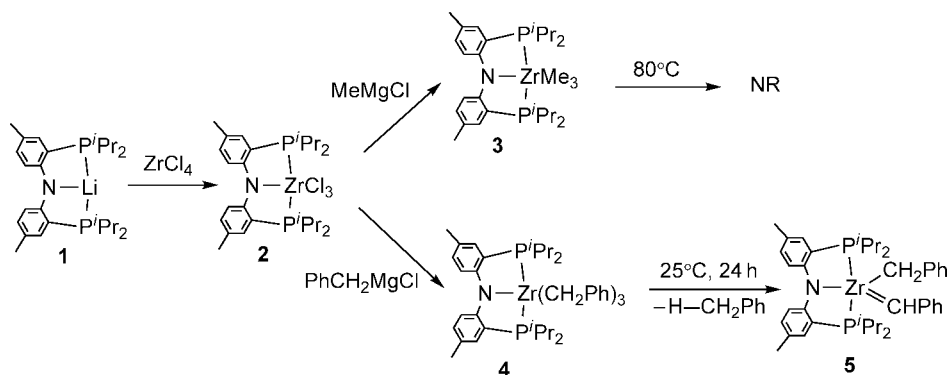


Fig. 13.5. Zirconium alkylidene.

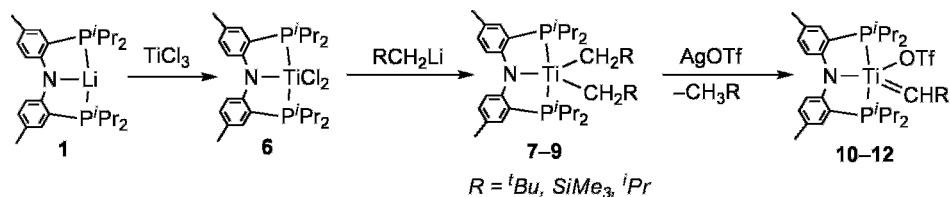


Fig. 13.6. Titanium alkylidene.

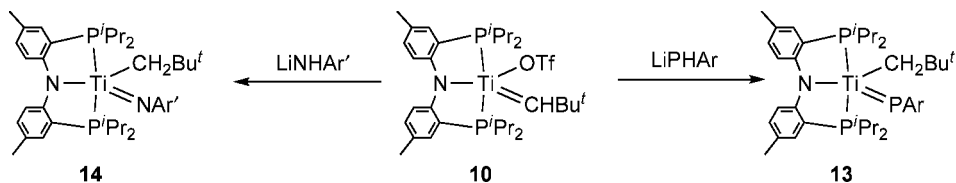


Fig. 13.7. Titanium imido and phosphinidene complexes.

its alkylation by $(\text{PhCH}_2)_2\text{Mg}$ led to a multitude of undesired products, including possibly those arising from the reduction of the Ti^{IV} center [45].

The Mendiola group had successfully developed a new approach to Ti^{IV} alkylidene formation in the diketiminate-supported systems that entails alkylation of a Ti^{III} precursor followed by one-electron oxidation [23]. This strategy proved successful for the PNP derivatives as well (Fig. 13.6). Alkylation of **6** with alkyl lithium reagents and subsequent one-electron oxidation gave rise to the structurally authenticated alkylidenes **10–12** in high yield [45–48].

10 reacted with lithiated bulky arylphosphine or bulky aniline to ultimately produce complexes **13** and **14**, respectively (Fig. 13.7) [45]. Experimental data and DFT calculations indicate multiple bonding between Ti and N or P in these compounds.

Further alkylation of **10** leads to **15** [48]. **15** undergoes α -abstraction to ostensibly produce a highly reactive and very much unprecedented Ti alkylidyne **16** (Fig. 13.8). **16** was not observed directly, but its intermediacy was strongly supported by kinetic and computational findings. **16** displays extraordinary reactivity, undergoing C–H activation of SiMe_4 and benzene, as well as ring-opening of pyridine, all at ambient temperature [47, 48]!

In the context of this reactivity, it is indeed remarkable that the PNP ligand remains untouched by the highly reactive metal centers. This is in marked contrast with the diketiminate ligands that have been shown to be much less tolerant of metal–carbon multiple bond functionalities. A plausible view is that the phosphine donors of the PNP ligand are much less attractive targets for a reactive early metal center than the imine donors of the diketiminate [23]. Thus, while soft phosphines are perhaps counterintuitive as supporting ligands for hard early metals, this mismatch may be critical for the robustness of the auxiliary ligand.

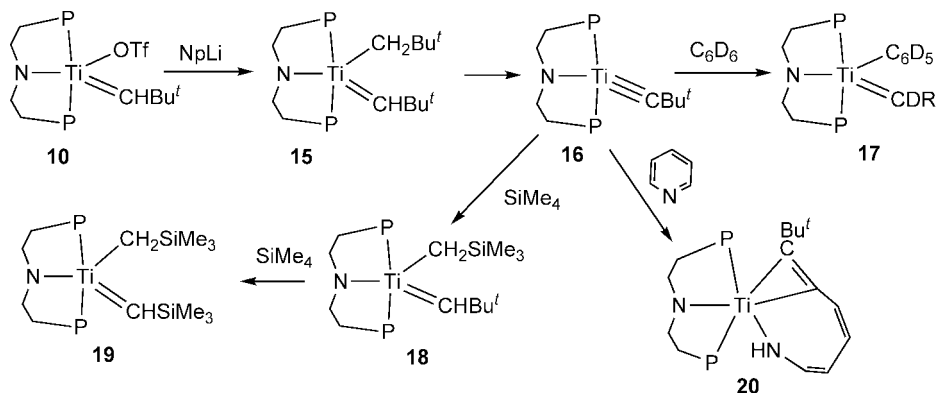


Fig. 13.8. Reactivity of transient Ti alkylidyne.

13.4 RUTHENIUM: CO ABSTRACTION

Selective activation of C–C bonds is one of the basic synthetic challenges [49]. While C–C(O) bonds in ketones may be regarded as activated compared with C–C bonds in hydrocarbons, examples of selective activation of ketonic C–C bonds are rare and most require rather forcing conditions. By contrast, activation of aldehydic R(O)C–H bonds is well established and commonly leads to the abstraction of CO in the form of a metal carbonyl complex [50, 51].

We recently discovered that (PNP)RuH₃ (**22**) is capable of abstracting CO out of acetone and carbonate under mild conditions (Fig. 13.9) [52]. The synthesis of **22** requires avoidance of carbonate bases and primary or secondary alcohols. Reaction of **21** with [(COD)RuCl₂]_n in secondary alcohols with K₂¹³CO₃ as base led to the formation of (PNP)RuH(CO) (**23**) with *ca.* 75% incorporation of ¹³C into the carbonyl ligand. The same product **23** (natural abundance of C) was formed if Et₃N or NaOH was used as bases. Ostensibly, the Ru center abstracts CO from both carbonate and the secondary alcohol.

We therefore surmised that **22** ought to abstract CO from acetone (which would form from ⁱPrOH during the synthesis of **23** from **21**). Indeed, thermolysis of **22** in neat acetone or in fluorobenzene in the presence of 4 equiv. of acetone led to near-quantitative formation of **23**. In the course of the reaction, (PNP)RuMe(CO) (**25**) was observed as an intermediate; methane (but not ethane!) was also observed as a by-product. We proposed a reaction mechanism outlined in Fig. 13.9.

Computational studies by Watson on a model ligand system (Fig. 13.10) determined that the overall transformation is exergonic by –51.5 kcal/mol [52]. The major contributor to this was traced to be the 38.9 kcal/mol preference of the (PNP)Ru^{II}H fragment to bind CO vs. H₂. DFT studies indicated approximately square-pyramidal structures for **22'** and **23'** with hydride in the apical position and either η²-H₂ or CO *trans* to N. The computed structure of **23'** closely matches the structure of **23** determined experimentally through X-ray diffraction.

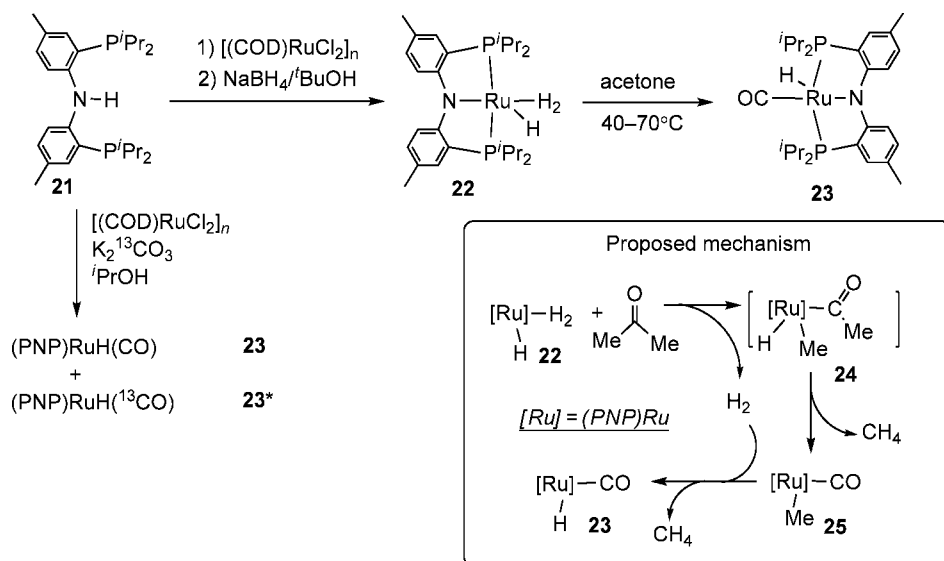


Fig. 13.9. Abstraction of CO from acetone.

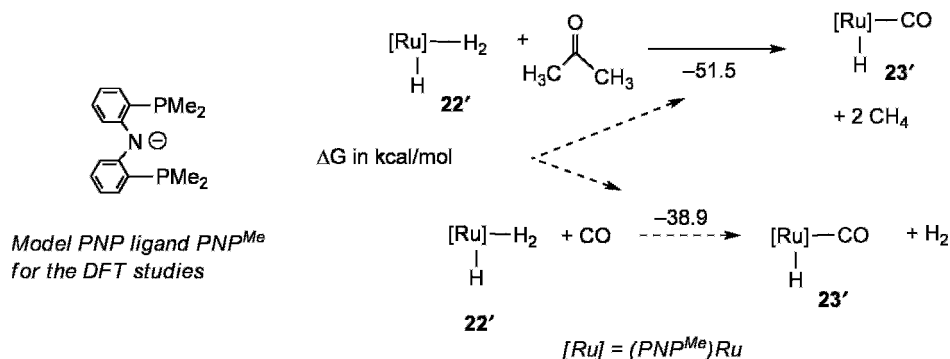


Fig. 13.10. Computed reaction energies for the CO abstraction.

13.5 GROUP 9 METAL CHEMISTRY

13.5.1 Intramolecular N–H, N–C, and C–H Oxidative Addition Reactions

The investigations of the oxidative addition reactions of the N–H and N–Me forms of the PNP ligands were inspired by the work of Milstein and co-workers on the topologically similar C–C vs. C–H oxidative addition with PCP ligands [2, 49]. The PN(H)P ligand **21** reacts cleanly with Rh^{I} and Ir^{I} precursors by N–H oxidative addition and formation of deep-green Rh^{III} and Ir^{III} products **26/27** (Fig. 13.11) [26]. The PN(H)P ligand **28** also reacts with an Rh^{I} source to give **29** in the presence of THF [20].

In the case of the reaction of the N-methylated ligands **30/31/36**, a greater diversity of products was observed (Fig. 13.12) [26, 28]. With Rh and **30/31**, initially Rh^{I} adducts

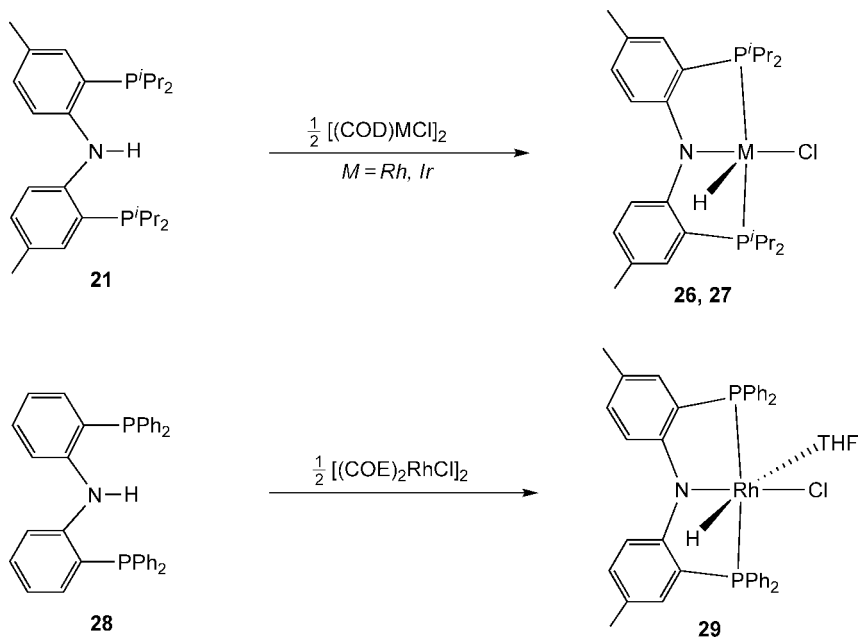


Fig. 13.11. N-H oxidative addition to Rh and Ir.

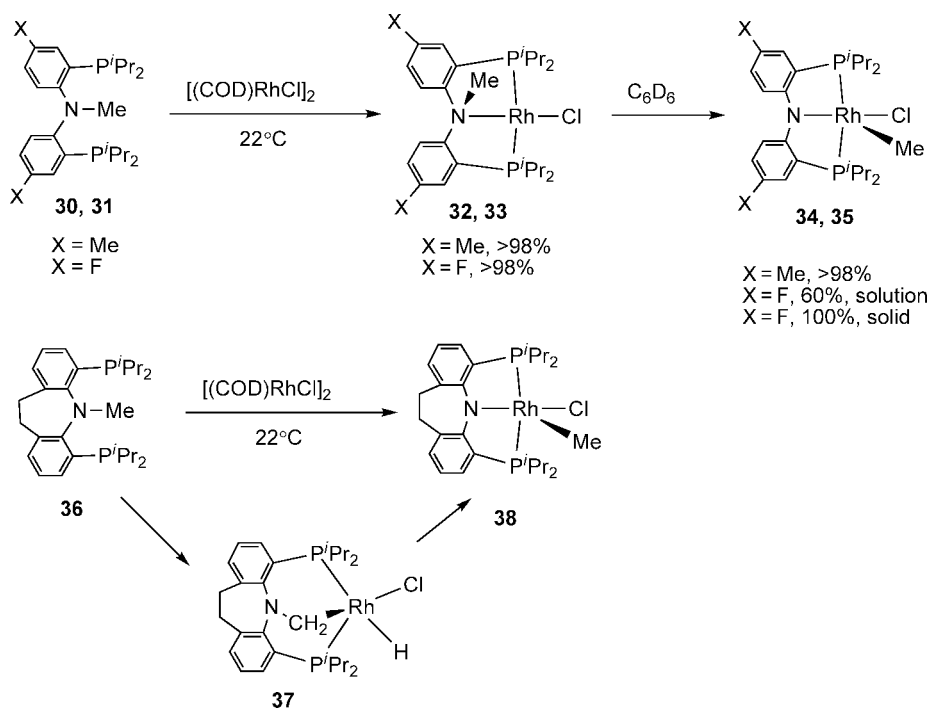


Fig. 13.12. N-C oxidative addition to Rh.

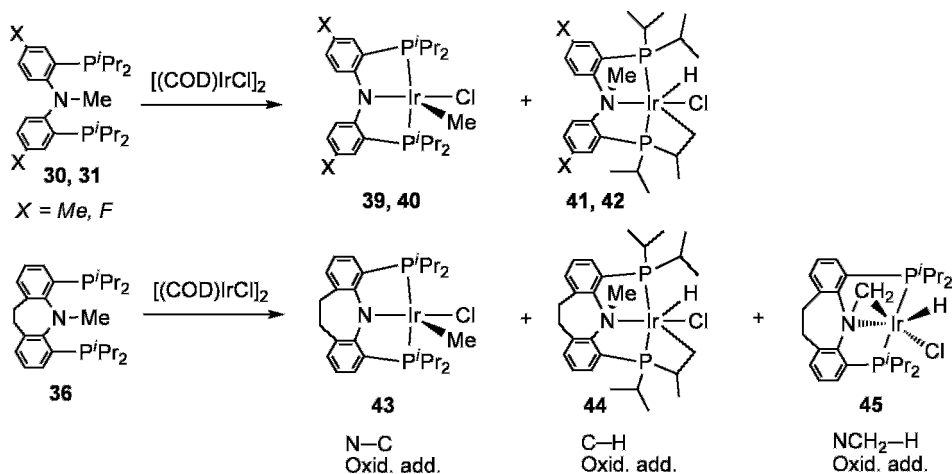


Fig. 13.13. N–C vs C–H oxidative addition to Ir.

32/33 are produced cleanly. **32** ($\text{X} = \text{Me}$) converts to **34** cleanly in both solution and solid state. The solution kinetics reveals the near-zero entropy of activation for the conversion from **32** to **34**. This is consistent with an intramolecular migration of the Me group from N to Rh. The solid-state conversion of **32** to **34** is remarkable, in that it proceeds as a crystal-to-crystal reaction. Even more remarkable is that the solid-state thermolysis of **33** ($\text{X} = \text{F}$) quantitatively produces **35**, while the corresponding solution reaction leads to a variety of unidentified products. Reaction of **36** with an Rh^{I} precursor in solution ultimately leads to the N–Me oxidative addition product **38** as well. An intermediate C–H oxidative addition product **37** (that evolves into **38** over time) can also be observed.

Reactions of **30/31** with $[(\text{COD})\text{IrCl}]_2$ result in a mixture of **39/40** and **41/42** (two diastereomers for each of **41** or **42**, Fig. 13.13). **39/40** and **41/42** do not interconvert at room temperature. **36** reacts with $[(\text{COD})\text{IrCl}]_2$ to produce **43** and **44**, and also **45**. Utilization of $\text{N}-^{13}\text{CH}_3$ -labeled $\text{PN}(\text{Me})\text{P}$ ligands proved exceedingly helpful in identifying the nature of the Ir and Rh products [28].

13.5.2 Competitive C–H vs. C–Hal Oxidative Addition Reactions of Haloarenes

13.5.2.1 (PNP)Ir and haloarenes

The PNP ligand provided a robust platform for the investigation of intermolecular oxidative addition reactions of haloarenes to Rh^{I} and Ir^{I} [53, 54]. We discovered that addition of norbornene to **46** in chlorobenzene generates products of C–H oxidative addition (**48**) almost exclusively [53]. In analogy with the PCP chemistry by Goldman and co-workers [55], norbornene likely serves to remove the two hydrides from the Ir center via hydrogenation of the double bond. This generates the unobserved **47** in solution, which is capable of attacking the C–H bonds of the aromatic solvent.

Thermolysis of the mixture of isomers of **48** at 70°C resulted in the conversion to a single isomer **48°**, in which the Cl is found in the *ortho*-position of the aromatic ring with a weak Cl...Ir interaction present in the solid state. Thermolysis at 120°C led to the conversion to **49**, a product of C–Cl oxidative addition.

Thus, in this Ir system, C–H oxidative addition is a kinetically favored process. Of the C–H oxidative addition isomers **48**, the one with the *ortho*-Cl (**48°**) is thermodynamically preferred. However, the global oxidative addition minimum in the (PNP)Ir/PhCl system is the C–Cl oxidative addition product **49**. Analogous findings were made in reactions with bromobenzene. By contrast, reaction with fluorobenzene led only to C–H oxidative addition products. It is possible that the barrier to C–F oxidative addition is too high to be surmounted under reasonable experimental conditions (Fig. 13.14).

Interestingly, these findings contrast with the reactivity of **50** reported by Milstein and co-workers. Experimentally, only C–H oxidative addition products (**51**) were observed with halobenzenes [56]. Computational studies indicated that C–Cl oxidative addition of PhCl to **50** is not thermodynamically favored over C–H oxidative addition [57]. A potentially useful conclusion is that the preference for C–H vs. C-heteroatom oxidative addition to a given metal center can be tuned by changing the auxiliary ligand(s).

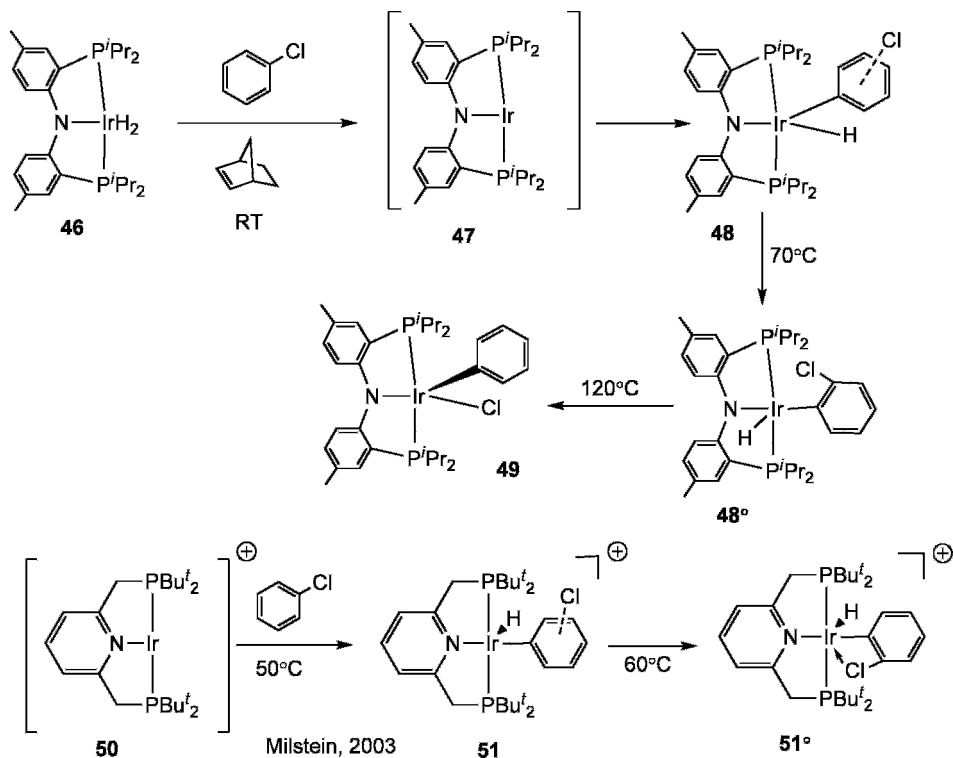


Fig. 13.14. C–Cl vs C–H oxidative addition to Ir.

13.5.2.2 (PNP)Rh and halobenzenes

In contrast to the chemistry of (PNP)Ir, the Rh analog **53** was only observed to undergo carbon–halogen oxidative addition reactions with PhCl, PhBr, and PhI (Fig. 13.15) [54]. The unsaturated **53** can be accessed by C–C reductive elimination from **52**. While the exact structure of the unobserved **53** under the experimental conditions (e.g., whether agostic interactions, or weak solvent coordination is involved) has not been ascertained, the kinetic studies indicate that it functions as a kinetic equivalent of three-coordinate (PNP)Rh. Thus, C–C reductive elimination from **52** proceeds as a clean first-order reaction and shows no dependence on the concentration of PhBr. The elementary steps of C–Hal oxidative addition and C–C reductive elimination observed in a well-defined fashion with (PNP)Rh are closely related to the several recent examples where non-pincer Rh catalysts enable C–C coupling of aryl halides, the reactivity that is typically achieved with Pd⁰ catalysts [58–62].

Because the C–H oxidative addition products were not observed, we endeavored to prepare one by an independent synthetic route (Fig. 13.15). However, when **55** (made by C–Cl oxidative addition of *p*-dichlorobenzene) was allowed to react with an NaBEt₃H (a hydride donor), **56** was not observed, and instead, **54** was registered as the major product of the reaction. Thus it appears that in the case of (PNP)Rh, similar to (PNP)Ir, the thermodynamic preference lies on the side of C–Cl oxidative addition.

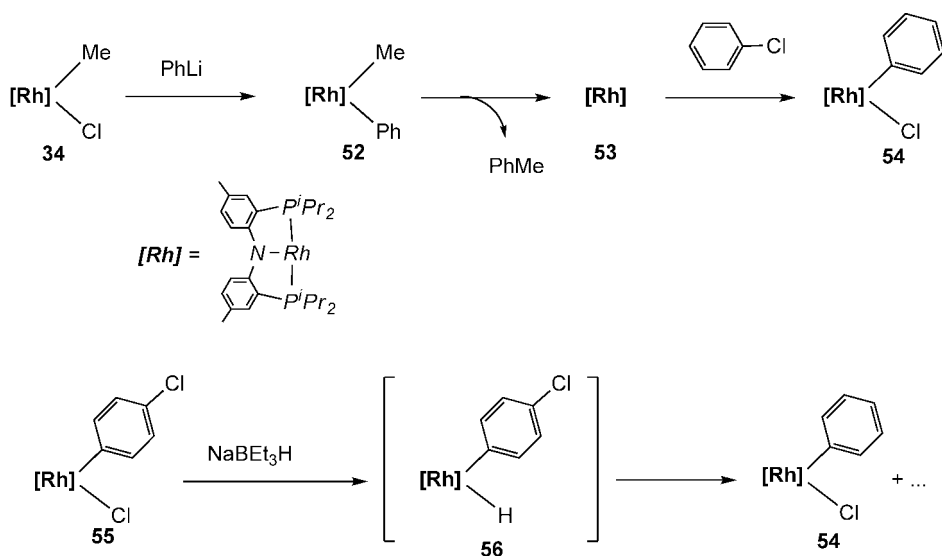


Fig. 13.15. C–Cl oxidative addition to Rh.

13.5.3 Catalytic Alkyne Dimerization

Alkyne dimerization is an attractive way of synthesis of conjugated enynes, important building blocks in organic synthesis [63]. We discovered that compounds **57/58/59** all act as catalysts for dimerization of terminal alkynes (Fig. 13.16) [64]. The catalyst **57** bearing the ‘tied’ PNP ligand proved to be the most active and highly selective for the

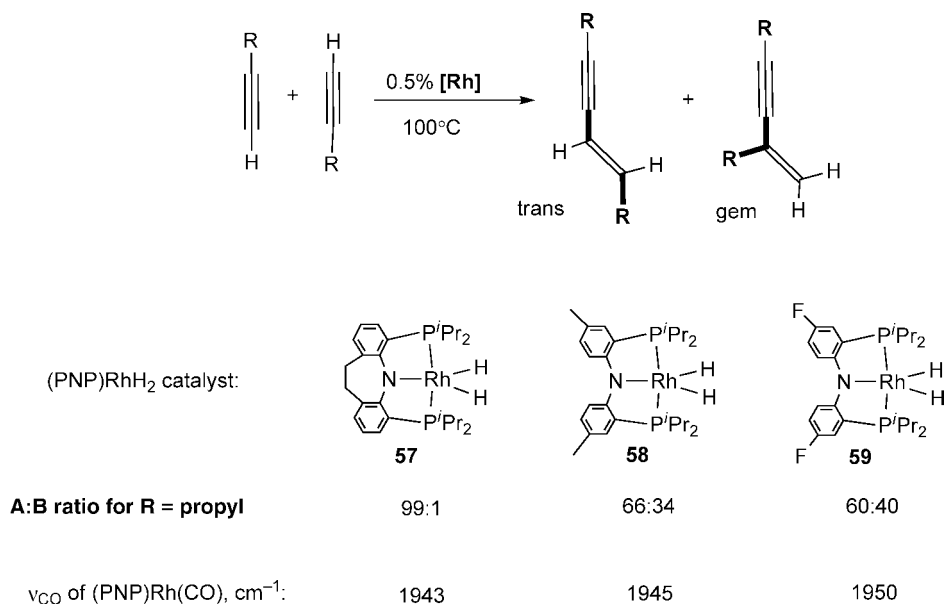


Fig. 13.16. Regioselective alkyne dimerization.

trans-enyne isomer. The dimerization proceeded with high selectivity for a variety of terminal alkynes of different steric and electronic properties. The process was tolerant of water and even, to some degree, air, and was compatible (without loss of selectivity) with hydroxyl groups in the alkyne. Turnover numbers in excess of 600 were achieved. All in all, **57** is unmatched in its high selectivity for the *trans*-enyne isomer and breadth of scope.

We ascribed the higher selectivity of **57** to the greater effective steric bulk of the ‘tied’ PNP ligand. This can be illustrated by the results of the dimerization of 1-pentyne by **57/58/59** (Fig. 13.16). **59** is essentially identical to **58** sterically, yet differs from **58** electronically to a greater degree than does **57**. **58** and **59** give very similar product distributions pointing to the steric origin of the higher selectivity of **57**.

13.5.4 PNP Complexes of Cobalt

Mindiola and co-workers reported several Co complexes of the PNP ligand with Co in various oxidation states (Fig. 13.17) [65]. The installation of the PNP ligand is accomplished by salt metathesis of (PNP)Li (**1**) with CoCl₂ to produce **60**. Reduction of **60** under argon leads to the dimeric species **61**. A monomeric three-coordinate (PNP*)Co complex utilizing a Fryzuk-type PNP ligand was recently reported by Caulton and co-workers [12]. Reduction in the presence of excess of CO leads to the 5-coordinate **63**. A monocarbonyl complex **64** can be prepared by reaction of **61** with stoichiometric amount of CO. Reduction of **60** under N₂ leads to the formation of the dimeric anionic N₂ complex of apparently Co⁰ (**62**). A bridging Co^I dinitrogen complex **65** can be accessed via reaction of **61** with N₂.

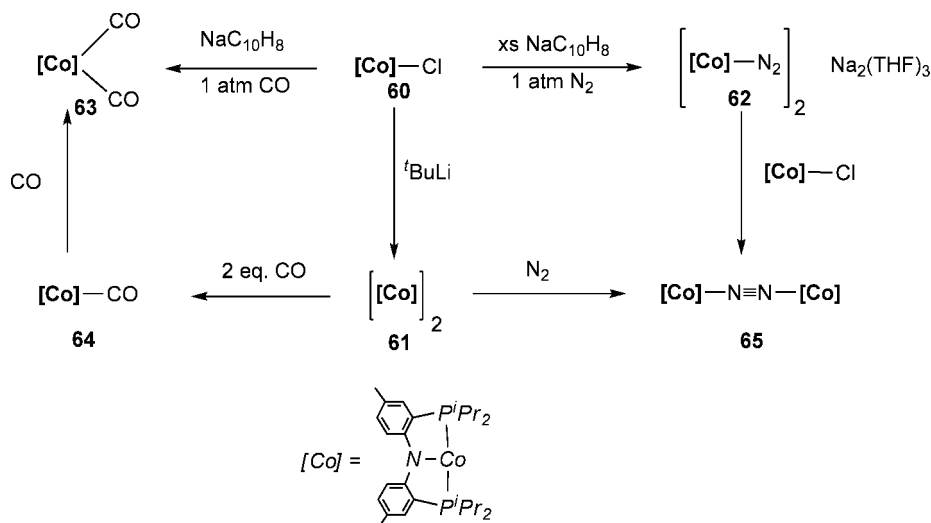


Fig. 13.17. PNP complexes of cobalt.

13.6 GROUP 10 CHEMISTRY

13.6.1 Synthesis of Various (PNP)MX Complexes

13.6.1.1 Introduction of the PNP ligand into the coordination sphere

The PNP ligands are ideally suited to support a variety of square-planar complexes of the general formula (PNP)MX (M = Ni, Pd, Pt). Three forms of the ligand precursor (N–Li, N–H, or N–Me forms) can be used to introduce the amido-PNP ligand into the coordination sphere of a group 10 metal. The reactions can be separated into four categories.

Salt metathesis between a (PNP)Li derivative and a group 10 metal halide or acetate reliably produces (PNP)MX and LiX as the by-product (Fig. 13.18) [19, 31].

Direct reaction of the neutral (PNP)H form of the ligand (**21**) with the group 10 metal halide or acetate (for Pd) is also possible (Fig. 13.19) [21]. In the case of Pd(OAc)₂, base is not required, and the reaction produces (PNP)PdOAc, with AcOH as the by-product. In the case of L_nMCl₂ precursors, the HCl by-product of the formation of (PNP)MCl

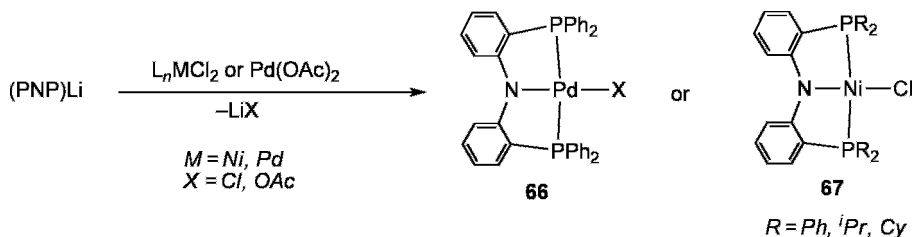


Fig. 13.18. Salt metathesis synthesis of PNP complexes of Pd and Ni.

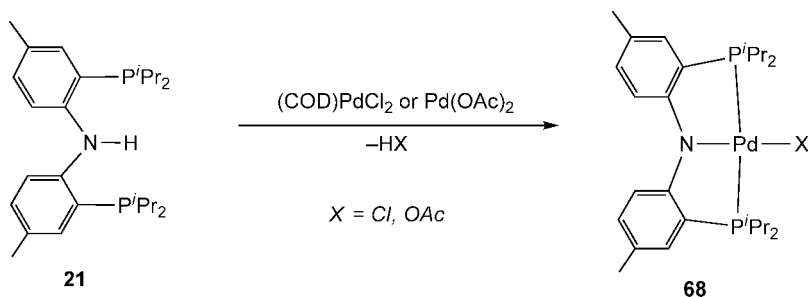


Fig. 13.19. N–H cleavage by Pd(II).

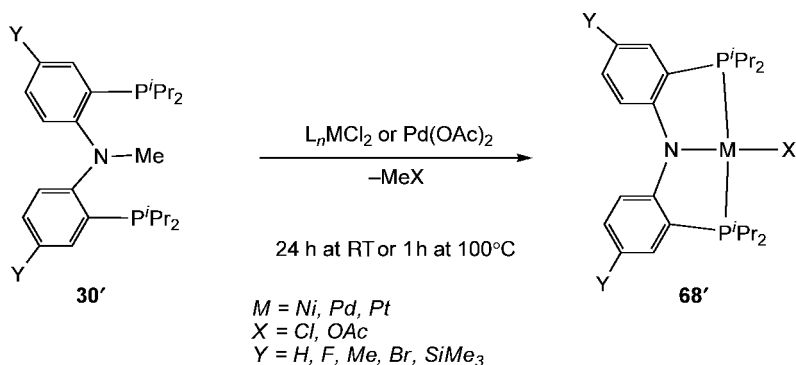


Fig. 13.20. N–C cleavage by Pd(II).

can be removed by addition of a weak base (e.g., Et_3N) or even simply by application of vacuum.

With certain PNP ligands, the methylated form of the ligand (PNP)Me may also be used in a reaction with MX_2 precursors to produce (PNP)MX and MeX as the by-product (Fig. 13.20). The N–C cleavage reaction works for the PNP ligands bearing PPr_2 arms, but not PPh_2 arms [27, 28]. The exact mechanism of the N–C cleavage here (particularly, whether N–Me oxidative addition to produce M^{IV} intermediates is involved) remains unclear, although some pathways were ruled out [27].

Both (PNP)H (**21**) and (PNP)Me (**30/31**) ligands bearing PPr_2 arms can react with L_nM^0 precursors ultimately by N–H or N–C oxidative addition to produce (PNP)MH (**69**) and (PNP)MMe (**70**) compounds (Fig. 13.21) [66]. Although N–H and N–C oxidative addition is of interest being atypical for group 10 metals, as a preparative method, this is only viable for the (PNP)H ligands. The N–C oxidative addition reactions with (PNP)Me ligands did not proceed to completion. M^0 precursors are more expensive and less enduring than M^{II} precursors, and (PNP)MH (**69**) and (PNP)MMe (**70**) compounds are more conveniently accessed via replacement of X in (PNP)PdX (**68'**).

13.6.1.2 Substitution reactions

Compounds (PNP)MX (**71**, Fig. 13.22) undergo a range of reactions resulting in substitution of X. The hydride ligand can be installed by action of NaBH_4 in an alcohol to

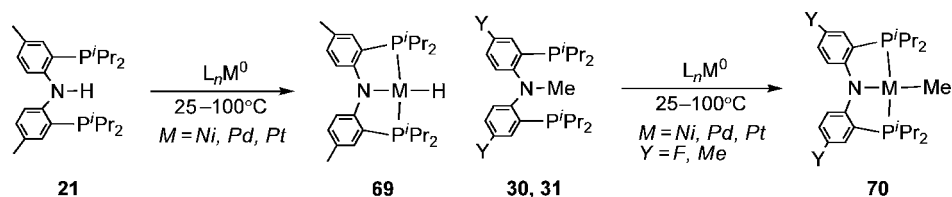


Fig. 13.21. N-H and N-C oxidation addition addition to Ni(0), Pd(0), and Pt(0).

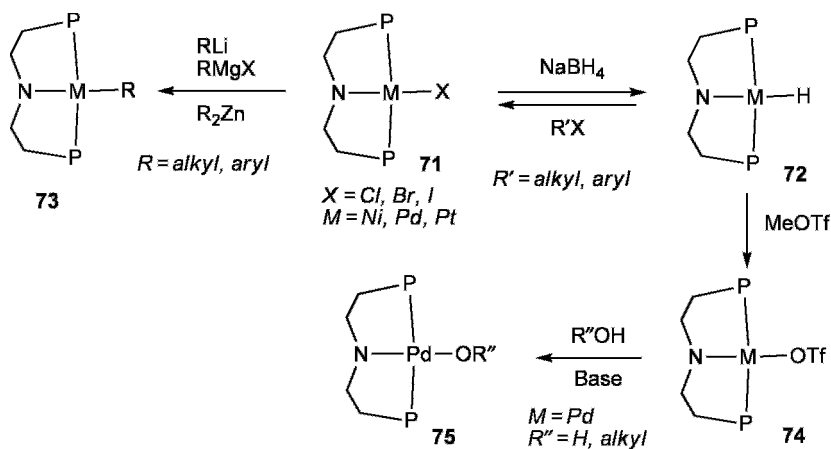


Fig. 13.22. Transformation of (PNP)MX complexes.

produce **72** [21]. Alkyl and aryl derivatives **73** can be prepared by reaction of **71** with corresponding organo-magnesium, lithium, or zinc reagents [19, 34, 66]. (PNP)MH (**72**) reacts with halogenated hydrocarbons to revert to **71** [21, 34, 66]. Certain (PNP)NiR react with halogenated hydrocarbons similarly [34]. (PNP)MH (**72**) also reacts with $MeOTf$ to produce (PNP)MOTf (**74**) [67]. (PNP)PdOTf is a convenient precursor for the synthesis of alkoxide and hydroxide derivatives **75** [68].

13.6.1.3 *Trans-influence issues*

(PNP)MX complexes offer opportunities for convenient comparative analysis of the *trans*-influence of the amido donor in the PNP ligands. Crystallographic data on the Pd-Cl bond length in several known (PNP)PdCl and (PCP)PdCl compounds allow one such comparison (Fig. 13.23) [21, 69–72]. The Pd-Cl distances in the (PNP)PdCl complexes are 0.05–0.12 Å shorter than in the (PCP)PdCl analogs.

Spin-spin $^{195}Pt-^1H$ coupling in (PNP)PtH [66] allows another measure of the *trans*-influence of the amido ligand. *trans*-(Cy_3P)₂PtHX compounds reported by Bercaw and co-workers represent a useful comparison (Fig. 13.24) [73]. The higher $^1J_{Pt-H}$ values should correspond to weaker *trans*-influence ligands *trans* to the hydride. The amido donor of the PNP can be ascribed a *trans*-influence that is intermediate between those of the hydride and hydrocarbyls and of the halides.

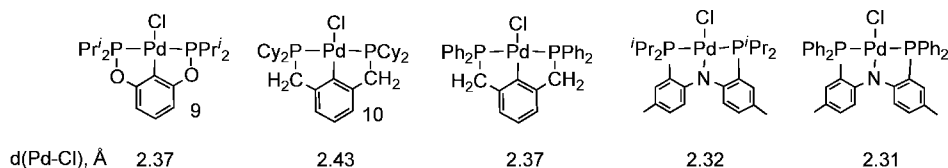


Fig. 13.23. Structural comparison of pincer complexes of Pd.

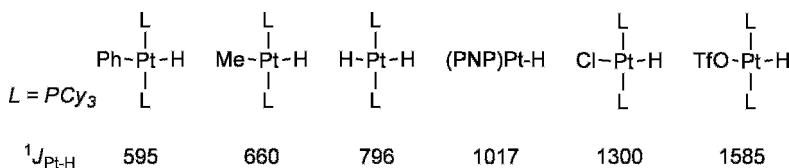
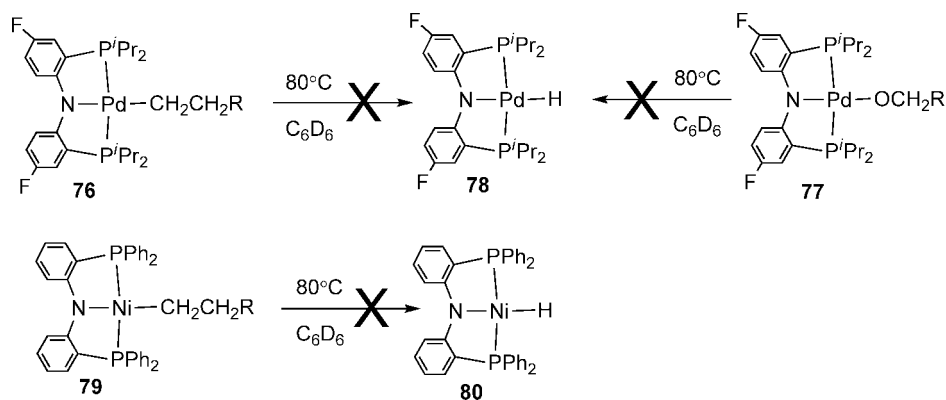


Fig. 13.24. Comparison of trans-influence of ligands on Pt(II).

13.6.1.4 β -Hydrogen elimination or the lack thereof

(PNP)PdR (**76**) [68] and (PNP)NiR (**79**) [19] with β -hydrogen containing alkyl ligands display remarkable thermal stability (Fig. 13.25). (PNP)NiH (**80**) reacts irreversibly with 1-hexene to produce **79** (R = *n*Bu), indicating that the lack of β -hydrogen elimination in this Ni system is uphill thermodynamically [34]. By contrast, (PNP)PdH does not react with ethylene; thus, the question of whether the stability of Pd-alkyl derivatives is of thermodynamic or kinetic origin remains open.

Pd alkoxides that contain β -hydrogens (**77**, Fig. 13.25) also showed thermal resistance to β -H elimination in benzene as solvent [68]. Slow β -H elimination from (PNP)PdOEt (**77**, R = Me) with formation of **78** did occur in ethanol. The thermal stability of **77** in benzene is thus of kinetic origin. This stability can be ascribed to the rigid tridentate coordination of the PNP ligand blocking the empty sites in the square plane of the complex. Conventional β -H elimination mechanism would require such an empty site. In more polar solvents such as ethanol, an alternative mechanism that involves

Fig. 13.25. Resistance to β -hydrogen elimination.

alkoxide dissociation and transfer of hydride without maintaining a Pd–O bond may become operative for alkoxides. A similar mechanism was proposed for the β -hydrogen elimination from a saturated Ir^{III} methoxide by Milstein and Blum [74].

13.6.1.5 C–H activation of benzene at a (PNP)Pt center

Liang et al. described C–H activation of benzene at the (PNP)Pt center (Fig. 13.26) [75]. Treatment of (PNP)PtOTf (**81**) with a base or of (PNP)PtMe (**82**) with a Lewis acid in benzene led to the production of (PNP)PtPh (**83**). This reactivity is reminiscent of that reported earlier by Peters et al. for the (NNN)Pt system (**84–86**) [76, 77].

13.6.2 Catalytic Applications of (PNP)MX

13.6.2.1 Aryl halide coupling reactions

Similar to a number of other pincer complexes of Pd [2], (PNP)PdX compounds have been shown to be active as catalysts in the Heck olefination (Fig. 13.27) [21, 75]. The Pd complexes bearing the PPh_2 arms were more active [75]. As is typical, the activity was higher for aryl iodides than for aryl bromides and only marginal for aryl chlorides. Jensen and co-workers originally proposed a $\text{Pd}^{\text{II}}/\text{Pd}^{\text{IV}}$ catalytic cycle for the Heck reactivity of (PCP)PdX [78]. However, later studies showed that at least for some PCP pincer systems, the active catalyst is some ill-defined form of $\text{Pd}(0)$ and the pincer complex apparently serves merely as a precursor [79, 80]. Whether this applies to the PNP systems remains unknown.

Liang et al. demonstrated that complexes (PNP)NiX are viable catalysts for the Kumada coupling between iodo- and bromoarenes on the one hand and aryl- and alkylmagnesium reagents on the other (Fig. 13.28) [31]. Alkyl Grignards containing β -hydrogens could be used successfully. Variations in the PNP ligand structure did not result in systematic effects on the activity. The exact mechanism by which this coupling

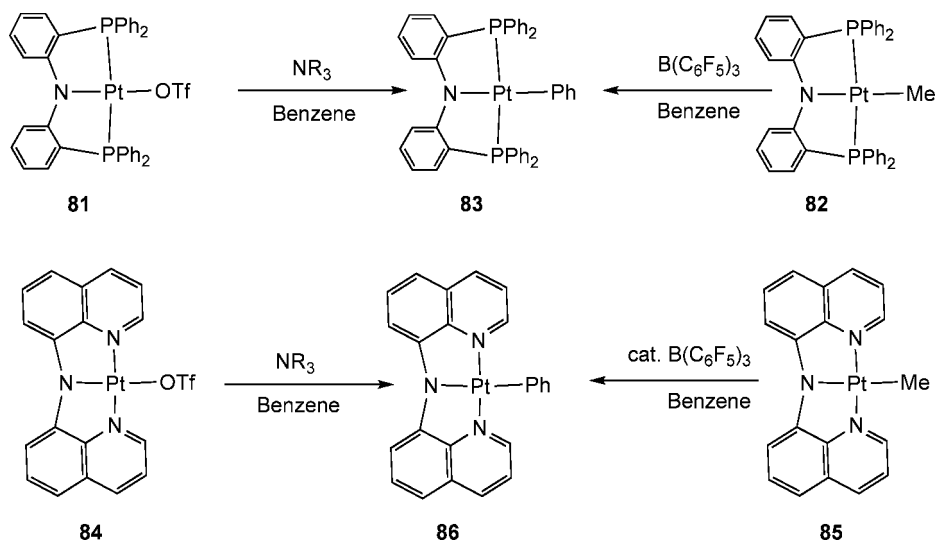
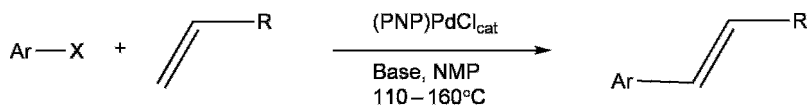


Fig. 13.26. C–H activation of benzene at pincer-ligated Pt(II).



$\text{R} = \text{Ph}, \text{CO}_2\text{Et}$

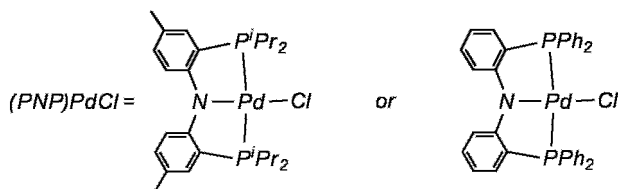
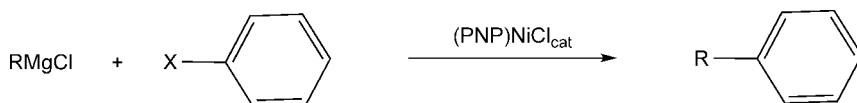


Fig. 13.27. Heck coupling catalyzed by PNP complexes of Pd.



$\text{X} = \text{Br}, \text{I}$

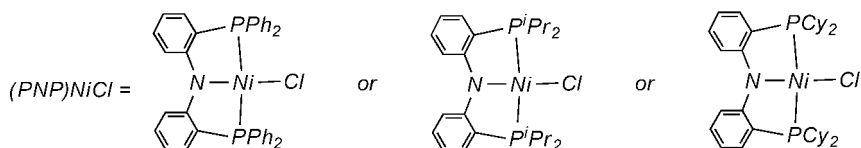


Fig. 13.28. Kumada coupling catalyzed by PNP complexes of Ni.

reaction takes place remains unknown, although kinetic studies by Liang et al. showed that aryl halide oxidative addition is not the rate-limiting step.

13.6.2.2 Lewis acid-catalyzed coupling of acetonitrile with aldehydes

Catalytic coupling of alkylnitriles with aldehydes under mild conditions is surprisingly challenging. Few efficient catalytic reactions have been reported, and achieving high enantioselectivity remains an unsolved problem [81–83]. As pointed out by Shibasaki and co-workers [81], soft Lewis acids would appear to be appropriate candidates for catalysis. We recently reported that $(\text{PNP})\text{NiOTf}$ is a viable catalyst for coupling of acetonitrile, with aldehydes with DBU as base and at temperatures not exceeding 50°C (Fig. 13.29) [67]. Interestingly, the Pd and Pt analogs were not catalytically active. A variety of aldehydes were surveyed. The reaction works best for electron-deficient aryl aldehydes. The steric bulk of the aldehyde is not at all a detriment. Aliphatic aldehydes with branched but not straight chains could also be successfully coupled with acetonitrile. The choice of DBU as base was necessary; Et_3N and ‘proton sponge’ were not effective. The mechanism was not fully elucidated. However, the triflate ligand in $(\text{PNP})\text{NiOTf}$ is easily replaced by acetonitrile and thus may be viewed as a synthon

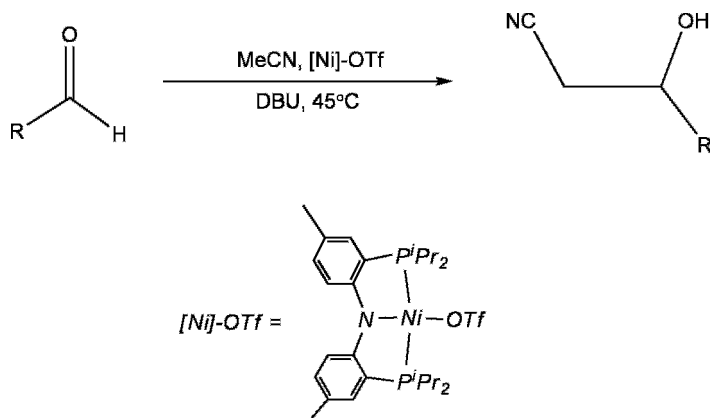


Fig. 13.29. Coupling of acetonitrile with aldehydes.

for the $[(\text{PNP})\text{Ni}]^+$ fragment. Coordination to $[(\text{PNP})\text{Ni}]^+$ increases the C–H acidity of acetonitrile, allowing for the use of a mild base for the coupling.

13.7 COPPER COMPLEXES

Peters and Harkins reported a dimeric $[(\text{PNP})\text{Cu}]_2$ complex **88** (Fig. 13.30) [24]. **88** displays two reversible oxidation waves in cyclic voltametry. The most interesting property of **88** is that it is an exceptional luminophore possessing a high combined quantum yield and relatively long lifetime.

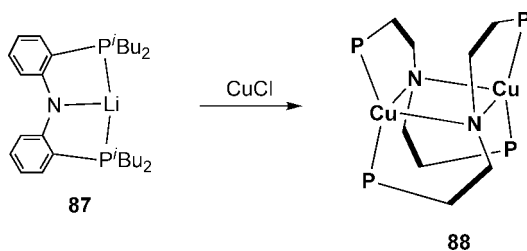


Fig. 13.30. A dimeric $[(\text{PNP})\text{Cu}]_2$.

13.8 SUMMARY

The new family of rigid PNP pincer ligands has been demonstrated to support a wealth of exciting transition metal chemistry. The usefulness of the PNP ligands extends to both borders of the transition metal series. Such versatility is largely owing to the rigid backbone that prearranges the three donor atoms for binding a transition metal and also to the hybrid nature of PNP, incorporating both the hard amido donor and the soft phosphine donors. For the early metals, the chemistry of group 4 metal–carbon multiple

bonds has been significantly extended beyond previously known precepts. For the late metals, particularly those of groups 9 and 10, the PNP ligand serves as robust ancillary ligand in several diverse catalytic processes. In addition, the new PNP ligands have been used to engender unusual organometallic reactions and to support new structural motifs.

ACKNOWLEDGMENTS

I am grateful to the members of my group who have contributed to our work on the PNP systems: Lei Fan, Wei Weng, Vyacheslav Papkov, Remle Çelenligil-Çetin, Claudia Fafard, Sylvain Gataud, Lauren Gregor, Jessica DeMott, Laura Gerber, Mayank Puri, and Shannon Finnell. Their energy, motivation, and intellect have made all the difference. I am thankful for the good will and the expertise of my collaborators, Prof. Bruce Foxman and his students Liang Yang and Chengyun Guo (XRD studies), Dr. Sean Parkin (XRD studies), and Prof. Lori Watson (DFT studies). I also thank Profs D. Mindiola, J. Peters, K. Caulton, N. Hoffman, and A. Goldman for stimulating discussions pertaining to the substance of the chemistry described in this chapter. Our group's contributions would not be possible without the support from Brandeis University, the US National Science Foundation, Petroleum Research Fund, Research Corporation, and the Sloan Foundation. The generous support of these agencies is acknowledged with gratitude.

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Pincer, chelate and spirocyclic metal carbene complexes from bis(iminophosphorano)methane ligands

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14.1 INTRODUCTION AND OVERVIEW

The remarkable growth of organometallic chemistry over the last 50 years has provided an enormous selection of compounds which present different metal–carbon binding environments. Relevant to the series of complexes described in this chapter are those situations in which the carbon is directly bound to a metal with a reduced coordination environment (<4) forming ‘carbene’ structures. We will focus on the formation of bis(chelated) ‘pincer’ complexes obtained from backbone-deprotonated bis(diphenyliminophosphorano)methane (**1**) [1] (the methandiide, dianionic form) and related ligands. Typically, the $M=C$ structure is supported by chelation of the two imino functionalities of the ligand although, as will be seen below, this is not required for formation of the $M=C$ entity. This particular system of pincer complexes is characterized by a carbon–metal link wherein, notably, this carbon is not part of a ring structure. We shall also survey the bis(diphenyliminophosphorano)methandiide complexes containing a doubly deprotonated carbon center with a carbon coordination geometry of four and the carbon either bridges two metals (to form a ‘bridging carbene’) or forms a spirocyclic carbon center with two metals attached to the same carbon center.

Our system rests on an extensive body of transition metal phosphinimine and phosphinimide complex chemistry [2–4]. Most common are monodentate ligand structures. Recent applications to the development of new commercially viable olefin polymerization catalysts using these ligands is notable [5]. In the bis(iminophosphorano)methane system, early work employed the monolithiated bis(iminophosphorano)methane ligand [**1-(H)Li**] to form chelated imine complexes [6–11]. Others have monolithiated related bis-($P=O$) and -($P=S$) ligand systems to form chelates (see [12]).

Our explorations with the bis(iminophosphorano)methane ligands thus created a system of constrained geometry, pincer, bis-chelate, complexes (Chart 14.1, **A**) to expand the substantial collection of carbon bound pincer systems (Chart 14.1) which had been developed by others. Recent reports have provided some related complexes of the

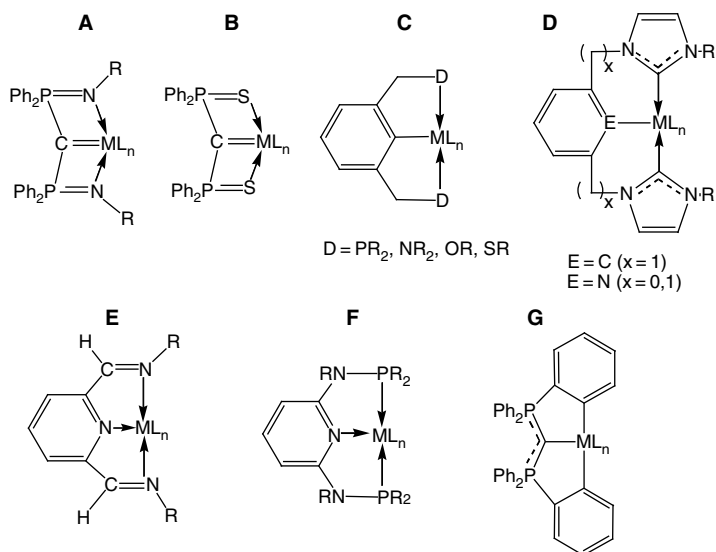


Chart 14.1

bis(diphenylthiophosphinyl)methandiide ligand (Chart 14.1 **B**) (see [13]). The extensive (and growing) collection of pincer systems have been typically based on a C-bound ortho-disubstituted phenyl ring attached to the metal (Chart 14.1, **C**) [14f–i, 15]. The two ortho-positioned arms carry Lewis base donors (typically an amine or phosphine) which chelate the metal to produce the tridentate pincer complex. Four-, 5- or 6-coordinate pincer complexes are obtained. Recent extensions have included NHC (nonheterocyclic carbenes) as elements of the bis(ortho) substituents (Chart 14.1, **D**) [15] which provides a (C,C,C) pincer motif. Gibson and co-workers developed the bis(ortho-imine)-substituted pyridine ligand system to synthesize many (N,N,N) pincer-type bis(chelate) complexes wherein the central feature is a N–M dative bond (Chart 14.1, **E**) [16] and bis(phosphinomethane)- and bis(phosphinoamino)-pyridine ligands have recently been expanded to a present suite of (P,N,P) pincers (Chart 14.1 **F**, see [17] and references therein).

Monometallic pincer complexes of the type depicted in Chart 14.1 continue to receive considerable widespread attention. The incentive is the search for metal complexes which will support effective catalytic processes. In the case of the pincer systems, the presence of reactive metal centers supported by flexible multidentate ligands with the concomitant possibility of, perhaps, controllable dissociation through selective adjustment of the substituents offered by the ligand suggests a significant potential for applications to homogeneous catalysis. In addition, the relative bulkiness of the substituents on these pincer systems offers steric protection to the reaction site. Many successful applications have been recorded [14–16]. The geometrical constraints imposed on the metal reaction center by the ligand structure and connectivity and the stabilization of the complex through the retention of the ligand by the metal as the result of the pincer or chelate structure places these systems into the class of constrained geometry catalysts. The characteristic properties of these pincer complexes mimic the numerous varieties of cyclopentadienyl

metal derivatives widely used for catalysis, especially for polymerization of olefins. Much related metal–ligand complex chemistry has been developed with these structural aims in mind. Our monometallic systems differ from the usual pincer systems in that the carbon center is not itself part of a cyclic substituent structure.

Later in this chapter we shall describe related bidentate chelate bis(iminophosphorano)methandiide complexes in which the carbon is again fully deprotonated to create a dianionic ligand but only one of the two available nitrogen atoms is bound to the metal and thus the complex is not a pincer complex. Other related complexes have been prepared which have pincer structures but the carbon is a normal, tetracoordinate, (methine) bound to metal, with two phosphorus and one H substituent. We shall focus on the $M=C$ fully deprotonated chelates mentioning only briefly, and only where directly relevant, derivatives of these methine species which will generally be in the context of the discussion of derivatives or products of reactions of our pincers and chelates. Previous studies of similar monochelated methine complexes have been described elsewhere [6–12].

Elsewhere (Chapter 15) we consider related triple (C,C,C) pincers (Chart 14.1, **G**) and bidentate chelates formed by the carbodiphosphorane ligand system which can be regarded as a formal derivative of the bis(iminophosphorano)methandiides. There are substantial similarities between both sets of ‘carbene (ylide) pincers’ because the central structure of both systems in each case is the $P-C(=M)-P$ core with a tricoordinate, metal-bound, carbon which appears to exhibit a closely related bonding structure.

Finally we shall summarize the chemistry of some new derivatives of the bis(iminophosphorano)methane ligand system which contains two (identical or dissimilar) metals each singly bound to carbon in two configurations, one in which two metals are attached to only one carbon to form a geminal, bridging spirocyclic carbon structure or, alternatively, the case where the metal is attached to two different carbon atoms to form a bridging carbene ring structure. This collection of tricoordinate pincer carbenes and tetracoordinate ‘bridging and spirocyclic carbenes’ has provided a wealth of interesting new complexes, the full scope and versatility of which has yet to be defined.

Bimetallic systems in general excite considerable interest, in part because of the possibility that cooperative interactions might be established which may provide enhanced catalytic activity. Overall this is one sector of the larger theme; creating special complexes for catalytic assistance. We will focus on a limited area, our ‘carbenic’ bis(iminophosphorano)methane-based systems, but note that there are many other bimetallic examples wherein two metals are bridged by a single carbon (and in many of these cases the carbon is called a bridging carbene [18–22]). Also, our bimetallic, bridging carbene, complexes differ from the usual bimetallic complexes which are typically either ‘A’ frame structures bridged by bis(phosphine) ligands [23] or systems which possess a $M-M$ direct bond (see [24] and references therein).

In spite of this importance and interest, there is a scarcity of direct and efficient general synthetic routes to the simple bimetallic complexes. Existing preparations are often tedious with poor yields. Our first examples of bridging carbenes based on the bis(iminophosphorano)methanes were homo-bimetallic but recent advances which we will describe below have opened a relatively simple synthetic route to geminal, spirocyclic, homo- or heterobimetallic, complexes linked by a single (substituted methylene) carbon-connecting bridge. The resultant, new, complexes also demonstrate some additional reactivity, particularly in the formation of an unusual, stable, ketene complex

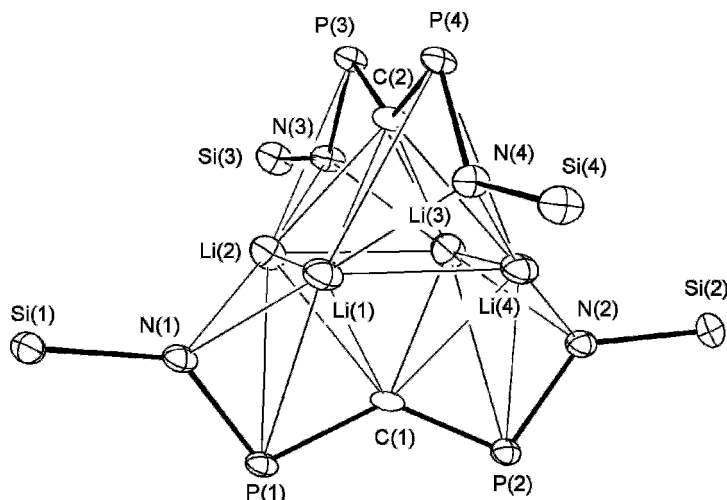


Fig. 14.1. Core structure of the dimeric dilithium salt $[1\text{-Li}_2]_2$. For clarity, phenyl and methyl substituents have been removed [26]. Reproduced by permission.

which can release incorporated CO under mild conditions suggesting a potential catalytic utility [25].

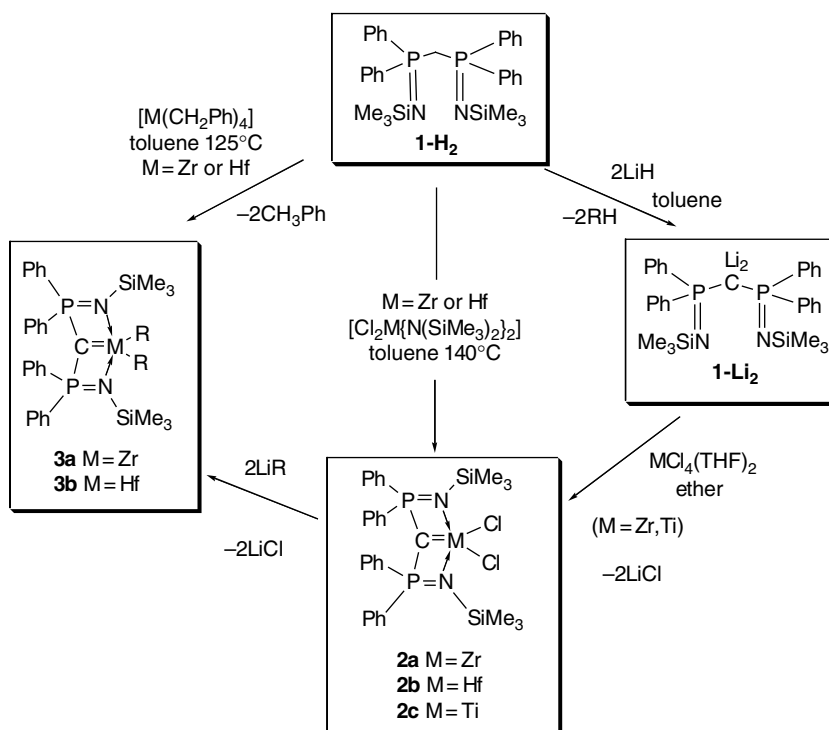
Our first pincer bis(iminophosphorano)methandiide complexes were those of the early transition metals which excited initial interest because the carbon appeared to possess distinct carbene character [4]. Starting with the bis-phosphinimine ligand, $\text{H}_2\text{C}(\text{R}_2\text{P}=\text{NSiMe}_3)_2$ (which we style **1-H₂** [1]) or the (dimeric) dilithio-methane derivative, $[\text{Li}_2\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2]_2$ (Fig. 14.1), styled $[1\text{-Li}_2]_2$ [26, 27], pincers and bimetallic bridging carbenes of low-valent early metals could be prepared. The dilithium salt is a versatile reagent which reacts with many simple halide precursors of the early metal groups (Sm, transition metals, e.g., Cr, Fe, and lanthanides), main group metals (particularly Al and Zn) and also the late transition metals (Rh, Pd, Pt, etc.) [28] – all of which then provide examples of various types of monometallic and bimetallic carbene complexes.

In addition to this dilithium dimer [26, 27], central to our studies, we have explored the alkali metal ($\text{M} = \text{Li}, \text{Na}, \text{K}$) derivatives of the methanide ligand $[1\text{-H}]\text{M}$ system as potentially useful reagents [29, 30]. In contrast to many alkali metal complexes which are often complicated polymers, these phosphinimine derivatives proved to be simple monomers or dimers. Explorations by others have provided extensions to the chemistry and revealed more complex structures [31].

Recently Leung et al. reported a number of methylene-carbon-bridged, bimetallic, Pb-C-Pb and Sn-C-Sn bis(iminophosphorano)methandiide complexes. Most of the work of this group has been done with the pyridine-substituted monophosphinimine ligand system which, although interesting and analogous, does not integrate with this short chapter on the bis(iminophosphorane)methane system. Nevertheless, one intriguing system developed by them with the deprotonated bis(iminophosphorane)methandiide ligand will be highlighted below.

14.2 THE BEGINNING: PINCERS OF EARLY TRANSITION METALS

The discovery of the first example was unexpected and serendipitous. Being unable to transmetallate the silyl iminophosphorane functionality with TiCl_4 (a facile reaction with CpTiCl_3 wherein Me_3SiCl was eliminated as expected, see [32]; we obtained only a stable TiCl_4 adduct which did not eliminate Me_3SiCl even under forcing conditions), we opted to use $\text{Zr}(\text{NT}_2)_2\text{Cl}_2$ as the metal precursor. The result was deprotonation of the methylene unit of the ligand backbone with elimination of hexamethyldisilazane [HMDS] to form complex **3a** (Scheme 14.1). The Hf analog behaves similarly to form **3b** [33].



Scheme 14.1 The essentials of the group 4 series of methandiide complexes.

Thus, reaction of $[\text{MCl}_2\{\text{N}(\text{SiMe}_3)_2\}_2]$ (M=Zr, Hf) [34] with $\text{CH}_2(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2$ [**1-H₂**] at relatively high temperatures (refluxing toluene) gave $[\text{MCl}_2\{\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2-\kappa\text{C}, \kappa\text{N}, \kappa\text{N}'\}]$ [M=Zr, Hf], **2a,b** [33]. The Ti analogs $\text{TiCl}_2(\text{NT}_2)_2$ are not thermally stable; at these reaction temperatures they scramble to equilibrium mixtures containing all possible substituent arrangements, thus general application of this procedure in which the metal precursor deprotonates the ligand was of limited use. This impediment was removed by the discovery of the remarkably stable, dimeric, dilithium salt [**1-Li₂**]₂ which could be obtained by the simple expedient of the reaction of [**1-H₂**] with two moles of alkyl lithium [26, 27]. A metathetical reaction

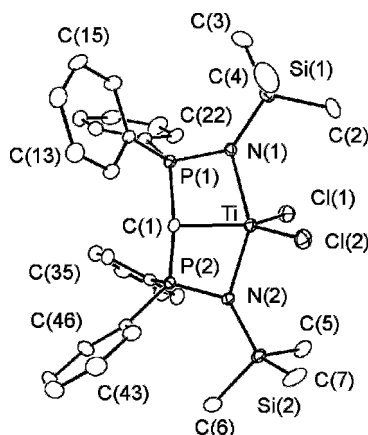


Fig. 14.2. The structure of the titanium pincer complex **2c**. For clarity all hydrogen atoms have been removed [35]. Reproduced by permission.

with TiCl_4 then readily gave the Ti analog **2c** ($M = \text{Ti}$, Fig. 14.2) [35]. The lithium salt route also yields **2a** and **2b** from the other MCl_4 precursors but the metal amide precursor route for these metals is somewhat cleaner, so is more efficient.

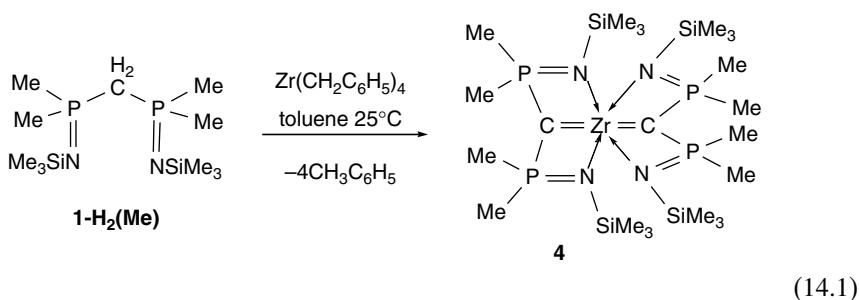
A particular feature of this group 4 early metal system was also that it provided a complete triad of metal complexes of Ti, Zr and Hf [33], in which all metal centers were coordinated by the same ligand. The complexes were isostructural thus allowing the comparison of the chemistry throughout a periodic metal series. Generally, the organometallics of periodically related transition metals can be prepared for only limited combinations of ligand and metal so that direct analogs are generally not provided down a periodic column. In this system, the hafnium bis(iminophosphorano)-methandiide complexes display the same metal–carbon bond features and essential reactivity (as discussed below) as was observed for Ti and Zr complexes [4, 33, 35, 36].

It was realized very early that metal alkyls, $\text{M}(\text{CH}_2\text{Ph})_4$ would also deprotonate the ligand **1-H₂** with the elimination of toluene to form the alkylated analogs **3a** and **3b** [36] (Scheme 14.1). Again the instability of the Ti alkyl analog did not allow general application of this route. The halide complexes (**2a, c**) could be readily transformed into the alkylated complexes (**3**) with either alkyl lithium or Grignard reagents so access to a complete group series of metal alkyls could be provided with reactions of $[\mathbf{1}\text{-Li}_2]_2$ with halides followed by standard alkylations of the complexes. The reactions of metal amide complexes and metal alkyls with **1-H₂** (and the lithiation procedure itself) capitalizes on the relatively high acidity of the methylene backbone protons of **1-H₂** and the weak basicity of the eliminated protonated species. Such methylene deprotonation reactions have considerable precedent.

This system also showed that the *N*-adamantyl imine [36] analog followed the same chemistry as the Me_3Si imine system; thus it appears that considerable substituent bulk and/or electronic variations can be tolerated on the nitrogen center. Likewise, the successful methylene deprotonation of the Cy_2P analog of **1-H₂** by $\text{Hf}(\text{CH}_2\text{Ph})_4$ leading to the cyclohexyl (Cy)-substituted complex **3b'** ($\text{Ph} = \text{Cy}$) indicates that differently substituted phosphorus centers do not completely lose the acidity of the methylene protons

upon which this synthetic route depends. Notably, also, this alkylated pincer complex **3b** [36] provided an example of an organometallic Hf carbene, a relatively rare species.

Although the variation of both P and N substituents of the bis(phosphoranimine) offers enormous possibilities for 'tuning' the ligand and introducing control of complex reactivity, this facet of the system has not yet been extensively explored. An example of the effect of substituent on the chemistry was provided by the fact that the bis(carbene) complex of Zr, $[\text{Zr}\{\text{C}(\text{Me}_2\text{P}=\text{NSiMe}_3)_2-\kappa\text{C}, \kappa\text{N}, \kappa\text{N}'\}_2]$ (**4a**) (Eqn 14.1, Fig. 14.3), was accessible to us only in the case of the methyl phosphine ligand analog of **1-H₂** (Ph=Me) [37] but it is still not clear if such results are general or the outcome of a particular combination of ligand and metal precursor characteristics because generality has been difficult to establish.



As mentioned, deprotonation of the backbone methylene unit of bis(iminophosphorano)methane ligands is well preceded. The moderate acidity of these methylene protons has been previously employed for the synthesis of singly deprotonated, monolithiated derivatives [6–12]. Although double deprotonation of bis(phosphino)methanes has not been systematically exploited it has been previously encountered in a number of cases, often as the result of further decomposition of singly deprotonated precursors [38]. In these quoted cases, a dimetallated carbon spirocycle resulted. Several group 10 and group 13 metal complexes obtained in this

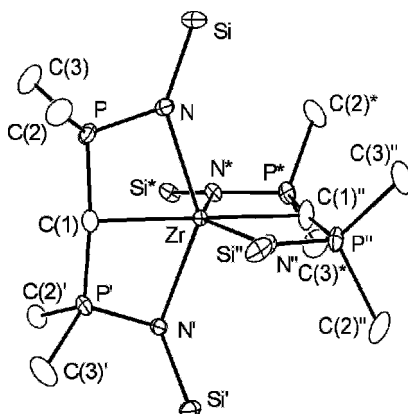


Fig. 14.3. The structure of the zirconium bis-pincer complex **4**. For clarity all hydrogen and all trimethylsilyl carbon atoms have been removed [37]. Reproduced by permission.

way have been structurally described [38–42]. In addition, the presence of a few doubly deprotonated methandiide ligands has been suggested for other systems [43, 44] but without crystal structure evidence. In our studies we have encountered a number of products through purposeful preparation and as the result of reactivity studies [4, 45–47] wherein the carbon bound to the metal is singly protonated creating a (four coordinate), C(H) methine, center. Some are described in subsequent sections in the context of reactivity discussions of the carbenes but, because this chapter is concerned with the carbene-ylidic pincer system, only brief mention will be made, where appropriate.

Overall these systems of complexes are potentially very versatile because there is a wealth of established phosphorus and nitrogen ligand substitutional chemistry which can be applied to the construction of the ligand framework in order to control complex stability and ligand–metal reactivity. The system has substantial potential versatility which is presently underexploited. Our system has added a new and unique set of members to the group of constrained geometry complexes. We have a system which possesses considerable carbene character but offers nonmetallocene, noncarbonyl, constrained organometallic centers with structural characteristics related to the organometallic catalyst systems derived from the metallocenes. Likewise, many of the other pincer systems [13–17] do not carry any cyclopentadienyl substituents and so they also offer constrained geometry environments with reactivity which is different from the metallocenes (and our carbenes). The particular character of our pincer complexes which differs from the general form of most pincer complexes is that ours contain a $M=C$ bond (or metal–carbon link with an electron-rich carbon) feature which is not part of a cyclic structure. Thus the geometry, flexibility and reactivity of our systems is different to that of the other pinchers. The fact that the metal-bound carbon in these systems is subtended by two phosphorus atoms with ‘ylidic’ delocalization adds another facet to the nature of the resultant complexes. Although a ‘heteroatom’, P shows substantial similarity to C in many aspects of its chemical behavior [48].

For a given metal, the nature and reactivity of prototypical carbene complexes, $M=CR_2$ depends greatly on the electronic and steric nature of the substituent, R. Those containing one or two highly electronegative heteroatom substituents, such as O, N or S, are designated as ‘Fischer carbenes’ whereas those with only hydrogen or carbon atom substituents are designated as ‘Schrock carbenes’ or alkylidene complexes. Chemically, the former are generally electrophilic in character whereas the latter are generally nucleophilic [49]. The chemical behavior of the present series of ‘carbene-ylides’ suggests that, rather than behaving as typical heteroatom (Fischer) carbenes, they resemble the alkylidene (Schrock) carbenes. This is consistent with the mimicry of C by phosphorus [48]. Until recently there were few carbenes with phosphorus substituents but this field has been greatly expanded in recent years to include even NHC analogs by the Bertrand group and others (see [50–53] and references therein).

14.2.1 Structures

Selected structural metrical data and NMR parameters for the pincer carbene complexes and their relatives have been summarized in more detail elsewhere [4, 45]. The structural data was essential to the proof of structure and to elaborate on the nature of the bonding interactions between the metal and the carbon center. The molecular structures of the group 4 system are quite similar; being based on a framework which is composed of

two nearly planar, fused, four-membered rings (formed by M, N, P and the carbene C) subtended from the shared edge defined by the M=C carbene bond. The carbene atom is displaced by varying amounts from the plane defined by the atoms P, N, M, N, P; the two four-membered rings are not consistently coplanar, they form a distorted 'open book' conformation which is defined by a dihedral angle ranging from 0 to 37° and the P-C-P angles range from 138 to 168° ([45], Table 1). There does not appear to be a systematic relationship to this distortion which can be related to the nature of the metal or to the particular substituents. However, the P-C-P unit seems to be generally quite flexible so we suspect that packing forces may play a significant role in addition to the electronic character of the ligand and the metal. The M=C bond distances are relatively short but are not remarkably or extraordinarily so.

The presence of relatively short M=C bonds and the fact that addition reactions across this bond could be carried out (with bond lengthening of approximately 10%), as described below, provide some support for a designation of a M=C bond with an order higher than one. The details of the bonding description of these metal carbenes is presently the topic of considerable discussion. Overall the complexes are highly soluble in relatively polar and aromatic solvents such as diethyl ether, benzene and toluene and they also have relatively high thermal stability which can be attributed to the steric protection of the carbene center by the formation of the tridentate chelate pincer structure.

14.2.2 Reaction Chemistry of the Group 4 Pincers

The interesting aspect of the reactivity of the complexes, as illustrated by the studies on the group 4 set, is that, in some cases, they behave as alkylidene carbenes and in other cases the reactivity is unique to the system. The reactivity delineated for the group 4 series suggests a multiple bond character for the linkage between the metal and the carbon.

14.2.2.1 Simple nucleophilic substitution

As mentioned above, the halide substituents of **2** are readily replaced by alkyl groups using simple lithium or magnesium Grignard reagents (Scheme 14.2(i)). Thus, reaction of **2b** with NpLi (Np = neopentyl) gave (**3b''** R = neopentyl) [HfNp₂{C(Ph₂P=NSiMe₃)₂-κC,κN,κN'}] [54]. It is notable that the carbon center in the complex is not attacked under these reaction conditions as is also the case for alkylidene complexes and so this reactivity evidence points to Schrock-type carbene behavior [54]. In contrast to Fischer-type carbene complexes, an alkyl lithium would attack the carbene center to form an anionic carbon species [55, 56].

Similar dialkylbis(iminophosphorano)methanide group 4 complexes were accessed directly by reacting the metal tetra-alkyl precursor with [**1-H₂**] [36].

14.2.2.2 Metal acidity

The bis(iminophosphorano)methanide complexes, **2**, readily form Lewis base adducts [M(L)Cl₂{C(Ph₂P=NSiMe₃)₂-κC,κN,κN'}] {M = Hf, L = THF **5a**; M = Hf, L = AdCN **5b** (Fig. 14.4) [54] (Ad = adamantyl); M = Zr, L = CN(C₆H₄Me₂-2,6) **5c**} with coordinating solvent (e.g., THF, a nitrile or an isonitrile) (Scheme 14.2(ii)). Because M=C complexes generally yield insertion products with isonitriles or nitriles [56–58] the formation of adducts in the present case is unique and may be due to the strong electrophilic character and coordinative unsaturation of the metal center.

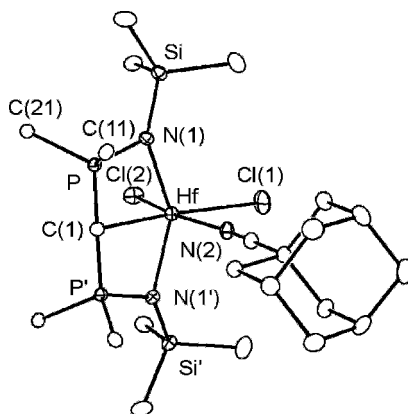


Fig. 14.4. The structure of the Hf pincer adduct of AdCN [54] (**5a**, M = Hf, L = AdCN, X = Cl). For clarity all hydrogen atoms have been removed. Reproduced by permission.

14.2.2.3 The nature of the $M=C$ bond: (A) [1, 2]-addition

The methandiide complexes **2** react smoothly with compounds containing acidic protons such as aromatic amines, phenols or aliphatic alcohols to yield the $C\alpha$ -(methine)-protonated product (X = halide, E = Me or H) $[MCl_2(X)\{EC(Ph_2P=NSiMe_3)_2-\kappa C, \kappa N, \kappa N'\}]$, as a result of 1,2-addition of the substrate across the $M=C\alpha$ bond (Scheme 14.2(iii)). Products of this (methine) type may also be obtained directly from the reaction of metal halides with **[1-(H)Li]**.

Representative products **6a** (M = Zr) [54] and **6b** (M = Hf) [54], isolated from the addition reactions of *p*-toluidine and adamantanol (Fig. 14.5), respectively, are shown in Scheme 14.2. A similar addition reaction was observed with methyl iodide, giving a low yield of $[HfCl_2(I)-\{(Me)C(Ph_2P=NSiMe_3)_2-\kappa C, \kappa N, \kappa N'\}]$ **6c** [54] undoubtedly because of halogen-scrambling reactions. The electrophilic (E) moiety adds specifically to the carbene center thus further supporting the assignment of a nucleophilic character to the carbene center [55]. The metal–carbon bond order is clearly reduced in the products (vide infra) again substantiating the attribution of a multiply bonded nature to the parent complexes but, notably, M–C connectivity remains.

14.2.2.4 The nature of the $M=C$ bond: (B) [2+2] cycloaddition

Heteroallenes such as $RNCO$ (R = Ad, N(*p*-tolyl)) and $RN=C=NR$ (R = Cy) react readily with methandiide complexes **2** (M = Zr, Hf) to form [2+2]-cycloaddition products. Representative structures of these cycloaddition products are $[ZrCl_2\{C(NCy)NCy\}C(Ph_2P=NSiMe_3)_2-\kappa C, \kappa N, \kappa N', \kappa N'']$ **7a** (Scheme 14.2(iv) and Fig. 14.6) and $[HfCl_2\{C(O)N(Ad)C(Ph_2P=NSiMe_3)_2-\kappa^4 C, N, N', N''\}]$ **7b** (Scheme 14.2(iv) and Fig. 14.7) [46, 54]. The addition of the heteroallene to the pincer chelate creates a tetradentate propeller shaped, dianionic, ligand bonded to the metal by the central carbon, the two original nitrogens and the remaining appropriate NR fragment of the heteroallene. Two chloride ligands complete the sixfold coordination of the metal. Notably the oxygen of the isocyanate group is *not* bound to the oxophilic metal center. The three nitrogen substituents of the expanded ligand adopt a tripodal arrangement and lie at the corners of an almost regular triangle but notably, again, the

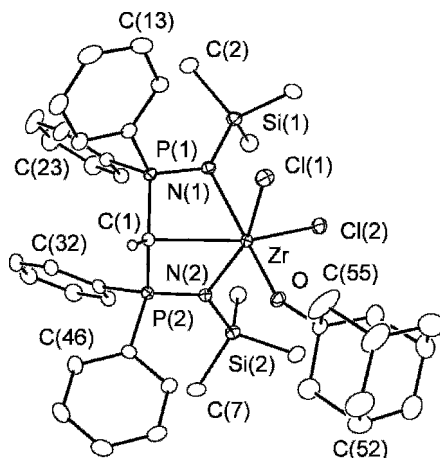
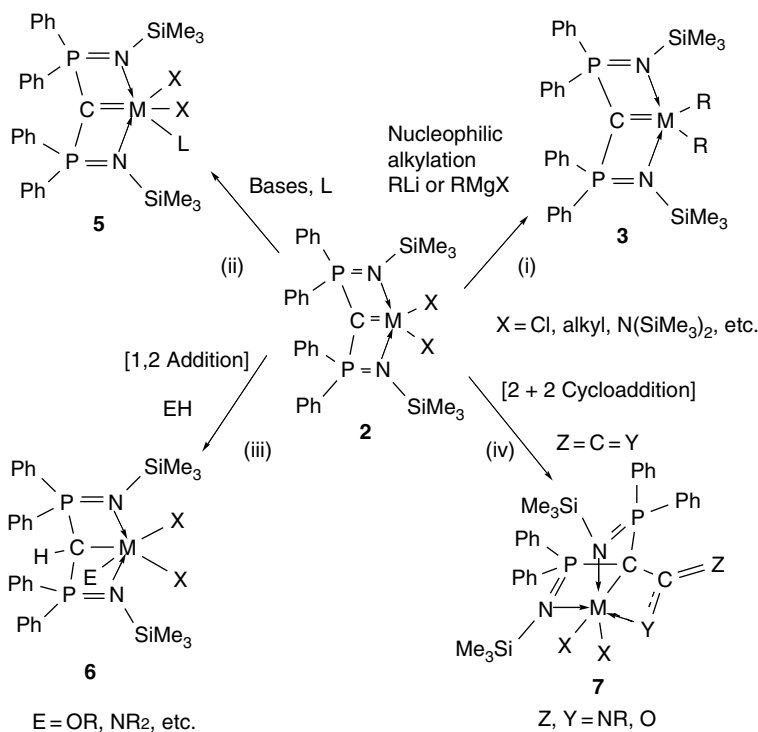


Fig. 14.5. The structure of the Zr pincer adduct of AdOH **6b**, M=Zr, X=Cl, E=oAd. For clarity all hydrogen atoms have been removed [54]. Reproduced by permission.



Scheme 14.2 Reactions of early metal pincer complexes.

ligand remains bound through the carbon to the metal. The M–C distance increases relative to the metal–carbon distance in the parent compound which is expected for a reduction of bond order from two to one by the cycloaddition. Because the carbon is

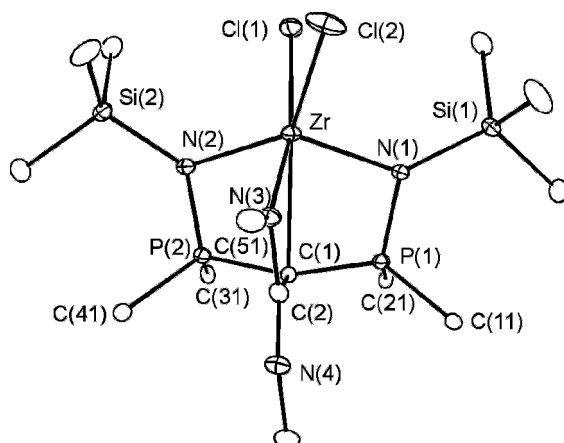


Fig. 14.6. The structure of the Zr pincer adduct of cyclohexylcarbodiimide **7a** ($M = \text{Zr}$, $X = \text{Cl}$, $Y = Z = \text{NCy}$) [54]. For clarity all hydrogen atoms and all (but the ipso) carbons of phenyl and cyclohexyl groups have been removed. Reproduced by permission.

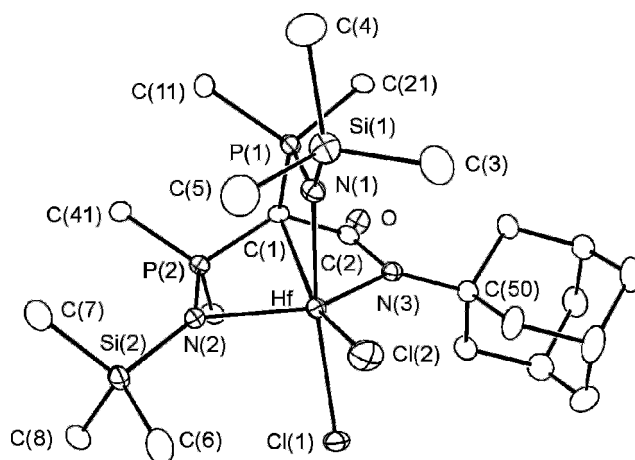


Fig. 14.7. The structure of the Hf pincer adduct of AdNCO **7b**, $M = \text{Hf}$, $X = \text{Cl}$, $Y = \text{NAd}$, $Z = \text{o}$. For clarity all hydrogen atoms and all (but the ipso) carbons of phenyl groups have been removed [54]. Reproduced by permission.

still attached to the metal it is however clear that the original $M=\text{C}$ interaction has preserved metal–carbon bonding following addition thus supporting the assignment of a type of $M=\text{C}$ carbene character to the original complexes. Were this metal–carbon interaction to be removed completely by the addition, then the complex would adopt a typical tripodal, tridentate ligation structure as is the case for tris(pyrazolyl)borate complexes or, as demonstrated below by the zinc and monoaluminum methane complexes, the bis(iminophosphorano)methanide ligand would adopt ‘acac’-like geometry [59, 60].

14.2.3 The Nature of the M=C Bond: Theory

The above reaction chemistry suggests that there is an enhanced bond between the carbene carbon and the metal. The changes in bond length values that accompany additions across the M=C bond and the fact that a clear M–C linkage remains after such additions (*vide supra*) leads to a labeling of the carbon as a carbene which is justifiable with the proviso that this system has considerable ylidic character. There is evidence that the basic M–C σ -bond may lie rather deep in the molecular orbital framework and the π -character mainly resides on the carbon, so the bonding is not the classical C=C double bond type. The bond distances within the bicyclic framework are also considerably altered in comparison with related values in parent bis(iminophosphorano)methanes [7, 46, 47]; the P=N bond distances are slightly elongated and the endocyclic P–C bond distances are significantly shorter but the exocyclic P–C bond distances are not affected. These factors suggest that there is a significant delocalization of π -electron density within each of the two four-membered rings arising from the effective conjugation of the M=C bond and the P=N bonds which develops ylidic character thus the debate oscillates between presenting these systems as carbenes and as simple ylides. The appropriate ‘proper’ description undoubtedly lies between these limiting models.

In Chapter 15 we describe σ and π M–C components in the pincer carbodiphosphorane complex of Rh which provide a model. There are two relatively deep σ - and one π -orbital which are themselves bonding with respect to the Rh–carbene axis. One of these σ - and both π MOs are paired with occupied antibonding orbitals so the overall result appears to be no net Rh–C bonding from these orbitals. One Rh–carbene σ orbital remains. The HOMO is a largely C-based p_z orbital with small contributions from Rh – this provides significant electron density on the carbene and is the source of the nucleophilicity. The deep (HOMO-14) M–C σ component provides a strong link between the metal and the carbon. Thus electrophilic reactions may occur at the carbon center through the HOMO which do not break the framework of the molecular system which is maintained by the deep σ component. The system does not fit the classical description of a σ and π ‘double bond’ but reaction behavior and structural artifacts manifest themselves in a way which creates the essential character of σ and π multiple bonding interaction between metal and carbon; the ability to add fragments across the bond without breaking the connection, thus the reaction patterns of these complexes exhibit the double bond character seen above without being classical examples of double bonds. Our own single-point DFT level calculations on the Zr alkyl complex (**3a**) indicated a substantial negative charge at the carbene carbon (–1.82e) [36, 45–47] which is consistent with a dianionic formulation of the ligand.

Other recent calculations on related systems yield slightly different but comparable pictures. Ru(II) complexes of bis(iminophosphorano)methandiide ligands in the hands of other workers yielded a chelate complex with one free substituent (the other imino center) [61] similar to our chelated carbene Pt complex described below (*vide infra*). They also reported relatively loose pincer complexes formed by coordination of the remote donor on the dangling arm. This chelate complex has a short Ru=C bond (1.976 Å) (not as short as in Grubb carbenes (~1.85 Å) but substantially shorter than the value associated with a C sp^3 bond (2.22 Å)) [61]. These workers also reported a methine (CH) chelate of the ligand system with a Ru–C bond length of 2.23 Å. The short Ru=C bond length of the Ru carbene chelate complex is comparable to that of a true pincer. The carbon in the Ru=C chelate is also planar (Σ of angles about

carbon: 359.2) [61]. Limited DFT calculations were described which did not give orbital characters but indicated that the carbene carbon has significant electron density ($-1.19e$). In another study [62], the analogous carbene chelate of Ru(II) was not observed but their more detailed DFT report indicated that there were several orbitals holding the metal C framework together; a metal-based set (HOMO, HOMO-2, HOMO-3) forming a metal d^6 configuration. HOMO-4 is a Ru–carbene single σ bond and the HOMO-1 is a C lone pair directed outward which carries the negative charge on the carbene. This orbital provides a nucleophilic reaction center. Bond ellipticities were also analyzed therein to evaluate σ and π character [62].

Recent studies on the related dianionic bis(diphenylthiophosphinyl)-methandiide, $Li_2[C(Ph_2(S)P)_2]$, complexes of Pd(II) [63] and Ru(II) [13] suggest, in both cases, a clear dianionic, alkylidene carbene character with some difference in detail as to the actual composition of the various orbitals involved. In the Ru case the carbenic carbon is essentially planar whereas in the Pd complex, substantial folding around the Pd–C axis was recorded. Previously this folding has been invoked to deny the carbenic character of this center; however, as mentioned, there seems to be a substantial flexibility to this connection, perhaps because the core bonding and the frontier electron density distribution which provide the enhanced interaction between the metal and the carbon are not interconnected as in the case of classical σ – π interactions of the C–C system. Similar variations of folding along the M=C axis occurs through the group 4 bis(iminophosphorano)methandiide complexes [4, 45, 46].

The DFT analyses of the bis(diphenylthiophosphinyl)methandiide, Pd(II) [63] and Ru(II) [13] complexes differ in the particular relationship of internal σ and π bonds between the metal and the carbene and the electron-rich π orbital which is close to the frontier, but provide similar pictures of high electron density on the carbene center close to the frontier and a deep structure which holds the carbon to the metal which is not likely to be easily broken.

14.2.4 Other Early Transition Metals

The monomeric complex of Sm, **8**, which shows the same M=C bond feature as the group 4 complexes was readily formed by the same route, double deprotonation of the bis(iminophosphorano)methane ligand **1-H₂** by samarium tris(dicyclohexylamine) (Eqn 14.2) [64]. Only two of the amides were eliminated and, because the reaction was done in ether, a solvent molecule was added to the coordination sphere to produce the same type of pincer structure as was seen earlier in the group 4 complexes. The structure of the Sm complex $[Sm\{C(Ph_2P=NSiMe_3)_2-\kappa C, \kappa N, \kappa N'\}(NCy_2)(THF)]$, **8**, (Fig. 14.8), which is a yellow, air-sensitive, crystalline solid, was similar to that of the group 4 complexes showing a similar core structure of two nearly planar, fused four-membered rings with a Sm–C(1) shared edge. The samarium to carbon bond distance $\{Sm-C(1) = 2.467(4) \text{ \AA}\}$ while shorter than average Sm–neutral carbene bond distances [65–68], supposedly falls within the typical Sm–C single bond length range (see Ref. [68] footnote 50). The formulation of the Sm=C linkage as one of ‘multiple bond character’ will presumably turn out to be a description very similar to that derived for the group 4 (and the noble metal) complexes as described above.

The only previously known carbene complexes of lanthanide metals were the adducts of the neutral carbene ligands [65–67]; however, recently Sm (and Tm) complexes of the bis(diphenylthiophosphinyl)methandiide system have been reported [69, 70].

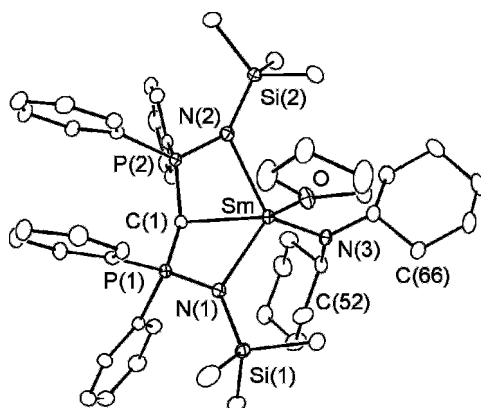
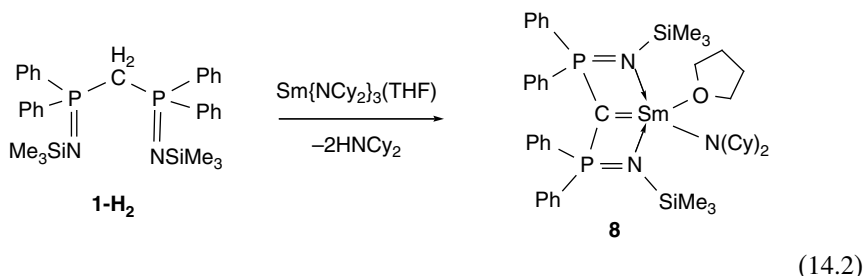


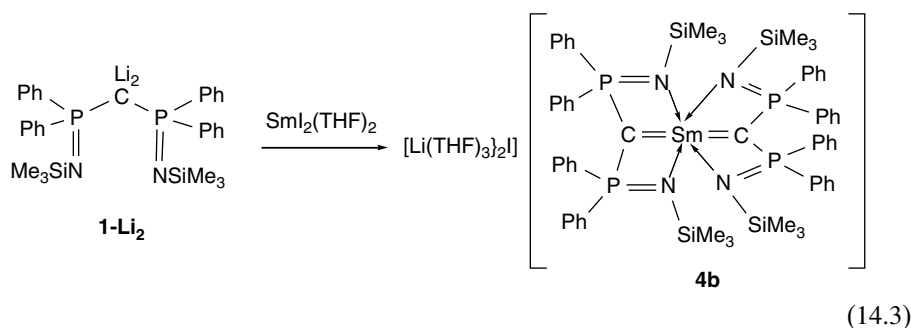
Fig. 14.8. The structure of the Sm pincer complex **8**. For clarity all hydrogen atoms have been removed [64]. Reproduced by permission.



14.3 BIS-LIGATED COMPLEXES

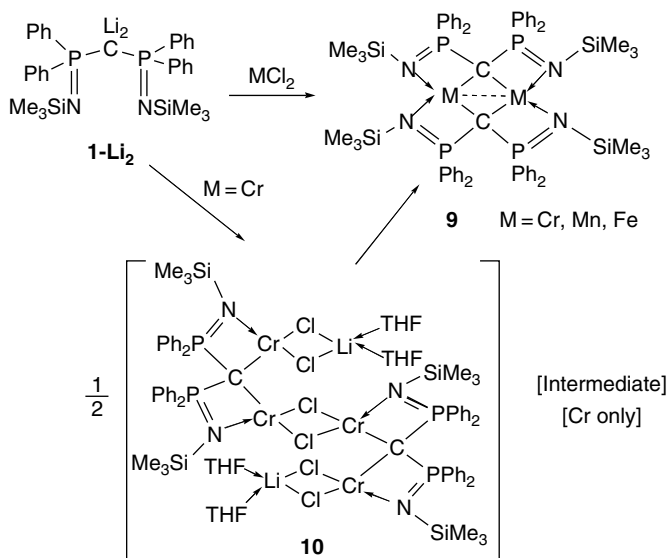
As mentioned above, the reaction of the methylated version of the bis(iminophosphorano)methane ligand, **1-H₂(Me)**, with tetrabenzyl zirconium gave **4a** (Eqn 14.1), one of the two known examples of a bis(iminophosphorano)methandiide complex substituted by two fully coordinated pincer ligands [37]. The other is a complex of Sm(III) with the usual phenyl-substituted form of the ligand, $[\{\text{Li}(\text{THF})_3\}_2\text{I}]^+ [\text{Sm}\{\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2-\kappa\text{C},\kappa\text{N},\kappa\text{N}'\}_2]^-$, **4b** (Eqn 14.3, [46]). Complex **4b** was prepared from reaction of the dilithiated salt, $[\textbf{1-Li}_2]_2$, with $\text{SmI}_2(\text{THF})_2$. Complex **4b** was formed by a redox disproportionation and Sm metal appears to be deposited in the reaction [46]. The valence requirements imposed by the dianionic ligand results in a paramagnetic anionic complex. The structure of the Sm bis(carbene) anion in **4b** [46] is virtually identical to that of the neutral Zr(biscarbene), **4a** (Fig. 14.3, [37]). We had initially thought, following the preparation of the Zr bis-ligated complex **4a** (which succeeded only with the methylated form of the ligand) that bis-substitution on a metal required a reduction in ligand bulk; however, the isolation of the Sm bis-ligated complex with phenyl substituents on P clearly indicates that this is not the

case. More important for synthetic success is the appropriate choice of metal precursor and ligand reagent. These bis-ligated complexes show a slightly longer M=C bond perhaps due to some internal crowding but the effect is not large. Reactivity of these bis-ligated complexes has not been investigated, but the metal appears to be fully encapsulated hence the reactivity will probably be dominated by the carbene centers. The related dianionic bis(diphenylthiophosphinyl)-methandiide has also yielded a bis-ligated complex of Sm(III) and Tm(III) [69, 70]. Although the solid state structure of the disubstituted bis(thio) Sm complex (and that of the high-temperature form of the Tm complex) [69, 70] do not have perfect planarity at the carbene carbon (in contrast to the perfect symmetry of the C=M=C unit in complexes **4** [37]), the values are close to the required sum and bis-carbene M=C character has been assigned. The low-temperature form of the Tm complex has a very asymmetric ligand structure) [70].



14.4 EARLY METAL-BRIDGING CARBENES

The preparation of the dilithium salt **[1-Li₂]₂** allowed the ready exploration of complex formation with the simple halide precursors of other metals. Thus the Cr(II) complex $[\text{Cr}\{\mu_2\text{-}[(\text{C}(\text{NCy})_2\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{-}\kappa\text{C},\kappa\text{N},\kappa\text{N}',\kappa\text{N}'')]_2\}]_2$ **9**, could be accessed from metathetical reaction of CrCl_2 and **[1-Li₂]₂** [71] (Scheme 14.3, Fig. 14.9). This complex is a bimetallic, dimeric system which shows a central square-plane framework made of two chromium atoms bridged by two carbene centers to form a Cr_2C_2 four-membered ring. The ligand backbone forms four fused, four-membered, rings which are assembled from the bridging carbene carbon, the metal, the phosphorus and the imine nitrogen atoms in a saddle shape. The geometry around each Cr is approximately tetrahedral and the iminophosphorane nitrogen units coordinate to the metal to confer a $\mu_2\text{-}\kappa^4$ coordination. Bond distances and angles throughout the bicyclic ligand framework again suggest that there is a delocalization of π -electron density within each of the two four-membered rings [4, 45]. The geometry about the Cr is approximately tetrahedral and the $\text{Cr}\cdots\text{Cr}$ separation is 2.65 Å. The magnetic moment is 2.76 BM which is low for the d^4 electron configuration of Cr(II) in a tetrahedral environment and the short $\text{Cr}\cdots\text{Cr}$ distance suggests that there might be some interaction between the metal centers. Magnetic measurements to 4 K do not indicate any unusual interaction [46, 72]. This was the first of the bimetallic complexes to be encountered in our system and the structure represents an example of a bridging carbene. The Mn(II) and Fe(II) analogs



Scheme 14.3 Early metal bis-carbenes.

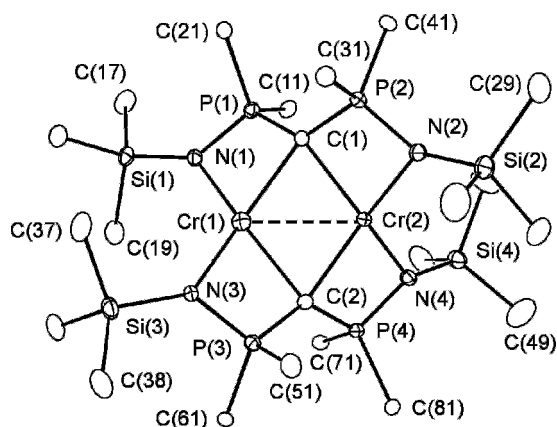


Fig. 14.9. The structure of the Cr bridging carbene dimer complex **9** (M=Cr). Note that an intermediate (**10**) has also been identified and crystallographically characterized in the Cr system [71]. For clarity all hydrogen and all phenyl carbon (except ipso) atoms have been removed. Reproduced by permission.

were subsequently isolated and shown to be isostructural, but crystal quality was not good enough for full refinement [46, 72]. A Cr(II) intermediate **10**, which interestingly showed Li incorporation and participation was also isolated and structurally characterized. In this latter complex the Cr...Cr separation is about 2.95 Å. Later we found significant Li participation in a heavy metal system (vide infra) with very interesting chemical consequences.

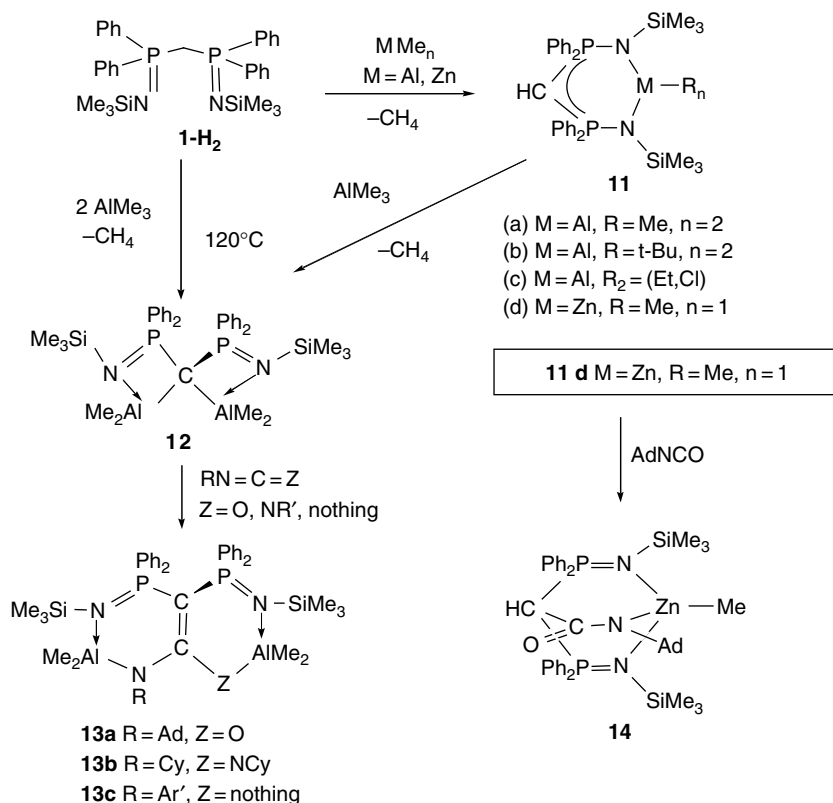
14.5 MAIN GROUP METAL COMPLEXES

14.5.1 Aluminum

Aluminum [60] and zinc [59] methyls reacted at room temperature with $[1-H_2]$ to give *N,N*-chelated methanides via single deprotonation events. Thus, reaction of $[1-H_2]$ with one equivalent of $AlMe_3$ in toluene solution at room temperature gave the monomeric aluminum bis(iminophosphoranomethanide), $[AlMe_2\{CH(Ph_2P=NSiMe_3)_2-\kappa N, \kappa N'\}]$ [60] (**11a**) (Scheme 14.4, Fig. 14.10) which has a tetrahedral Al center and an $R_2M(acac)$ -like structure. This aluminum product was unstable and decomposed to the dialuminum spirocycle, $[Al_2Me_4\{\mu-C(Ph_2P=NSiMe_3)_2-\kappa C, \kappa N: \kappa C, \kappa N'\}]$ [60] (**12**, Fig. 14.11). Complex **12** could be obtained directly by the reaction of $1-H_2$ with 2 molar equivalents of $AlMe_3$ at higher temperatures. Other Al alkyl precursors gave differently substituted versions of the methanide system **11** (**11b** and **11c**, Scheme 14.4 and vide infra).

14.5.1.1 Reactions of aluminum complexes

The reactions of **12** with heteroallenes resulted in the formation of new carbon–carbon bonds, most remarkably C=C double bonds between



Scheme 14.4 Al and Zn complexes.

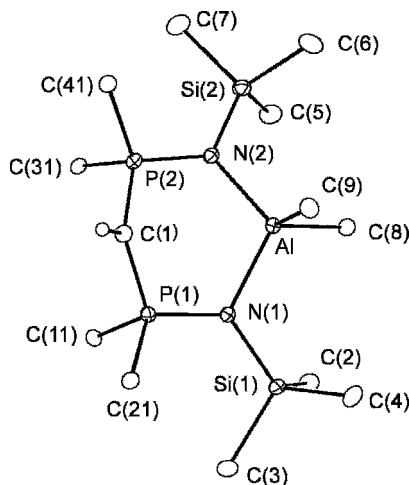


Fig. 14.10. The structure of the Al-methine complex **11**. For clarity all hydrogen and all phenyl carbon (except ipso) atoms have been removed [72]. Reproduced by permission.

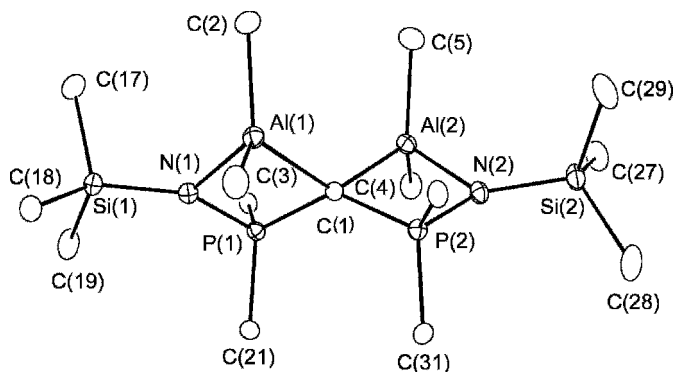


Fig. 14.11. The structure of the diAl-bridged spirocyclic carbene dimer complex **12**. For clarity all hydrogen and all phenyl carbon (except ipso) atoms have been removed [60]. Reproduced by permission.

the formerly bridging methylene carbon atom in **12** and the central carbon atom in the heteroallene; thus adamantylisocyanate, $\text{AdN}=\text{C}=\text{O}$, gave $[(\text{AlMe}_2)_2\{\mu\text{-}((\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{C}=\text{C}(\text{AdN})(\text{O}))\text{-}\kappa\text{N},\kappa\text{N}':\kappa\text{N}'':\kappa\text{O}}]$, (**13a**, Scheme 14.4 and Fig. 14.12) [73].

Reaction of bis(cyclohexyl)carbodiimide with **12** gave $[(\text{AlMe}_2)_2\{\mu\text{-}((\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{C}=\text{C}(\text{CyN})_2)\text{-}\kappa\text{N},\kappa\text{N}':\kappa\text{N}'':\kappa\text{N}'''']]$ (**13b**, Scheme 14.4, Fig. 14.13) [73]. In both cases, an excess of the heteroallene gave neither further homologation nor insertion into the available $\text{Al}-\text{Me}$ bonds. The isonitrile $\text{Ar}'\text{NC}$ ($\text{Ar}' = \text{C}_6\text{H}_4\text{Me}_2\text{-2,6}$) gave $[(\text{AlMe}_2)_2\{\mu\text{-}((\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{C}=\text{C}(\text{Ar}'))\text{-}\kappa\text{N},\kappa\text{N}':\kappa\text{C}}]$ (Scheme 14.4, **13c**) [72] wherein a new $\text{Al}-\text{C}$ bond was formed as well as a new $\text{C}=\text{C}$ bond.

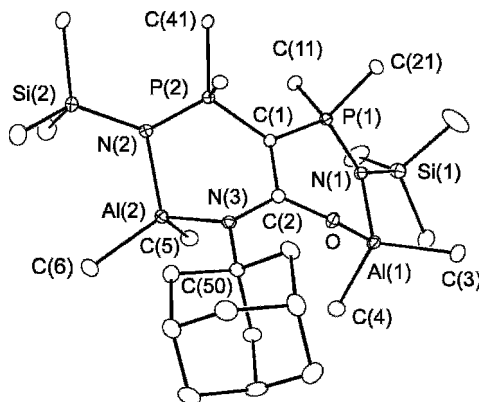


Fig. 14.12. The structure of the Ad-isocyanate adduct **13a** with the dialuminum spirocycle **12**. For clarity all hydrogen and all phenyl carbon (except ipso) atoms have been removed [60]. Reproduced by permission.

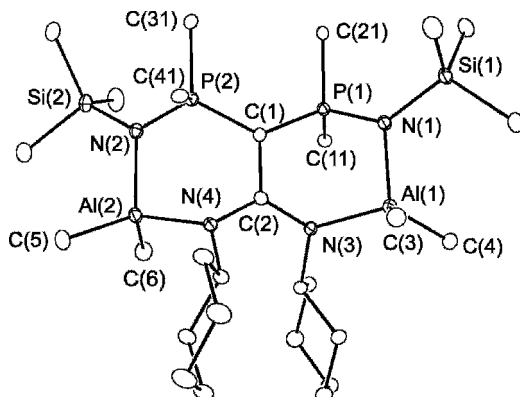


Fig. 14.13. The structure of the cyclohexyl carbodiimide adduct **13b** with the dialuminum spirocycle **12**. For clarity all hydrogen and all phenyl carbon (except ipso) atoms have been removed [73]. Reproduced by permission.

Double deprotonation of the related ligands $\text{CH}_2(\text{Ph}_2\text{P}=\text{E})_2$ ($\text{E} = \text{O}, \text{S}$) by AlMe_3 had been observed in earlier work by others but the products were structurally complex-bridged tri- and tetrametallic complexes, $[\text{Al}(\text{R})\{\text{C}(\text{Ph}_2\text{P}=\text{E})_2\}]_2[\text{Al}(\text{R})_2]_2$ ($\text{E} = \text{O}, \text{R} = \text{Me}, \text{Et}; \text{E} = \text{S}, \text{R} = \text{Bu}$) [40–42]. Our system differed in allowing the stepwise synthesis and isolation of both mono and bimetallic methanide and methandiide complexes with monomeric structures. The former can be readily converted to the latter. We suspect that the steric bulk of the trimethylsilyl substituents on the phosphoranamine nitrogen atoms confers a greater degree of steric control and some electronic stabilization which supports the observed behavior.

The dialuminum spirocyclic carbene **12** proved to be a very effective, transition metal-free, ethylene polymerization precatalyst when activated by one molar equivalent of trityl tetrakis(pentafluorophenyl)borate [74]. By contrast, the monometallic aluminum

precatalysts, $[\text{AlR}_2\{\text{C}(\text{H})(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2-\kappa\text{N},\kappa\text{N}'\}]$ ($\text{R} = \text{Me}$ (**11a**), Bu (**11b**)) or $[\text{Al}(\text{Cl})\text{Et}\{\text{C}(\text{H})(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2-\kappa\text{N},\kappa\text{N}'\}]$, (**11c**), which contain monoanionic *N,N*-chelating ligands and which have structures that are all similar to $\text{AlR}_2(\text{acac})$ complexes, were only modestly active under similar conditions. This suggests that dialuminum species may prove to be generally more effective polymerization catalysts than monometallic complexes. Although the group 4 metal complexes were also effective as catalysts for the polymerization of ethylene (comparable to the metallocenes), the reaction required the traditional large molar excess (1500 molar equivalents) of the usual MAO (methylalumoxane) co-catalyst.

14.5.2 Zinc

The reaction of ZnMe_2 with $[\mathbf{1-H}_2]$ gave the analogous tricoordinate Zn complex $[\text{ZnMe}\{\text{CH}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2-\kappa\text{N},\kappa\text{N}'\}]$ [59] (**11d**, Scheme 14.4) but in this case there is a close interaction between the Zn atom and the methine CH group that gives a pronounced boat conformation to the structure instead of the more open acac structure of the Al analogs. There appears to be no pincer-forming ability in this system presumably because the metal center is too electron rich but an analogous bond formation addition reaction proceeds in any case. This Zn complex, **11d**, added adamantylisocyanate to form **14** (Scheme 14.4), in which a new C–C bond to the methine carbon atom has been created (Fig. 14.14) [59]. Even though the carbon in the ligand backbone is an unconnected methine, there appears to be sufficient electron density at this center to promote electrophilic attack. The end product is probably stabilized by the formation of the N–Zn coordinate link.

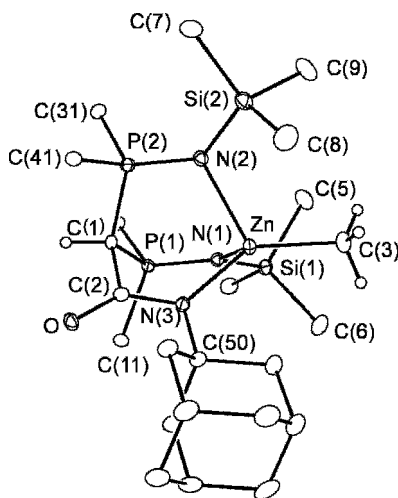
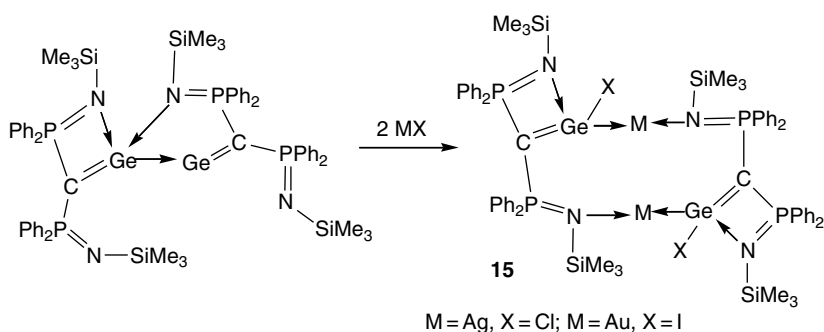


Fig. 14.14. The structure of the Ad-isocyanate adduct **14** formed from the zinc complex **11d**. For clarity all hydrogen and all phenyl carbon (except ipso) atoms have been removed [59]. Reproduced by permission.

14.5.3 Other Main Group Metals

Some interesting bis(phosphoranamide) complexes of Ge and Sn with $M=C$ bonds have been reported by Leung et al. [75–77]. These bidentate chelates show interesting, additional Ge–Ge, Ge–Ni, Ge–Pd and Ge–Ag bonding which is somewhat related to our Cr complex cited above and the Pt complex cited below. The bimetallic chelate, **15** [75], has a rather unusual structure and shows further adduct complexation to form tetrametallic complexes (Eqn 14.4). This group has prepared complexes of an asymmetrical pyridine-phosphoranamide ligand, which have some similarity to our bis(iminophosphorano)methane complexes (see [78]).



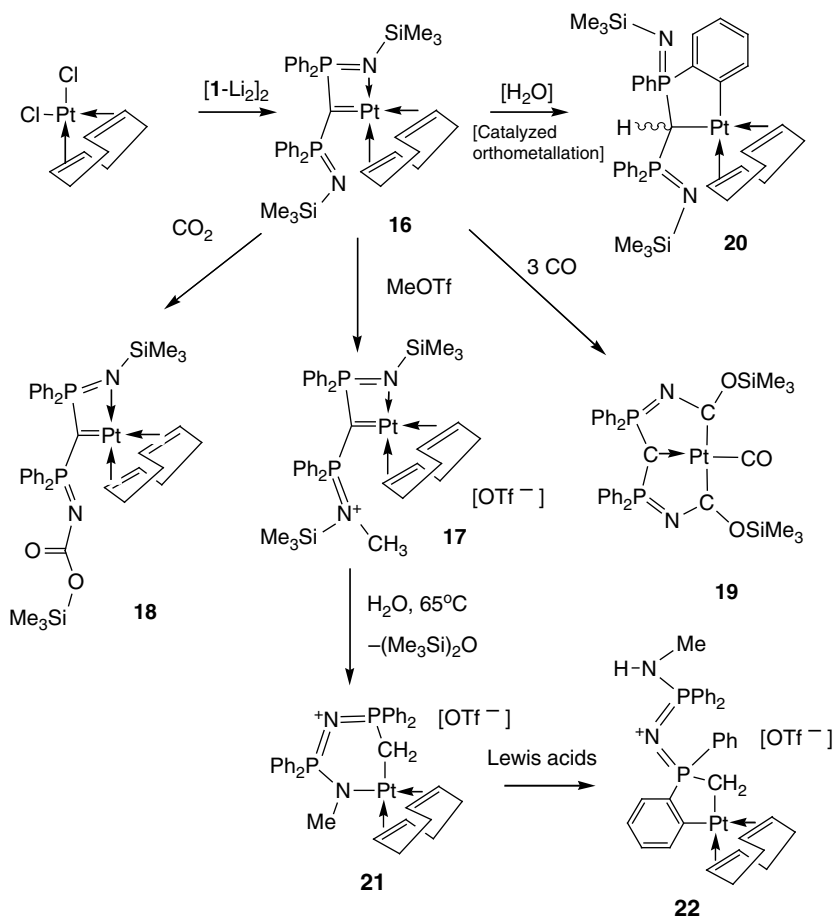
(14.4)

We also found that the alkali metals formed monomeric or dimeric complexes with this ligand system [29, 30] instead of the frequently encountered polymeric materials. These complexes could become useful reagents similar to the dilithiated species, $[\mathbf{1-Li}_2]_2$, and others have reported [31] extensions.

14.6 PLATINUM GROUP METALS

Following the successful development of the chemistry of a considerable fraction of early and middle portions of the transition metal block, it was appropriate to explore the synthesis and reactivity of carbene complexes of the late transition elements. The dilithiated salt reagent provided an efficient route to these compounds. Thus, reaction of $[\mathbf{1-Li}_2]_2$ with 2 equiv. of $[\text{PtCl}_2(\eta^4\text{-cod})]$ in Et_2O gave $[(\eta^4\text{-cod})\text{Pt}\{\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2-\kappa\text{C},\kappa\text{N}\}]$ (**16**, Scheme 14.5, Fig. 14.15) [28]. Here the ligand forms a chelate wherein the coordination environment around the Pt-atom is a slightly distorted square plane. This was the first $\kappa\text{C},\kappa\text{N}$ chelate carbene (as opposed to chelated methanides) of any metal in this system. Recent studies by Cadierno et al. on the Ru(II) system has provided a $\text{Ru}=\text{C}$ chelate which is very similar to **16** [61]. In this coordination mode only one of the two N-atoms of the ligand coordinates to the metal forming a four-membered chelate ring, the other is 'dangling'. Earlier work had shown that a monolithiated ligand **1-(H)Li** would bind to noble metals and form a methanide chelate system [6–8, 11, 79]. The question had arisen in the context of our earlier work as to whether coordination of both N-centers was necessary for the formation of stable carbene complexes; however, **16** showed that one coordinated N-atom could also support the metal–carbene structure. Clearly the nature of the metal exerts a strong influence. It is still not clear whether

M=C complexes of **1** (as the dianion) in which neither nitrogen is coordinated can also be made although recent work by Marrot et al. [53] on PHC carbene complexes suggests that the chelation support is not required for stability.



Scheme 14.5 Platinum group metal complexes.

The carbene C-atom in **16** is planar and the chelate ring C(1), P(1), N(1) and Pt is nearly planar. Likewise P(t), C(1), P(1) and P(2) are coplanar. The Pt–C(carbene) distance in **16** is appreciably longer (2.021(5) Å) than those typically found for both NHC complexes of two- and four-coordinate Pt (1.93–1.97 Å) [67, 80, 81] and Fischer carbene complexes of 4-coordinate Pt (1.87–1.96 Å) [82–87]. Indeed, the Pt–C(carbene) distance in **16** is unusual in that it is more like those found for Fischer carbene complexes of five- [88] and six-coordinate [89] Pt (1.99–2.01 Å). Nevertheless, the Pt–C(carbene) bond in **16** is notably shorter than typical Pt–C(alkyl) single bonds (2.07–2.15 Å) [90] and subsequent chemistry developed at this center again suggests that the system

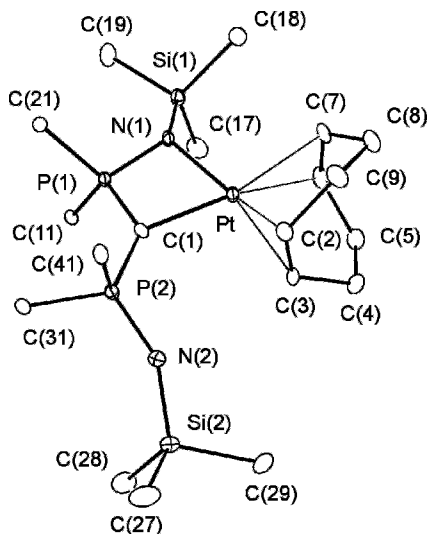


Fig. 14.15. The structure of the platinum carbene chelate **16**. For clarity all hydrogen and all phenyl carbon (except ipso) atoms have been removed [28]. Reproduced by permission.

behaves as if there is a $M=C$ bond with order >1 . The $Ru=C$ chelate in $[(\eta^6\text{-}p\text{-cymene})Ru(\kappa C, \kappa N)C[P\{=NP(=O)(O\text{Ph})_2\}Ph_2][P\{=NP(=O)(OEt)_2\}Ph_2]]$ also shows a short $Ru=C$ bond ($1.976(6)$ Å) and a planar carbon center (Σ angles at the carbene chelate is 359.2°) [61].

In contrast to the early transition element pincer chemistry, the reactivity of **16** was dominated by the presence of the uncoordinated N-atom; reactions with electrophiles demonstrated that this latter center was more nucleophilic than the carbene C-atom. Thus, $MeOSO_2CF_3$ ($MeOTf$) gave the *N*-methylated complex, $[Pt(\eta^4\text{-cod})\{C(Ph_2P=NSiMe_3)(Ph_2P=N(Me)SiMe_3)-\kappa C, \kappa N\}][OTf]$ (**17**), while reaction with CO_2 resulted in an 'insertion' to the N–Si bond to give $[Pt(\eta^4\text{-cod})\{C(Ph_2P=NSiMe_3)(Ph_2P=NC(O)OSiMe_3)-\kappa C, \kappa N\}]$ (**18**) (Scheme 14.5). None of the reactions which attempted to add an electrophile to the carbene carbon atom in **16** were successful. Another notable feature of the reactivity of **16** was the poor lability of the cod substituent which normally can be easily replaced by better bases or π -acids [28].

14.6.1 A Triple Carbene Pincer

The nucleophilicity of the N-donors and C-to-O migration of the trimethylsilyl group is evident in the reaction between **16** and 1 atm of CO gas at room temperature, which resulted in the rapid and quantitative formation of the remarkable triple carbene pincer complex $[(CO)Pt\{\eta^3\text{-}C(Ph_2P=NCOSiMe_3)_2\}]$ (**19**, Scheme 14.5, Fig. 14.16) [91]. This transformation presumably occurred via initial displacement of the cod and twofold attack by free iminophosphorane nitrogen atoms on coordinated CO followed by trimethylsilyl group migration. This ultimately resulted in the insertion of CO into both N–Si bonds and the concomitant formation of two new (nominally Fischer) carbene donors.

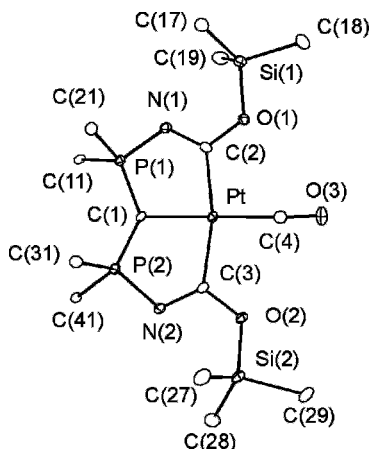


Fig. 14.16. The structure of the platinum ‘triple carbene’ **19**. For clarity all hydrogen and all phenyl carbon (except ipso) atoms have been removed [91]. Reproduced by permission.

All three carbons of the ligand bound to the metal are planar and the bond lengths are short. The central carbene center provides the shortest bond: the Pt–C(1) bond length is 2.002(5) Å, but the others are comparable (Pt–C(2) 2.059(6) Å and Pt–C(3) 2.048(6) Å). All are slightly shorter than the corresponding bond length found in the parent **16**.

14.6.2 Orthometallation and Rearrangements

The carbene complex **16** undergoes an orthometallation reaction to form the complex, $[(\eta^4\text{-cod})\text{Pt}\{\text{C}(\text{H})(\text{PhP}(\text{C}_6\text{H}_4)\text{NSiMe}_3)(\text{Ph}_2\text{PNSiMe}_3)\text{-}\kappa\text{C},\kappa\text{C}'}\}]$ (**20**, Scheme 14.5, Fig. 14.17) [28]. The reaction appears to be catalyzed by small amounts of water because there was no reaction in dry solvent under the same conditions. The orthometallated complex **20** does not display the kind of charge delocalization found in **16**, but rather resembles normal orthometallated aryl Pt complexes. The C–P and P=N distances in **20** are longer and shorter, respectively, than the corresponding lengths in **16** and fall within the accepted ranges of single C–P and double P=N bonds.

The N-methylated complex **17** reacted (Scheme 14.5) with stoichiometric quantities of H₂O diluted in solvent (uncontrolled addition of water gave intractable products) to give an unusual platinacycloposphazene, $[(\eta^4\text{-cod})\text{Pt}\{\text{CH}_2\text{P}(\text{Ph}_2)\text{NP}(\text{Ph}_2)\text{N}(\text{Me})\text{-}\kappa\text{C},\kappa\text{N}}\}]$ (**21**) wherein both N–Si bonds have been hydrolyzed and a remarkable N–P–C–P–N to C–P–N–P–N rearrangement took place (Scheme 14.5) [92]. The rearranged platinacyclic carbaphosphazene **21** (Fig. 14.18) was insensitive to and insoluble in H₂O and, in the solid state, it was likewise insensitive to several days’ exposure to air. In the presence of Lewis acids, **21** converted into an orthometallated isomer, $[(\eta^4\text{-cod})\text{Pt}\{\text{CH}_2\text{P}(\text{C}_6\text{H}_4)\text{PhNPPH}_2\text{NH}(\text{Me})\text{-}\kappa\text{C},\kappa\text{C}'}\}]$ (**22**, Scheme 14.5) in which the N–Pt bonding formed in the water-catalyzed rearrangement resulted in the complex being converted back to a C–Pt bonding situation [92, 93]!

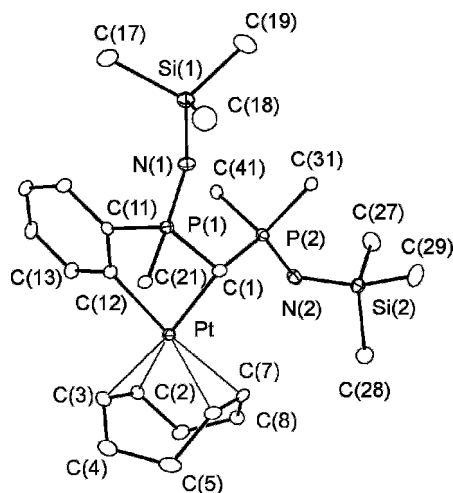


Fig. 14.17. The structure of the orthometallated chelated carbene **20**. For clarity all hydrogen and all phenyl carbon (except ipso) atoms have been removed [28]. (Note *Erratum* wherein correct structure will be found). Reproduced by permission.

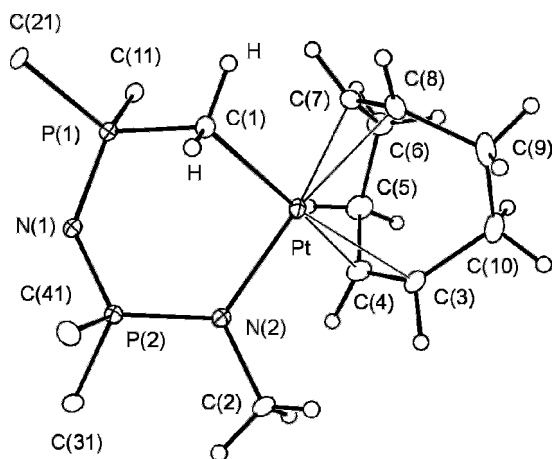


Fig. 14.18. The structure of the rearranged platinum carbocycle, **21**. For clarity all hydrogen and all phenyl carbon (except ipso) atoms have been removed [92]. Reproduced by permission.

14.7 BIMETALLIC SPIROCYCLES

14.7.1 Synthesis and Characterization

Reaction of $[\mathbf{1-Li}_2]_2$ with one equivalent of the rhodium dimer, $[\text{Rh}(\mu\text{-Cl})(\eta^4\text{-cod})]_2$, proceeded smoothly in THF at room temperature to give $[(\eta^4\text{-cod})\text{Rh}\{\mu\text{-C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{-}\kappa\text{C},\kappa\text{N}:\kappa\text{C},\kappa\text{N}'\}\text{Li}(\text{OEt}_2)]$ (**23**, Fig. 14.19), a Li–Rh heterobimetallic spirocycle which contains a reactive carbon nucleophile [25, 93]. This complex proved

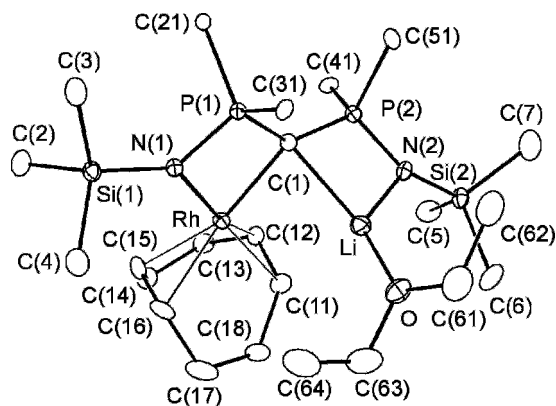


Fig. 14.19. The structure of the Li–Rh bimetallic spirocycle, **23**. For clarity all hydrogen and all phenyl carbon (except ipso) atoms have been removed [25].

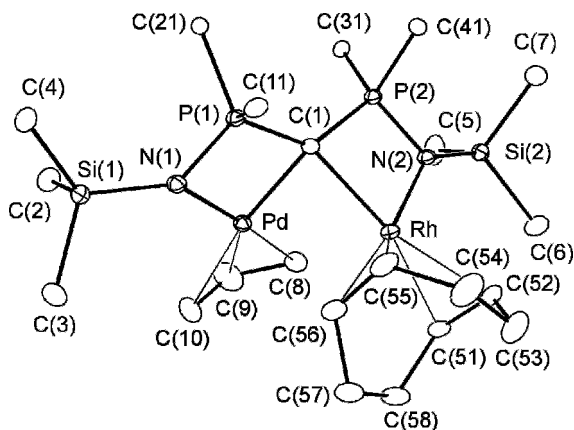


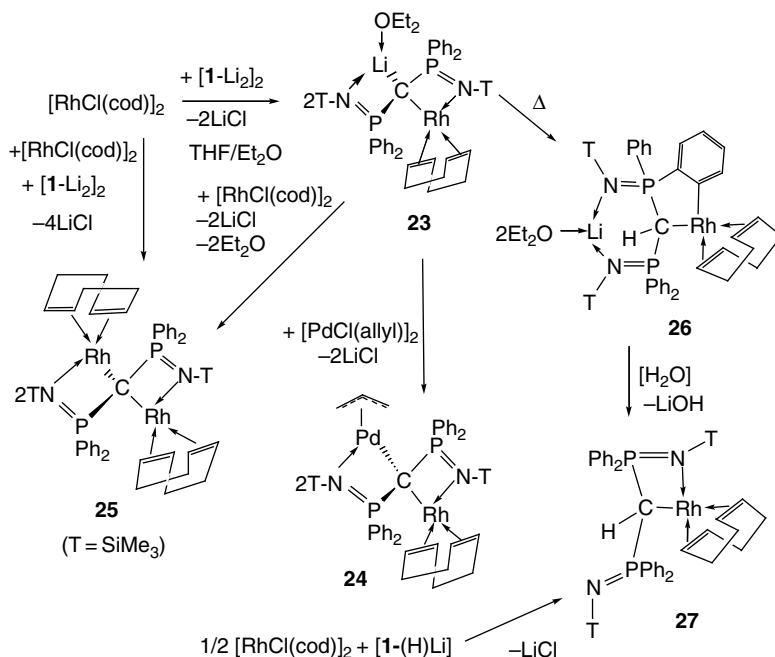
Fig. 14.20. The structure of a typical bimetallic spirocycle, that of the Pd–Rh complex, **24**. For clarity all hydrogen and all phenyl carbon (except ipso) atoms have been removed [47, 93].

to be an ideal precursor to other homo- and heterobimetallic species via simple elimination of lithium halide. This discovery has opened the door to the development of bimetallic complexes of this ligand system.

A different metal may be introduced at this point. For example reaction of **23** with $[\text{Pd}(\mu\text{-Cl})(\eta^3\text{-allyl})]_2$ gave $[(\eta^4\text{-cod})\text{Rh}\{\mu\text{-C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{-}\kappa\text{C},\kappa\text{N}:\kappa\text{C},\kappa\text{N}'\}\text{M}]$ **24**, $\text{M} = (\eta^3\text{-allyl})\text{Pd}$. The structure of **24**, shown in Fig. 14.20, is representative of Rh–Pd [25, 93] bimetallic spirocycles.

Complex **23** was readily transformed (Scheme 14.6) into the homobimetallic Rh-bridging methylene spirocycle, $[(\eta^4\text{-cod})\text{Rh}\{\mu\text{-C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{-}\kappa\text{C},\kappa\text{N}:\kappa\text{C},\kappa\text{N}'\}\text{M}]$ (**25**, $\text{M} = (\eta^4\text{-cod})\text{Rh}$), upon reaction with a second mole of $[\text{Rh}(\text{cod})\text{Cl}]_2$ [93]. This

dirhodium complex **25** can be accessed directly by the one-step reaction of $[\mathbf{1-Li}_2]_2$ with a twofold molar ratio of $[\text{Rh}(\text{cod})\text{Cl}]_2$ [93].



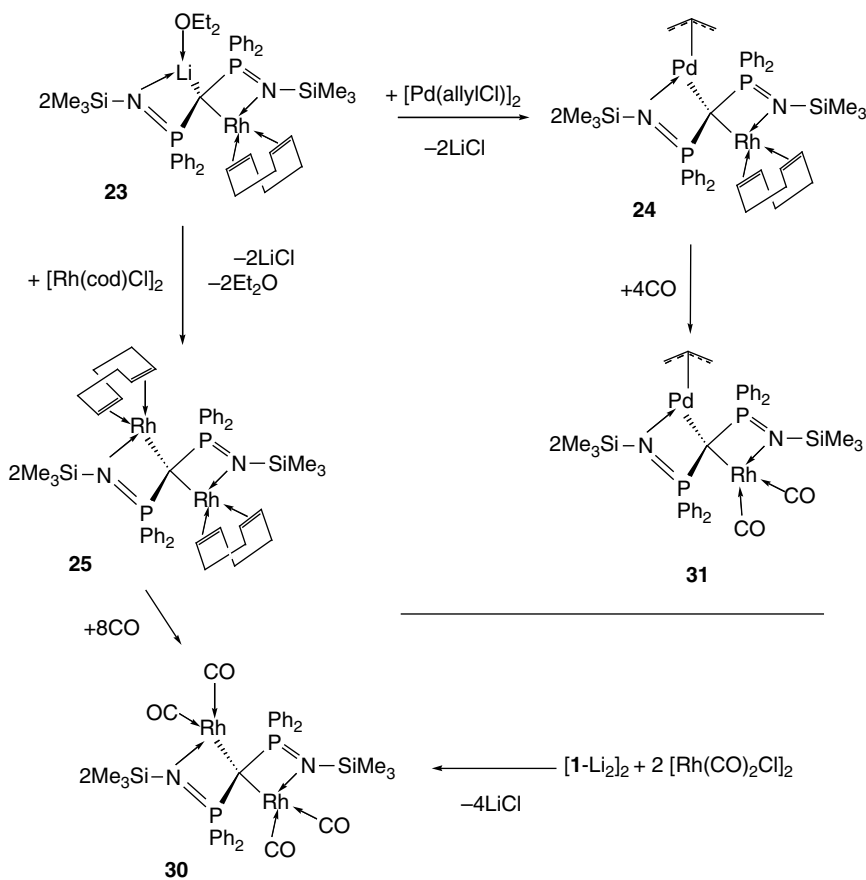
Scheme 14.6 Bimetallic spirocycles.

As complex **23** is easily prepared from the straightforward, stoichiometrically controlled (1:1), metathetical reaction of the dilithiated salt $[\mathbf{1-Li}_2]_2$ and $[\text{Rh}(\text{cod})\text{Cl}]_2$ [93], subsequent metathetical reactions of **23** with additional aliquot of different metal precursors would appear to provide routes to a variety of spirocyclic bimetallics. Although there are many examples wherein an organometallic complex has been prepared by metathetical replacement of the Li in a lithiated precursor [4, 28, 71, 76, 94] this synthetic route, to the best of our knowledge, has not been systematically applied to prepare bimetallic complexes. It has yet to be demonstrated that different metal analogs of **23** can themselves be prepared but there appears to be no reason in principle why this cannot be done, therefore the potential for extensive bimetallic spirocycles appears to be limitless. It should be noted that appropriate combinations will yield chiral complexes which might be efficacious as chiral catalysts.

14.7.2 Reactions of Bimetallic Complexes

While evaluation of the lability of the organometallic substituents was the goal (to contrast with the surprising inert character of the cod on the Pt carbene **16**) carbon monoxide reactions with **24**, **25** (and **27**) were conducted with the knowledge that CO insertions into the N–Si bond could also occur as was the case in our hands for the

reaction of **16** with CO, but in the bimetallic, **24**, the allyl group on Pd was not displaced (Scheme 14.7). To complete the circle, the CO complex **30** could be obtained from metathetical reaction of the appropriate Rh–CO precursor with the appropriate lithiated form, $[1\text{-Li}_2]_2$, of the ligand [93]. The cod substituents in this system are labile so we expect further transformations to be facile.



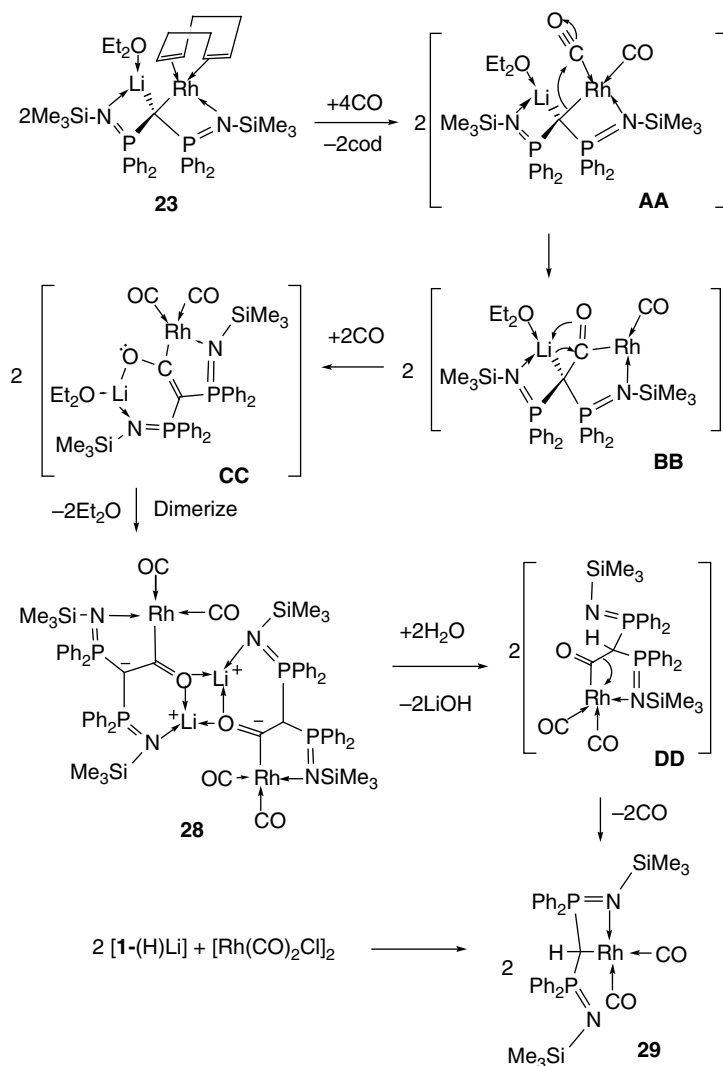
Scheme 14.7 Substitution reactions of spirocycles.

14.7.3 Reactivity of the Lithiated Spirocycle

Complex **23** was not exceptionally thermally unstable but heating it in solution led to an orthometallation transformation to the bimetallic lithiated methanide (Scheme 14.6) $[(\eta^4\text{-cod})\text{Rh}\{\mu\text{-CH}(\text{Ph})(\text{C}_6\text{H}_4)\text{P}=\text{NSiMe}_3)(\text{Ph}_2\text{P}=\text{NSiMe}_3) \kappa\text{C}, \kappa\text{C}': \kappa\text{N}, \kappa\text{N}'}\text{-Li}(\text{OEt}_2)]$, **26**, wherein one of the phenyl rings has suffered orthometallation at rhodium, the resulting hydrogen has been transferred to the formerly carbenic carbon atom and the lithium center has become *N,N*-chelated.

14.7.4 A Ketene Complex

In addition to the cod replacements by CO described for **24**, **25** and **27** (Scheme 14.7), complex **23** itself reacted smoothly with CO with replacement of cod but simultaneously there was an additional formal C–C bond formation insertion reaction (Scheme 14.8) into the spirocyclic Rh–C bond to yield **28**, a fully characterized dimeric ketene complex (Fig. 14.21) [25, 93]. We surmise that **28** probably arise from a Li-mediated insertion reaction which follows the normal substitutional replacement of the cod ligand on Rh with CO. Thus, a CO ligand on Rh inserts into the Rh–C bond to form an acyl (Scheme 14.8 intermediate [AA]). The terminal oxygen on the Li attacks and opens the Li–C



Scheme 14.8 Ketene formation and decomposition.

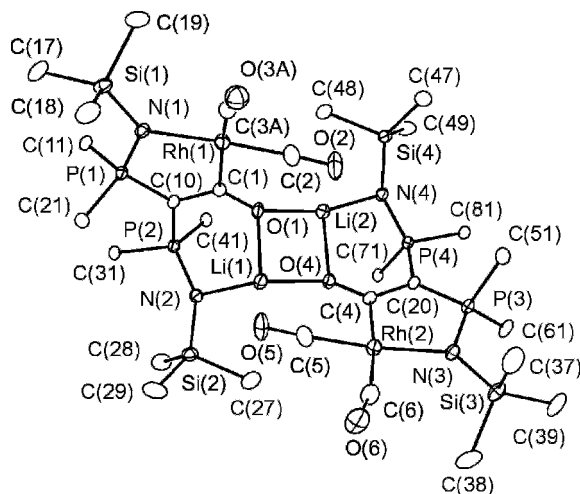


Fig. 14.21. The structure of the dimeric ketene complex **28**. For clarity all hydrogen and all phenyl carbon (except ipso) atoms have been removed [25, 93]. Reproduced by permission.

bond to form a (likely stronger) Li–O bond (Scheme 14.8 [BB]). The coordination unsaturation at Rh which is created by this process is readily overcome by the addition of one more molecule of CO (Scheme 14.8 [CC]) which then dimerizes with loss of ether to **28**. The overall result is that CO has been inserted into each of the Rh–C(carbene) bonds. The dimerization probably enhances the stability of the final product. Notably, complexes analogous to **23**, such as **24** and **25** (Scheme 14.7) which do not contain Li but have weaker Rh–CO bonds (lengths are 2.137(3) in **24**; 2.148(2) in **25**; versus 2.015(6) in **23**), which would presumably be susceptible to insertion to form a ketene, do not insert CO [25, 93] suggesting that Li plays a key role in promoting the CO insertion reaction demonstrated by **23** probably by inducing, through increased polarity at the bridging carbene center, a higher nucleophilicity of the proximal carbon in **23**. The nearly quantitative formation of **28** also implies that a direct CO insertion to the Li–C bond is not operative because it is known that such reactions are generally nonspecific at room temperature [95, 96].

14.7.5 The Reactivity of the Ketene

Notably, complex **28** reacts with H₂O at room temperature as illustrated in Scheme 14.8 to give the bidentate rhodium methine complex, **29**. No intermediate was observed in the NMR [25, 93]. The ketene dimer is split and the ketene functionality is destroyed by the ejection of CO. A possible reaction pathway begins from the presumption that the PCP carbons likely possess significant negative charge, as suggested by the illustrated resonance structure, (**28**), therefore a likely first step of the hydrolysis involves attack of water at Li to form LiOH with protonation of the carbene center (intermediate **DD**, Scheme 14.8) with concomitant dissociation of the dimer. This then rearranges with the destruction of the ketene structure, possibly involving an intermediate with highly carbonylated Rh which would readily lose CO to yield **29**. This final methine complex can be synthesized from **1-(H)Li** and the appropriate Rh–carbonyl dimer precursor.

14.8 SUMMARY

The bis(iminophosphorano)methandiides, obtained by spontaneous or deliberate double deprotonation of the backbone carbon of bis(iminophosphorano)methane, have provided an extensive series of metal complexes spanning the periodic table from group 3 to group 15 which, for the most part, offer metal–carbon bonds of unusual character. Many different geometries have been encountered; pincer and chelate carbenes with $M=C$ bonds and examples of bimetallic carbenes with either the bridging carbene structure wherein two metals are linked with two carbon atoms to provide a M_2C_2 plane or a M_2C spirocyclic bimetallic system wherein two metals connect to a common carbon. The system has provided some unusual reactivity, the scope of which has not yet been fully defined. There are many fruitful avenues which could be pursued, especially toward the exploration of the utility of these new systems for catalytic transformations. In this application, the most potentially useful group could be the new system of bimetallic spirocycles.

ACKNOWLEDGEMENTS

Our work has been supported throughout by the Natural Sciences and Engineering Research Council (NSERC) of Canada, the Killam Foundation of the University of Alberta, the Petroleum Research Foundation of the American Chemical Society (ACS-PRF), our industrial sponsor, NOVA Chemicals, and the University of Alberta (UA). I am indebted to all the skilled postdoctoral researchers who have worked on this project; Rупpa Poonchary Kamalesh Babu, Kasani Aparna (after 2000 styled as Aparna Kasani, by choice), Guanyang Lin, Nathan Jones (UA Killam Postdoctoral Fellow), Min Fang and (courtesy of an ACS PRF-summer faculty fellowship) Robert Gossage (Acadia University). I am also indebted to the undergraduate researchers; Kristina Friesen, Robert Lukowski and Jim Tjathas who worked on various aspects of the system described herein. My thanks to the UA staff crystallographers, Robert McDonald and Mike Ferguson, for providing so many illuminating structures. My thanks also to Kazuyuki Kubo (1-year Faculty visitor at UA from Hiroshima University sponsored by the Japan Ministry of Education, Sports, Science and Technology). Professor Kubo developed the carbodiphosphorane application (see Chapter 15) to the point where it really connected to the phosphine imine system! I thank UA for the provision and maintenance of excellent NMR and crystallography facilities in the department which have proven to be essential for our work. I also thank my contacts and collaborators at NOVA Chemicals of Canada who contributed substantially to the development of the system which has already provided patented examples of catalytic capability [97].

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Pincer and chelate carbodiphosphorane complexes of noble metals

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15.1 INTRODUCTION

Recently we and others have revisited the metal chemistry of hexaphenyl carbodiphosphorane, $\text{Ph}_3\text{P}=\text{C}=\text{PPh}_3$ (**1**), a ligand which offers potential for ‘carbene’ donation of one or two pairs of electrons (see Chart 15.1). Our curiosity was prompted by the question of the independence of the carbene center in the (dianionic) bis(phosphoranimino)methandiides $[\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2]^{2-}$ (**2**), (Chapter 14) particularly, whether the N-coordination so frequently observed was necessary for stabilization. In this chapter we describe chelate and pincer (see Chart 15.2, **C**) carbene complexes of Pt, Rh and Pd which are obtained from single and double orthometallations, respectively, of the phenyl rings of **1**. The pincer complexes of the carbodiphosphorane system represent a wholly new class of *C, C, C*-pincer complexes and expand the relatively small supply of pincers containing only carbon atoms bonded to the metal. Most pincers which have this structure have a bound carbon atom which is part of an aromatic ring structure (such as Chart 15.2, **D, E**); not so in our cases. In our systems (here and the rather unique example of a Pt complex obtained via a migratory CO insertion reaction reported previously by us [1], Chapter 14), the central carbon is not part of any ring, rather it is single and bound only to two phosphorus centers. Most recent examples of *C, C, C*-pincer complexes have included NHC components in the ligand structure (e.g., Chart 15.2, **E**, where atom E = C) [2, 3].

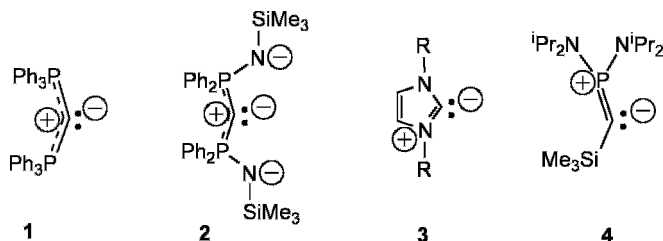
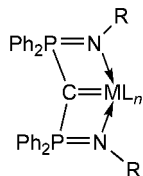
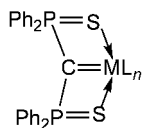
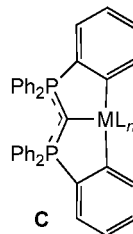
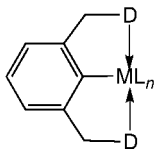
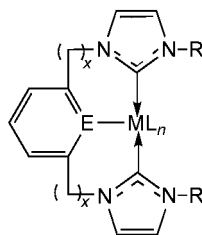


Chart 15.1 Some types of carbenes.

Dianionic "carbenes"

**A****B****C**

Classic pincers

D = PR₂, NR₂, OR, SR**D****E**

E = C (x = 1) (yielding C,C,C pincers)

E = N (x = 0, 1)

Chart 15.2 Dianionic carbenes, carbodiphosporanes and classic pincers.**15.2 BACKGROUND**

The intriguing (double ylide) carbodiphosporane, Ph₃P=C=PPh₃ (**1**) (which may be written Ph₃P⁺–C^{2–}–PPh₃⁺), was first reported 45 years ago by Ramirez et al. [4]. The synthetic phosphorus chemistry of this system was then expanded by Schmidbaur, Appel and others with the bulk of the work being done over 20 years ago [5, 6]. A number of potentially useful ligands can be extracted from this work. The bis(phosphoranimino)methandiides [C(Ph₂P=NSiMe₃)₂]^{2–} (**2**) (Chart 15.1) can be considered as formal derivatives of **1**. We have described elsewhere in this volume (Chapter 14) the pincer and some related chelate complexes of this system (e.g., Chart 15.2, **A**).

As demonstrated by the following chemistry, **1** forms pincer complexes in which the C–M interaction may be thought of as a dative, two-electron C → M σ-bond. The complexes appear to be stabilized by orthometallation of one of the phenyl rings on each phosphorus atom to form the pincer. These new pincer complexes (Chart 15.2, **C**) add new examples of cyclometallated pincers [3].

Formally (**1**) may offer a carbene-type carbon to bind to metals. Although a formal carbene resonance form (six valence electrons on the central carbon atom) cannot be drawn for either the type **1** or type **2** systems (see Chart 15.1), there appears to be a useful concept parallel with the Arduengo (*N*-heterocyclic) (**3**) and the Fischer-type Bertrand (phosphanyl-aryl or -silyl)carbenes (**4**) in that **1** and **2** have ylidic resonance forms that allocate eight valence electrons to the 'carbenic' carbon. These ligands can then form complexes in which they act as bent, two-electron, σ-donors (Chart 15.1). Like the Bertrand and Arduengo carbenes, the carbodiphosporanes are electrically neutral.

However, in contrast to the Arduengo (which have been designated as ‘push–push’) carbenes and Bertrand (‘push–pull’) carbenes, the noncoordinated carbodiphosphoranes can be thought of as ‘pull–pull’ carbene systems because the electron-withdrawing phosphonium substituents deplete electron density on the central, formally C^{2-} , atom thus giving it a distinct carbenic character. In efforts, parallel to ours, other filled-octet, phosphorus-containing compounds for which formal carbene resonance forms cannot be clearly drawn, such as the bis(thiophosphinoyl)methandiides [7] (Chart 15.2, **B**), and more elaborate variations of the bis(phosphoranimino)methandiides [8] have recently begun to be regarded as carbene types.

15.3 METAL COMPLEXES OF HEXAPHENYLCARBODIPHOSPHORANE

The initial metal chemistry (Mn, W, Pt, Ni and Ir) of **1** was pioneered by Kaska and co-workers; however, some results were inconclusive [9]. Thus complexes of Pt could be made but no structural characterization was achieved. Recently Petz has shown a simple monodentate coordination of **1** to $Ni(CO)_3$ [10] and Petz and co-workers have reinvestigated the Pt system [11] providing new insight into some of the early work. In addition this group has explored other ligand chemistry of **1** [11].

These investigations of **1** by ourselves and others have led to the discovery of an entirely new and intriguing class of pincer complexes (Chart 15.2, **C**) for $M = Pt, Pd$ and Rh as well as additional nonchelate chemistry. In the context of this present chapter, only the chelates and pincers of these metals will be considered. A collection of relevant references to metallic complexes of **1** which do not contain chelate or pincer structures can be found in the introduction of Ref. [11].

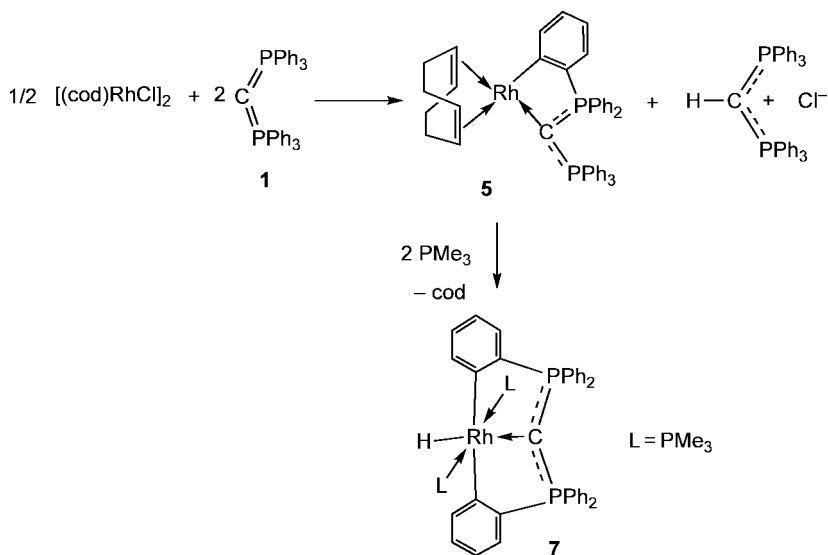
15.3.1 Synthesis

Reaction of **1** with coordinatively unsaturated metal complex precursors readily gave access to carbodiphosphorane complexes. Common halide and sulphide-bridged bimetallic complexes of the late metals proved useful in this regard because we had found that $Ph_3P=C=PPh_3$ (**1**) was not effective in ligand-replacement processes even with ligands presumed to be quite labile and that is because although **1** is strongly basic, it is only weakly nucleophilic. This is supported by the observation that typical Wittig reactivity is almost completely unknown for the carbodiphosphoranes.

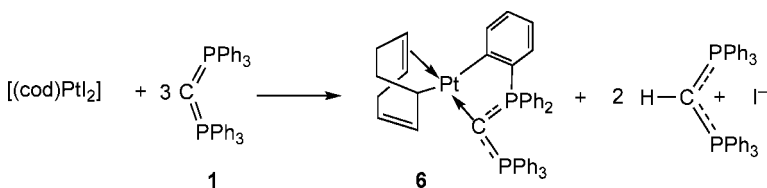
Thus, $[Rh(\mu-Cl)(\eta^4-cod)]_2$ reacted with **1** first to form the *C, C*-chelated carbene complex, $[(\eta^4-cod)Rh\{\eta^2-C(P(C_6H_4)Ph_2)(PPh_3)\}]$ (**5**, Scheme 15.1, Fig. 15.1) probably through an $Rh(III)$ hydride intermediate [12]. Structurally this complex shows the carbene bound to the metal with one pendant PPh_3 group. Interestingly, in the light of related work [11], the *cod* substituent on Rh is unchanged.

In contrast Petz and co-workers, beginning with $[(cod)PtI_2]$, obtained an orthometallated chelate complex of Pt, **6** (Scheme 15.2), in which one phenyl of one PPh_3 unit is orthometallated and the other PPh_3 unit remains free. In this case the platinum valence is satisfied through a second orthometallation with the *cod* unit with rearrangement of the electronic structure of the *cod* ligand [11].

Subsequent treatment of **5** with 2 equiv. of PMe_3 gave the $Rh(III)$ *C, C, C*-pincer carbene complex, $[HRh(PMe_3)_2\{\eta^3-C(Ph_2P(C_6H_4))_2\}]$ (**7**, Fig. 15.2) in high yield



Scheme 15.1 Preparation of rhodium chelate and pincer.



Scheme 15.2 Preparation of a platinum chelate [11].

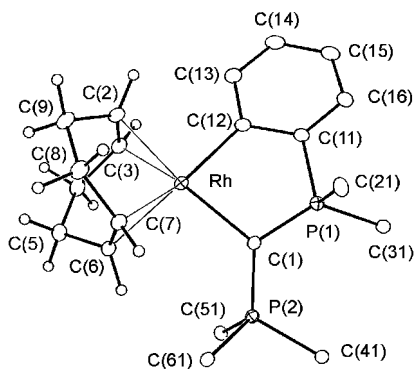


Fig. 15.1. The molecular structure of **5**. The atoms are represented as 20% ellipsoids. Only the ipso carbon atoms of all but the orthometallated phenyl rings are shown [12]. Reproduced with permission.

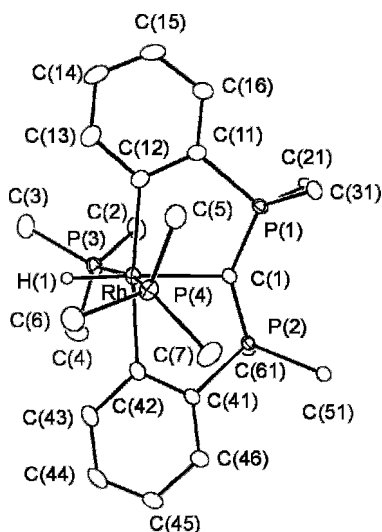


Fig. 15.2. The molecular structure of **7**. Only the ipso carbon atoms of the phenyl rings are shown and all but the hydride hydrogen atoms have been omitted for clarity. The atoms are represented as 20% ellipsoids [12]. Reproduced with permission.

Table 15.1. Metal–carbon bond lengths (Å) in selected chelates and pincers.

	Metal	M–C(1)	M–C(12) ^a	M–C(42)
Chelates				
5	Rh	2.165(2)	2.072(2)	–
6^b , Ref. [11]	Pt	2.072(3)	2.086(4) (C31)	–
10	Pd	2.108(3)	2.108(3)	–
Ref. [13]	Pd	2.127(7)	2.057(7) (C3)	–
Pincers				
7	Rh	2.202(3)	2.092(3)	2.075(3)
8	Pt	2.032(3)	2.080(3)	2.077(3)
9	Pt	2.086(3)	2.087(3)	2.067(3)
Triple carbene ^c Ref. [1]	Pt	2.002(5)	2.059(6) (C2)	2.048(6) (C3)

^a Atom designations are as depicted in the figures unless other structural data carries different labels. The different labels are indicated where appropriate.

^b A short Pt–C(38) distance to one cod carbon (2.139(4) Å) completes the Pt valence.

^c Data from Ref. [1] (also Pt–C(4) of CO is 1.868(6) Å.)

through replacement of the cod ligand and inducing a second phenyl orthometallation event on the free PPh₃ end of the ligand [12]. See Table 15.1 for selected structural data for **5** and **7**.

Reaction of **1** with [Me₂Pt(μ-SMe₂)]₂ gave directly the Pt(II) C, C, C-pincer carbene complex, [(Me₂S)Pt{η³-C(Ph₂P(C₆H₄)₂)}] (**8**, Scheme 15.3) directly via double orthometallation with elimination of 2 equiv. of CH₄. No intermediate species were

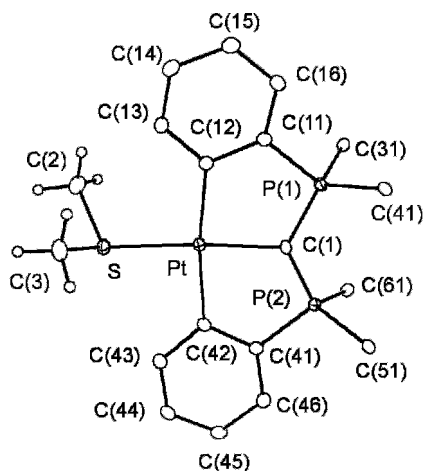
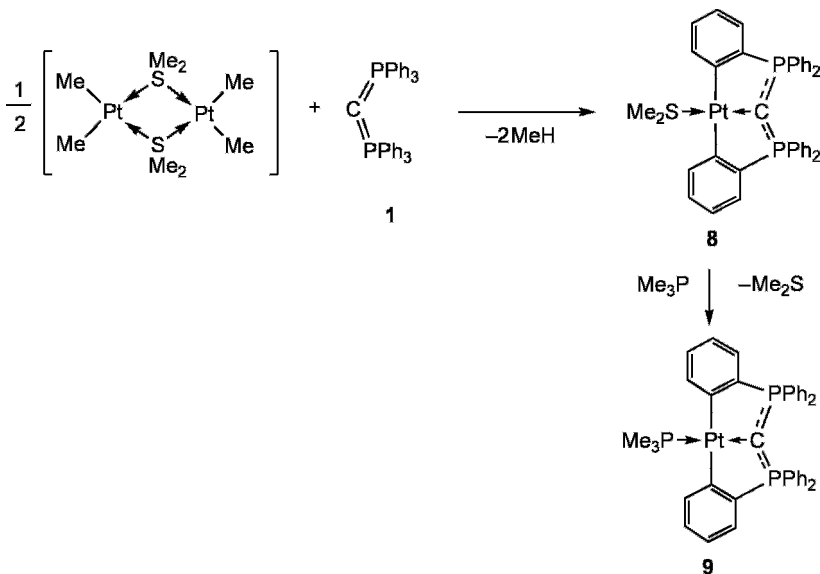


Fig. 15.3. The molecular structure of **8**. The atoms are represented as 20% ellipsoids. Only the ipso carbon atoms of the singly bound phenyl rings are shown and all but the hydride hydrogen atoms have been omitted for clarity [12].

observed in this reaction [14]. The Me_2S ligand was readily replaced with PMe_3 to give **9**. The structure of **8** is shown in Fig. 15.3 and a few important distances are given in Table 15.1.



Scheme 15.3 Platinum pincers.

In contrast, the reaction of **1** with $[(\eta^3\text{-allyl})\text{Pd}(\mu\text{-Cl})_2]$ results in a single orthometal-lation event (Scheme 15.4). A representation of the molecular structure of **10** is given in Fig. 15.4. A structure of this same product was briefly reported elsewhere [13]. Selected relevant bond lengths are given in Table 15.1.

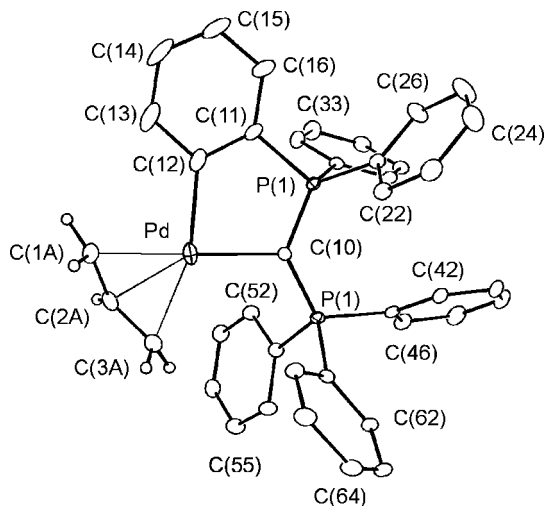
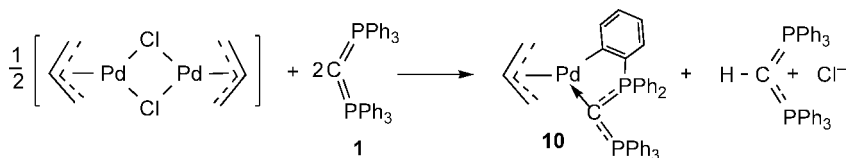


Fig. 15.4. The structure of **10**. Only the ipso carbon atoms of the singly bound phenyl rings are shown and all but the hydride hydrogen atoms have been omitted for clarity [14].



Scheme 15.4 Palladium chelate.

Preliminary density functional electronic structure calculations (Gaussian 98 DFT B3LYP/LANL2DZ) [15] for the model compound $\text{HRh}(\text{PH}_3)_2[\eta^3\text{-C}\{\text{H}_2\text{P}(\text{C}_6\text{H}_4)\}_2]$ (**7'**) [14, 15], revealed one π and two relatively deep σ molecular orbitals which are themselves bonding with respect to the $\text{Rh}-\text{C}_{\text{carbene}}$ axis. One of these σ - and the π -bonding MOs are paired with occupied antibonding orbitals and so the overall result appears to be no net $\text{Rh}-\text{C}_{\text{carbene}}$ bonding from these orbitals. One σ $\text{Rh}-\text{C}_{\text{carbene}}$ bonding orbital remains. The HOMO is largely a C-based p_z -orbital with small contributions from Rh and H. The $\text{Rh}-\text{C}$ interaction can therefore be described as a single σ -bond between a Rh-based d-orbital and an sp^2 -like orbital on $\text{C}_{\text{carbene}}$ plus (as the HOMO) an occupied p_z -orbital on the $\text{C}_{\text{carbene}}$. The Mulliken charges are: Rh +0.26, $\text{C}_{\text{carbene}}$ -0.87, P +0.40 (including H atoms), C_{phenyl} +0.17. This calculation suggests that the metal-carbon interaction in these compounds may be described as a dative, two-electron, $\text{C} \rightarrow \text{M}$ σ -bond which is buried in the core bonding orbitals. The HOMO in this case shows a pair of electrons on C localized as a p_z (π -type) orbital which will be influenced by the character of the metal and are also available as a point of nucleophilic attack. We suggest that bis(phosphoranimine)methandiide ligands might have similar character so, while neither of these systems has a formal six-electron resonance form, each may be considered as ligands with pull-pull Fischer carbene character. The electron density distribution is not firmly defined by the ligand itself so the metal to which the ligand becomes coordinated will ultimately dictate its chemistry.

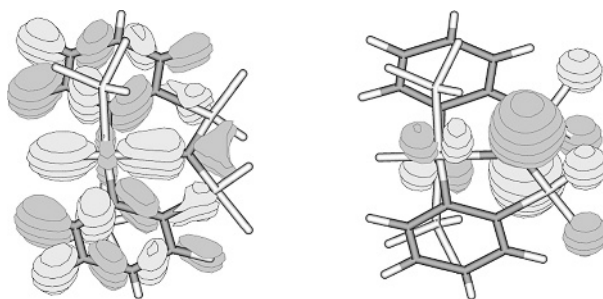


Fig. 15.5. Two MOs of the model compound **7'**: (a) the HOMO-14 σ -bonding level and (b) the π HOMO levels [15].

ACKNOWLEDGEMENT

Our work has been supported throughout by the Natural Sciences and Engineering Research Council (NSERC) of Canada, the Killam Foundation of the University of Alberta, the Petroleum Research Foundation of the American Chemical Society (ACS-PRF) and the University of Alberta (UA). Special thanks go to Dr Kazuyuki Kubo (1-year faculty visitor at UA from Hiroshima University, sponsored by the Japan Ministry of Education, Sports, Science and Technology) for his work delineating this system. Our thanks go to the UA staff crystallographers, Robert McDonald and Mike Ferguson, for providing so many illuminating structures and we thank UA for the provision and maintenance of these excellent crystallography and NMR facilities in the department which have proven to be essential for our work. We thank Dr Nathan Jones (UA Killam Postdoctoral Fellow) for his input to the area and for the calculations shown in Fig. 15.5.

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Hypervalent organotin, aluminium, antimony and bismuth Y,C,Y-chelate complexes

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16.1 INTRODUCTION

The extensive investigations of hypervalent compounds of main groups are due to the work of last two decades. The large number of publications and reviews deal with aspects of the chemistry of these compounds concerned with extra-coordinated species [1–14]. This increasing interest in hypervalent, so called hypercoordinated, derivatives of main group elements is caused by their structural peculiarities, high reactivity and also by the presence of interesting dynamic processes enabling the studies of nucleophilic substitution reactions at the central atom.

According to Akiba's formalism [15], hypervalent compounds of main group metal elements (sp element, groups 1, 2 and 13–18) are compounds containing number of formally assignable electrons (N) of more than the octet in the valence shell directly associated with central atom (M) that is directly bound with a number (L) of ligands. This N - M - L designation is very useful for the classification of hypervalent structures, where a trigonal bipyramid (TBP), square pyramid (SP) or octahedral (Oh) arrangement are the most typical ones in the chemistry of hypercoordinated compounds.

The hypercoordination of central atom is usually accompanied by the presence of the inter- or intramolecular $Y \rightarrow M$ donor–acceptor bond. The intermolecular complexes of main group metal compounds with halide ions and neutral N-, P-, O- and S-donors, including electron-donor solvents, with general formula $nY \rightarrow MX_m$ (where Y is donor atom, MX_m is metal compound) have been known for a long time [1, 2, 16–20]. The stability, composition and structure of organometallic complexes depend especially on the central metal and the mutual ratio of organic substituents bound to the metal by direct M–C bond (R), ligands (L) and polar groups (X).

The existence of intramolecular $Y \rightarrow M$ donor–acceptor bond can be achieved by the introduction of additional donor atom Y into an organic group that has been already bound to main group metals M . Such an organic group is then monoanionic bidentate

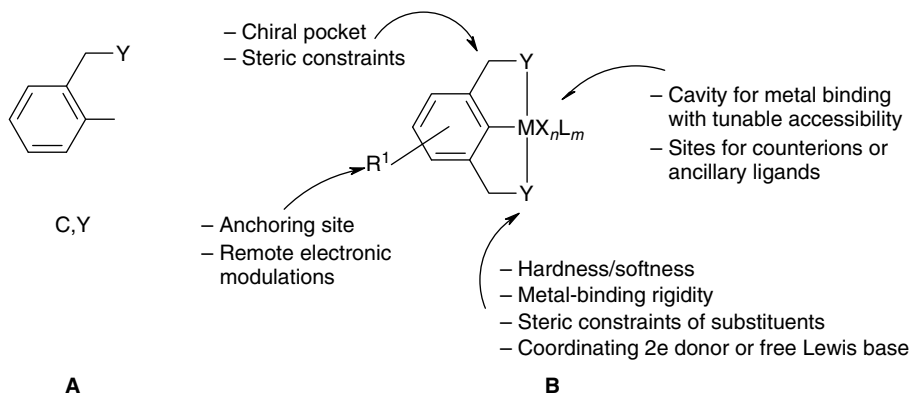


Fig. 16.1. C,Y-chelating ligand (A) and Y,C,Y-complexes (B).

X,Y-chelating ligand (X, Y = C, N, P, O, S) [1, 2, 16]. Among them, the C,Y-chelating ligand (Y = N, O) (Fig. 16.1A) seems to be the most popular one and has been widely used for the preparation of both hypercoordinated main group (see for example [21–26]) and transition metal complexes (see for example [27–39]). In such organometallic complexes containing a direct metal–carbon bond, chelation led to the formation of metallacycles through the $Y \rightarrow M$ donor–acceptor bond, which provides additional stabilization of the $M-C$ bond [17, 18, 40]. It has been also shown that the binding of C,Y-chelating ligand to a metal through two bonds is a versatile method to control the properties of metal centres by a well-defined ligand system.

Additional exploration in the field of such well-defined ligand systems resulted in the synthesis of terdentate monoanionic ligands as the most promising ones in the control of the metal centre properties. The first organometallic complexes containing these ligands were reported in the late 1970s [41–43]. These so-called ‘pincer’ ligands have the general formula $[2,6-(YCH_2)_2C_6H_3]^-$ (Y,C,Y) and comprise a potentially Y,C,Y terdentate coordinating, monoanionic array, where Y is a neutral two-electron donor such as NR_2 , PR_2 , AsR_2 , OR or SR, while C represents the anionic aryl carbon atom, of the 2,6-disubstituted phenyl ring (Fig. 16.1B), that can be substituted by R^1 group, most frequently in the 4-position [44–46]. The pincer ligands have a lot of modification sites that can affect the properties of metal centres, and their complexation with pincer ligands usually occurs with the formation of two five-membered metallacycles to afford complexes $[MX_n(Y,C,Y)L_m]$.

Most probably the first main group metal complex containing pincer-type ligand has been mentioned in the early work on organotin compounds containing N,C,N-ligand $(C_6H_4(CH_2NMe_2)_2-2,6)$, where N,C,N-chelate ligand was used in an attempt to make chiral, water-soluble triorganotin compounds [42, 43]. After that the N,C,N-ligand emerged in the chemistry of both main group metals [47–73] and transition metals (TM) (for example [74–83]). However, while the chemistry of TM has been explored by other pincer ligands (P,C,P; S,C,S, etc.) (see for example [84–93]), there was no mention of them being used in main group metal chemistry and the studies dealing with hypercoordinated organotin(IV) compounds containing an aryldiphosphonic ester $(C_6H_3[P(O)(OR)_2]_2-1,3-t-Bu-5)$, as the O,C,O-chelating ligand were mentioned in the late 1990s [94] and has been used for the preparation of hypercoordinated organosilicon

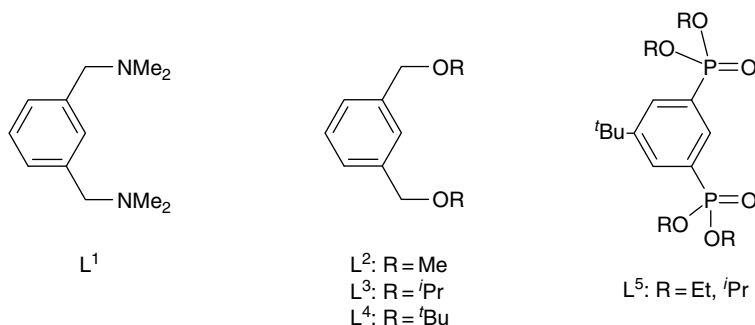


Fig. 16.2. Y,C,Y-chelating ligands discussed in this chapter.

[95–99], tin(II) [100] and lead [101, 102] compounds. Similarly, another O,C,O-chelating ligand ($\text{C}_6\text{H}_4(\text{CH}_2\text{OR})_2$ -2,6) has been applied for the preparation of hypercoordinated organotin [103, 104], aluminium [105, 106] and bismuth [107] compounds until quite recently.

The purpose of this chapter is to review the investigation dealing with the synthesis, structure and reactivity of selected hypervalent main group metal compounds (organotin(IV), aluminium(III), antimony(III) and bismuth(III)) containing Y,C,Y-chelating ligands L^{1-5} (Fig. 16.2). The structure and properties of these compounds still remain a challenge. Many novel and unusual structures were elucidated by X-ray diffraction technique.

16.2 ORGANOTIN COMPOUNDS CONTAINING Y,C,Y-CHELATING LIGANDS

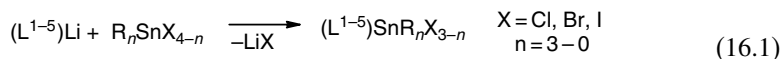
As mentioned above, organotin compounds containing N,C,N-chelating ligand (L^1) were most probably the first prepared main group metal complexes bearing pincer-type ligand and they are investigated so far. Besides these, several papers dealing with organotin compounds containing both classical O,C,O-pincer ligands L^{2-4} and nonclassical one L^5 have been reported recently that enable us to compare the influence of pincer ligands L^{1-5} on the same tin fragment. Because the strength of $\text{Y} \rightarrow \text{Sn}$ donor–acceptor bond depends on the Lewis acidity (LA) of the central Sn atom, the organotin compounds containing ligands L^{1-5} are arranged in the order of increasing LA of tin fragment.

16.2.1 Preparation of Organotin Compounds Containing Y,C,Y-Chelating Ligands L^{1-5}

Several methods are used for the preparation of organotin compounds and the selected ones seem to be the most common and useful for organotin L^{1-5} pincer complexes preparation.

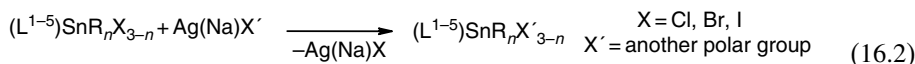
16.2.1.1 Reactions of Li salts of Y,C,Y-chelating ligands with organotin halides

Reactions of Li compounds of Y,C,Y-chelating ligands with organotin halides (Eqn 16.1) are used for the preparation of both organotin halides and tetraorganotin compounds substituted by ligands L^{1-5} . The structures of starting lithium salts LiL^1 and LiL^5 have been characterized by X-ray diffraction and both have dimeric structures consisting of two Li atoms and two monoanionic-chelating aryl ligands, similar to other dual side arm-coordinated lithium salts [51, 108–113].



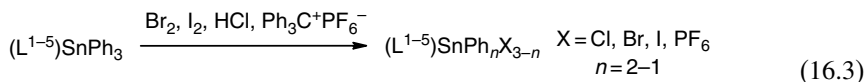
16.2.1.2 Halide abstraction

The halide abstraction (Eqn (16.2)) has been widely used for the preparation of organotin L^{1-5} pincer complexes containing different polar groups and sodium or silver salts of polar groups were applied for this purpose [104, 114–116].



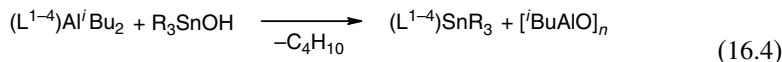
16.2.1.3 Phenyl abstraction

Similarly, the phenyl abstraction is used for the introduction of polar group to the organotin L^{1-5} pincer complexes. Tetraorganotin compounds are starting compounds in that case (Eqn (16.3)) [94, 104, 114, 117, 118].



16.2.1.4 Transmetallation reaction

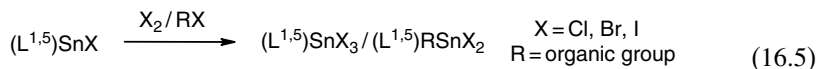
A new method for the preparation of tetraorganotin compounds containing L^{1-4} ligands has been reported recently (Eqn (16.4)). The preparation is based on the selective aryl transfer of pincer ligands L^{1-4} from intramolecularly coordinated aluminium compounds to the organotin compounds (vide infra) [119].



16.2.1.5 Oxidative addition

Oxidative addition (Eqn (16.5)) is very useful method for the preparation of various organotin(IV) compound containing L^{1-5} starting from organotin(II) precursors and has

been applied for the preparation of triorgano, diorgano and monoorganotin compounds containing L^1 and L^5 ligands [68, 100, 117, 120–122].

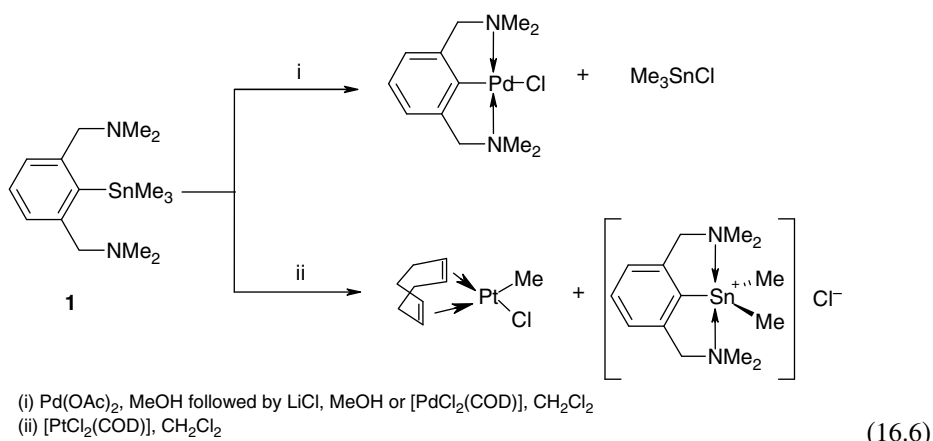


16.2.2 Structure, Dynamic Behaviour and Reactivity of Organotin Compounds Containing Y,C,Y-Chelating Ligands L^{1-5}

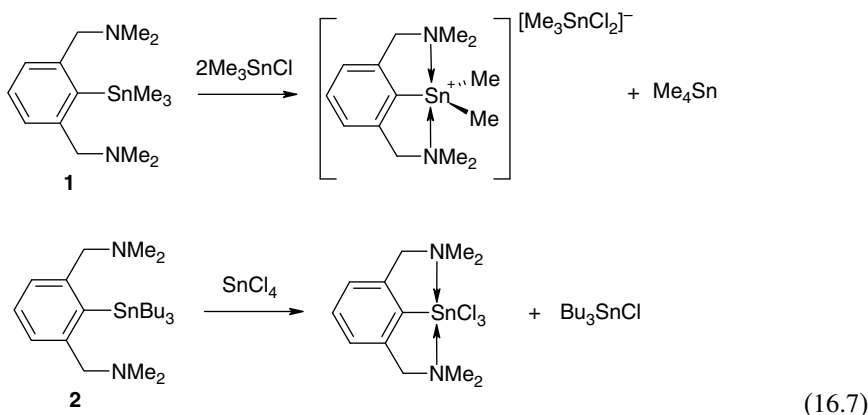
16.2.2.1 Tetraorganotin compounds

Several tetraorganotin compounds of general formula $(L^{1-5})SnR_3$ (R = organic group) have been prepared so far, most of them by method 16.2.1.1. The molecular structures that have been determined by a single-crystal X-ray diffraction study revealed bicapped tetrahedral arrangement of the central atom for all L^{1-5} ligands and the value of $Sn-Y$ bond lengths (the range of 2.908(1)–3.063(4) Å) demonstrates the presence of weak $Sn-Y$ interactions [94, 103, 119, 123]. These facts clearly indicate similar structures of $(L^{1-5})SnR_3$ (R = Me, Bu, Ph) without any substantial effect of the pincer ligands as well. The same structures have been detected in solution of the compounds.

Despite their tedious structural behaviour, tetraorganotin compounds of type $(L^{1-5})SnR_3$ have been studied for their reactivity because compared to tetracoordinate tetraorganotin compounds, these are more reactive. While the reaction of L^1SnMe_3 (**1**) with $Pd(OAc)_2$ or $PdCl_2(COD)$ resulted in the products of aryl transfer (Eqn (16.6)), the reaction of **1** with $PtCl_2(COD)$ led to the product of alkyl transfer (Eqn (16.6)) [123–126]. What else, this single methylation of $PtCl_2(COD)$ by **1** requires less forcing conditions than in the case of Me_4Sn [127–129].

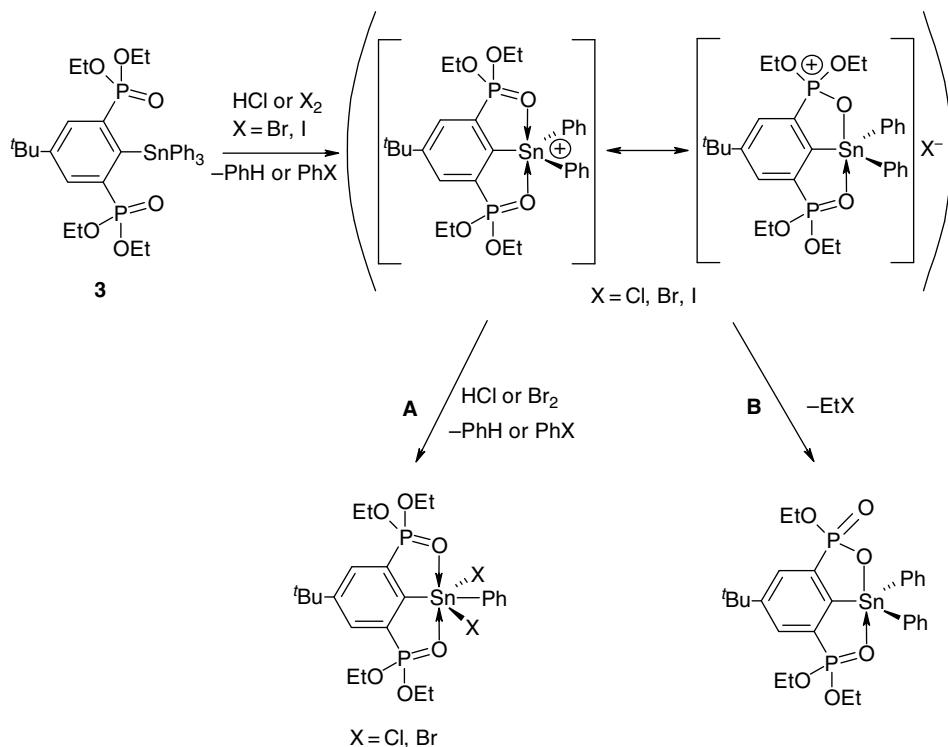


Similarly, while the reaction of **1** with Me_3SnCl includes the methyl transfer, the reaction of L^1SnBu_3 (**2**) with $SnCl_4$ involves aryl transfer of L^1 pincer ligand (Eqn (16.7)) [123, 130].



In addition to the mentioned reactivity, tetraorganotin compounds ($\text{L}^{1-5}\text{SnR}_3$) have been widely used for the preparation of other organotin pincer ligands-containing compounds (see Section 16.2.1.3).

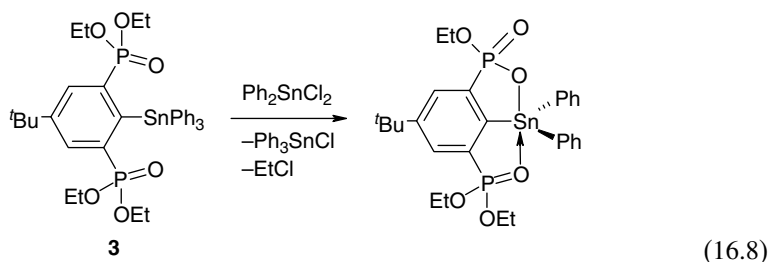
One of the most remarkable results has been observed for the L^5SnPh_3 (**3**) [117]. The reaction of **3** with 2 equiv. of HCl and Br_2 resulted in, besides the expected diorganotin compounds (Scheme 16.1, path A) as the major products, 2,3,1-benzoxaphosphastannole



Scheme 16.1 Proposed mechanism of intramolecular donor-assisted cyclization.

as a byproduct (path B). Attempt to prepare corresponding diorganotin diiodide by the reaction of **3** with 2 equiv. of I_2 were unsuccessful and the reaction of **3** with one molar equivalent of I_2 led to 2,3,1-benzoxaphosphastannole (Scheme 16.1, path B). Proposed mechanism of this intramolecular donor-assisted cyclization of **3** is given in Scheme 16.1.

Additional studies have shown the intramolecular cyclization to proceed in other reactions of **3** as well (Eqn 16.8) [117].



16.2.2.2 Triorganotin compounds

The substitution of one organic group by a polar one results in the increase of LA of tin atom, which has caused the different behaviours of individual L^{1-5} ligands in the triorganotin compounds. These triorganotin compounds of general formula $L^{1-5}R_2SnX$ (R = organic group, X = polar group) may be separated to four basic groups in agreement with both the presence or absence of $Sn-X$ covalent bond and the nature of pincer ligand.

16.2.2.2.1 Ionic triorganotin compounds containing N,C,N-chelating ligand L^1 . As mentioned above, first fully characterized organotin compound containing pincer-type ligand has been characterized in the late 1970s and this triorganotin compound containing L^1 ligand of formula $[L^1MePhSn]^+Br^-$ is ionic in nature [43]. After that time, there were several reports dealing with the ionic triorganotin compounds of general formula $[L^1R_2Sn]^+X^-$ (Fig. 16.3) [116, 123, 130–135]. In general, these ionic triorganotin compounds are soluble in water and some of them have been tested in vitro against potentially pathogenic fungi [116, 136].

The structures of several compounds have been determined by X-ray diffraction technique [43, 116, 123, 130–135]. These compounds contain an organotin cation, while the polar group X is outside of the primary tin coordination sphere. The central tin atom is coordinated by a carbon atom and two nitrogen atoms of the L^1 ligand in a tridentate fashion and by two carbon atoms of organic groups R . The resulting geometry is pseudo-*trans*-trigonal bipyramidal formed by three carbon atoms in the equatorial plane and two *trans*-nitrogen atoms. The equivalent $Sn-N$ bond distances (range of $Sn-N = 2.440(1)–2.4273(13) \text{ \AA}$) indicate strong $Sn-N$ interactions in the cations.

The ionic nature of these compounds is also retained in the solution as indicated by ^1H and ^{119}Sn NMR spectroscopy. While observed values of $\delta(^{119}Sn)$ indicate the existence of [3+2]-coordinated organotin cations [104, 137, 138] with the polar groups outside of the primary tin coordination sphere in these compounds, the ^1H NMR spectroscopy at various temperatures showed no decoalescence of signals of the CH_2 and CH_3 groups indicating the symmetrical arrangement of the tin coordination sphere.

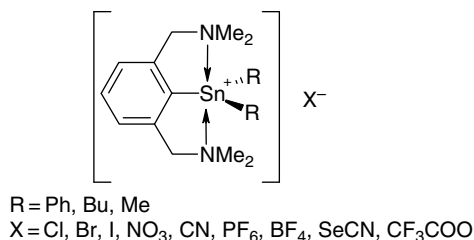


Fig. 16.3. Prepared ionic triorganotin compounds $[\text{L}^1\text{R}_2\text{Sn}]^+\text{X}^-$.

16.2.2.2.2 Molecular triorganotin compounds containing N,C,N -chelating ligand L^1 . While the ionic triorganotin compounds containing L^1 ligand are known for a long time, the triorganotin derivatives of L^1 ligand of general formula $\text{L}^1\text{R}_2\text{SnX}$ containing covalent $\text{Sn}-\text{X}$ bond have been prepared recently (Fig. 16.4) [114, 130, 139].

There are only two structures that have been determined by X-ray diffraction technique to date [114, 139]. The values of the $\text{Sn}-\text{N}$ bond lengths (range of 2.5957(18)–3.0372(14) Å) indicate that the presence of the covalently bonded polar group results in a decrease of the $\text{Sn}-\text{N}$ bond strength in these compounds compared to the ionic ones. The shape of the coordination polyhedron is *trans*-TBP formed by three C atoms in the equatorial plane, one nitrogen and polar group in axial position. The values of the $\text{N}-\text{Sn}-\text{N}$ bond angles (range of 110.13(5)–116.37(6)°) demonstrate the *cis* position of both nitrogen donor atoms of L^1 -ligand. This contrasts with the *trans* coordination of both nitrogen atoms in the ionic compounds (range of $\text{N}-\text{Sn}-\text{N} = 151.4(2)$ – $152.18(7)^\circ$).

A nonionic character of these compounds is retained in solutions of noncoordinating solvents at ambient temperature. The observed values of $\delta(^{119}\text{Sn})$ are typical for five-coordinated triorganotin compounds containing covalent bond $\text{Sn}-\text{X}$ [140–143]. Because of the coordination of one nitrogen donor atom of the L^1 ligand, the second one being noncoordinated, the dissociation–association of both donor nitrogen atoms has been observed in solutions of noncoordinating solvents of these compounds as the expected dynamic process (Scheme 16.2A) [114, 130–133, 139, 144].

However, the second dynamic process was surprisingly observed by both ^1H and ^{119}Sn NMR spectroscopy [114, 139]. The decrease in the temperature resulted in the observation of new signals in the ^{119}Sn NMR spectra of molecular compounds $\text{L}^1\text{R}_2\text{SnX}$

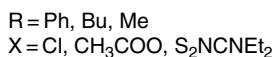
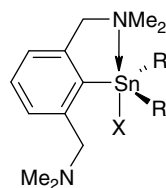
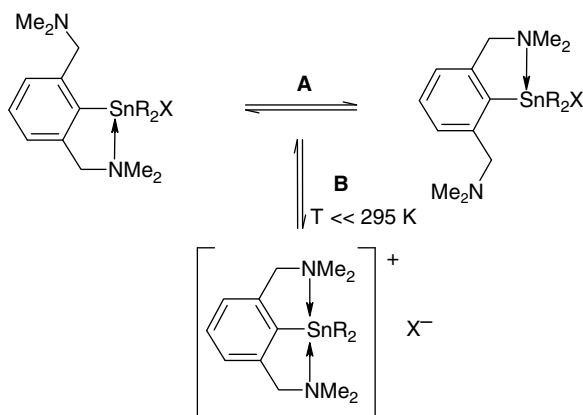


Fig. 16.4. Prepared molecular triorganotin compounds $\text{L}^1\text{R}_2\text{SnX}$.



Scheme 16.2 Dynamic processes found in the molecular triorganotin compounds.

(R = Ph, Bu, Me, X = CH₃COO and R = Bu, X = Cl, Br). While the intensity of the original signals decreased in the ¹¹⁹Sn NMR spectra, the intensity of the new signals increased during further decrease in temperature (Fig. 16.5). The values of the new signals are comparable to those found in the ionic triorganotin derivatives of L¹-ligand and so the ionization of these compounds was predicted to occur in CD₂Cl₂ solution at lower temperatures (Scheme 16.2B).

The influence of both organic group R and different solvents on the ionization process has been studied as well [114, 139].

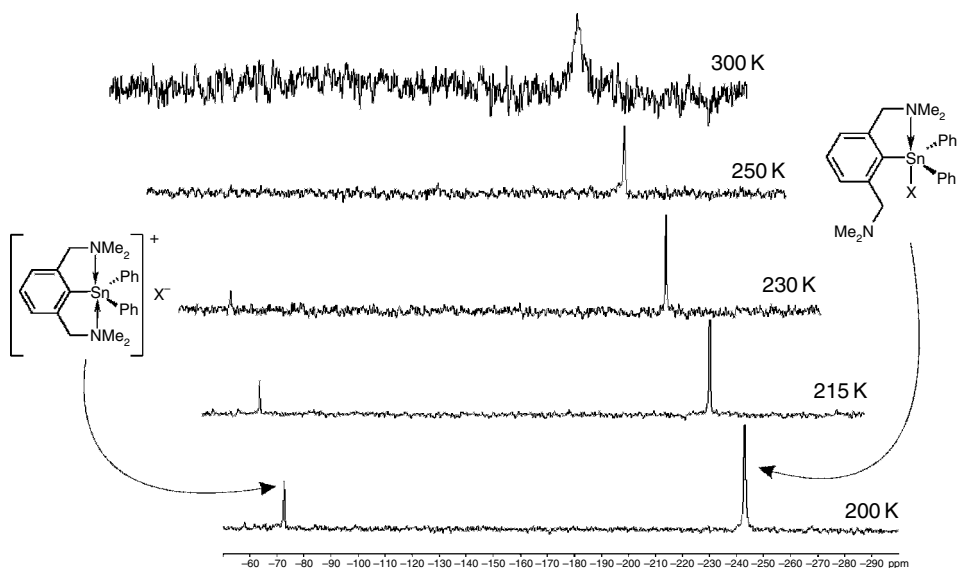


Fig. 16.5. The temperature dependence of ¹¹⁹Sn NMR spectra in CD₂Cl₂ solution.

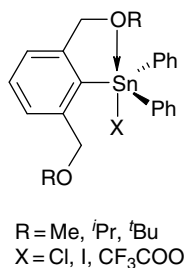


Fig. 16.6. Prepared molecular triorganotin compounds $\text{L}^{2-4}\text{R}_2\text{SnX}$.

16.2.2.2.3 Molecular triorganotin compounds containing O,C,O-chelating ligands L^{2-4} . In contrast to the L^1 analogues, nonionic triorganotin derivatives of L^{2-4} are air stable, fairly prepare-able compounds Fig. 16.6 [103].

The X-ray crystal structure determination showed similar results to L^1 analogues. The compounds have *trans*-trigonal bipyramidal geometry, the values of the Sn–O bond lengths (range of 2.567(2)–2.993(2) Å) indicate medium strong or weak interaction as the result of covalently bonded polar groups, the value of the O–Sn–O bond angle (range 109.60–117.24(4)°) demonstrates the *cis* position of both oxygen atoms of L^{2-4} ligand. The NMR studies proved their nonionic character in solutions of both noncoordinating and coordinating solvents [140–143]. The ${}^1\text{H}$ NMR spectroscopy at various temperatures showed the presence of the dissociation–association process (Scheme 16.2A) but excluded the presence of Sn–X bond dissociation (Scheme 16.2B). The comparison of energy barriers ($\Delta G^\ddagger$) of dissociation–association process shows that stronger Sn–O interaction is present in triorganotin derivatives of L^2 compared to L^4 so that the steric bulk of L^4 attenuates Sn–O interaction in these compounds [103].

16.2.2.2.4 Ionic triorganotin compounds containing O,C,O-chelating ligands L^{2-5} . The ionic triorganotin derivatives of L^{2-5} have been prepared very recently and possible formation of triorganotin cation of general formula $[\text{L}^{2-5}\text{Ph}_2\text{Sn}]^+$ requires the presence of low nucleophilic anions X^- (Fig. 16.7) [104, 118, 145].

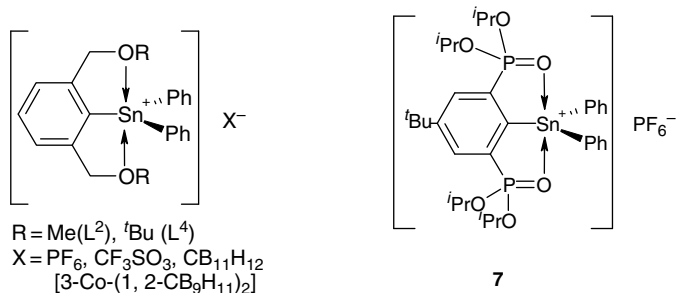
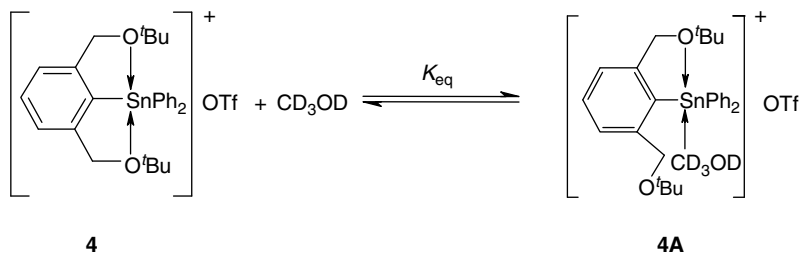


Fig. 16.7. Prepared ionic triorganotin compounds $[\text{L}^{2-5}\text{Ph}_2\text{Sn}]^+\text{X}^-$.

The structures of these air-sensitive compounds are similar to their ionic L^1 analogues, i.e. *trans*-trigonal bipyramidal geometry of organotin cation with two strong Sn–O interactions (range of Sn–O = 2.241(3)–2.394(3) Å). Their ionic nature is also retained in the solution as indicated by ^1H and ^{119}Sn NMR spectroscopies (vide supra) [104, 118, 145].

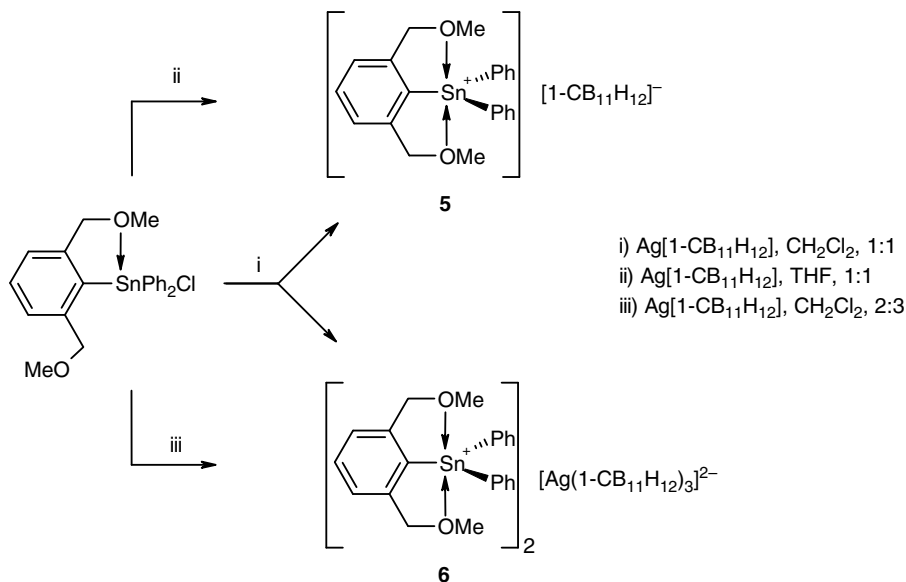
^1H NMR spectrum of CD_3OD solution of $[\text{L}^4\text{Ph}_2\text{Sn}]^+\text{OTf}^-$ (**4**) revealed the equilibrium between noncoordinated and its coordinated form **4A** (Scheme 16.3) and demonstrated weaker Sn–O interaction in **4** compared to L^2 analogue, $[\text{L}^2\text{Ph}_2\text{Sn}]^+\text{OTf}^-$, where both oxygen remained coordinated to Sn atom not forming such an adduct [104].



Scheme 16.3 Equilibrium between non-coordinated **4** and coordinated **4A** form of organotin cation $[\text{L}^4\text{Ph}_2\text{Sn}]^+\text{OTf}^-$.

During the preparation of triorganotin complex $[\text{L}^2\text{Ph}_2\text{Sn}]^+ [\text{1-CB}_{11}\text{H}_{12}]^-$ (**5**), compound $2[\text{L}^2\text{Ph}_2\text{Sn}]^+ [\text{Ag}(\text{1-CB}_{11}\text{H}_{12})_3]^{2-}$ (**6**) has been isolated as well (Fig. 16.8) [145].

Further study showed that the products strongly depend on reaction conditions (Scheme 16.4) [145].



Scheme 16.4 The preparation of organotin cations **5** and **6**.

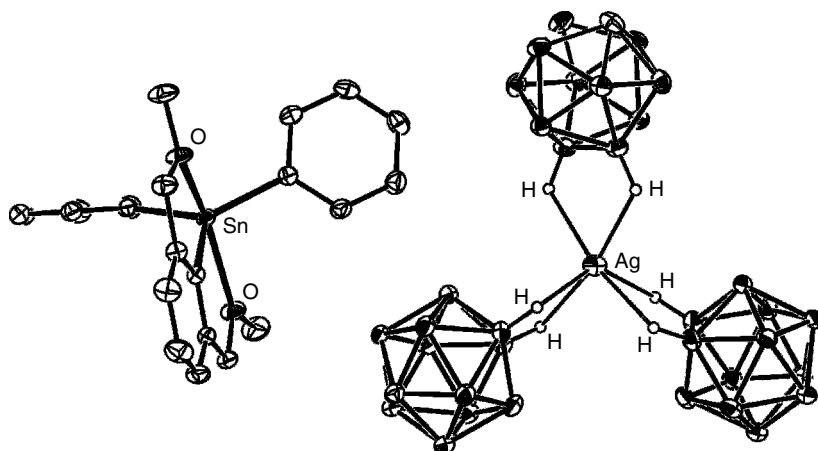
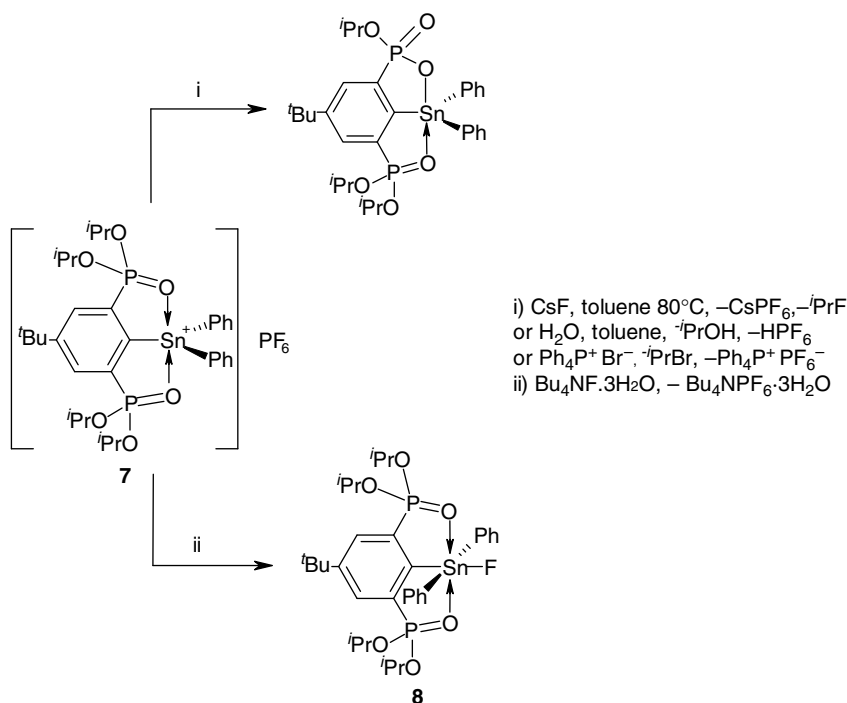


Fig. 16.8. The molecular structure of triorganotin compound **6**; hydrogen atoms and one molecule of $[L^2Ph_2Sn]^+$ have been omitted for clarity.

The reactivity of $[L^5Ph_2Sn]^+PF_6^-$ (**7**) has been investigated as well. It has been shown that compound **7** reacts similarly with CsF, H_2O and $[Ph_4P]^+Br^-$ to yield the same product, benzoxaphosphastannole $[1(P),3(Sn)-SnPh_2OP(O)(O^iPr)-6^iBu-4-P(O)(O^iPr)_2]C_6H_2$, but the reaction of the same cation **7** with $Bu_4NF \cdot 3H_2O$ resulted in the hexacoordinated triorganotinfluoride $\{[4^iBu-2,6-P(O)(O^iPr)_2]_2C_6H_2\}SnPh_2F$ (**8**) (Scheme 16.5) [118].



Scheme 16.5 The reactivity of triorganotin cation $[L^5Ph_2Sn]^+PF_6^-$ (**7**).

16.2.2.3 Diorganotin compounds

Substitution of another organic group R by polar X results in diorganotin compounds of general formula $L^{1-5}RSnX_2$. In such compounds, central tin atom increases its LA, thereby the strength of intramolecular interaction. There are several diorganotin compounds containing L^{1-5} ligands that have been prepared by different methods. The structure, dynamic behaviour and reactivity of organotin L^{1-4} derivatives, i.e. 'classical' pincer-type ligands, are mutually similar, while diorganotin compounds containing L^5 ligand show rather different behaviour and are discussed separately.

16.2.2.3.1 Diorganotin compounds containing Y,C,Y-chelating ligands L^{1-4} . Most common examples of diorganotin L^{1-4} derivatives are diorganotin halides (Fig. 16.9) [70, 103, 131–133, 138, 139]. Despite the increase of LA of tin atom, they are air stable both in solid state and solution and no hydrolysis products have been observed.

X-ray diffraction analysis showed common factor of the structures of diorganotin derivatives of L^{1-4} ligands, shape of coordination polyhedron is deformed octahedron for all determined halides [70, 103, 131–133, 138, 139]. However, the values of Y–Sn–Y bonding angles revealed important differences. While values of N–Sn–N (range $151.1(4)$ – $153.7(3)^\circ$) demonstrate that both nitrogen atoms are mutually in *trans* positions, the values of O–Sn–O angles (range $116.95(4)$ – $118.83(6)^\circ$) show *cis* arrangement of both oxygen atoms in diorganotin halides containing L^{2-4} ligands. These structures are retained in solutions. The values of $\delta(^{119}\text{Sn})$ indicate hexacoordinated tin atom [141] and ^1H NMR spectroscopy at various temperatures proved both *trans* (one sharp signal for benzylic CH_2 groups of L^1 ligand in the whole measured range 170–300 K) and *cis* (the presence of AX spin system for benzylic CH_2 groups of L^{2-4} ligands at low temperature) arrangements of donor atoms in deformed octahedrons of diorganotin L^{1-4} derivatives.

Despite the strong Sn–N intramolecular interaction in diorganotin halides $L^1\text{RSnX}_2$, the reaction of $L^1\text{BuSnCl}_2$ (**9**) with HCl led to zwitterionic diorganotin compound **10**, in which one NMe_2 group is coordinated to the tin atom, while the second one has accepted a proton leading to $[\text{CH}_2\text{NHMe}_2]^+$ (Eqn (16.9)) [130].

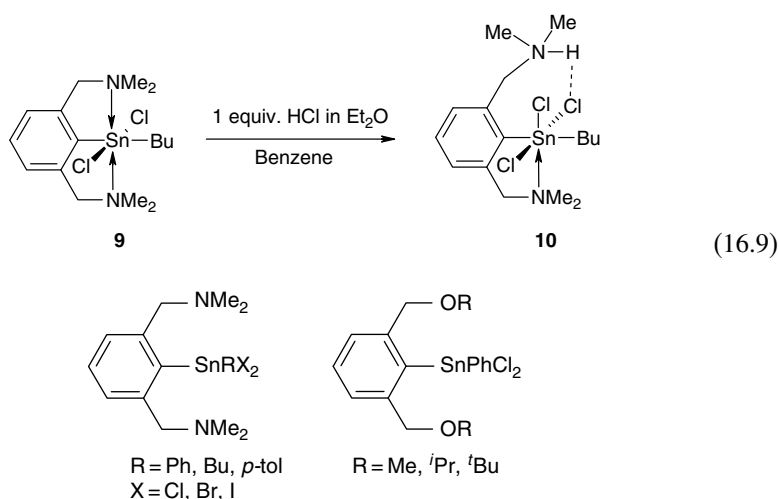


Fig. 16.9. Prepared diorganotin compounds $L^{1-4}\text{PhSnX}_2$.

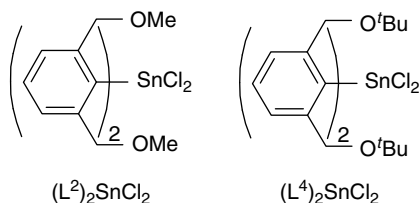
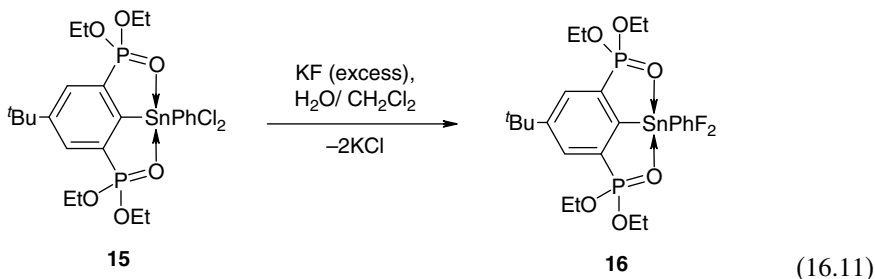


Fig. 16.11. Prepared double Y,C,Y-chelated diorganotin compounds $(L^{2,4})_2SnCl_2$.

However, substitution of chloride atom by low nucleophilic anions $X = CF_3SO_3$ or $CB_{11}H_{12}$ resulted in the preparation of ionic compounds $[(L^2)_2SnCl]^+[CF_3SO_3]^-$, $[(L^2)_2Sn(CF_3SO_3)]^+[CF_3SO_3]^-$ and $[(L^2)_2SnCl]^+[1-CB_{11}H_{12}]^-$ only [115].

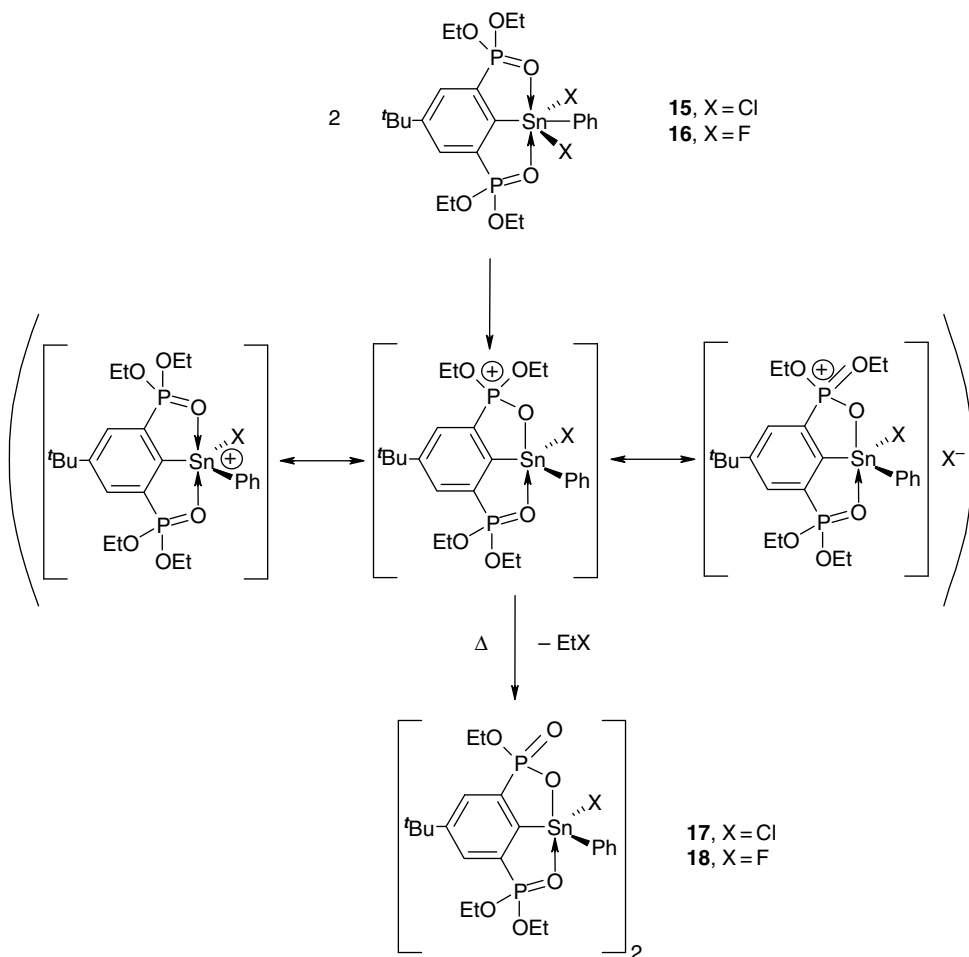
16.2.2.3.2 Diorganotin compounds containing O,C,O-chelating ligand L^5 . Diorganotin compounds of type L^5PhSnX_2 (Cl, Br) have been prepared by the reaction of tetraorganotin compound L^5SnPh_3 (**3**) with 2 equiv. of HCl or Br_2 (Scheme 16.1) [94]. The crystal structure showed distorted Oh configuration of the tin atom with both oxygen atoms mutually *trans* ($O-Sn-O = 161.2(1)^\circ$) and two strong Sn–O intramolecular interactions, with bonding lengths Sn–O = 2.203(5) and 2.278(5) Å. These Sn–O bonds are comparable to the corresponding values found for ionic triorganotin compounds $[L^{2-5}Ph_2Sn]^+$ [104, 118, 145].

The reaction of $L^5PhSnCl_2$ (**15**) with aqueous solution of KF led to diorganotin difluoride L^5PhSnF_2 (**16**) (Eqn (16.11)) that has been characterized by NMR spectroscopy and X-ray diffraction [147], and geometrical parameters (Sn–O bond lengths = 2.244(2) and 2.243(2) Å, $O-Sn-O = 159.8(1)^\circ$) indicate that the geometry of central tin atom is similar to the chloride analogue **15** [94]. However, molecule of **16** crystallizes with 0.5 mol of water so that two molecules are connected via unsymmetrical hydrogen bonds $F \cdots H-O-H \cdots F$.



Both compounds **15** and **16** are thermally unstable in solutions and decompose after 2 weeks at 110°C to dimeric both chlorine (**17**) and fluorine (**18**) substituted benzoxaphosphols (Fig. 16.12) [147].

The dissociation of Sn–X bond is assumed as the first step of this cyclization process, followed by nucleophilic attack of the halide anion at the methylene carbon of the ethoxy group. The last step is the transfer of ethyl halide (Scheme 16.6) [147]. This mechanism



Scheme 16.6 Proposed mechanism of cyclization reaction of **15** and **16**.

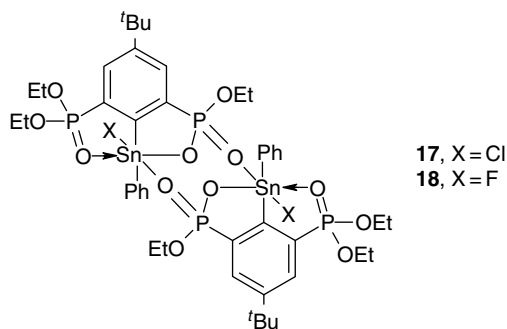
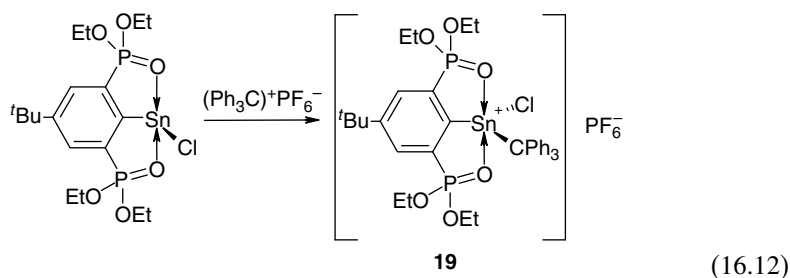


Fig. 16.12. The products of temperature decomposition of **15** and **16**.

also explains the reason, why the covalent triorganotin compounds of the type L^5Ph_2SnX could not be isolated while the ionic triorganotin compound $[L^5Ph_2Sn]^+PF_6^-$ (**7**) could be isolated (Scheme 16.6).

The ionic diorganotin compound $[L^5(Ph_3C)SnCl]^+PF_6^-$ (**19**) containing ligand L^5 has been prepared by oxidative addition of trityl cation $[Ph_3C]^+PF_6^-$ to the stannylenes L^5SnCl (Eqn (16.12)) [100].

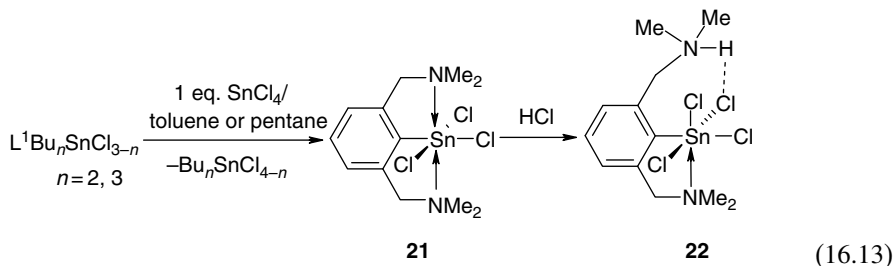


16.2.2.4 Monoorganotin compounds containing Y,C,Y-chelating ligands L^{1-5}

There are reports on the preparations of only several monoorganotin compounds containing L^{1-5} ligands. Since the monoorganotin compounds contain very LA tin centre they are reactive and moisture-sensitive species (Fig. 16.13) [103, 117, 130, 148].

As the result of this LA, monoorganotin L^{1-5} derivatives contain strong Sn–Y interactions, as has been proved by X-ray diffraction analyses of L^2SnCl_3 [103] and L^5SnCl_3 (**20**) [117], where two strong Sn–O donor–acceptor bonds have been found (the range of Sn–O = 2.221(3)–2.583(2) Å). Although both compounds adopt Oh geometry, a different arrangement of both donor oxygen atoms has been found in the compounds, being *cis* in L^2SnCl_3 and *trans* in **20** (compare values of O–Sn–O = 114.9(6) and 161.1(2)°). The similar structures are retained in solutions.

Compound L^1SnCl_3 (**21**) that has been prepared by aryl transfer reaction of $L^1Bu_nSnCl_{3-n}$ ($n = 2, 3$) with $SnCl_4$ is very reactive and immediately reacts with HCl to give compound $[L^1SnCl_3 \cdot (HCl)]$ (**22**) as the only one isolable product (Eqn (16.13)) [130].



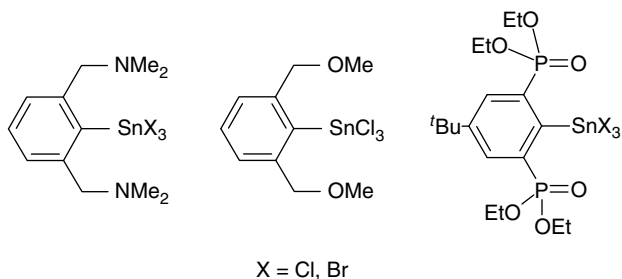
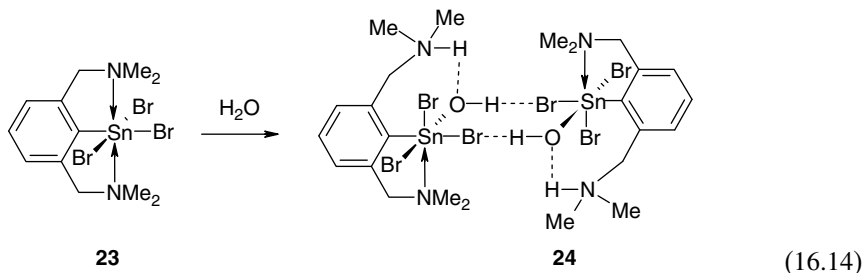
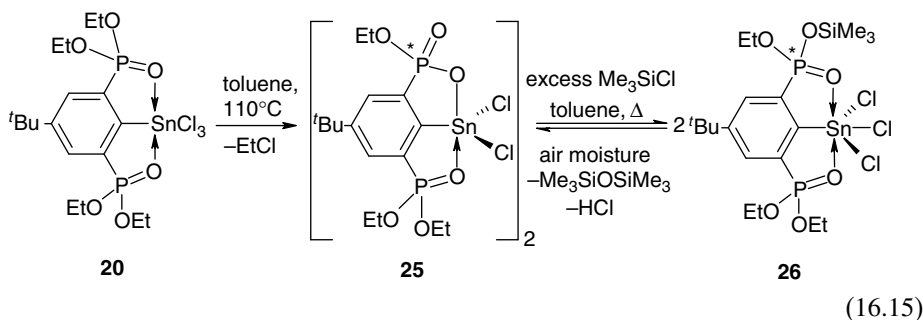


Fig. 16.13. Prepared monoorganotin compounds $L^{1-5}\text{SnX}_3$.

Similarly, compound $L^1\text{SnBr}_3$ (**23**) is unstable and hydrolyse on air to give zwitterionic compound $[\text{L}^1\text{SnBr}_3 \cdot (\text{H}_2\text{O})]_2$ (**24**) with intra- and intermolecular hydrogen bonds (Eqn (16.14)) [148].



While the reactivity of L^2SnCl_3 has not been reported yet, the reactivity of **20** has been studied in more detail. It has been shown that **20** is thermally unstable in solution, similarly to the diorganotin derivatives **15** and **16**, and decompose in refluxing toluene after several hours to provide dichloro-substituted 2,3,1-benzoxaphosphastannol **25** (Eqn (16.15)) that dimerizes (similarly to compounds **17** and **18**) leading to the mixture of diastereoisomers as the result of intermolecular $\text{Sn}-\text{O}$ interaction [117]. What else, the compound **25** reacts with Me_3SiCl leading to organotin trichloride **26** that is moisture sensitive and it hydrolyses to give starting compound **25** by loss of HCl and $(\text{Me}_3\text{Si})_2\text{O}$ (Eqn (16.15)) [117].



It has been also shown that reaction of **20** with 3 equiv. of $\text{Bu}_4\text{NF}\cdot\text{H}_2\text{O}$ gave the mixture of products L^5SnClF_2 and L^5SnF_3 . However, attempts to isolate L^5SnF_3 failed and compound $[\text{L}^5\text{Sn}(\text{OH})\text{F}_2]_2$ has been isolated instead [147].

16.3 ORGANOALUMINIUM, ANTIMONY AND BISMUTH COMPOUNDS CONTAINING Y,C,Y-CHELATING LIGANDS L^{1-4}

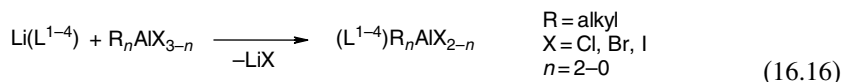
The investigation of organoaluminium, antimony and bismuth compounds bearing pincer ligands provides unique opportunity to study synthesis, reactivity and structural characteristics of both electron-deficient compounds (aluminium) and metals containing lone pair of electrons (heavy 'pnictogens' derivatives in formal oxidation state 3+).

The application of intramolecularly coordinated organometallic compounds based on aluminium as co-catalysts for Ziegler–Natta process [149], antimony and bismuth for C–C coupling reactions [150, 151] are legitimate reasons for scientific research in the field of these main group metals.

The investigation of compounds bearing central metal atom from group 13 or 15 was restricted to ligands L^{1-4} and no compounds bearing ligand L^5 emerged.

16.3.1 Synthesis of Organoaluminium(III) Derivatives

The reactions of organolithium precursors with corresponding aluminium halides in hexane or toluene are usually used for the synthesis of organoaluminium derivatives containing L^{1-4} ligands (Eqn (16.16)) [105, 152, 153].



However, the special procedure was necessary for the preparation of $(\text{L}^{2-4})\text{AlCl}_2$, where LA of AlCl_3 was hardened by triethylamine [106]. Aluminium hydrides were prepared by metathesis using complex $\text{AlClH}_2\cdot\text{NMe}_3$ as starting material as well [154].

16.3.2 Structure and Dynamic Behaviour of Organoaluminium(III) Compounds

All organoaluminium compounds of type $(\text{L}^{1-4})\text{AlX}_2$, $(\text{L}^1)\text{RAIX}$ and $(\text{L}^{1-4})\text{R}_2\text{Al}$ (X = polar group, R = organic group) that has been characterized by X-ray diffraction techniques in the solid state to date, display similar structures. The central aluminium atom is located in the centre of distorted TBP, both donor atoms Y are in axial positions and almost planar equatorial plane is formed by *ipso*-carbon atom of L^{1-4} ligands and two remaining substituents X or R . The values of $\text{Al}-\text{Y}$ ($\text{Y} = \text{N, O}$) bonding length indicate the presence of two strong almost identical $\text{Al}-\text{Y}$ interactions and compound $\text{L}^4\text{Al}(i\text{-Bu})_2$ is the only exception, where the $\text{Al}-\text{O}$ bond lengths differ significantly 2.1237 versus 2.6137 Å [105].

The structure and dynamic behaviour in solution of organoaluminium compounds has been elucidated by ^1H , ^{13}C and ^{27}Al NMR spectroscopies, where the later is informative for coordination number of central aluminium atoms [155].

High LA of central aluminium atom led to strong coordination of both ligands' donor atoms to the central aluminium in monoorganoaluminium compounds $\text{L}^{1-4}\text{AlX}_2$ resulting in coordination number five of central atom (as corroborated by ^{27}Al NMR spectroscopy) and trigonal bipyramidal array with donor atoms in axial positions (Fig. 16.14A) [152–154].

On the other hand, the concentration equilibrium was established in solution of compounds $\text{L}^{2-4}\text{AlCl}_2$ [106]. The structure of $\text{L}^{2-4}\text{AlCl}_2$ is analogous to Fig. 16.14A in diluted solution, but in more concentrated samples the monomer/dimer equilibrium occurred (Fig. 16.14B).

Organoaluminium derivatives of type $\text{L}^{1-4}\text{AlR}_2$ or $\text{L}^1\text{Al}(\text{X})\text{R}$ display coordination number four for aluminium atom in solution. This situation cannot be explained by rigid coordination of only one donor atom to aluminium, rather fast dynamic process of dissociation/association of both donor groups is more appropriate explanation (Fig. 16.15) [152].

16.3.3 Reactivity of Organoaluminium(III) Derivatives

Monoorganoaluminium compounds L^1AlX_2 were utilized for the preparation of organoaluminium dihydrides L^1AlH_2 using LiAlH_4 or NaH [152, 154] and their reaction with elemental selenium afforded the dimeric arylaluminium selenide $(\text{L}^1\text{AlSe})_2$ and teluride $(\text{L}^1\text{AlTe})_2$ [25]. The reaction with lithium 2,6-dimethyl-*N*-(trimethylsilyl)anilide yielded sterically crowded organoaluminium amide $\text{L}^1\text{Al}(\text{Br})[\text{N}(\text{SiMe}_3)\text{-2,6-(Me)}_2\text{C}_6\text{H}_3]$ [153].

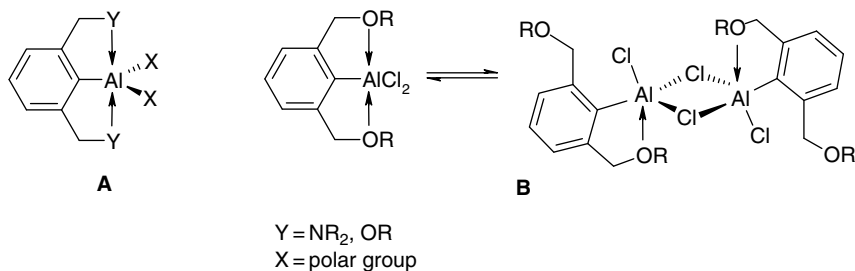


Fig. 16.14. Structure of $\text{L}^{1-4}\text{AlX}_2$ in solution.

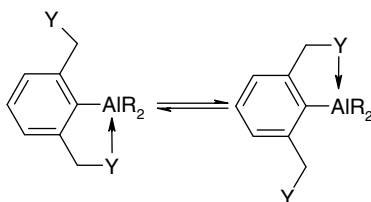
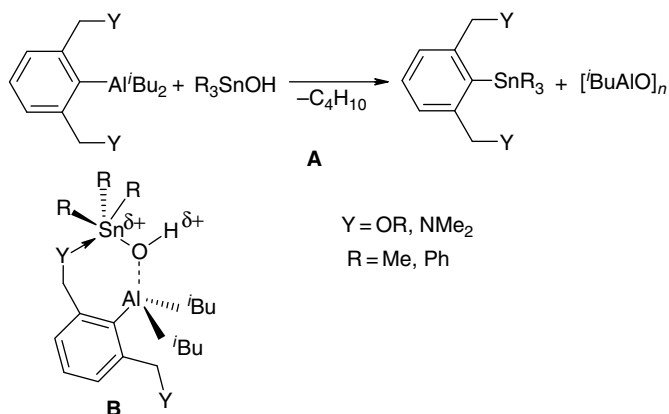


Fig. 16.15. Dynamic behaviour of $\text{L}^{1-4}\text{AlR}_2$ and $\text{L}^1\text{Al}(\text{X})\text{R}$ in solution.

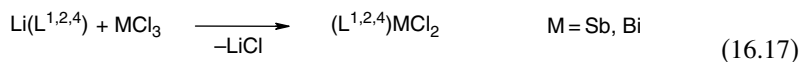
While compound L^4AlMe_2 was used for synthesis of organoaluminium alkoxides and iodides [105], compounds $(L^{1,2,4})Al(i-Bu)_2$ have found application as transmetallating agents in the reaction with organotin reagents (Scheme 16.7A) [119]. These reactions proceed through selective migration of $L^{1,2,4}$ ligands from aluminium to tin atom and represent rare examples of migration of Y,C,Y ligands between two main group metals. The presence of pendant donor arms of pincer ligands was suggested to play an important role in this reaction and in the transition state (Scheme 16.7B). Similar reaction of organoaluminium precursors with organosilicon compounds did not lead to products of transmetallation rather expected alkane elimination and Al—O—Si bond formation was observed [119].



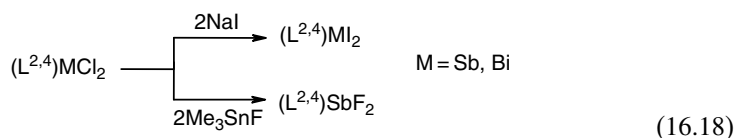
Scheme 16.7 Transmetallation using aluminium pincer-type compounds.

16.3.4 Synthesis and Reactivity of Organoantimony(III) and Organobismuth(III) Derivatives

Similar to organoaluminium compounds, the derivatives of heavier pnictogens (Sb, Bi) known to date contain only $L^{1,2,4}$ ligands. Organoantimony and organobismuth dichlorides have been prepared by the reaction of organolithium compounds with metal chlorides (Eqn (16.17)) [72, 107].



While the reactivity of $(L^{2,4})MCl_2$ ($M = Sb$, or Bi) has been restricted to the preparation of corresponding iodides and fluorides to date (Eqn (16.18)) [107], the reactivity of L^1MCl_2 has been investigated in more detail.



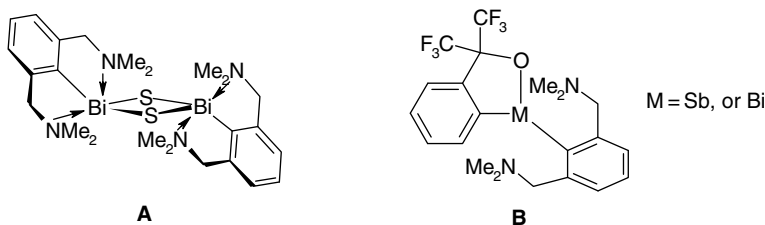
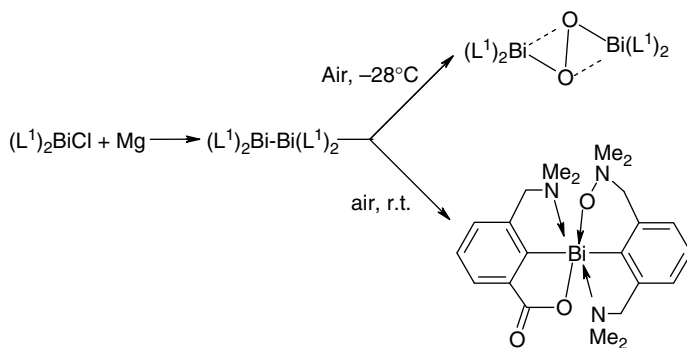


Fig. 16.16. Prepared organoantimony(III) and bismuth(III) derivatives of L^1 ligand.

Reaction of L^1BiCl_2 with Na_2S resulted in novel heterocyclic compound $(L^1BiS)_2$ and X-ray diffraction showed the presence of Bi_2S_2 ring with aryl groups in *trans* positions (Fig. 16.16A) [156]. These compounds have been used for preparation of antimony and bismuth derivatives containing Martin ligand as well (Fig. 16.16B) [73].

The possibility to isolate organobismuth species containing bismuth–bismuth bonds supported by ligand L^1 has emerged very recently [157]. Any resulting Bi–Bi bond was used for preparation of peroxo-compound stabilized by L^1 (Scheme 16.8). The X-ray diffraction studies proved the presence of oxygen molecule coordinated between two bismuth centres. The bonding length O–O 1.515 Å indicate single bond between both oxygens. Another reaction of starting dibismuthane yielded product with partially oxidized L^1 ligands' arms (Scheme 16.8) [157, 158].



Scheme 16.8 Preparation of organobismuth peroxo complexes containing L^1 .

16.3.5 Structure of Organoantimony(III) and Organobismuth(III) Derivatives

16.3.5.1 Solution

Organoantimony and organobismuth chlorides of type L^1MCl_2 ($M = Sb$ or Bi) have symmetrical rigid structure in solution, with both nitrogen atoms coordinated in *trans* fashion. The overall geometry is best described as a square pyramid, with *ipso*-carbon of the L^1 ligand in the apical position and *trans*-placed chlorine atoms [72].

The examples of organoantimony and bismuth compounds containing L^2 and L^4 are more plentiful, covering $L^{2,4}MX_2$ ($M = Sb$, or Bi , $X = F$, Cl , or I). The organoantimony fluorides and chlorides differ in their structure from those found for L^1SbCl_2 .

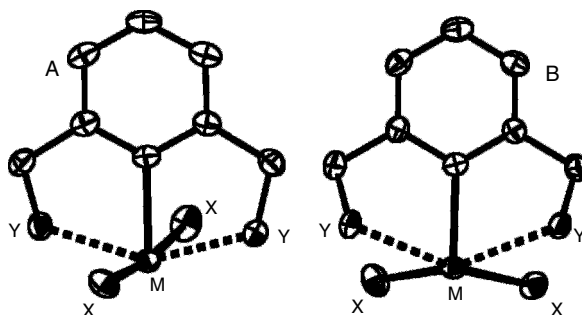


Fig. 16.17. Different types of coordination polyhedron in organoantimony and organobismuth pincer complexes.

The structure of O,C,O chelates is fluxional at ambient temperature, but lowering of temperature in solution results in *cis* coordination of both oxygen donor atoms and the polyhedron is best described as bicapped trigonal pyramid (distorted *cis*-tetragonal pyramid is alternative description) [107].

In contrast to these compounds all organobismuth derivatives and organoantimony diiodides bearing ligands L^2 and L^4 display analogous structure to this found for L^1SbCl_2 , i.e. square-pyramid on central atom with *trans*-coordinated oxygen atoms [107].

16.3.5.2 Solid state

The square-pyramidal shape of the antimony coordination polyhedron in L^1SbCl_2 is retained in the solid state in comparison with solution [72]. Both nitrogen atoms and chlorine atoms are coordinated in basal plane in *trans* positions (Fig. 16.17A) (angles $N-Sb-N = 147.3^\circ$ and $Cl-Sb-Cl = 174^\circ$).

Analogous structure to L^1SbCl_2 was detected also for some of the O,C,O-chelated antimony and bismuth compounds $L^{2,4}SbI_2$ and $L^{2,4}BiX_2$ ($X = Cl, I$) (Fig. 16.17A) (range of angles $O-M-O = 142.3-148.3^\circ$ and $X-M-X = 172.4-176.2^\circ$, where $M = Sb$ or Bi and $X = Cl$ or I) [107].

On the other hand in organoantimony compounds $L^{2,4}SbX_2$ ($X = F, Cl$) the ligand arms are coordinated in *cis* fashion (angle $O-Sb-O = 116.7^\circ$) and the overall geometry is bicapped trigonal pyramid similar to solution *vide supra* (distorted *cis*-tetragonal pyramid is alternative description) Fig. 17B. Interesting structural feature of organobismuth O,C,O compounds is dimerization of L^2BiCl_2 via nearly symmetrical $Cl-Bi-Cl$ bridges [107].

ACKNOWLEDGEMENT

The authors wish to thank all their colleagues who have been involved in the chemistry of hypervalent organotin, aluminium, antimony and bismuth Y,C,Y-chelate complexes and whose names have been cited in the text.

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Stability of supported pincer complex-based catalysts in Heck catalysis

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17.1 INTRODUCTION

In today's world, the need to limit the use of nonrenewable resources and the importance of recycling has been recognized. One important contribution of chemists toward the general goal of limiting their use is to find catalysts that can be reused and recycled, thereby limiting the need for expensive metal precursors and metal waste. Strategies to recycle catalysts are multifold and range from the employment of soluble polymers as catalyst supports to the use of membrane-encapsulated catalysts. Clearly, not all catalysts can be supported in a straightforward fashion. Suitable catalyst candidates amenable toward the supporting process and the overall materials should be robust under all catalytic reaction conditions. Furthermore, the supported catalyst has to have comparable reaction rates to its small molecule counterpart and must allow for easy recycling and reuse. One class of catalysts that has been identified as successful candidates in supported catalysis is palladacycles. Among known palladacycles, palladated pincer complexes have been suggested to catalyze a variety of carbon–carbon bond-forming reactions and to be the most stable palladacycles and therefore the prime candidates to be supported.

Pincer molecules are defined as monoanionic tridentate ligands with an anionic core flanked by two neutral two-electron donors on each side of the metal. They are usually named after the three atoms that coordinate to the metal center, for example, SCS, PCP, NCN, CNC, and CCC (Fig. 17.1). These ligands can be complexed with a vast library of metals ranging from common metals such as palladium [1] to exotic ones such as uranium [2]. The resulting complexes can be employed in a variety of catalytic transformations. Palladated pincer complexes have been widely used not only for coupling chemistries such as the Heck, Suzuki, or Sonogashira couplings [1, 3–9] but also for Michael additions [10, 11], boronations of allyl alcohols [12], and asymmetric allylations [13].

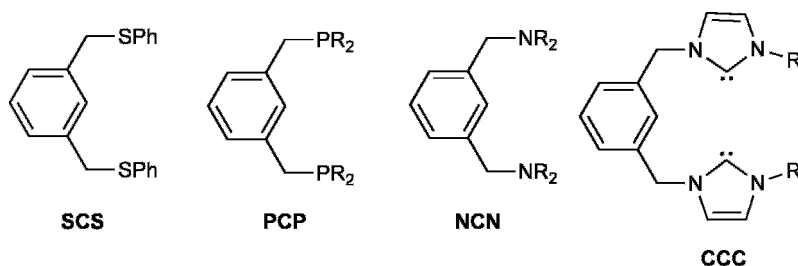


Fig. 17.1. Different types of pincer ligands reported in the literature.

Iridium pincer complexes have been studied extensively as dehydrogenation catalysts [14, 15]. Rhodium and ruthenium pincer complexes have also been reported, but only a few studies have been carried out to investigate their catalytic activities [16, 17]. The second area of intense research activity using metallated pincer complexes is the employment of these pincer complexes as tunable metal coordination recognition units in self-assembly [7, 18–20].

With the wide variety of transformations that metallated pincer complexes are able to catalyze and the notion that metallated pincer complexes are stable under a wide range of conditions and at high temperatures, several groups started to investigate the activity of such complexes on supports (some examples of supported pincer complexes are shown in Fig. 17.2) [1, 6]. The goal of these studies was to synthesize highly stable, recoverable, and recyclable catalysts. To accomplish this goal, metallated pincer complexes, in particular palladated complexes, were immobilized on different supports ranging from polymers to clays. Bergbreiter and coworkers immobilized Pd-SCS pincer complexes onto poly(ethylene glycol) and investigated their catalytic activities in the Heck coupling of iodobenzene with methyl acrylate and styrene [3, 4, 21–23]. In general, the authors claimed that the activities of these supported complexes are comparable to their small molecule analogs. Furthermore, they were able to show that the supported complexes can be recycled by simple precipitation of the polymer and reused [3, 4, 21–23]. It was noted that some decomposition was occurring for some supported Pd-SCS pincer complexes. However, Bergbreiter et al. seemed to circumvent this problem by modifying the tether of the ligand to the polymer [3, 4, 21–23]. A similar system was reported by Pollino and Weck using poly(norbornene) to support Pd-SCS-type pincer complexes [7].

Using a modified approach toward supported pincer complexes, Dijkstra et al. synthesized different generations of metallo dendrimers with Pd-NCN pincer complexes as peripheral groups [24, 25]. The authors studied the activity of their second-generation dendrimers containing 12 palladated pincer complexes in a continuous nanofiltration membrane in the Michael addition of methyl vinyl ketone with α -cyanoacetate. Only slight decreases in conversion after five cycles were observed [24, 25]. Silica-immobilized second-generation PAMAM dendrimers with Pd-PCP pincer complexes at the periphery were also employed as supported catalysts. Chanthateyanonth et al. investigated the cyclocarbonylation of 2-allylphenol using these supported complexes [26]. Conversions ranging from 87 to 99% after three catalytic cycles were obtained [26]. A similar support was used by Giménez et al. to support dinuclear Pd-SCS pincer complexes [27]. In this work, the authors studied the activity of their catalysts

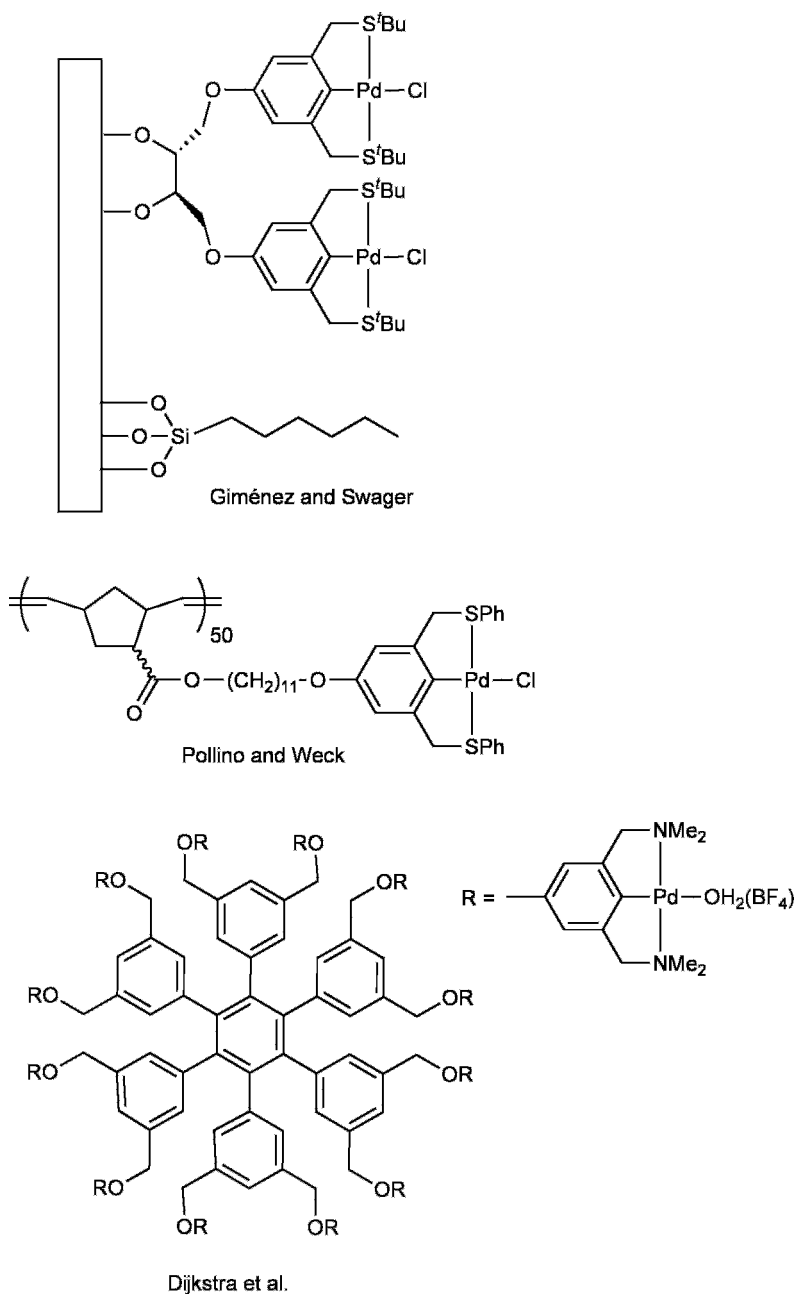


Fig. 17.2. Selected examples of supported palladated pincer complexes in the literature.

in the aldol reaction of methylisocyanoacetate. They found similar activities for their system in comparison to the small molecule analogs [27]. A less common support was used by Poyatos et al., who supported Pd-CNC pincer complexes onto montmorillonite K-10 clay and investigated the activity of these complexes in the Heck coupling reaction

of bromobenzene with styrene [28]. They were able to recycle their catalyst up to 10 times without noticing any significant decrease in conversions [28, 29]. The most recent example in this field came from Atlava et al. who supported Pd-CCC pincer complexes onto Merrifield resins as potential catalysts for the Heck reaction between aryl halides and various alkenes [30]. Quantitative conversions for several supported complexes within 24 h were obtained. However, extensive kinetic studies showed that for all catalytic transformations studied, induction periods were observed [30].

While these examples demonstrate that metallated pincer complexes can be supported on a wide variety of supports, they do not establish if the complexes themselves are catalytically active species. Only a few authors carried out leaching or kinetic experiments to investigate the stability of their supported complexes [30, 31]. According to available kinetic data, an induction period was always observed. This suggests that a change in the metal pincer complexes has to occur to generate the catalytically active species. One possible explanation for this phenomenon is the leaching of the metal from the ligand [31].

The nature of the active species and the catalytic mechanism of the palladacycles used to be highly controversial. In contrast to the more common Pd(0) Heck catalysts, Pd pincer complexes and their closely related half pincers contain a Pd(II) center in the resting state. The known mechanism of the Heck catalysis involves the reduction of a palladium (II) to palladium (0), which is the active species and follows a classic oxidative addition, olefin insertion, and reductive elimination mechanism. This basic mechanism is not easily applicable to palladacycles since they can not be reduced to Pd(0) without removing the ligand from the metal center. One possible pathway could be the formation of an anionic catalyst species. However, no experimental evidence has been reported to date that would verify such a hypothesis. Therefore, for half pincers and palladacycles, a highly controversial Pd(II)–Pd(IV) mechanism was introduced by Milstein et al. and Jensen et al. (Fig. 17.3) [1, 32]. The bond between the carbon of the benzene ring and the Pd was believed to be very strong and virtually unbreakable during the catalytic conditions spurring the idea of the Pd(II)–Pd(IV) mechanism. However, to date, no clear experimental evidence of any Pd(IV) species during Pd pincer complex catalysis has been reported.

17.2 STUDIES INTO THE STABILITY OF Pd-PINCER COMPLEXES

Recently, motivated by the conflicting reports in the literature and the importance of supported catalysts, we and others started to investigate the stability and activity of supported Pd pincer complexes in catalysis [33, 34]. In a collaborative effort, we investigated a variety of supports and palladated pincer complexes (Fig. 17.4). Two basic classes of supports were investigated: supports that are soluble under reaction conditions and insoluble supports. Poly(norbornene) was chosen as the soluble support. The ring-opening metathesis polymerization (ROMP) of functionalized norbornenes is a demonstrated living polymerization that permits good control of catalyst loading and the incorporation of other functionalized co-monomers [18, 35–41]. Furthermore, these polymers have the advantage that one can control their solubility by simple modifications of the pendant side chains. Finally, because of the polymers solubility under reaction conditions, the catalysis can be carried out under homogeneous conditions

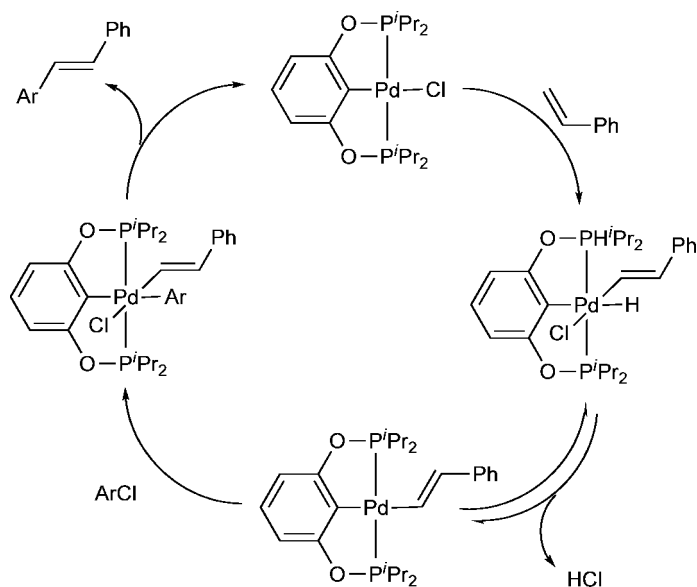


Fig. 17.3. Proposed Pd(II)–Pd(IV) catalytic cycle by Jensen et al.

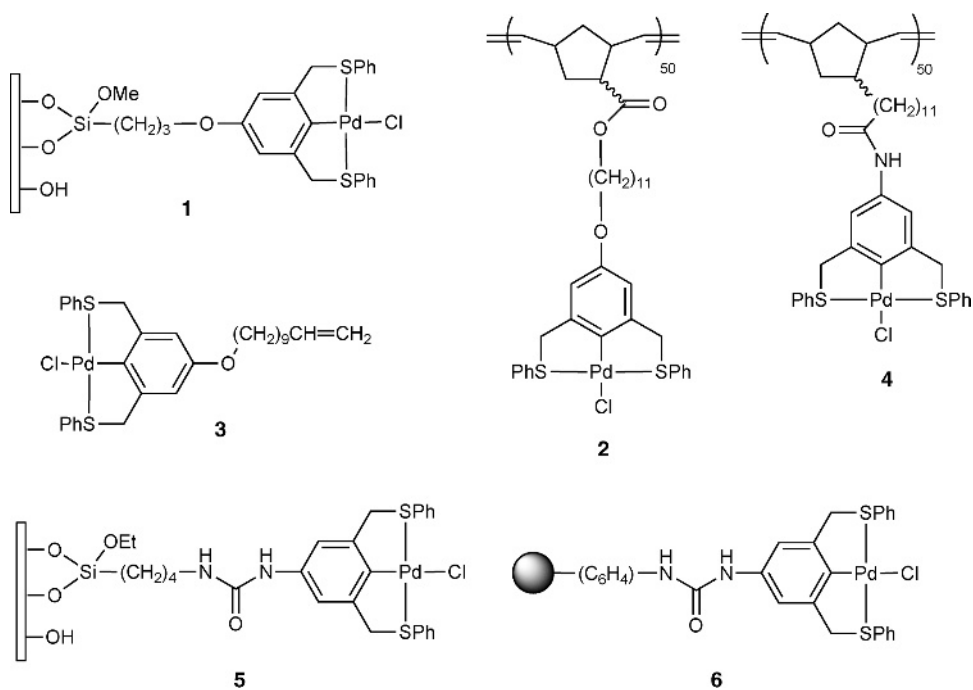


Fig. 17.4. Supported Pd-SCS Pincer complexes studied by Jones, Weck, and coworkers.

while having the ability to recover the polymer-supported catalysts through simple precipitation methods [7, 18, 19, 33, 34, 42]. Additionally, the use of nanoporous silica SBA-15 as a solid support was also investigated. The advantage of heterogeneous silica-supported catalysts is their easy recovery [33, 34, 42].

17.2.1 Stability of Pd-SCS Pincer Complexes

17.2.1.1 Initial observations

The first metallated pincer complexes that we investigated for their stability under reaction conditions were Pd(II)-SCS pincer complexes supported on SBA-15 (100 Å pore size) and poly(norbornene). Initially, Pd-SCS complexes that were tethered to the supports via an ether linkage were studied (Pd-SCS-O-pincer complexes). The stability of all catalysts was investigated through a series of kinetic studies as well as poisoning experiments. In the leaching studies, induction periods of up to 20 min were observed. Furthermore, when the silica-supported catalysts were recycled, a decline in conversions after each run was detected. To strengthen our findings further, a three-phase test was used. This test, consists of anchoring one of the reagents onto a solid support while using a solid-supported catalyst [43]. Catalysis cannot occur unless the catalyst or the substrate leaches from the support to interact with the anchored substrate. We immobilized iodobenzene onto nanoporous silica, with **1** as the catalyst. Under the Heck reaction conditions, conversions of the anchored iodobenzene were observed. These results suggested that some Pd was leaching out of the Pd-pincer complexes. To verify this hypothesis, a filtration test was carried out by removing the silica-supported catalyst from the reaction mixture, followed by the addition of new reagents to the filtrate. Conversions of the newly added reagents were observed, confirming our hypothesis that leached Pd species were at least partially responsible for the catalysis.

17.2.1.2 Poisoning studies

To further investigate whether catalysis occurred on the supported Pd-pincer complexes, a variety of poisoning studies were carried out. These poisons were selected to bind selectively to unprotected Pd(0) and Pd(II) sources, *i.e.* Pd species that are not protected by a well defined ligand. These poisons were designed to remove any unprotected Pd(0) species from the reaction solution, thereby shutting down any catalytic activity arising from them. If the supported Pd(II) pincer complexes were responsible for the catalysis, conversions should be observed even in the presence of the poisons. The first poison that was employed was poly(vinyl pyridine) (PVPy). PVPy is heterogeneous under reaction conditions and is known to coordinate to Pd(0) [33, 34, 44, 45]. The second poison was mercury which is able to form an amalgamate with Pd(0), thereby removing the palladium from the reaction solution. Both methods terminate any catalytic activity of unprotected Pd(0) species by sequestration and removal from the reaction medium [44, 46, 47]. Again, it is important to note that both of these poisons have no effect on molecular organometallic catalysts.

The PVPy tests were carried out with all supported Pd(II)-SCS-O-pincer complexes by adding the poison at the beginning of the reaction and in a different reaction after 40% conversion was achieved. If PVPy was added at the beginning of the Heck reaction containing either **1** or **2**, no conversions were observed. When adding the PVPy poison after 40% conversions, catalysis was completely quenched (Fig. 17.5). Addition of Hg(0)

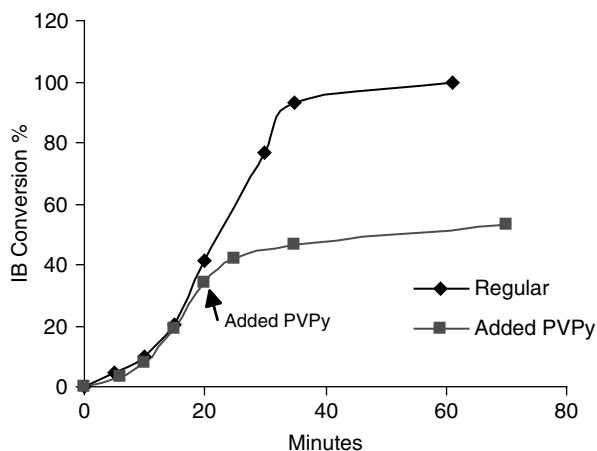


Fig. 17.5. Kinetic study of the Heck catalysis between iodobenzene and *n*-butyl acrylate using **1** as catalyst and PVPy as poison.

to a reaction mixture containing either **1** or **2** resulted in negligible conversions in all cases. The combination of these kinetic, three-phase test and poisoning studies proved that Pd(II)-SCS pincer complexes tethered with an ether linkage onto supports such as mesoporous silica or onto poly(norbornene) are not catalytically active in the Heck reaction but act solely as a Pd reservoir. This conclusion was not fully unexpected because Bergbreiter et al. evocated a decrease in activity when they examined Pd(II)-SCS pincer complexes tethered to poly(ethylene glycol) (**7**) via an ether linkage in the Heck reaction (Fig. 17.6). In the same contribution, supported Pd(II)-SCS pincer complexes attached to the poly(ethylene glycol) support via an amide linkage (**8**) instead of the

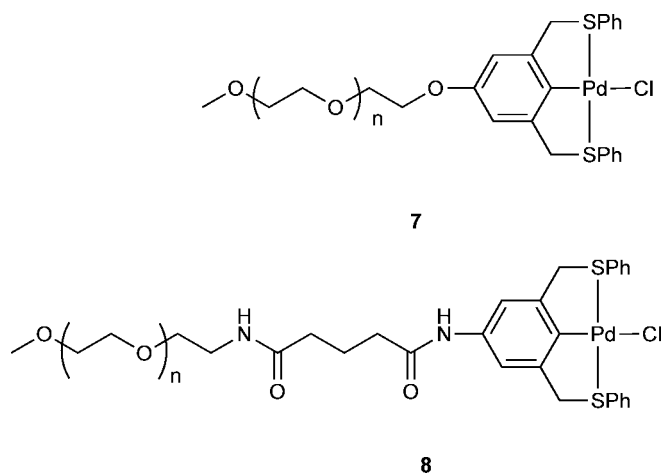


Fig. 17.6. Supported pincer complexes employed by Bergbreiter et al.

ether linkage were suggested as fully stable catalysts because no decrease in activity was observed when carrying out recycling experiments [33, 34].

To investigate these potentially stable complexes, our research team synthesized supported Pd(II)-SCS pincer complexes that were tethered to their respective support with an amide linkage (Pd(II)-SCS-N-pincer complexes). Three supports were investigated: poly(norbornene) (**4**), nanoporous silica (**5**), and Merrifield resin (**6**). The activities of these Pd-pincer complexes in the Heck catalysis of iodobenzene and n-butyl acrylate were faster, with no induction times observed for the majority cases. However, when **5** was recycled and reused, an induction time of up to 10 min was observed after the first run and the activity decreased for each additional run. Kinetic and poisoning tests as outlined for the Pd(II)-SCS-O-pincer complexes were run to test the true active species of these catalysts. The use of PVPy or Hg(0) yielded negligible reactivities with any of the amide-linked supported catalysts. When the solid-supported Pd(II) pincer complexes were removed by filtration, the filtrate was still able to convert freshly added reagents. Clearly, the amide-tethered Pd(II)-SCS complexes are not stable under Heck reaction conditions. At the same time, Bergbreiter et al. conducted mechanistic studies on their supported Pd(II)-SCS pincer complexes **7** and **8** [48]. They conducted kinetic experiments where significant induction times were observed, which were dependent on the amount of reactants, water, and other additives present. Additionally, a series of 'competition' reactions by adding phosphines to the Heck reaction were carried out. They observed a reduction in activity when phosphines were added, suggesting that Pd(0) was trapped by the phosphine ligands. They also carried out a split test by removing their polymer from the reaction mixture and adding fresh reagents to the filtrate. They noticed significant conversions from the 'catalyst-free' solution. The overall conclusions from their studies were similar to ours, confirming that supported SCS-Pd pincer complexes are not the actual catalysts during the Heck reaction [33, 34, 48]. Clearly, these conclusions suggest that no supported Pd(II)-SCS pincer complex is stable under the Heck reaction conditions, and the actual catalyst is a leached Pd(0) species following the well-known Pd(0)–Pd(II) catalytic cycle. Because all other palladium-catalyzed coupling reactions follow a closely related catalytic cycle to the Heck reaction, Pd(II)-SCS pincer complexes might also be unstable under other palladium coupling reaction conditions.

17.2.2 Stability of Pd-PCP Pincer Complexes

17.2.2.1 Small molecule leaching studies

In 2004, Eberhard studied the catalytic activity and stability of Pd(II)-PCP pincer complexes **9–12** [49]. The PCP-type pincer complexes have been suggested in the literature as being more stable than their SCS-type counterparts [22]. To investigate the activity of these complexes, Eberhard carried out detailed kinetic studies of the Heck coupling of styrene with benzyl chloride and noticed an induction period in all cases. He also used PPh₃ and CS₂ as poisons to coordinate to Pd(0) and reported that the reaction was fully inhibited after addition of these poisons. Furthermore, the ³¹P NMR spectra of the complexes before and after catalysis differed, suggesting that the Pd-PCP pincer complexes decomposed during the reaction. He concluded that his Pd(II)-PCP pincer complexes were only precursors for the true catalytic species (Fig. 17.7). However, he pointed out that he can not rule completely small amounts of catalysis by non-decomposed catalyst through the controversial Pd(II)–Pd(IV) mechanism.

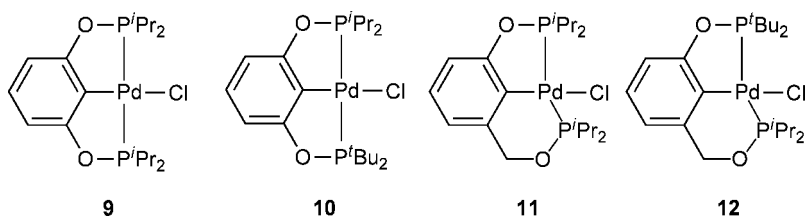


Fig. 17.7. PCP-pincer complexes studied by Eberhard.

17.2.2.2 Supported Pd-PCP pincer complex poisoning studies

To further investigate the stability of Pd(II)-PCP pincer complexes we synthesized a series of supported Pd(II)-PCP pincer complexes (Fig. 17.8). As mentioned above, these complexes were commonly reported to be significantly more stable than SCS pincer complexes due to the stronger bonds between the two phosphorous atoms and the palladium center [22]. We synthesized three different supported complexes: Pd(II)-PCP pincer complexes supported on mesoporous silica via an ether linkage (**13**), poly(norbornene) ether-tethered Pd(II)-PCP pincer complexes (**14**), the amide analogs (**15**) and a small molecule version (**16**) which was used as the standard to compare the activities of the supported catalysts. To investigate the stability of the different supported complexes, we used the same reaction conditions and poisoning methods outlined above coupled with kinetic and in situ NMR spectroscopy experiments. The activities of the Heck catalysis of iodobenzene with *n*-butyl acrylate using **13–15** as catalysts were similar to **10**, with quantitative conversions observed within 20 min. When PVPy or mercury was used as poisons during the Heck reaction, no conversions were observed for any supported Pd(II)-PCP pincer complexes. Again, these results suggest that the Pd(II)-PCP pincer complexes are not stable under the Heck conditions and act solely as a soluble palladium reservoir.

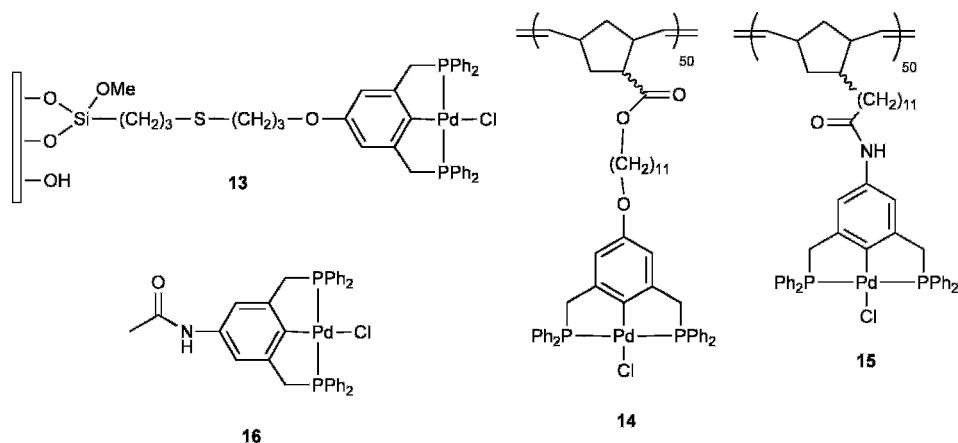


Fig. 17.8. Supported Pd(II)-PCP pincer complexes evaluated by Jones, Weck, and coworkers.

17.2.2.3 Supported Pd-PCP pincer complex NMR studies

One question that had not been addressed in our previous studies is the mechanism of decomposition of pincer complexes. To gather some insight into the mechanism, we employed *in-situ* ^{31}P NMR spectroscopy. For these studies we employed complex **16** using CD_2Cl_2 as the solvent. All *in situ* NMR experiments were run at 120°C . We first investigated complex **16** without the addition of any other chemicals. The ^{31}P NMR spectrum of **16** showed a single signal at 15.7 ppm. We then started to add the reactants for the Heck reaction in a stepwise fashion to the NMR tube and took a ^{31}P NMR spectrum after each step. The expectation from this experiment was to see either new ^{31}P NMR signals in the NMR spectrum when carrying out the Heck catalysis in case of complex decomposition or no new signals if the complex is stable under reaction conditions. When several equivalents of iodobenzene and/or *n*-butyl acrylate were added to **16**, no changes in the ^{31}P NMR spectra were observed. This suggests that the reactants alone do not play a key role in the decomposition pathway. However, when seven or more equivalents of triethylamine were added to **16**, the appearance of two new signals at 7.7 and -4.2 ppm were observed, suggesting decomposition of **16** (or at least the formation of a new palladium complex). Furthermore, palladium black was observed at the bottom of the NMR tube after the experiment confirming our hypothesis that palladium leached out of the complex. These NMR studies suggested that the base rather than the reactants play a key role in the decomposition of Pd(II)-PCP pincer complexes.

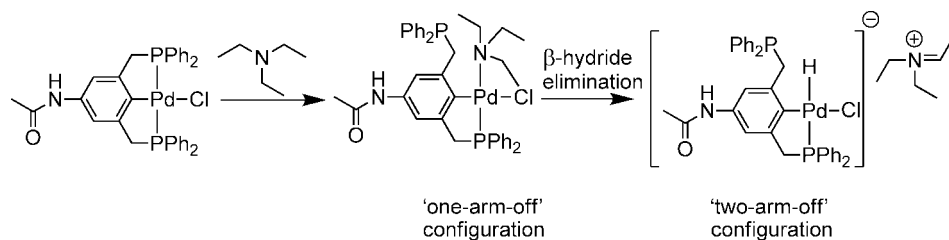
17.2.2.4 XAS studies

We collaborated with the R.J. Davies group in chemical engineering at the University of Virginia to probe the reactions of palladium pincer complexes *in situ*. The Davis group carried out *in situ* XAS spectroscopy experiments on Pd(II)-SCS pincer complexes (**1–6**) under Heck reaction conditions to investigate whether any Pd(IV) species could be detected during catalysis. As mentioned above, stable palladium pincer complexes were suggested to follow a Pd(II)/Pd(IV) catalytic cycle. Therefore, the detection of any Pd(IV) species during the catalysis would support the conclusion that at least some palladium pincer complexes are active catalysts. However, no Pd(IV) species were observed for any supported complexes under any reaction conditions. Instead, the formation of palladium iodide species was detected in solution. It has been reported in the literature that soluble palladium species are often stored as $[\text{Pd}_2\text{I}_6]^{2-}$ [50]. While these results did not fully exclude a Pd(II)–Pd(IV) catalytic cycle, the results were consistent with the poisoning studies that effectively ruled out catalysis by intact pincer species.

17.2.2.5 Computational studies into the decomposition pathway

Finally, we collaborated with the C.D. Sherrill group at GeorgiaTech to investigate potential decomposition pathways using computational methods. Due to the complexity of the calculations, only nonsupported Pd-SCS and Pd-PCP pincer complexes were modeled. Based on some reports by Hartwig and Louie, who have shown that half-pincer complexes in the presence of an amine base are able to undergo a β -hydrogen elimination resulting in the formation of a palladium hydride species [51], we proposed the first steps of a decomposition pathway of palladated pincer complexes in the presence of amine bases as outlined in Scheme 17.1.

Following the proposed decomposition pathway, optimized geometries of both PCP and SCS pincer complexes as well as relative energies were obtained using the BP86



Scheme 17.1 Proposed first steps of the decomposition pathway.

density functional method with a LAV3P/6-31G* basis set. The results from these calculations strengthened our hypothesis, as it was found that only 7.0 kcal/mol separated the Pd(II)-SCS pincer complex from the one arm-off configuration, with an amine base replacing the sulfur atom bonded to the palladium center (Scheme 17.1). Furthermore, the configuration with both arms off and two amines bonded to the palladium center was calculated to be even 0.6 kcal/mol lower than the one arm-off conformation. Similar calculations were run for the Pd-PCP pincer complex. While the removal of one arm (21.1 kcal/mol) and both arms (34.1 kcal/mol) required more energy than Pd(II)-SCS pincer complexes, it is not unreasonable to suggest that Pd(II)-PCP complexes follow this pathway under the high-temperature reaction conditions usually employed during the Heck catalysis. Furthermore, when both arms are uncoordinated, solvent or base molecules can coordinate to the free sites on the metal to stabilize it. These results track very well with literature reports that suggest that PCP pincer complexes are more stable than SCS pincer complexes, that is, the Pd–phosphorus bond is stronger than the Pd–sulfur bond, resulting in faster leaching of Pd(II)-SCS pincer complexes. To gather experimental proof for the computed decomposition pathway, a series of mass spectroscopy experiments were carried out. Hartwig and Louie established that the amine base exists as an iminium ion after hydride elimination. This iminium ion can be hydrolyzed to yield a secondary amine. We employed dicyclohexylamine as the base in the Heck catalysis of iodobenzene and *n*-butyl acrylate using **16** as catalyst. Mass spectroscopy characterization of the reaction mixture showed a molecular ion signal at 182.3 *m/z*, indicative of the presence of dicyclohexylamine giving strong support to our proposed decomposition pathway.

While these preliminary studies suggest a possible decomposition pathway, it is important to note that this is only applicable when using an amine base. The decomposition mechanism for inorganic bases has to be different because these bases do not have a β -hydrogen available for an eventual elimination.

17.3 CONCLUSIONS

Over the past 3 years, several studies have been published that question the stability of palladated pincer complexes under Heck catalysis conditions. Through a series of poisoning tests, kinetic and spectroscopic studies and computational experiments, these studies have proved that any supported as well as small molecule Pd-pincer complexes

decompose during Heck catalysis. Furthermore, no experimental proof could be obtained for the proposed Pd(II)/Pd(IV) catalytic cycle, which is a requirement for the Heck promoted by stable Pd(II) pincer complexes. While no detailed studies have been carried out to evaluate the stability of palladated pincer complexes in other palladium-catalyzed coupling reactions, the decomposition results might be applicable to other Pd-coupling chemistry because they follow similar catalytic cycles.

Unfortunately, despite the detailed kinetic and poisoning studies described in the literature over the past 24 months and in this chapter, the very recent literature still shows a plethora of articles using palladated pincer complexes as ‘catalysts’ for coupling chemistry where no studies to investigate the stability of the Pd pincer complexes have been carried out. One has to question and evaluate the literature reports carefully.

ACKNOWLEDGMENTS

We gratefully acknowledge the support and enthusiasm of former and current group members and colleagues. In particular, the fruitful collaboration with the Davis, and Sherrill groups is acknowledged. The research from our group described in this chapter is supported by the US DOE Office of Basic Energy Sciences through the Catalysis Science Contract No. DE-FG02-03ER15459. M.W. gratefully acknowledges a 3M Untenured Faculty Award, a DuPont Young Professor Award, an Alfred P. Sloan Fellowship, a Camille Dreyfus Teacher-Scholar Award, and the Blanchard Assistant Professorship.

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Dendrimers incorporating metallopincer functionalities: synthesis and applications

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18.1 INTRODUCTION

The utility and application of dendrimers to organic and medicinal chemistry, polymer science and catalysis is a burgeoning and active field of chemical and materials research. Initially introduced by the groups of Vögtle [1], Tomalia [2–5], Fréchet [6–9] and Newkome [10, 11], dendrimers are a narrowly defined subclass of hyperbranched polymers that are uniquely regular in composition and generally spherical or globular in shape [12, 13]. The term ‘dendrimer’ for these specially designed macromolecules was derived from the word *dendros*, Greek for tree [14]. As shown in Fig. 18.1, it is convenient to define regions and structural features, such as a central core, branch points and the periphery, based on a ‘tree-like’ or *dendritic* architecture. Dendrons, the constituent branches or wedges of dendrimers, contain a focal point in place of the central core.

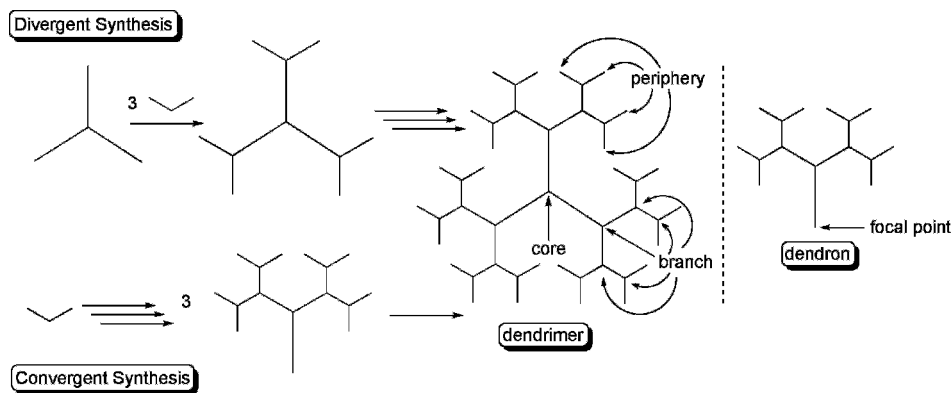


Fig. 18.1. Synthetic strategies for dendrimer construction and schematic structures of a dendrimer and dendron.

Due to their well-defined and regular structures, dendrimers are attractive platforms for materials investigations as the dendritic species often exhibit different properties than the more randomly distributed hyperbranched polymer analogs/isomers. Also, new medicinal research involving dendrimers as nanocapsules for drug delivery or as synthetic immunoreceptors is attracting attention [15, 16].

Two related and conceptual simple methodologies have been introduced for the synthetic design of dendrimers, see Fig. 18.1. First, a divergent synthesis originates from a core molecule and successively adds additional layers or dendrimer generations in a stepwise, 'inside-out' fashion. Conversely, convergent methods utilize preformed individual dendritic wedges and, in the final step, attach these dendrons to a central hub. With a divergent strategy, problems may arise due to incomplete reactions, especially at higher generations. To fully substitute the outer shell, multiple transformations need to be performed sequentially on the same molecule, and if not perfectly quantitative, a mixture of species results and separations can be potentially difficult. Convergent methods avoid this as the dendritic wedges are synthesized separately. However, as each of the dendrons is potentially very sterically bulky, the final coupling of multiple wedges to a single core may require forcing conditions. Regardless of these potential roadblocks, both of these two methods have found wide utility in the synthesis of a variety of dendrimers.

An important and growing subclass of dendrimers are the transition metal-containing metallo dendrimers [17–22], species incorporating organometallic or coordination compounds as either an integral part of the dendrimer framework or grafted onto the dendritic skeleton. The combination of metal complexes with dendrimers, as well as the construction of heteroatom-containing dendrimers [23], has proved to be a very fruitful area of study [17–22, 24]. The position of the metal complex in the dendritic structure can have important consequences to reactivity. Fig. 18.2 gives a schematic representation of the possible positions metals can occupy within a dendrimer. Core-functionalized metallo dendrimers have a metal complex encapsulated at the center of the dendrimer. Conversely, peripherally substituted systems incorporate multiple metal species on the outer dendritic surface. In branch-functionalized complexes, the metal coordination environment is acting either as a branch point or as a linker between the branches in each dendrimer generation. Dendrimers can also act as hosts for metal complexes or discrete metal (nano)particles [25, 26] and, via covalent or noncovalent interactions, graft these to the dendrimer skeleton in the voids or cavities between the dendrimer arms. All of these classifications of metal position can be transposed to dendritic wedges as well. Among their most important attributes in catalytic applications [27] is the ability of the dendritic framework to either locally isolate metal complexes within the dendrimer structure or concentrate the catalytically active metal centers on the surface, factors which can have a tremendous impact on catalyst lifetime, stability and/or reactivity. Also, they provide a soluble support which is amenable to separation techniques, such as nanofiltration [28], which potentially allows for catalyst recycling [29].

Metal complexes of the 'pincer' ligand have been employed in numerous applications in catalysis, materials chemistry, as chemosensors and in fundamental bonding and structure investigations [30–36]. Amongst the pincer ligand's most important attributes are the facile preparative routes which allows for a high degree of modularity in design. In metallopincer complexes, direct or remote tuning of both the steric and electronic environment about the metal and, often, metal complex stability are key characteristics.

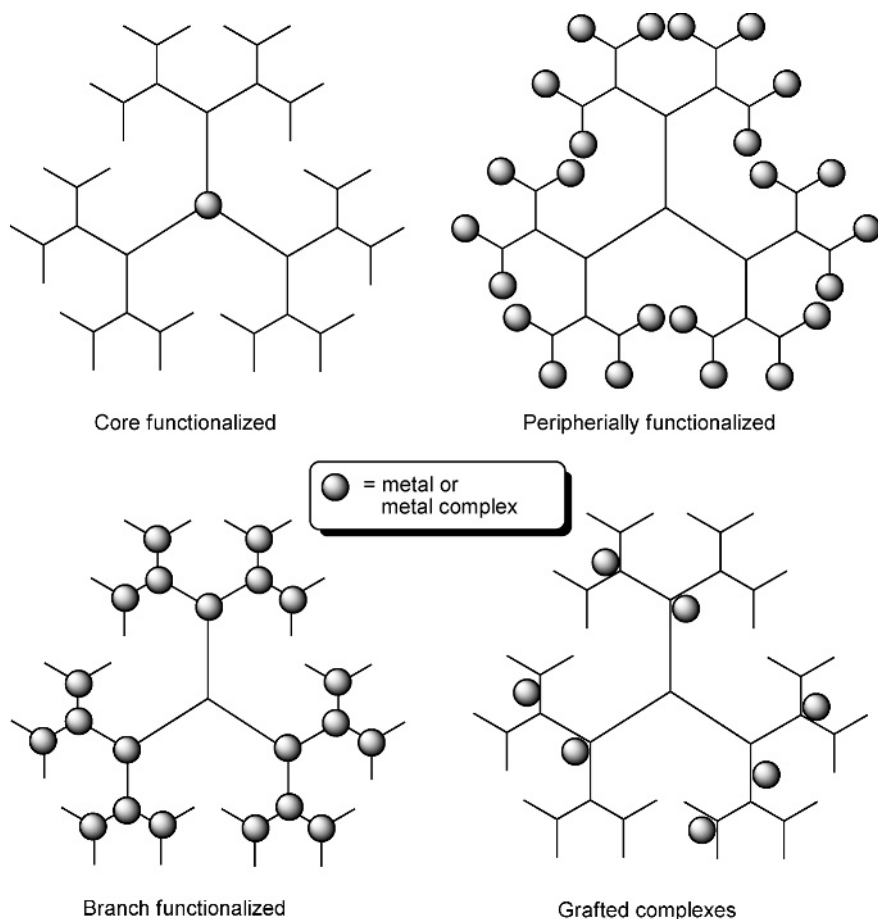


Fig. 18.2. Possible positions of metal complexes in a dendrimer.

These large molecules can be difficult to purify so the stability of M–C bond is crucial in this respect and the direct organometallic σ -bond also prevents metal leaching, a potentially deleterious side reaction known for a number of other metallodendrimers. Due to these properties, in particular complex stability, pincers can be efficiently incorporated into the structure or onto the surface of dendrimers. As described herein, the combination of the dendrimer scaffold with the pincer ligand has proved very useful for applications in catalysis, green chemistry, materials and nanochemistry.

This chapter provides a detailed synopsis of the current research on dendrimers containing a single or multiple pincer metal complexes within the dendritic structure with a focus on catalytic and materials applications. The sections are separated based on the positioning of the metallopincer fragment within the dendrimer structure, either on the peripheral surface, distributed throughout the branches, or buried within the core.

18.2 PERIPHERALLY SUBSTITUTED SYSTEMS

18.2.1 Early Studies

The first example of the incorporation of a pincer-ligated metal functionality into a dendrimer was reported by van Leeuwen and van Koten in 1994 [37]. Carbosilane (CS) dendrimers incorporating terminal SiMe_2Cl groups were reacted with nonmetalated NCN pincers, *para*-substituted with a terminal alcohol, in the presence of NEt_3 to give a dendrimer with a siloxane linker between the pincer ligand and the dendritic core. The nickel centers were introduced by oxidative addition of the pincer $\text{aryl}-\text{Br}$ bond with $\text{Ni}(\text{PPh}_3)_4$. Both zeroth- and first-generation dendrimers **1-G₀** and **1-G₁**, respectively, were synthesized and structures are given in Fig. 18.3.

In addition to the synthesis of these new species, the peripherally grafted NCN-Ni halide groups were active in the Kharasch addition of polyhaloalkanes to olefins [34, 38]. This represented one of the first successful applications of a transition metal containing dendrimer to catalysis. A representative Kharasch addition reaction is shown in Scheme 18.1. It is an example of an atom transfer radical addition (ATRA) reaction between a polyhalogenated alkane and an olefin. The specific reaction investigated was the addition of CCl_4 to methyl methacrylate (MMA), Scheme 18.1. The activity of the dendritic species was somewhat less (74 and 63% for **1-G₀** and **1-G₁**, respectively) than that of the monomeric parent pincer **2-H** (80%) after 2 h reaction. However, as the reaction conversion was based on total incorporation of Ni into the dendrimer, the results for the dendrimers are somewhat underestimated. Incomplete metalation was observed for the first-generation dendrimer by NMR experiments, and on average, 11 Ni centers were incorporated per dendrimer. Also, the specificity of the monomeric catalyst for the selective production of the 1:1 coupling product was retained with both dendritic systems.

18.2.2 Dendrimers with NCN-Ni Groups

Alternate dendrimers containing the NCN-Ni motif were further studied to help explain the effects that the dendritic framework exerted on the catalysis chemistry of the system [39, 40]. A number of related NCN-Ni systems (**3-G_n**, **4** and **5**) were synthesized utilizing a similar CS dendritic scaffold, see Figs 18.4 and 18.5. In the original synthesis of **1** the pincer units were attached to the dendrimer via carbamate and siloxy linkages, relatively reactive functionalities that are not compatible with some common synthetic reagents, such as organolithiums. As such, a more inert anchor was desired. This was accomplished via a four-step reaction sequence, shown in Scheme 18.2, that results in a direct $\text{aryl}-\text{Si}$ bond between the pincer group and the dendrimer. The steps include (1) hydrosilylation of the terminal allyl substituents with HSiMe_2Cl ; (2) salt metathesis with an excess of 3-Li-1,5- $(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3$; (3) selective *ortho-ortho* lithiation between the pincer arms; and (4) metalation with $\text{NiCl}_2(\text{PEt}_3)_2$.

Species **3-5** differ only by dendrimer generation or by the substitution pattern at the branching points. For example, the first-generation dendrimer **3-G₁** incorporates three pincer units per branch point, for a total of 12 Ni centers/dendrimer, while the related complex **4** integrates two metallopincers and one methyl group to give eight Ni centers/dendrimer, see Figs 18.4 and 18.5. An 'extended' first-generation system **5**, synthesized by one additional cycle of allylation and hydrosilylation prior to pincer

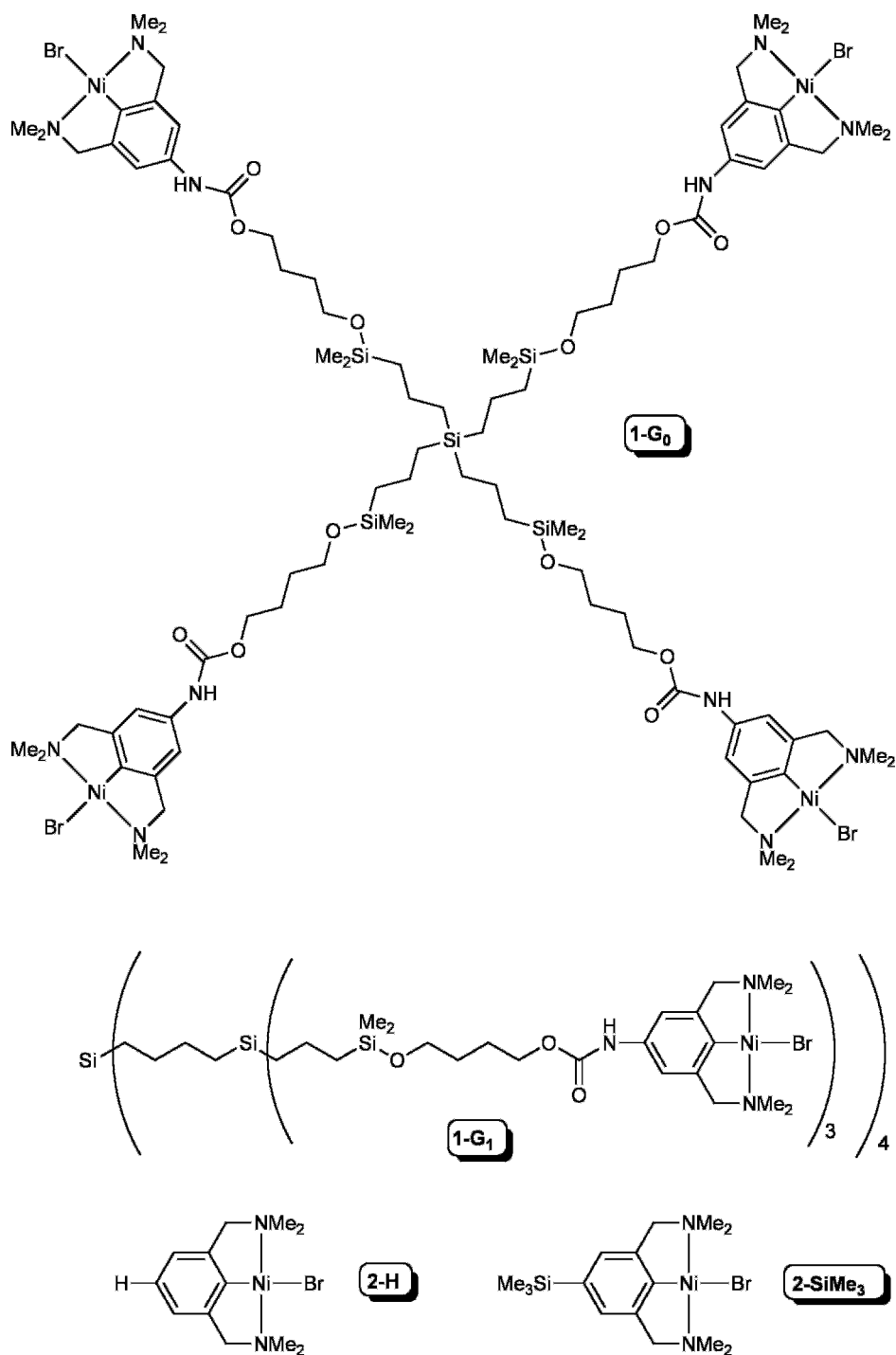
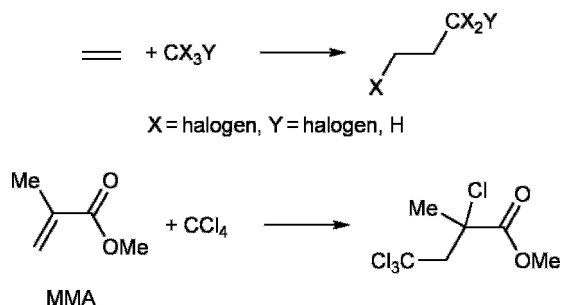


Fig. 18.3. Structures of zeroth- and first-generation CS NCN-Ni dendrimers **1-G₀** and **1-G₁** and model NCN-Ni pincers **2** [37].



Scheme 18.1 A general and a representative Kharasch addition reaction.

insertion, contains an additional $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2-$ group between the dendrimer and the peripheral NCN-Ni pincer unit and, akin to **3-G₁**, incorporates 12 NCN-Ni groups.

Again, problems with incomplete metalation of the dendrimer periphery were observed. In this case, the highly reactive, in situ-generated NCN-Li groups were found to be useful for the introduction of the Ni centers but are also extremely sensitive towards traces of moisture. Analysis of NMR spectroscopic, mass spectrometric and elemental analysis data indicated that, on average, 80–90% nickellation of the pincer sites was achieved. This was due to partial hydrolysis of the NCN-Li groups during the metalation step. Independent quenching studies showed that >98% of the NCN pincer sites were lithiated so incomplete metalation was likely the result of trace water present in the Ni reagents.

The electrochemistry of these dendritic systems was also investigated. As the redox reaction for this system involves both an electrochemical and a chemical step, simple Nernstian behavior was not observed. During oxidation, the highly reactive $[\text{NCN-Ni}^{\text{III}}\text{Cl}]^+$ abstracts a halide from the supporting electrolyte ($n\text{Bu}_4\text{NCl}$) to generate a neutral, metal-based radical NCN-NiCl₂. All the dendrimers only exhibit a single oxidation and reduction wave; there is no coupling between the Ni centers and all NCN-Ni groups in a given dendrimer are electrochemically equivalent. The calculated $E_{1/2}$ values (average of E_{ox} and E_{red}) were also essentially identical (−0.32 to −0.35 V) irrespective of dendrimer generation or degree of substitution. A monomeric NCN-NiCl model incorporating a SiMe_3 group *para* to the metal (**2-SiMe₃** in Fig. 18.3) exhibited $E_{1/2} = -0.33$ V.

One of the most striking results, especially in light of the similarity of the electrochemical data, was the strong dependence of dendrimer generation and composition on catalyst performance. Again, the test reaction studied was the Kharasch addition of CCl_4 to MMA. The zeroth-generation dendrimer **3-G₀** showed somewhat lowered catalytic activity compared to monomeric system **2-SiMe₃**, see Fig. 18.3, whereas the second-generation dendrimer **3-G₂** was essentially inactive, see Table 18.1. The various first-generation dendrimers also exhibit large differences in reactivity. The highly metalated, compact dendrimer **3-G₁** showed initial turnover rates (per Ni center) of approximately half of that of **3-G₀**. In addition, significant catalyst deactivation was observed and, after 60 min, essentially no additional conversion was noted (20% conversion total). In contrast, dilution of the surface Ni concentration either by reduction of the number of pincer groups (**4**) or by extension of the distance between the Ni centers (**5**) significantly boosts catalyst stability and, in the case of **5**, activity. Complexes **4**

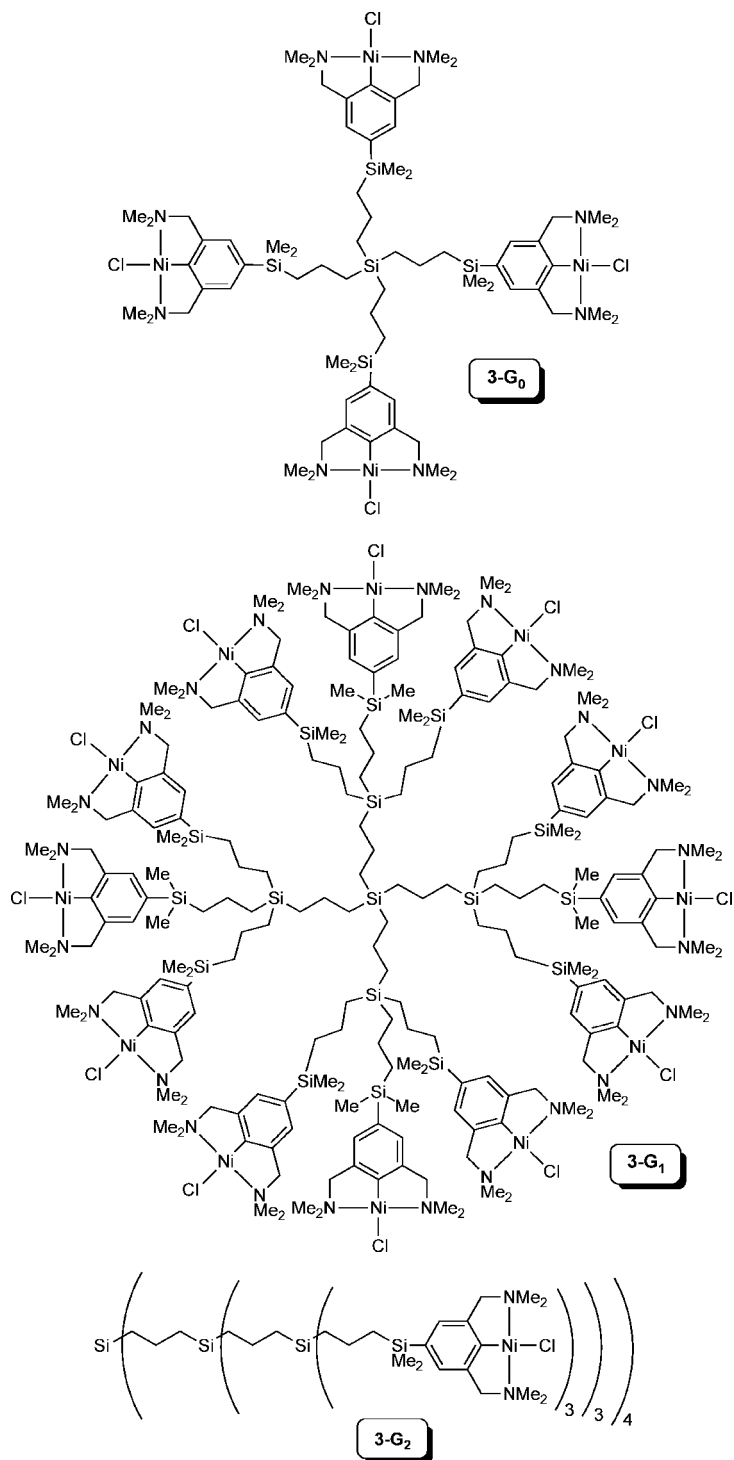


Fig. 18.4. Structures of zeroth- to second-generation CS NCN-Ni dendrimers 3-G_n [40].

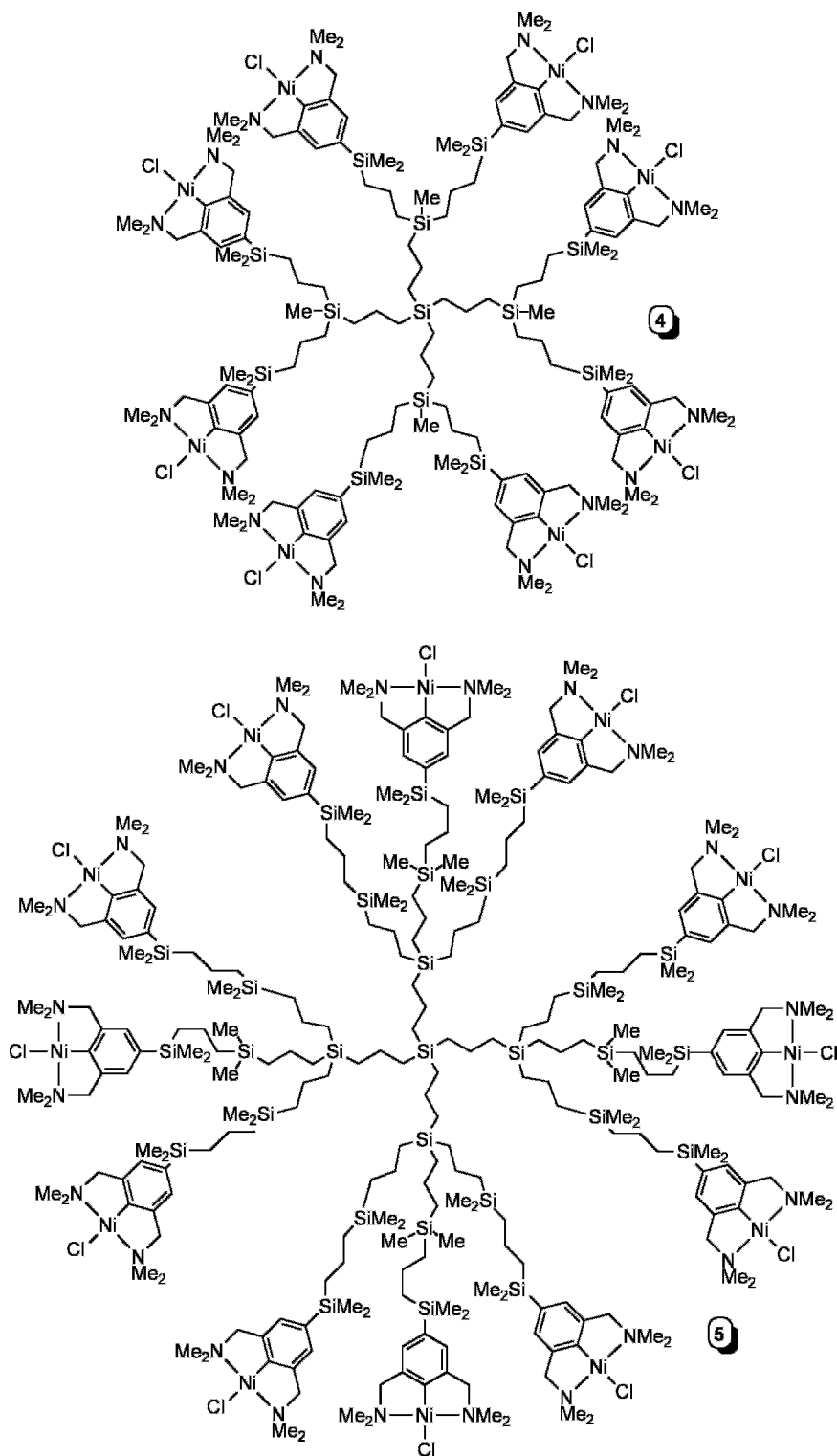
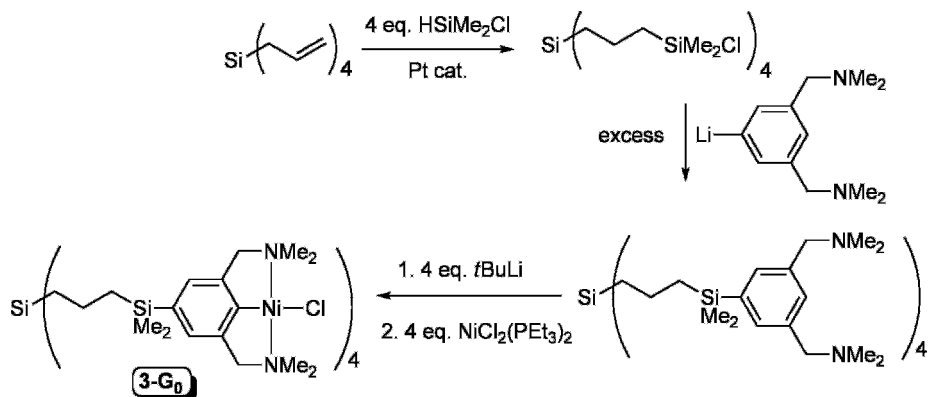


Fig. 18.5. Structures of modified first-generation CS NCN-Ni dendrimers **4** and **5** [40].



Scheme 18.2 Reaction sequence for generation of CS NCN-Ni dendrimers **3–5** [39, 40].

and **5** show no signs of catalyst degradation and full conversion is achieved after 22 h. Catalyst activity of **4** was similar to that of **3-G₁** while **5** exhibited TOF (per Ni center) more closely related to **3-G₀**.

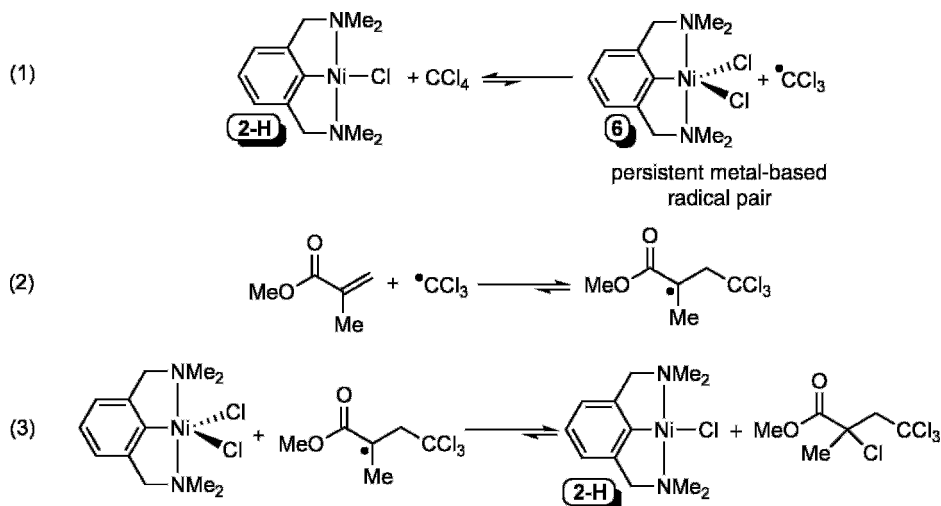
Varying the amount of active sites and the resultant impact on catalytic activity has provided a relatively rare opportunity to examine the root of a ‘dendritic effect’ in catalysis. The Kharasch addition is a radical-mediated process and is known to be sensitive to both catalyst and substrate concentrations. In nondendritic systems, altering the substrate:substrate ratio gives polymer via an atom transfer radical polymerization (ATRP) mechanism. Under conditions of low catalyst loading with the NiBr variant of **2-H** and substoichiometric amount of CCl₄, poly(methyl methacrylate) is generated via ATRP [41]. In this case with the dendritic NCN-Ni systems, the dendrimer covalently holds the metal centers in proximity and an effectively high localized concentrations of

Table 18.1. Catalytic data for Kharasch addition (ATRA) with NCN-Ni dendrimers [40]

Compound	Reaction time (h)	Conversion (%)	TOF (per Ni per h)
2-SiMe₃	0.25	15	163
	2	91	
3-G₀	0.25	9	111
	2	79	
3-G₁	0.25	3	44
	2	17	
3-G₂	0.25	0.2	3
	2	1	
4	0.25	5	53
	2	27	
5	0.25	8	102
	2	54	

Ni results, even though the overall bulk concentration of the dendrimers in solution is quite low ($\sim 9 \times 10^{-5}$ M).

The coloring of reaction solutions and precipitation of a purple solid gave qualitative evidence for the presence of metal-based radical species, which were found to be Ni^{III} compounds similar to **6**, see Scheme 18.3. The visual appearance of this purple product coincided with the observed reduction in catalyst activity. With the inactive systems, a purple precipitate was noted early in the reaction while for the active complexes, its formation was delayed until the end of the reaction where olefin concentration was low. Also, stoichiometric reactions of monomeric **2-SiMe₃** with 2 equiv. of CCl_4 resulted in the formation of a $\text{Me}_3\text{Si-NCN-NiCl}_2$ species, similar to **6** in Scheme 18.3, that was identified by X-ray crystallography. The EPR signals of both the monomeric and the dendrimer-trapped neutral Ni^{III} radicals are quite similar, strongly indicating the presence of persistent $\text{NCN-Ni}^{\text{III}}\text{Cl}_2$ groups in the dendrimer periphery.



Scheme 18.3 Mechanism for Kharasch addition (ATRA) with NCN-Ni pincers.

The three steps of the reaction mechanism for the Kharasch addition are shown in Scheme 18.3. Initially, the NCN-Ni halide couples with the haloalkane, in this case CCl_4 , to generate a trapped $\text{Ni}^{\text{III}}/\text{Cl}_3\text{C}^{\bullet}$ radical pair via a single electron transfer process. Second, the transient $\text{Cl}_3\text{C}^{\bullet}$ radical reacts with the olefin to generate an incipient ‘product-like’ radical that then, in the final step, abstracts a halide from the NCN- NiCl_2 to regenerate the active pincer catalyst. However, if two NCN- $\text{Ni}^{\text{III}}/\text{Cl}_3\text{C}^{\bullet}$ radical pairs are in proximity, an alternate, deactivation process via radical–radical coupling (to generate $\text{Cl}_3\text{C-CCl}_3$) can progress. The NCN- $\text{Ni}^{\text{III}}\text{Cl}_2$ groups are trapped and unable to participate in further catalytic reactions as one of the halides must be homolytically abstracted to regenerate the active Ni^{II} complex. Based on this data, a likely mechanism of catalyst deactivation can be envisioned and is shown in Fig. 18.6. Normally, due to its highly reactive nature, there will only be a low, steady-state concentration of $\text{Cl}_3\text{C}^{\bullet}$ (or ‘product-like’) radicals in solution under the conditions employed (high CCl_4/Ni ratio),

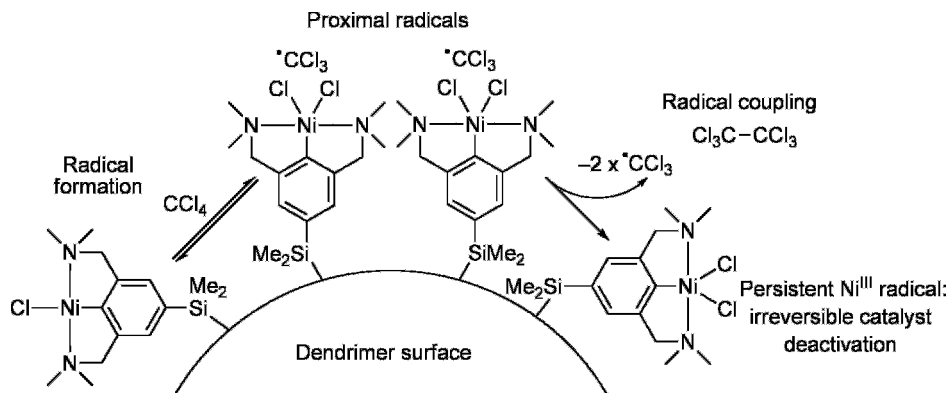


Fig. 18.6. Deactivation of NCN-Ni catalysts on dendrimer surface of **3**.

thus limiting the radical coupling-termination processes. However, with a dense, compact surface and a high local concentration of Ni centers, the chance for contact of two adjacent Ni^{III} /radical pairs is higher and thus catalyst deactivation occurs at a greater rate. Dilution of the number of Ni centers in a given volume, either by lowering the number of active surface sites or adding additional spacers, lowers the rate of catalyst deactivation and allows the reaction to proceed.

Membrane nanofiltration [28, 29] experiments were also performed on these systems to determine if it is possible to separate the dendritic catalysts from products. For nanofiltration to be effective, the desired compounds must be retained to a very high degree. As shown in Fig. 18.7, retentions of greater than 99.9% are necessary to

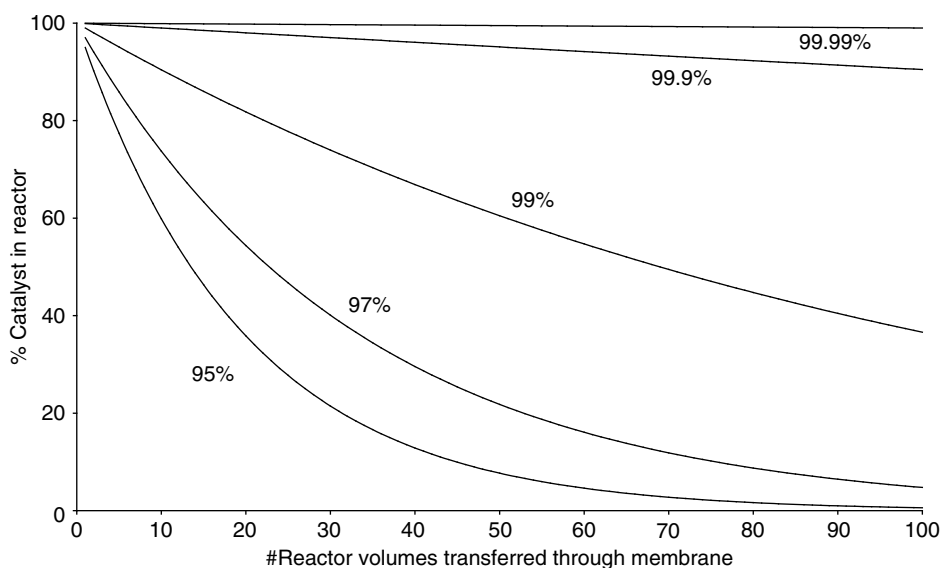
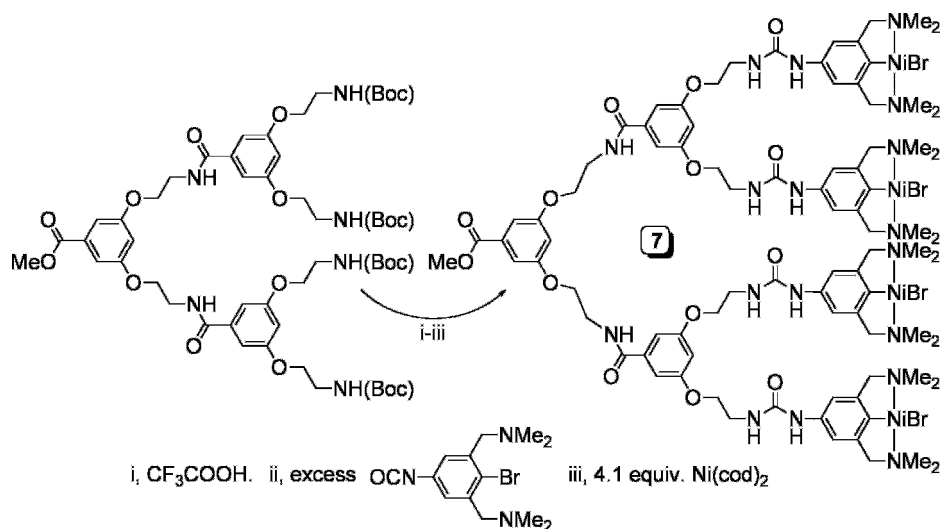


Fig. 18.7. Theoretical residence of a catalyst in a reactor at various percentage retentions.



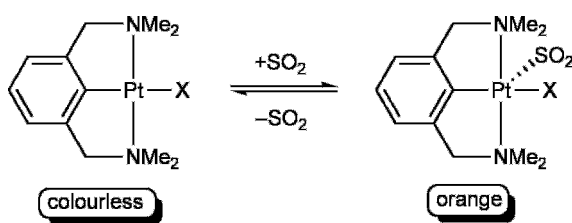
Scheme 18.4 Synthesis of amido/urea NCN-Ni-Br dendrimer **7** [42].

effectively sequester the catalyst if a large (>50) number of cycles or continuous flow systems are to be used. Here, with **3-G₀** and **3-G₁**, catalyst retentions of 97.4 and 99.75% were obtained, respectively, using a SelRO-MPF-50 membrane. As expected, the larger dendrimer was retained to the greatest extent. Both **3-G₀** and **3-G₁** were tested under batch-type conditions, but precipitation of the purple decomposition product was noted after 40 min in each case. Addition of $n\text{Bu}_4\text{NBr}$ helped inhibit the formation of the purple product, at the expense of initial reactivity rates and Br is incorporated into the product. Complex **3-G₁** was also examined under continuous flow conditions, and while no catalyst decomposition was noted visually, there was significant loss of catalytic activity after 33 h. Even though the catalyst was retained to a large extent (98.6%), the retained fraction showed no catalyst activity in further tests. This loss of reactivity was ascribed to reaction between the radical complexes and the membrane itself. Successful application of membrane-based separation technology to a dendrimer ATRA catalysis has been realized by isolating the catalyst within the core of a dendrimer (see Section 18.4).

As an alternative to the relatively apolar CS dendrimers, the NCN-Ni motif was incorporated into a highly polar amide and urea containing amino acid-based dendritic wedge [42]. The trifluoroacetate salt of dendrimer **7** (generated by reaction of the BOC-amine-protected dendrimer with trifluoroacetic acid) was reacted with a threefold excess of 1-bromo-2,6-bis(dimethylaminomethyl)-4-isocyano benzene ($p\text{-OCN-NCN-Br}$), see Scheme 18.4. This installs a urea linkage between the pincer ligand and the dendrimer skeleton. The four NCN-Br pincer groups were subsequently nickellated by reaction with $\text{Ni}(\text{cod})_2$. The catalytic performance of **7** in the Kharasch addition was quite similar to that of the zeroth-generation CS dendrimer **3-G₀**. This indicates that the drastically different polarity of the dendrimers does not adversely affect catalysis. Also, due to the presence of the urea functionalities, secondary interactions via hydrogen bonding are available to potentially modify the global dendrimer structure or to incorporate additional functional groups or ligands by self-assembly.

18.2.3 Dendritic Platinum and Palladium Pincers

Similar in structure to the ATRA Kharasch addition NCN-NiX catalysts, a number of dendrimers incorporating NCN-Pt units have also been reported. One interesting application of NCN-PtX (X = halide) pincers is as selective, reversible SO₂ chemosensors [43–46]. The colorless platinated pincer complexes form deep orange species in both the solution and the solid state upon exposure to SO₂ gas, see Scheme 18.5. Detailed studies of the kinetics and thermodynamics of the complexation reaction reveal that the SO₂ binds through the sulfur center directly to the Pt, resulting in a complex with an intense orange coloration [47]. Substitutions at the *para* position on the pincer aryl ring does not greatly affect SO₂ binding but subtle increases to the sterics at the amino donor prevent gas complexation [45, 46].



Scheme 18.5 Binding of SO₂ with NCN-Pt pincers [44].

The dendrimers **8-G₀** and **8-G₁** were obtained by a rapid esterification reaction between 4-hydroxy-NCN-PtX and an appropriately functionalized dendritic acyl chloride, see Fig. 18.8. Benzylic ether complex **9** was synthesized via reaction of hexakis(bromomethyl)benzene with 6 equiv. of 4-hydroxy-NCN-PtX, see Scheme 18.6. Due to the stability of the C–Pt bond in these pincers, the metal centers could be incorporated into the pincer synthon prior to dendrimer attachment. High-yielding reactions, such as esterification of an acyl chloride, could be employed to efficiently attach the premetalated pincers to the dendrimer, thus avoiding a potentially problematic multisite metalation in the final step.

In conjunction with the characteristic color change associated with SO₂ complexation, the solubility properties of dendrimers **8** were also influenced by introduction of the gas [45]. Both the zeroth- and first-generation dendrimers exhibited limited solubility in THF, while, on bubbling of SO₂ through THF suspensions of **8-G₀** and **8-G₁**, the dendrimers were completely solubilized. In addition, the strength of SO₂ binding to the individual Pt centers and the associated spectroscopic properties were not affected by the dendrimer framework, which indicates no strong interactions between Pt centers on the dendrimer periphery.

Platinated NCN pincers are also effective gas sensors in the solid state [44, 46]. The overall structural lattice remains crystalline but swells up to 25% during cycles of adsorption/desorption of SO₂, allowing efficient penetration of the gas into the lattice network. Based on this, there is potential for creation of stable, solid-state devices that colorimetrically or gravimetrically detect this potentially harmful gas. Towards the construction of a gravimetric variant of these sensors, a number of different NCN-Pt

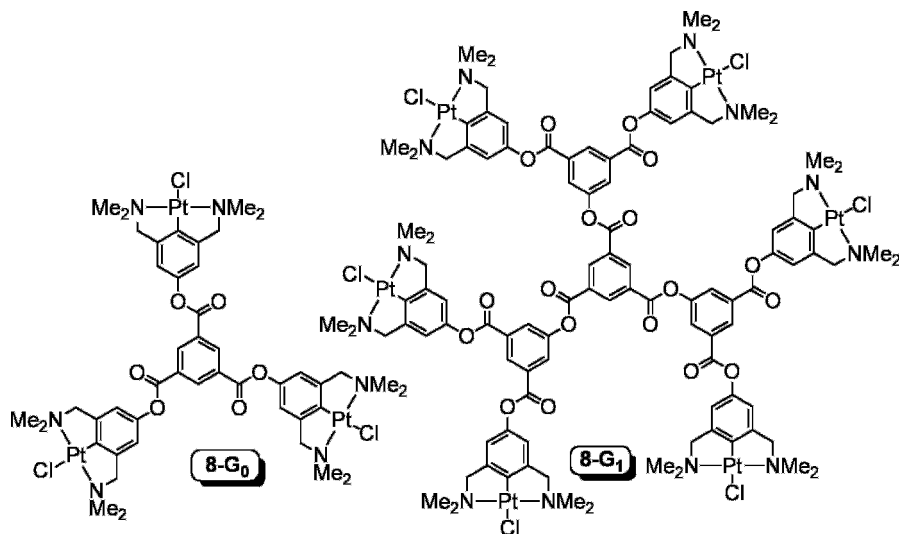
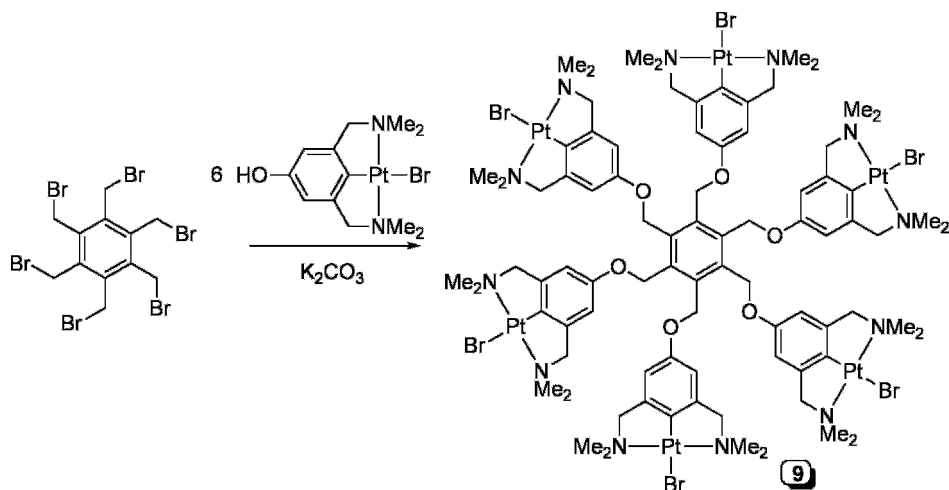


Fig. 18.8. Structure of NCN-Pt dendrimers **8** [45].



Scheme 18.6 Synthesis of NCN-Pt dendrimer **9** [48].

pincers were coated onto the disk of a quartz crystal microbalance [48]. The microbalance [49] is of sufficient sensitivity to detect the change in net weight of the grafted pincers upon SO_2 complexation. However, tests using devices fashioned from the simple *para*-hydroxy NCN-Pt pincer suffered from degradation due to loss of metallopincer. While the gas was efficiently detected, the pincer molecules slowly sublimed at the device-operating temperature (50°C); the slightly elevated temperature was necessary to desorb the bound SO_2 in a timely fashion. Incorporation of multiple NCN-Pt groups in a dendritic system increases the molecular weight (and sublimation temperature) while retaining a relatively

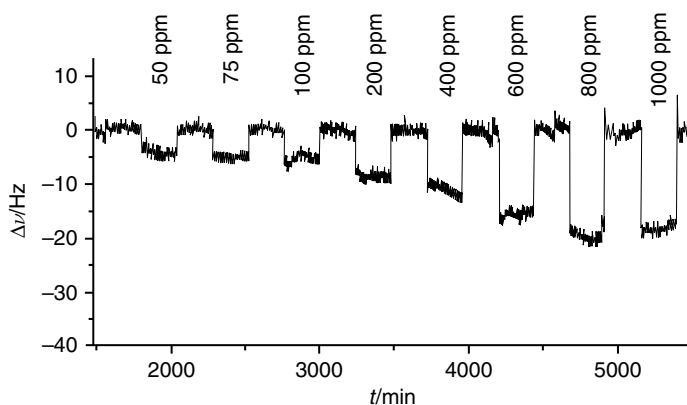
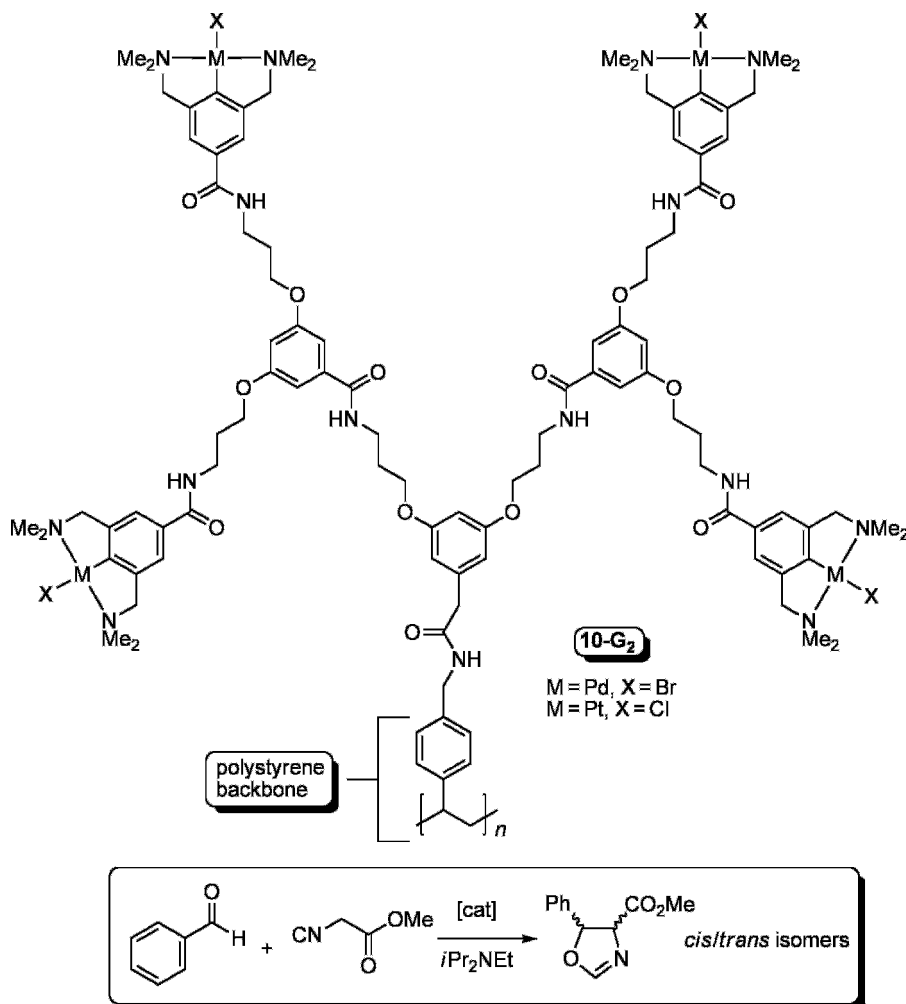


Fig. 18.9. Frequency response of quartz microbalance disc coated with NCN-Pt dendrimer **8-G₀** to changes in SO₂ concentration in gas stream [48].

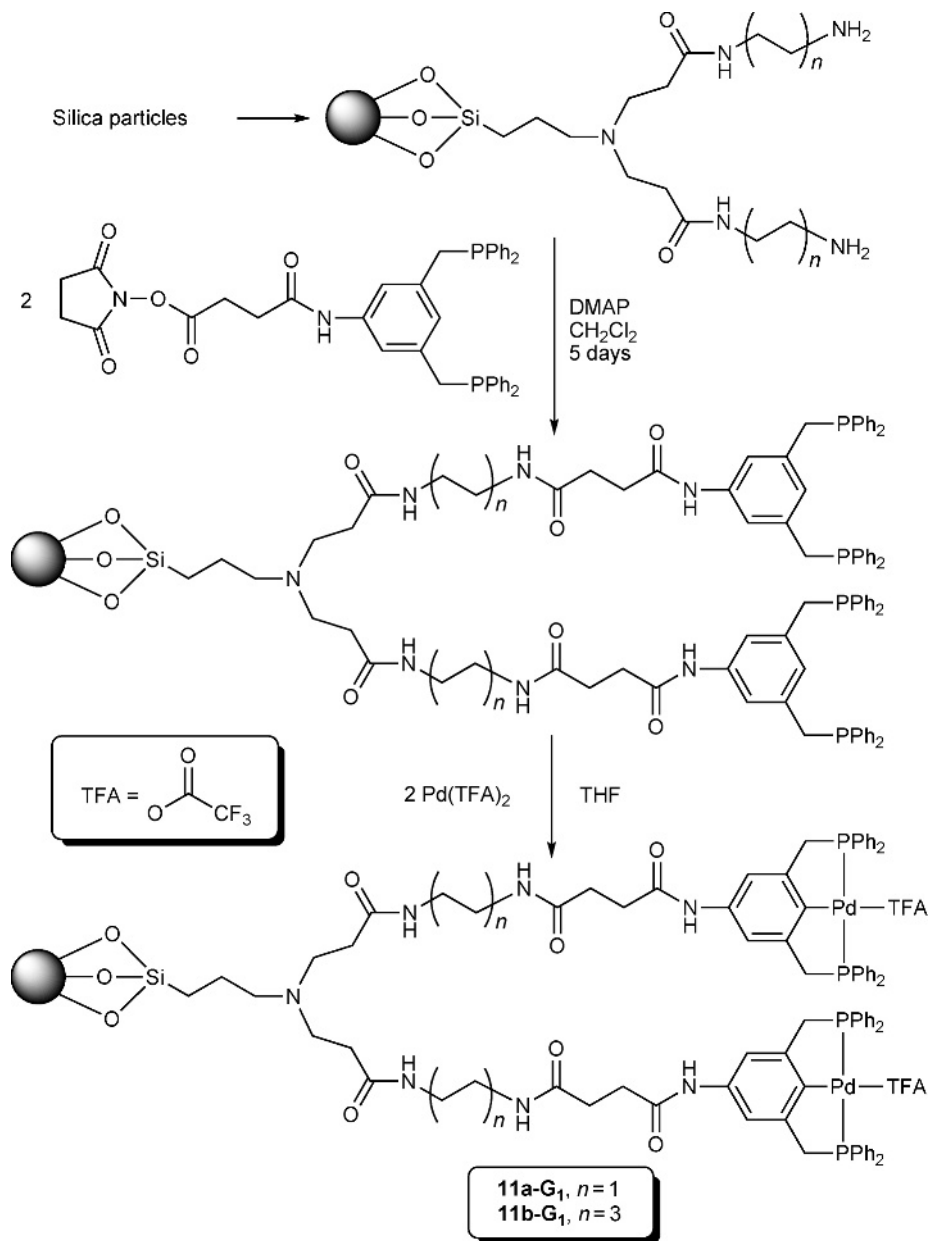
high %Pt ratio. Sensors developed utilizing both dendrimers of types **8** and **9** could reliably and reversibly detect SO₂ to a threshold of 5–10 ppm. The upper limit of detection was approximately 800 ppm for all systems. Notably, virtually instantaneous response to changes in the SO₂ concentration in the gas stream was observed under the optimized operating conditions, see Fig. 18.9. As well, changes could be reliably detected ‘on line’ and purging of the systems between analyses was unnecessary. In terms of selectivity and possible poisons or interferences, trace impurities such as solvents (benzene, toluene, aniline, methanol, nitromethane, H₂O) or other gases (NH₃, CO, CO₂) were all found to be completely innocuous and did not hamper SO₂ detection, a strong selling point for a potential device.

An intriguing subclass of functionalizable materials are dendronized polymers, species coined ‘DenPol’s’ [50, 51], which consist of a polymeric backbone regularly substituted with dendritic wedges. Here, a polystyrene polymer functionalized with first- to third-generation dendritic wedges is reacted with functionalized NCN-Pt and NCN-Pd pincers to metalate, via active ester chemistry [52], the periphery of the DenPols [53]. The structure of **10-G₂** is given in Scheme 18.7. The coupling reaction was quite efficient as only 7–9% of free amine was noted after reaction. Based on this degree of coverage coupled with polymer size measurements ($P_n=460$; PDI=1.8), 3400 metallopincers were incorporated on average per single molecule for the third-generation DenPols. First- and second-generation systems contain an average of 850 and 1700 metallopincers, respectively. The metal centers are quite accessible within the polymer network as exposure of the platinated DenPols to SO₂ results in a rapid and reversible color change from colorless to deep orange. In addition, the NCN-Pd DenPols were tested as catalysts for the aldol condensation of methyl isocyanoacetate with benzaldehyde, see Scheme 18.7. In contrast to the above NCN-Ni systems, all generations of DenPols performed nearly identically in terms of TOF and conversion, indicating that all the catalytically active metal centers are acting independently and that no deleterious side reactions are occurring in the dendrimer periphery. Tests with a monomeric analog show the DenPols to be somewhat less active, likely due to mass transfer effects. Recycling studies show that the reclaimed catalysts are about half as active as the initial run but each generation of dendrimer again performed equally.



Scheme 18.7 Structure of second-generation DenPol **10-G₂** and depiction of aldol condensation reaction between benzaldehyde and methyl isocyanoacetate [53].

In related work, Alper and coworkers recently reported the application of peripherally substituted dendritic pincers immobilized on silica to heterogeneous catalysis [54, 55]. PCP-type Pd complexes were fixed to silica particles that were functionalized with polyaminoamido (PAMAM) dendrons, species pioneered by Tomalia [2, 3, 56, 57]. The synthesis of prototypical first-generation systems **11a-G₁** and **11b-G₁** is given in Scheme 18.8 and second-generation complex **11-G₂**, also synthesized in a divergent fashion, is shown in Fig. 18.10. The silica-supported products were identified by ¹³C{¹H} and ³¹P{¹H} solid-state CP/MAS NMR spectroscopy and the %Pd incorporation was determined by ICP analysis. As with the NCN-Ni systems, first-generation dendrimers with varying short (**11a-G₁**) and long (**11b-G₁**) alkyl tethers were also generated. These



Scheme 18.8 Synthesis of first-generation PCP-Pd silica-supported dendrimer **11-G₁** [55].

were studied in the cyclocarbonylation of 2-allylphenols to generate lactones of varying ring size, see Scheme 18.9, with emphasis on the recyclability of the catalyst as well as product selectivity. In addition, **11-G₀** was tested as a catalyst for the Heck reaction.

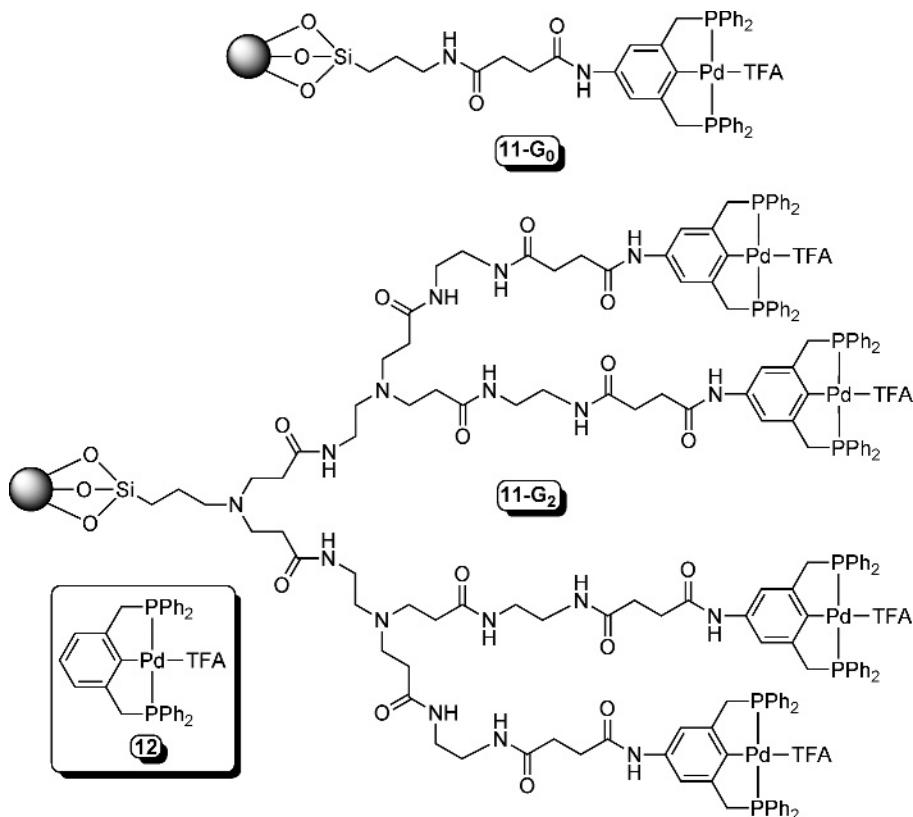
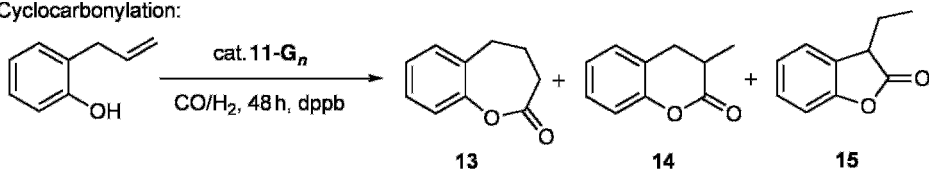
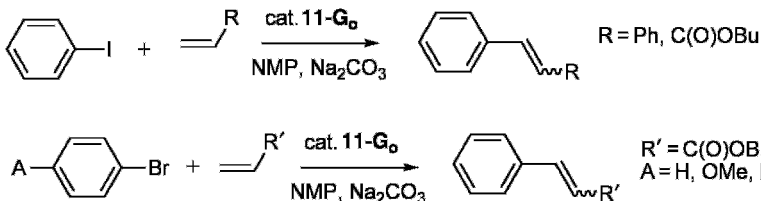


Fig. 18.10. Structure of zeroth- and second-generation silica-supported PCP-Pd dendrimers **11-G₀** and **11-G₂** and monomeric model **12** [55].

Cyclocarbonylation:



Heck reaction:



Scheme 18.9 Cyclocarbonylation of 2-allyl phenol catalyzed by silica-supported PCP-Pd dendrimers **11** to give lactones **13**, **14** and **15** and Heck reactions catalyzed by **11-G₀**.

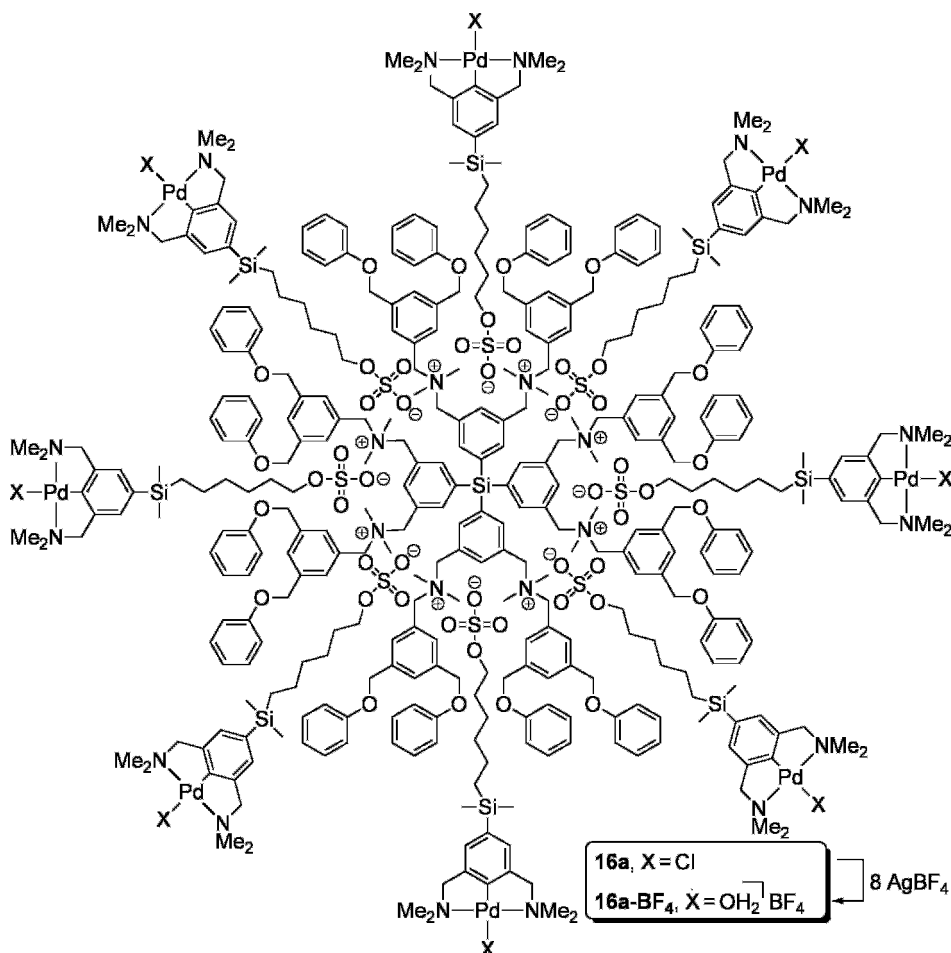
Changes to the reaction conditions were found to greatly influence both the activity of the catalyst and the distribution of ring sizes in the lactone products [54]. Variation of the pressure of CO and solvent (toluene, CH_2Cl_2), as well as addition of H_2 , was investigated with the zeroth-generation catalyst **11-G₀**. For example, at 140°C in CH_2Cl_2 with CO and H_2 pressures of 100 and 500 psi, respectively, the five-membered lactone **15** was predominantly formed (82%) with total consumption of starting material. Small amounts of the six- and seven-membered ring lactones, **14** and **13**, respectively, were also produced. Conversely, **13** was the preferred product (86%) in toluene with only CO present (400 psi). By reversing the concentrations of CO and H_2 (i.e., 5:1), again quantitative conversion to products was noted but the selectivity mimics that of the CO-only reaction, giving **13** with 83% selectivity. Under all the above conditions, the other silica bound dendritic catalysts performed comparably in terms of product yields and selectivity. Notably, monomeric, homogeneous catalysis with compound **12**, 5:1 CO/ H_2 and various additives (aminopropylated silica, free ligand) exhibited significantly lowered selectivity for the seven-membered lactone (48–59%) but did give >95% conversion. Thus, the dendritic structure is influencing the product distribution but further work is necessary to elucidate the source of this result. Also, addition of a large excess (to catalyst) of bidentate phosphine 1,4-bis(diphenylphosphino)butane was necessary for efficient reaction, calling into question the true nature of the actual catalyst and the mechanism of reaction. Indeed, the presence of Pd(0) has been invoked in a preliminary catalytic cycle based on the homogeneous reaction [58] (see below for further discussion).

Regardless of the reaction mechanism, the dendritic silica-supported PCP-Pd catalysts could be recycled but large differences were noted in the catalyst stability dependent on reaction conditions and dendrimer generation. Under the optimized 1:5 CO/ H_2 - and CO-only conditions, the second run with **11-G₀** gave comparable results to the first but the yield of products dropped precipitously after the third run to 38 and 11%, respectively. In addition, the product yield distribution was significantly altered in the 1:5 CO/ H_2 reaction during the third run, with the seven-membered lactone **13** formed with only moderate selectivity (54%). The higher-generation dendritic catalysts performed significantly better in terms of recycling in the CO-only reaction, but a noticeable drop in yield was again noted after the second run. Efficient recycling with all generations of catalyst was realized by utilizing the 5:1 CO/ H_2 conditions. Up to five separated runs with **11-G₀** and up to three runs with the remaining catalysts **11a-G₁**, **11b-G₁** and **11-G₂** were performed with nearly identical results in terms of selectivity and total yield. In addition, catalysis using **11-G₀** with a limited selection of substituted allylphenols shows this reaction to be fairly insensitive to substrate-based electronic effects but can be influenced by steric factors.

The silica-tethered PCP-Pd pincer **11-G₀** also showed decent activity in the Heck reaction between iodobenzene and styrene or butyl acrylate as well as with *para*-substituted bromobenzenes and methyl or butyl acrylate, see Scheme 18.9 [55]. All products were obtained in >90% yields with optimized conditions. As with catalytic lactone synthesis, the yields of the Heck coupling products are not greatly influenced by electronic effects, based on reactivity of a small selection of substrates. The catalyst recycling (up to five times) was quite efficient in some instances but in others, yields dropped significantly after two to three runs. One specific instance showed a drop of almost 40% by the third run.

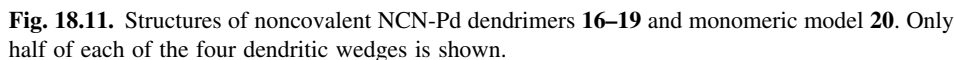
Recent detailed mechanistic, kinetic, poisoning and reactivity studies have strongly indicated that the Heck-type C–C coupling reactions are not catalyzed by the pincer complexes themselves. The cyclometalated species act as precatalyst reservoirs for soluble, extremely active, colloidal Pd(0) nanoparticles or mononuclear Pd(0) species, the true catalysts for the reaction [59–64]. However, there is still some debate on this issue, especially on the mechanism of Pd extrusion [59, 65], and some groups are still considering an unusual Pd(II)/Pd(IV) cycle as a viable alternative to the accepted Pd(0)/Pd(II) mechanism [66] with pincer complexes. In a detailed and excellent review in 2006 by Jones and coworkers on the nature of the active species in Pd-catalyzed Heck and Suzuki reactions [67], they conclusively state that the vast majority of pincer systems reported to date are indeed sources of Pd(0) under Heck conditions and catalysis is consistent with the normally evoked cycle. This also relates to other reactions traditionally involving Pd(0) that can be catalyzed by metallopincers, cyclocarbonylation, for example. As such, any reports on recycling studies on Heck or Suzuki, Stille, Sonogashira, etc., Pd(0)-catalyzed C–C coupling or other catalyzed reactions with supported palladopincers should be questioned critically. Poisoning experiments, (pre)catalyst stability under the reaction conditions, the degree of catalyst retention due to Pd metal leaching for supported catalysts and reaction kinetics should be studied in detail in each instance if any mechanistic details are to be investigated. In the work of Alper, the continued activity of the silica bound PCP-Pd pincers for Heck catalysis is likely due to their inherent stability which facilitates slow release of active Pd(0) under the conditions employed, leaving unreacted precatalyst within the support for reaction in subsequent runs.

Nonbonding, electrostatic interactions have been employed by Klein Gebbink and van Koten as an alternate method to incorporate pincer groups into dendrimers. This potentially combinatorial strategy allows for facile variation of the dendritic structures and the generation of mixed systems. Utilizing *para*-substituted NCN-Pd pincers with a sulfate-terminated alkyl tether as synthons, up to eight metallopincers have been introduced into the clefts of dendrimers containing an octacationic ammonium core with zeroth- to third-generation polar Fréchet (phenyl benzyl ether) dendrons (**16–18**) and a nonpolar (alkyl) dendritic wedge (**19**) [68, 69]. In addition, longer (**a**-series) and shorter (**b**-series) alkyl spacers can be simply incorporated into the tether and do not affect the introduction of the anionic sulfate into the dendrimer structure. Indeed, in associated chemistry with nondendritic ionic and zwitterionic organometallic pincer complexes similar to **20**, only small differences were noted in terms of molar conductivity, hydrogen bond strengths and NMR chemical shifts across systems with varying linkers [70]. The full structure of the polar dendrimer **16a** and the neutral **16a** and cationic Pd complex **16a-BF₄** is shown in Scheme 18.10 and schematic representations illustrating half of each dendritic wedge of **16–19** and the structure of **20** are given in Fig. 18.11. The syntheses of the were performed in two manners which gave complementary results: (1) reaction of eight pregenerated Pd species with a given dendrimer or (2) initial dendrimer/pincer complex formation followed by eightfold halide abstraction. Halide abstraction to generate the cationic Pd centers is performed by a stoichiometric reaction with AgBF₄. The dendrimers have been extensively characterized by multinuclear NMR spectroscopy, as well as 2D DOSY experiments, and by ESI-mass spectrometry (MS). Based on mass data, halide scrambling occurs but the spectra clearly indicate that the octameric species was formed and was stable. Results from transmission electron microscopy (TEM) and molecular mechanics (MMF94) support the dendrimer dimensions found in the NMR diffusion studies [69].



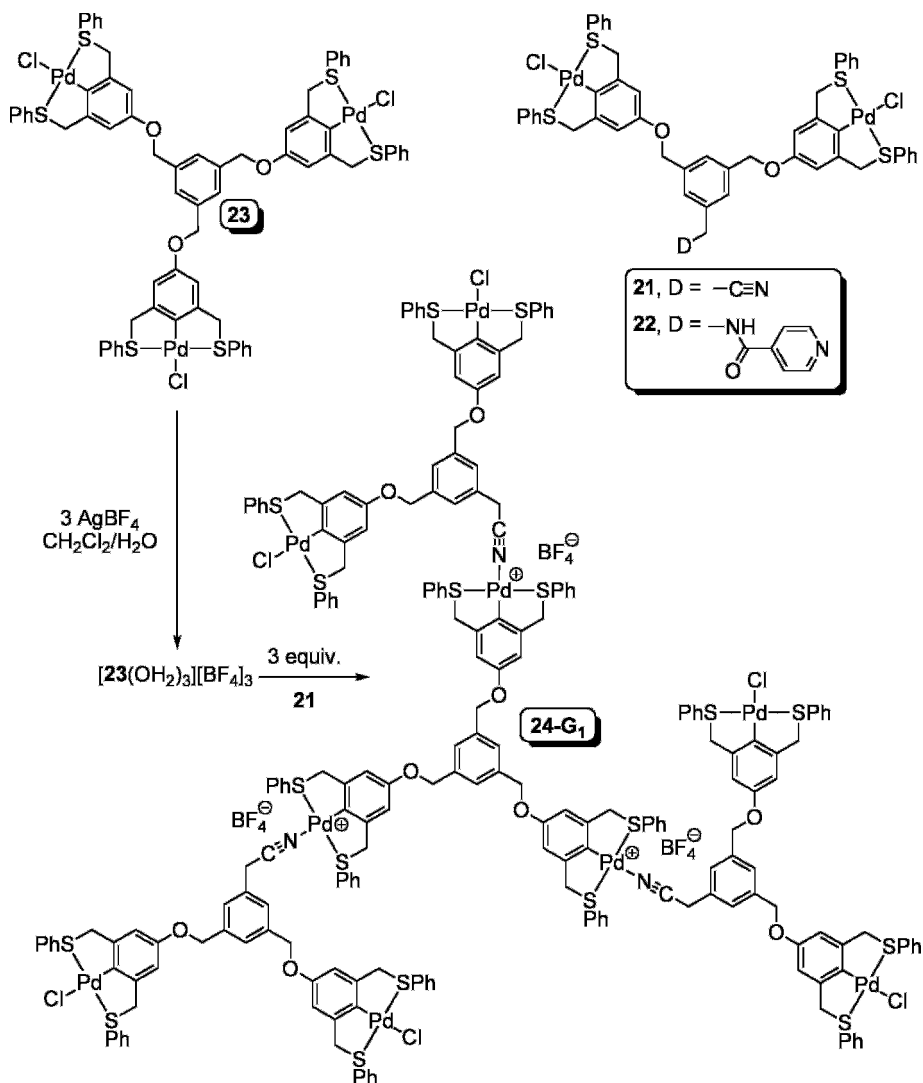
Scheme 18.10 Dendritic noncovalently bound neutral and cationic NCN-Pd pincers **16**.

The neutral Pd dendritic complexes **16–20** were also tested as Lewis acid catalysts in the aldol condensation of benzaldehyde and methyl isocyanoacetate, see Scheme 18.7 for the reaction. For example, dendrimer **16a** exhibited activity (per Pd center), turnover frequency and selectivity comparable to a model monomeric sulfate-terminated pincer complex **20**. Conversions of 82 and 95% were found for dendrimer **16a** and the pincer **20**, respectively, and both produced essentially the same amount of the *trans*-aldol product, with selectivities of 69 and 72%, respectively. Only subtle differences in activity and selectivity were noted within the homologous series of polar Fréchet-based dendrimers **16–18**, between the polar and nonpolar (**19**) dendrimers. Also, no differences could be observed based on the length of the alkyl linker (**a** vs. **b** series). This indicates that regardless of the dendrimer generation, length of tether or the polarity of the dendritic shell, these species are relatively open and allow ready access of reagents to the active catalytic sites and that the differing environments do not strongly interact with the cationic metal centers [69].



18.3.1 Dendrimers Containing Pincer-Ligated Palladium and Platinum Complexes

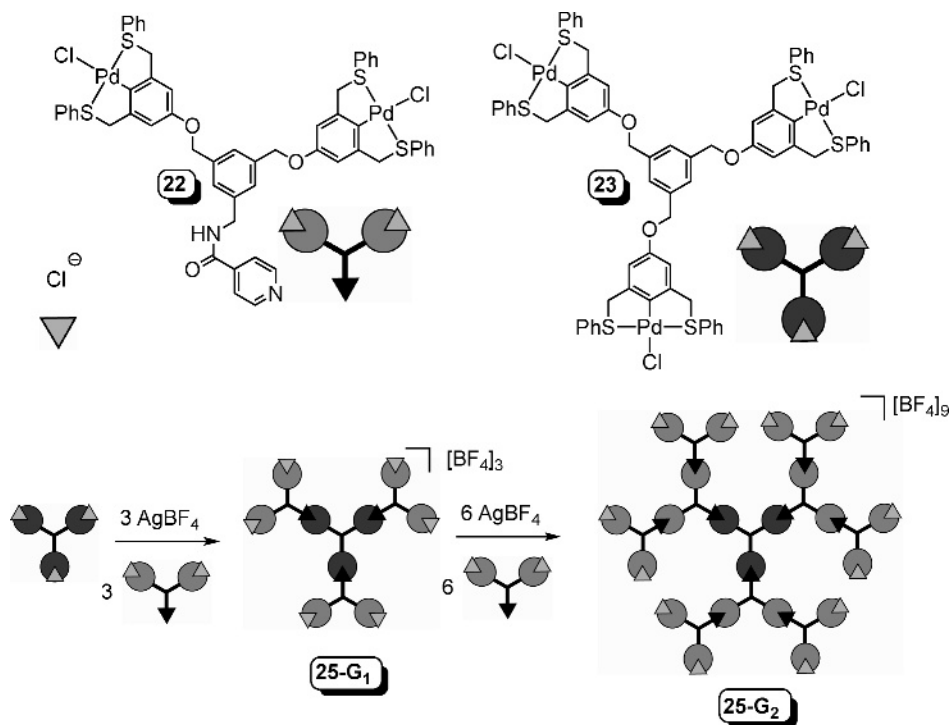
In a growing body of work, Reinhoudt, van Veggel and coworkers have employed dative metal–heteroatom interactions to install pincer functionalities as an integral portion of the dendritic framework (see Section 18.4 as well). Judiciously designed, multifunctional molecules that utilize simple Pd–nitrile, Pd–pyridine or Pd–phosphine dative bonds were employed to construct various dendrimers. In the original work, dendrons fusing two SCS-Pd pincers and a nitrile via an arene core (**21**) were used as branches for dendrimer construction in a divergent fashion [71, 72]. The dendritic core was comprised of a 1,3,5-trisubstituted benzene incorporating three SCS-Pd pincers (**23**). Dendrimers of type **24** were synthesized up to the fifth generation. Further work using a divergent synthetic approach has employed a pyridine-containing analog of **21** with an isonicotinoyl group in place of nitrile (**22**) [73]. Dendrimers of type **25**, exclusively incorporating the isonicotinoyl pyridine motif, were synthesized up to the third generation. The synthesis of the first-generation dendrimer **24-G₁** is given in Scheme 18.11 and expansion to larger dendrimers involves a simple, two-step procedure. First, the chlorides of the SCS-Pd-Cl pincers in the core are abstracted with the appropriate amount



Scheme 18.11 Synthesis of first-generation SCS-Pd dendrimer **24-G₁** [71, 72].

of AgBF_4 in $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ to give activated $[\text{SCS-Pd-OH}_2]^+$ cations. Subsequent addition of branching SCS-Pd pincer/nitrile **21** or SCS-Pd/pyridine **22** incorporates the next dendritic shell. As both reactions are essentially quantitative and rapid, large dendrimers can be efficiently synthesized; Scheme 18.12 depicts the synthesis of **25-G₁** and **25-G₂** schematically.

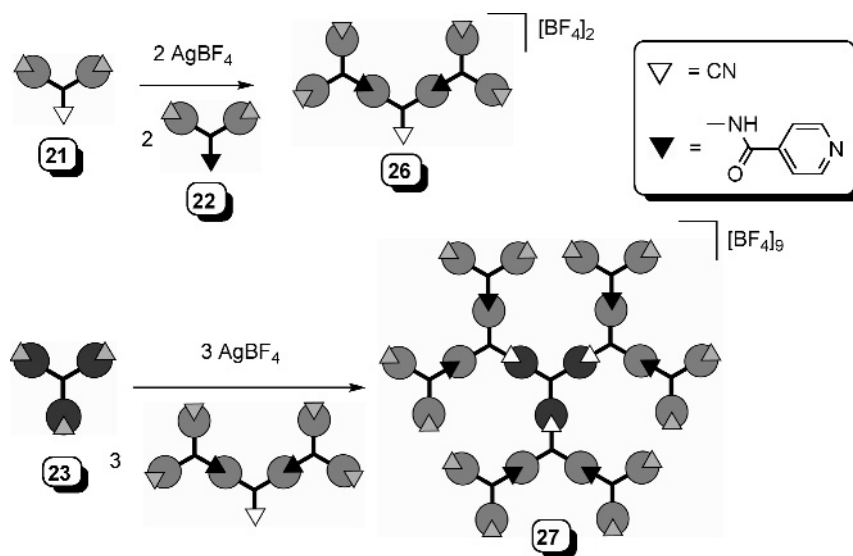
In addition to these well-defined dendrimers, self-assembly using analogous SCS-Pd nitrile interactions generated noncovalent hyperbranched polymers [74, 75]. These well-defined spheres had particle sizes that were tunable by incorporation of different thioether groups on the SCS pincers and by variation of anion.



Scheme 18.12 Schematic representation of the synthesis of first- and second-generation SCS-Pd dendrimers **25-G₁** and **25-G₂** [73].

All of these dendrimers were characterized in solution by NMR spectroscopy as well as by elemental analysis and, most importantly, mass spectroscopy. For many of these large, macromolecules, restricted rotation or slow molecular tumbling results in fairly broad NMR spectra, in spite of the highly symmetric structures inherent to dendrimers. However, in almost all cases, MALDI-TOF and ESI-MS measurements clearly show mass values for the complete defect-free dendrimer.

One of the advantages of a noncovalent approach to dendrimer synthesis is that the strength of the dative bonds can be used to influence the shape, composition and properties of the molecules. A detailed study of the bonding between SCS-Pd cations and various Lewis basic donors (LB) showed that Pd–LB bond strength follows the trend Pd–NCR < Pd–pyridine < Pd–PPh₃ [77]. In fact, a pyridine ligand can quantitatively displace a bound nitrile in SCS-Pd pincers. Based on this reactivity pattern, a number of dendrimers with varying properties were synthesized via an elegant convergent approach [73]. Dendrimers with Pd–nitrile coordination and Pd–pyridine bonds in the inner and outer shells, respectively, were formed by first assembling dendritic wedge **26**, see Scheme 18.13. The reaction is completely selective for formation of Pd–pyridine bonds. Next, the free-pendant nitrile group, which is at the focal point of the wedge, is complexed to a cationic trimeric core, giving a second-generation dendrimer **27**. Of note is that a different set of Pd–LB bonds is present in each of the dendrimer generations.



Scheme 18.13 Convergent synthesis of second-generation-mixed SCS-Pd dendrimer **27** [73].

One of the difficulties encountered with the noncovalently assembled SCS-Pd dendrimers incorporating pyridine linkages is their general lack of solubility in common solvents. For instance, the first- and second-generation dendrimers **25** were somewhat soluble in mixtures of $\text{CH}_2\text{Cl}_2/\text{MeNO}_2$ on slight warming (35°C), while the third-generation system only dissolved in MeNO_2 at elevated temperature (85°C). To help alter the solubility properties of these dendrimers, hydrophobic groups were added to the dendrimer periphery [76]. This type of surface modification is a known and proven method to alter and control the solubility of dendrimers [78, 79]. As such, the terminal SCS-Pd functionalities were used to anchor additional, functionalized dendritic wedges. As shown in Fig. 18.12, the fourth-generation ‘layered’ dendrimer **28** contained, from the outer shell to the core, solubilizing Fréchet-type phenyl–benzyl ether groups, Pd–phosphine branches, Pd–pyridine linkages and Pd–nitrile bonds. Higher-generation phosphine-appended Fréchet-type dendrons were also employed to give an even larger hydrophobic periphery. In contrast to the SCS-Pd-terminated dendrimers, these molecules showed a high degree of solubility in CH_2Cl_2 and CHCl_3 at room temperature. In a separate study, carbohydrate (**29**) and oligoethylene glycol functionalities (**30**), shown in Fig. 18.13, were similarly incorporated into the dendritic periphery via pyridine and phosphine linkages to induce water solubility on the metallodendrimers [80].

Attempts to extend this synthetic methodology to the PCP pincer system are of potential interest due to the catalytic activity of a number of metallopincer PCP complexes [31]. Also, the introduction of the PCP group could allow for the facile incorporation of a number of metals (Ni, Pt, Rh, Ir) via C–H activation; metal installation for the SCS pincer via this method is essentially limited to Pd with current methods. In addition to potential catalytic applications, this would add an extra layer of diversity to these functionalized dendrimers as mixed metal and/or mixed pincer systems are easily envisaged.

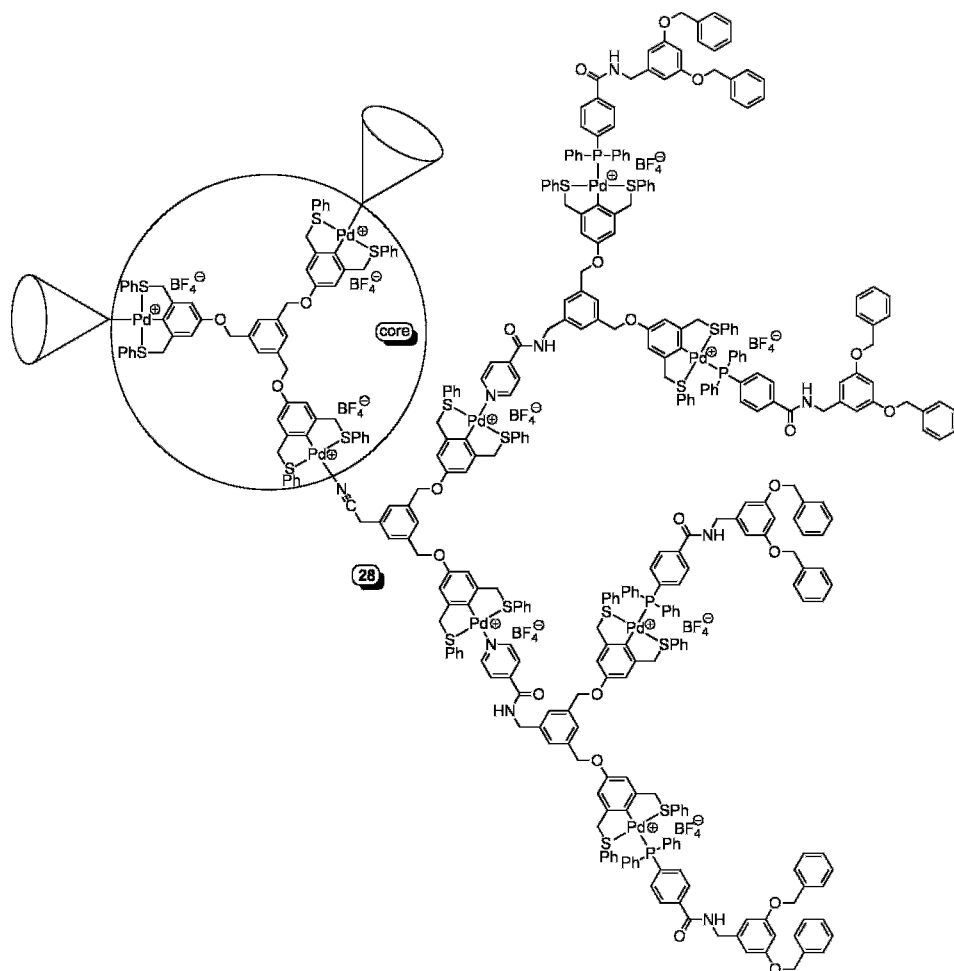


Fig. 18.12. Structure of fourth-generation-mixed SCS-Pd/phenyl benzyl ether dendrimer **28**. Only one of the three dendritic wedges is shown; cones represent the other dendrons [76].

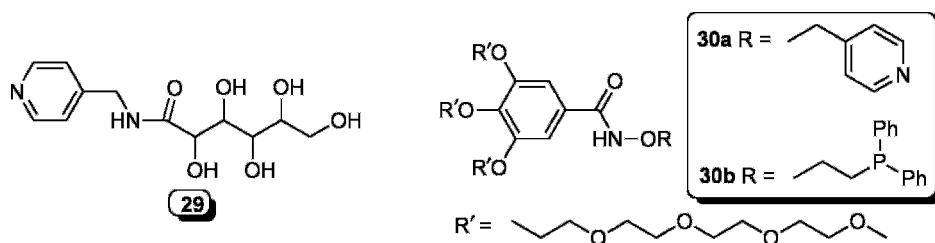


Fig. 18.13. Structure of water-solubilizing capping groups for SCS-Pd dendrimers containing carbohydrate (**29**) and ethylene glycol (**30**) functionalities [80].

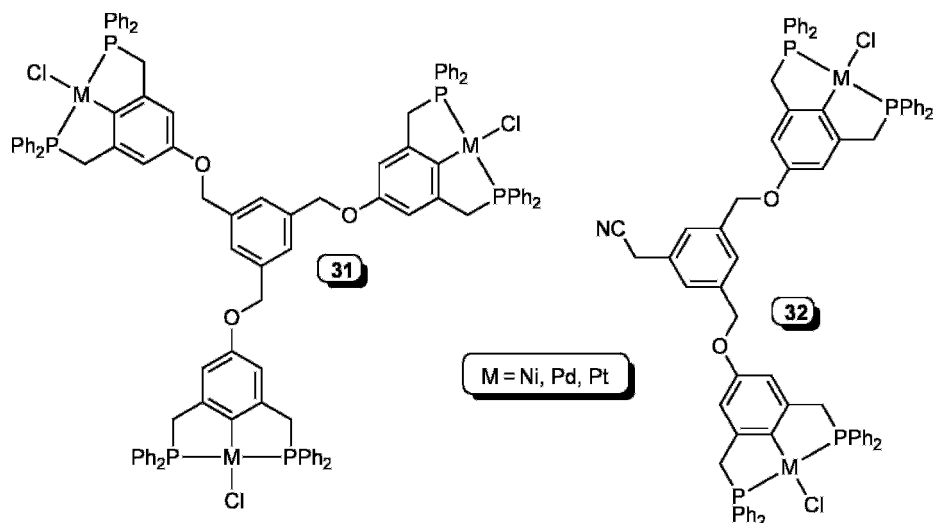


Fig. 18.14. Structures of Ni, Pd and Pt PCP pincer dendritic core **31** and dendron **32** [81].

Metallopincers with Ni, Pd and Pt centers were all incorporated into both a trimeric core molecule (**31**) as well as into a dendritic branch (**32**), see Fig. 18.14 [81]. Attempts to incorporate Ir(I) and Rh(I) via C–H activation with standard reagents were not successful. However, studies on the synthesis of homo- and heterodendrimers containing these dendrons are thus far limited, and while preliminary studies indicate dendrimer formation is possible, these species appear to be somewhat unstable and readily oxidize in solution.

Dendritic wedges containing SCS-Pd functionalities have been grafted onto gold surfaces [Au(111)] by means of a long-chain alkyl thioethers [82]. These dendrimers are isolated and confined on the Au surface and, due to their nanometer dimensions, they can be individually addressed and imaged by atomic force microscopy (AFM) and TEM techniques. Gold surfaces covered with a [D₂₁]decanethiol monolayer were treated with long-chain thioether-functionalized first- and second-generation SCS-Pd metallo-dendrimers **33**, see Fig. 18.15. The length of the tether allows the dendritic portion to protrude from the monolayer surface. The adsorption of dendrons on the surface was confirmed by contact angle measurements, AFM and secondary ion mass spectrometry (SIMS). Notably, tapping-mode AFM indicates that the average dimensions of the individual surface-confined dendrimers, especially the height above the monolayer surface, correlates well with the expected size from CPK models, if it is assumed that the dendrimers adopt a flat, disk-like geometry. The measured heights of **33-G**₁ and **33-G**₂ are 0.6 ± 0.2 and 0.9 ± 0.2 nm, respectively. Also, the surface concentration could be numerically evaluated by AFM. The number of individually adsorbed dendrimers varied with treatment time, and, after 20 h, a maximum of approximately 55 dendrimers were found per 200×200 nm area. This is in line with results on the degree of [D₂₁]decanethiol monolayer disruption induced by the solvent used in the adsorption reaction.

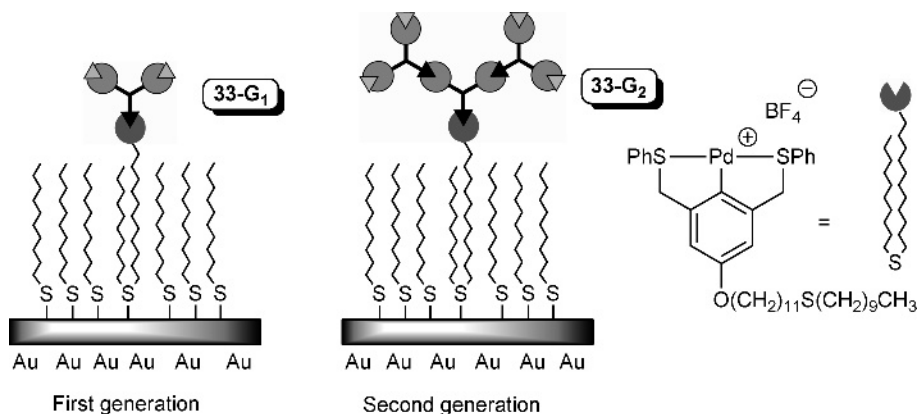
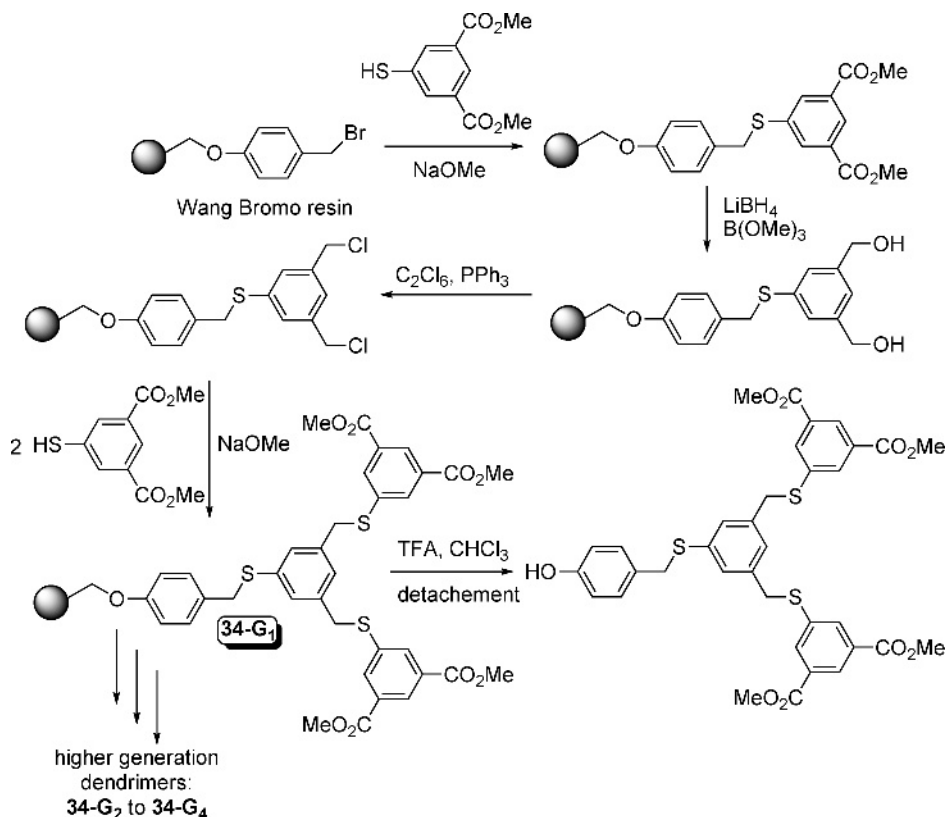


Fig. 18.15. Au surface-adsorbed SCS-Pd dendritic wedges **33** [82].

A novel synthetic strategy was employed by Portnoy and coworkers to assemble SCS-type dendrimers using solid-phase synthesis techniques [83]. First- to fourth-generation dendritic wedges **34-G_n** could be easily synthesized by repetition of a three-step reaction sequence shown in Scheme 18.14. Wang-Bromo resin was used as the solid support. The initial diester is attached to the Wang resin by nucleophilic substitution of the benzylic bromide with a thiolate. The esters are reduced to alcohols using borohydride and converted to benzylic chlorides by a chlorodehydroxylation reaction with PPh_3 and C_2Cl_6 . These pendant chlorides can then be converted to thioethers via the original nucleophilic substitution reaction. The fourth-generation dendrimer was isolated after detachment from the support in 42% overall yield over 10 steps, equating to an average of 92% yield/reaction. Selective cleavage of the resin-bound dendrimers was accomplished by treatment with trifluoroacetic acid; only the thioether adjacent to the resin surface was attacked to generate the 4-hydroxybenzyl-capped dendrimers.

Palladation of second- and third-generation dendrimers **34** to give integrated SCS-Pd pincer dendrimers **35** was accomplished by the reaction of resin-bound dendrimers with $\text{Pd}(\text{PhCN})_2\text{Cl}_2$, Fig. 18.16. The incorporation of Pd was noted by a color change from clear to deep red although definitive spectroscopic data supporting formation was not reported. The NMR spectra for both the resin-bound (solid-state NMR) and the detached dendrimers (solution NMR) were severely broadened. However, full characterization of model species **35-mod** did indicate that the palladation procedure was reliable. The resin-bound SCS-Pd dendrimers **35-G₂** and **35-G₃** as well as immobilized model **35-mod** were subsequently tested in the Heck coupling of iodobenzene and methyl acrylate. Preliminary catalytic data for all species indicate quantitative conversion using 2.5 mol% Pd loading and that the resin-bound immobilized catalysts could be efficiently recycled. Identical reactivity in terms of conversion and reaction rate was observed in a second run. Again, it is stressed that the catalysis is likely not performed by the pincer-bound SCS-Pd(II) complexes but by some active Pd(0) species that is leached into solution. The subsequent activity of the polymer-bound pincers is a result of incomplete reaction of the precatalyst, leaving bound SCS-Pd to participate in the next run.



Scheme 18.14 Solid phase synthesis of metal-free dendritic SCS pincers **34-G_n** [83].

18.4 FOCAL POINT AND CORE-FUNCTIONALIZED METALLOPINCER DENDRONS AND DENDRIMERS

The NCN-Pt group has been incorporated at the focal point of a Fréchet-type dendritic wedge and dendrimers of type **36** were reported up to the third generation, see Fig. 18.17 [84]. The metallopincer was attached to the preformed benzylic bromide-substituted dendron by reaction of 4-hydroxy-NCN-Pt-Br. The retention of the dendrimer by a nanofiltration membrane (SelRO-MPF-60) could be conveniently monitored colorimetrically by UV-Vis spectroscopy of SO_2 -saturated CH_2Cl_2 solutions on either side of the membrane. The amount of leaching decreased with increasing dendrimer generation; $t_{1/2}$ values for **36-G₁**, **36-G₂** and **36-G₃** were 108, 300 h and >60 days, respectively.

A third-generation dendrimer **37** where the NCN-Pt chemosensor was substituted with catalytically active NCN-Ni species was studied by van Koten et al. in the Kharasch addition reaction (see Sections 18.2.1 and 18.2.2) [84]. Particularly, the ability to separate products and recycle the catalyst by nanofiltration was studied. Membrane-capped vials containing the NCN-Ni dendrimer were immersed in solutions containing MMA and CCl_4 and the ATRA reactions were quantitative (>99% conversion) after 48 h.

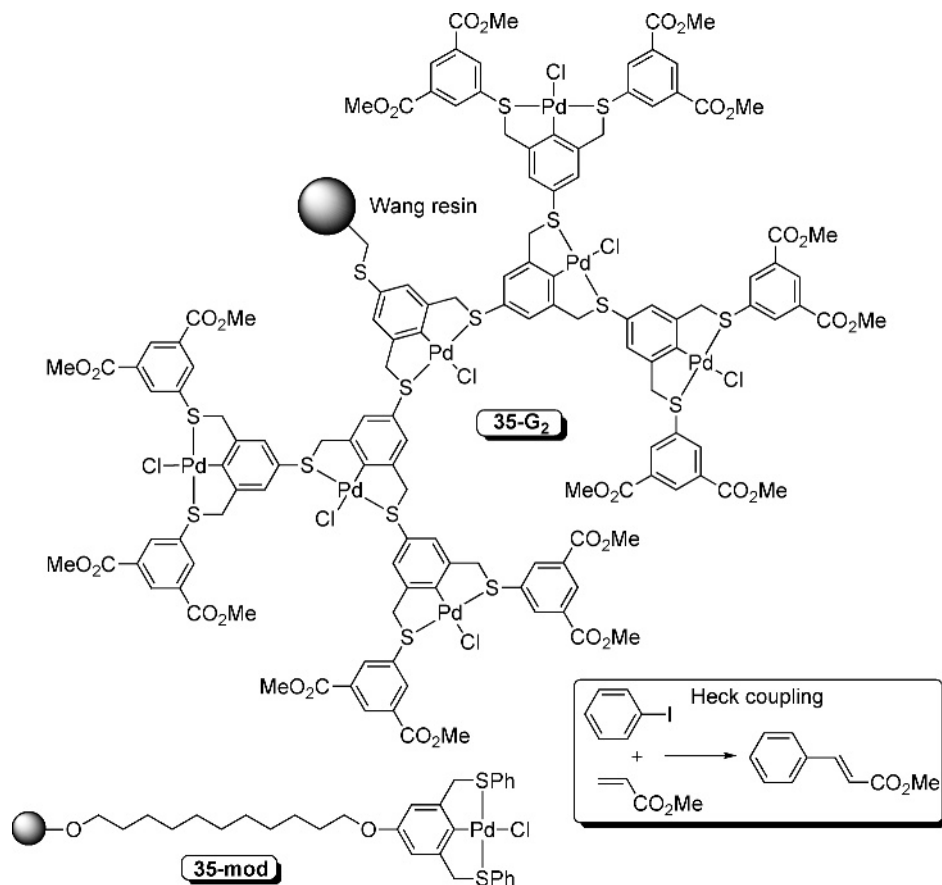


Fig. 18.16. Resin-bound SCS-Pd dendritic catalysts **35-G₂** and monomeric model **35-mod** for the Heck reaction depicted [83].

The slowed reaction rate (no pressure was applied) compared to nonmembrane experiments with nondendritic or peripherally substituted dendrimers (4 h, see Sections 18.2.1 and 18.2.2) was ascribed to mass transfer limitation of the membrane. Catalyst removal was simply achieved by removing the vial from the reaction solution. This study showed that nanofiltration is a viable method for catalyst separation utilizing pincer-substituted dendrimers. Importantly, encapsulating the active Ni center within the dendritic framework completely suppresses the bimetallic catalyst decomposition pathway noted for **3**, see Fig. 18.6, allowing for efficient reuse. Also, a single-pot ‘cascade’-type synthesis utilizing a number of different membrane-isolated dendritic catalysts could be potentially applied.

Reinhoudt and van Veggel have employed surface-bound SCS-Pd pincers to anchor isolated organic dendrimers and Au nanoparticles to self-assembled monolayer-coated Au surfaces [85]. Fig. 18.18 depicts the structures of the components used in this study. In a similar fashion to the previously discussed surface confined SCS-Pd dendrimers **33**, a long-chain alkyl thioether was used to implant a SCS-Pd pincer onto the Au(111)

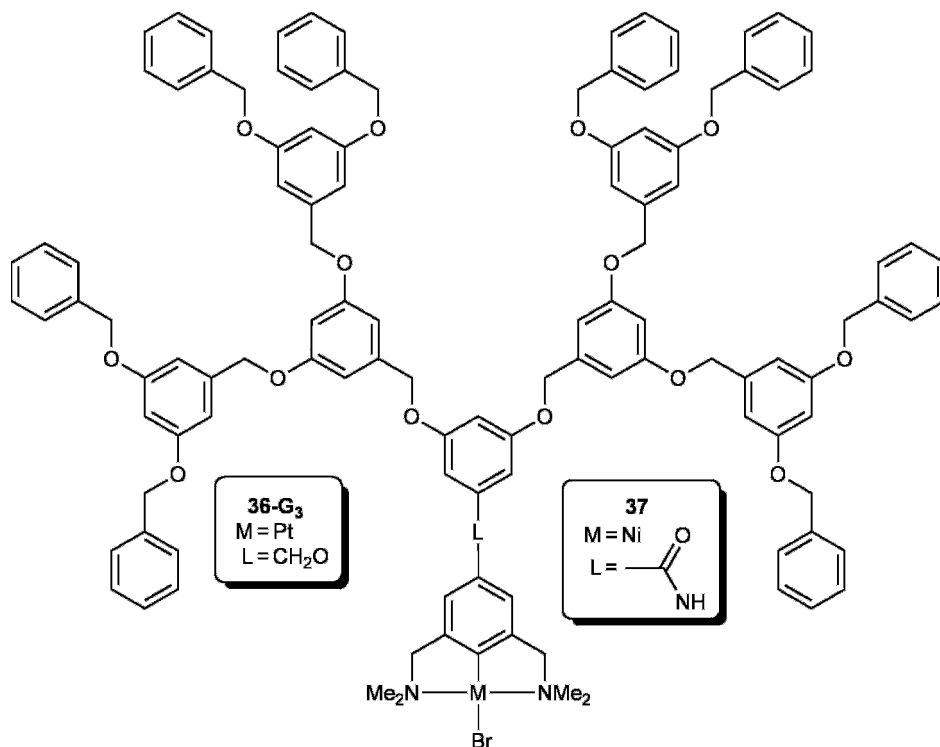


Fig. 18.17. Structure of third-generation core-functionalized NCN-Pt (**36-G₃**) and NCN-Ni (**37**) dendrimers [84].

surface. To avoid surface contamination with AgCl, cationic pincers were preformed prior to surface adsorption. With the pyridine ester dendritic wedge **38**, competitive intramolecular coordination of the thioether tail was noted by ^1H NMR spectroscopy, which may complicate surface attachment. However, quantitative coordination of the phosphine-containing dendron **39** obviated this problem due to the stronger affinity of the P center for Pd.

As shown in Scheme 18.15, surface-bound Fréchet-type dendritic wedges were synthesized by two separate methods [85]. First (method A), monolayers incorporating simple SCS-Pd-pyridine cations of type **40** were treated with solutions of dendrons **38** and **39**. As previously noted, the weaker coordinating pyridine ester wedge **38** caused problems and did not attach to the surface. Conversely, the phosphine dendron **39** was efficiently pulled down to the monolayer surface. The second method (method B) for dendrimer attachment with **42** involved direct insertion of the preformed dendritic thioether into the monolayer. The presence of isolated, surface-bound dendrimers was again verified by tapping mode AFM. An image of the AFM plots from the two synthetic methods is given in Fig. 18.19. Notably, the height profiles and average number of dendrimers per unit area, approximately 50 nanosized particles per 500×500 nm area, obtained for both methods A and B were very similar. Also, the measured dimensions of the nanometer-sized particles (height: 4.1–4.3 nm, width: 15.3–18.8 nm) on the surface

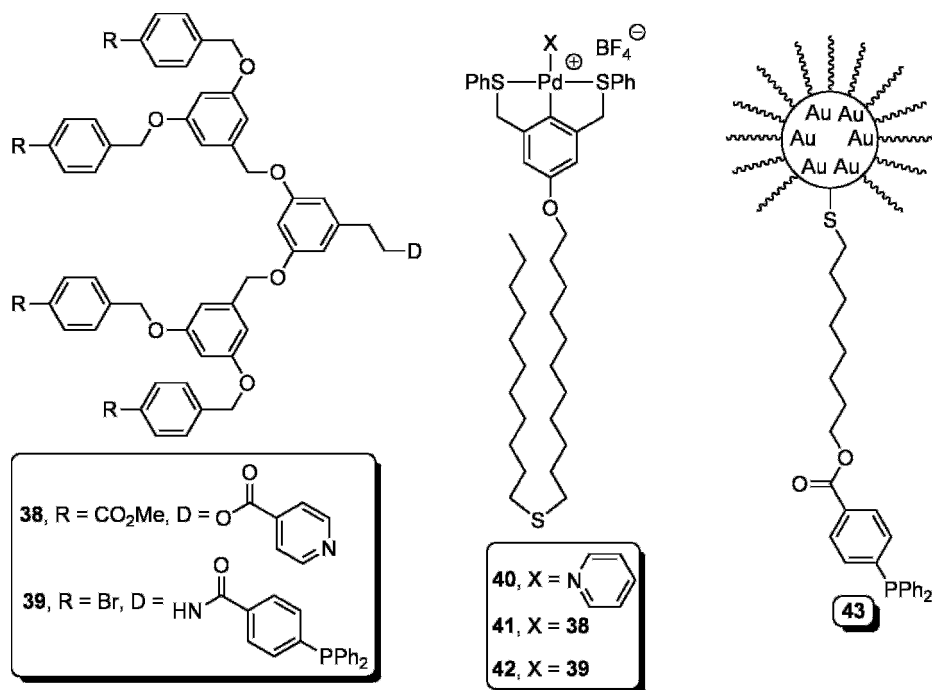
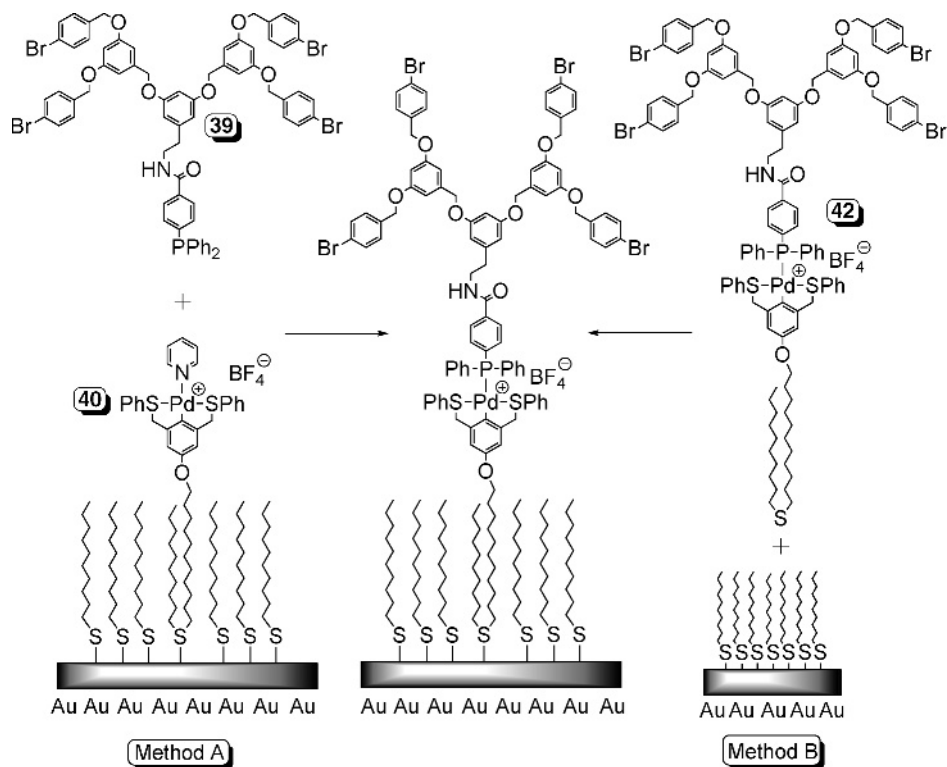


Fig. 18.18. Structure of dendrons **38** and **39**, SCS-Pd pincer **40**, dendritic wedges **41** and **42** and schematic of modified Au nanoparticle **43** [85].

corresponded to the expected size of the dendritic molecules. A number of control experiments were used to rule out simple physisorption processes and confirm that the specific metallopincer–ligand interactions are necessary for the assembly of the observed structures.

The terminal phosphine Au nanoparticles **43** were also complexed onto the pincer-functionalized Au(111) surface by similar methods [85]. To incorporate SCS-Pd coordinating groups on the nanoparticle, the stabilizing monolayer for the gold nanoparticle was impregnated with approximately 20% phosphine-terminated thiols (only one is shown in Fig. 18.18). By TEM, the dimensions for the nanoparticle were found to be 2.0 ± 0.5 nm. Au(111) surfaces containing simple SCS-Pd-pyridine cations **40** were exposed to the modified nanoparticles, see Fig. 18.20. By tapping-mode AFM, the isolated nanosized features found on the surface exhibited heights of 3.5 ± 0.7 nm, in line with size of the gold nanoparticles plus the organic shell. Again, control experiments clearly indicated that both adsorbed SCS-Pd pincers and the phosphine-modified Au nanoparticles are necessary for surface attachment.

A closely related study showed that multiple SCS-Pd-containing dendrons could be attached to a gold surface through a pyridine-functionalized first-generation, surface-confined dendrimers [86]. A monolayer-covered Au(111) surface incorporating a tetra(pyridine) terminated, thioether containing dendrimer **44** was reacted with a solution of SCS-Pd dendron **45**; Fig. 18.21 depicts a schematic representation of the surface-bound complex. Based on tapping-mode AFM, the overall average height of the



Scheme 18.15 Anchoring of SCS-Pd pincer dendron **42** to Au(111) surface [85].

species on the surface increased, but the distribution of values was much wider than previously noted. This indicates that there is incomplete reaction of the terminal pyridine groups, likely due to the steric strain imposed by the proximity of (up to) four dendrons in a limited area. From this, it was proposed that the surface-isolated species contained one to four SCS-Pd dendrons **45**.

18.5 CONCLUSIONS AND FUTURE PERSPECTIVES

As shown in this chapter, the integration of metallopincer functionalities into dendrimers and other dendritic macromolecules is a mature but still developing field. From the first reports on uses in catalysis, the chemistry has blossomed to include important contributions to materials chemistry and surface science as well as continued relevance in the realm of catalyst recycling, either by binding to heterogeneous supports or by homogeneous membrane nanofiltration techniques. One of the main advantages of the employ of pincer groups in these applications is the stability of metal-to-ligand organometallic σ -bond; many metallo dendrimers utilize dative interactions, for example, phosphine-to-metal bonding, that anchor the metal centers to the dendrimer framework. In terms of use as a recyclable catalyst, the dative-bonded complexes are generally more susceptible to

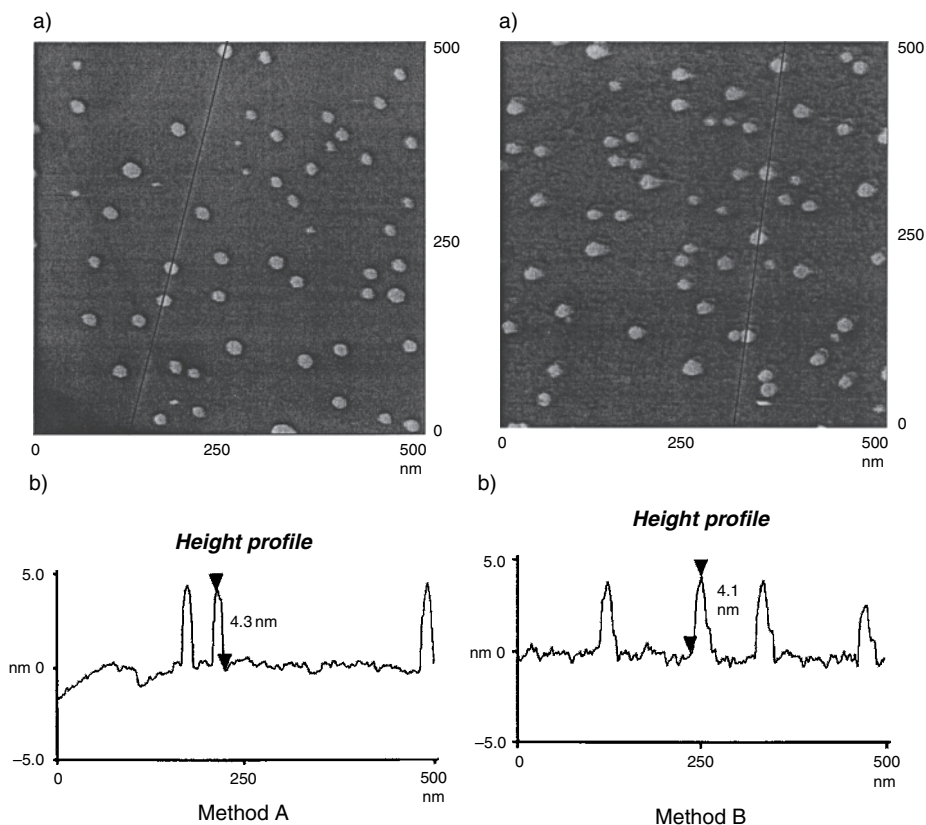


Fig. 18.19. TM AFM height images (500 × 500 nm) and height profiles of monolayer-coated Au(111) surface containing **42** prepared by method A (left) and method B (right). Reprinted with permission from ref. [85], Copyright 2001, American Chemical Society.

metal leaching, a drawback that is most often avoided with the metallopincers. A number of other metallodendrimers have direct σ - or π -bonds between the metal centers and the dendrimer framework [18, 21, 87–91], in particular cyclopentadienyl to iron π -bonds to incorporate ferrocenyl groups [20], but often these M–C linkages are sensitive to, for instance, strongly acidic or basic conditions. The stability of the metallopincer moiety also potentially allows for the use of these dendritic complexes in a much wider variety of conditions than other systems.

The use of dendritic metallopincers in catalysis can certainly be expanded. Unfortunately, the extremely active Heck catalysts based on PCP-, SCS- and SeCSe-Pd functionalities have, in most cases, been shown to simply be precatalysts for as-yet-to-be-identified soluble, highly active Pd(0) species, the actual catalysts of the reaction. Thus, supporting these complexes on dendrimers, if recycling or preventing Pd contamination in the products is the main goal, would not be fruitful due to this rare case of metal leaching from a pincer system. However, dendritic effects may result in differing rates of Pd(0) extrusion and thus affect observed activity. Site isolation within the dendrimer may also

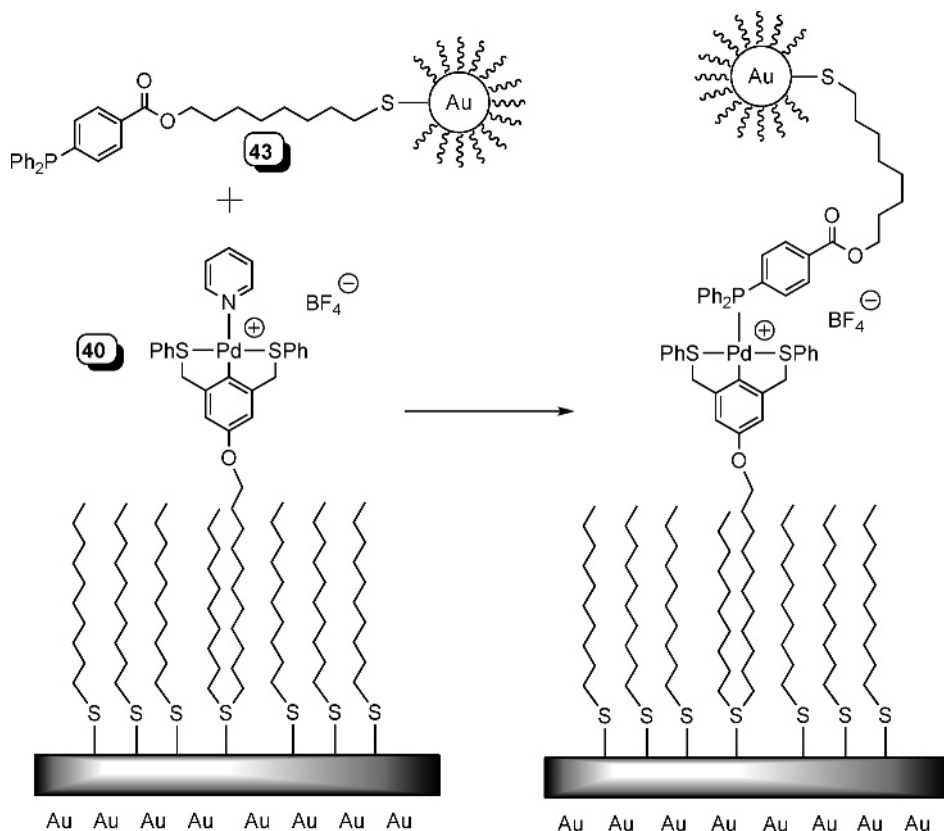


Fig. 18.20. Anchoring of Au nanoparticles **43** to Au(111) surface by SCS-Pd pincers **40** [85].

influence nanoparticle aggregation or coordination environment about a mononuclear Pd(0) species and thus also impact reactivity. In addition, dendrimer-like, rigid, nano-sized multimetallic SCS- and NCN-Pd pincer complexes have been synthesized, tested as catalysts in the Michael addition and subsequently applied in small-scale continuous flow (as opposed to batchwise) membrane reactors for the production of fine chemicals [92–96]. Multimetallic PCP-ligated Pd complexes were also tested as Heck catalysts [97–99]. Trimeric NCN-Pt complexes have been successfully employed as templates for the synthesis of pyridine-containing macroheterocycles [100–103], demonstrating the utility of these species. A selection of these compounds is given in Fig. 18.22. Furthermore, recent results from Szabó [104–116] detail the use of metallopincer complexes as catalysts for stannyl and silyl transfer reactions, the phenylselenylation of organohalides, allylic alkylations of carbonyls, imines and sulfonimines, direct boronation of allylic alcohols and cross coupling reactions. The mechanistic data strongly support an intact Pd metallopincer unit in all instances and that the Pd(II) oxidation state is present throughout. Additionally, a number of active PCP-Ir pincer-based catalysts for alkane [33, 117–126] and amine [127, 128] dehydrogenation have been well studied. Recycling of dendritic versions of these catalysts by nanofiltration can be envisioned as well as an examination of proximity and site-isolation effects.

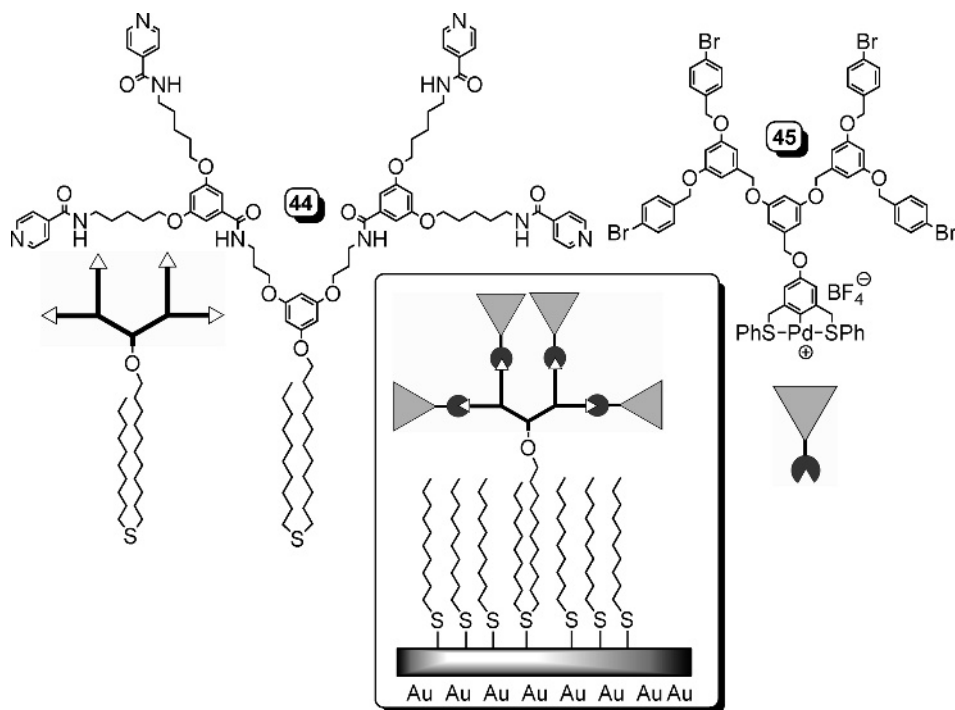


Fig. 18.21. Surface-confined tetra(pyridine) molecule **44** complexed to four SCS-Pd dendrons **45** [86].

In addition, a number of examples of supporting metallopincers on hyperbranched polymers, structurally related but polydisperse relatives of dendrimers, have also been reported. Modified polyglycerols have been utilized as amphiphilic nanocapsules for noncovalent support of NCN metallopincer catalysts and, while the supported catalysts were found to mildly enhance the reaction rate of a double Michael addition of ethyl cyanoacetate with methyl vinyl ketone over a blank, it was significantly less active than its nonencapsulated analog. The nanocapsules were also found to greatly increase the water solubility of the pincer complexes and the size of the supported catalysts allows for separation of catalyst and products by dialysis [129]. Metallopincers containing heavy platinum and iodine atoms were also covalently attached to a polyglycerol hyperbranched polymer, which allowed for visualization by TEM without any additional staining [130]. Chiral polyglycerols, synthesized from pure *S*- or *R*-glycidol, were used as both covalent and noncovalent supports with achiral pincer catalysts in an attempt to induce chirality in products of a double Michael addition [131]. However, no enrichment of a particular enantiomer was observed. A hyperbranched carbosilane polymer supported an active [Pd(NCN)] pincer-based catalyst for the aldol condensation of benzaldehyde with methyl isocyanoacetate [132].

Recently, we have reported the integration of metallopincers into the active site of cutinase, an enzymatic lipase isolated from *Fusarium solani pisi* [133]. In a sense, the effects provided by the tertiary structure of an enzyme, such as active site isolation or cooperative site proximity effects, are conceptually similar to those expressed in

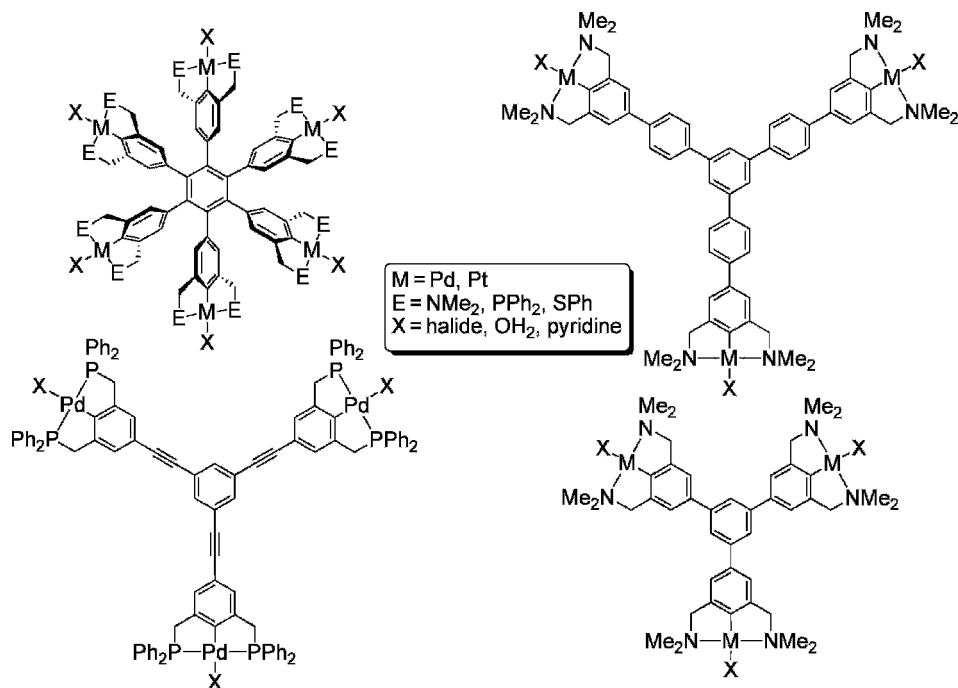


Fig. 18.22. Selection of structures of rigid multimetallic metallopincer complexes [92, 93, 95, 98].

dendritic systems. Additionally, dendrimers are being actively pursued as surrogates for pharmacologically active compounds by acting as nanocapsules for drug delivery and as synthetic immunoreceptors [15, 16]. As the understanding of the interrelation of the chemistry of complex biological systems and man-made macromolecules grows, the applications of dendrimers and metallodendrimers, specifically those incorporating metallopincer functionalities, are sure to increase.

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Perspective and prospects for pincer ligand chemistry

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Inorganic chemistry has undergone a tremendous transformation during the past century, beginning with the development and understanding of coordination chemistry through the work of Alfred Werner. These pioneering studies established the importance of ligands in dictating the properties of a central metal ion and demonstrated the rich diversity possible with a limited number of simple, unidentate ligands. The discovery of ferrocene in 1951 by Kealy and Pauson extended the horizons of inorganic chemistry to include covalent metal–carbon bonds, and in the following decades, hundreds of new cyclopentadienyl complexes appeared in the literature. Paralleling these synthetic achievements were a host of new chemical reaction pathways as the field of organometallic chemistry blossomed into existence. Phosphine donor ligands and their chelates appeared on the scene, and efficient new catalysts such as Wilkinson's catalyst showed unequalled activity and usefulness for the transformation of organic materials. More recently, the cyclopentadienyl analog trispyrazolylborate appeared and once again hundreds of new compounds were synthesized. In the midst of these developments, the specific desire for a meridional tridentate ligand became apparent and the pincer ligand was born out of the early work of Shaw and van Koten. This book is dedicated to presentation of the wide variety of tridentate pincer ligands that have been developed, the chemistry that they enable to take place at a metal center, and the catalytic reactions they can perform.

The range of types of pincer ligands is indeed quite broad. These ligands favor meridional coordination, although facial binding is occasionally observed. The pincers appear most often with a central aryl ring possessing two *ortho*-substituted arms containing donor ligands. The central attachment is typically directly through a carbon of the aryl ring, and the pendant arms can be found with C, N, P, O, S, or Se donor atoms. Other architectures have also been prepared, including pincers with a central pyridine or phosphinine ring, a central N-heterocyclic carbene, a phosphabarrelene, a cycloheptatriene, an anthracene, or a simple divalent carbene carbon. The use of a central diarylimido donor gives rise to a more rigid 'meridional enforcer' geometry for the pincer. Groups on the

pendant arms vary from phosphines, amines, thiols, ethers, and selenides to phosphine-sulfides, iminophosphoranes, and N-heterocyclic carbenes. S-C-S pincers have also been made from bis-diphenylphosphinomethane by conversion to the bis-sulfide and removal of the central hydrogens. Chiral pincer ligands have also been prepared using chiral oxazoline arms attached to a central pyridine (Pybox) or phenyl (Phebox) ring. Chiral-disubstituted tetrahydropyroles have also been employed to introduce chirality in the arms. These ligands impose a C_2 symmetry at the metal center, allowing for investigations of chiral induction in reactive substrates. One interesting class of pincers can be prepared by chloropalladation of difunctional alkynes, giving N-C-S and N-C-O derivatives in which there are a combination of hard and soft donor atoms. Pincer ligands have been supported on montmorillonite and bentonite clays, as well as on dendrimers to allow facile recovery of the metal.

The chemistry of pincer-containing compounds demonstrates a tremendous breadth in their applications. The tridentate P-C-P and N-C-N pincers force allyl ligands to be η^1 , which allows them to be transferred as nucleophiles to acyl derivatives. Palladium complexes with these ligands catalyze the transfer of allyl from tin to benzaldehydes or sulfonimides under mild conditions. These catalysts also transfer allyl from trifluoroallylborates to sulfonimine substrates. In addition, the palladium pincer complexes also serve as catalysts for the synthesis of allylboronic acids, allyltrifluoroborates, and allylstannanes, all of which are useful reagents in allyl transfer reactions. These pincers also catalyze stannylation and selenation of propargyl halides.

A large number of pincer complexes have been reported to be efficient catalysts for the Heck addition of olefins to aryl halides. Many of these pincer complexes have been shown to serve as controlled-release precursors of either a low-ligated Pd(0) species or Pd nanoparticle, as evidenced by poisoning of the activity with liquid mercury or polyvinylpyridine. Other systems appear to keep the metal pincer intact during catalysis, being resistant to poisoning or metal leaching. As a consequence, care must be taken in any newly developed system to carefully characterize the nature of the active catalyst. Fortunately, a number of tests are available (kinetic, three-phase, and poisoning) to sort out if a catalyst is truly homogeneous or if a tethered pincer catalyst stays bound to the substrate. In the absence of such tests, any mechanistic proposals should be regarded with due caution.

While some pincer ligand complexes have shown the ability to readily release the metal from the tridentate environment, other pincer ligands of the C-N-C type pyridine(NHC)₂ have shown high stability which has potential applications in radiopharmaceutical imaging applications. But an even more important application of these highly stable pincer complexes is in the catalytic dehydrogenation of alkanes. Wilkinson's catalyst, RhCl(PPh₃)₃, has been known for decades to be an excellent homogeneous catalyst for alkene hydrogenation, a process that is exothermic by >20 kcal/mol. Since Wilkinson's catalyst is a *catalyst*, this complex must be capable of accelerating both the forward and the reverse reactions. That is, if one could allow Wilkinson's catalyst to interact with an alkane and then remove the small amount of dihydrogen that would be formed at equilibrium, then an alkane could be converted to an alkene (+H₂), at least in theory. In practice, at the high temperatures required for such a reaction to occur and to drive off hydrogen at an appreciable rate, Wilkinson's catalyst decomposes via P-C cleavage, although early experiments by Mary L. Deem indicated that the possibility of this dehydrogenation existed, but were largely unnoticed. It was only with

the development of P–C–P pincer complexes of rhodium and iridium that this goal was ultimately achieved. The groups of Goldman and Jensen both produced strong evidence that both transfer dehydrogenation and catalytic dehydrogenation were possible and that the reason for this possibility was the robust nature of the pincer catalysts with these metals. Variation of the metal, arm linkage, and phosphine alkyl groups led to the development of catalysts that produced alkene (+ dihydrogen) from alkane in concentrations approaching 0.5 M upon reflux in open systems! While terminal olefins are the kinetic products in these dehydrogenations, competitive isomerization to give internal olefins is unavoidable with these catalysts. Perhaps of even more interest is the recent observation that the olefins produced in this reaction can undergo metathesis with Schrock alkylidenes to give re-distributed olefins which in turn are re-hydrogenated back to the saturated hydrocarbons, resulting in an overall ‘alkane metathesis’ process. This discovery has huge potential impact on the petroleum industry, as it will enable redistribution of alkanes from light and heavy hydrocarbon fractions to the more valuable mid-range diesel fractions. All of this chemistry results from the robust thermal stability of pincer ligands on transition metal catalysts.

Where are the developments for pincer chemistry going in the future? While prediction of specific applications are speculative at best, it is clear that the pincer ligand will have a strong impact on future research. The variability in the ligand structure is immense. One has control over donor/acceptor ability at both the central and adjacent side-arm positions. One has control over influences on the steric environment surrounding over 50% of the metal. One can influence electronics by adjustment of the donor ligand set in the meridional coordination environment. The ligand synthesis is relatively straightforward and, importantly, can be designed to be resistant to undesirable chemical side reactions. The important property of high thermal stability for some of the pincer ligand subset is an important accomplishment that should not be underestimated. One of the greatest drawbacks of organometallic catalysts is their lack of tolerance to elevated temperatures. Processes such as P–C cleavage of phosphines, undesirable ligand dissociation, and irreversible ligand oxidative addition are well documented with many catalysts. Some of the pincer systems developed to date appear to avoid these pitfalls, perhaps due to their restrictive environments, at least until much higher temperatures, so it appears as if the development of higher temperature catalytic processes appears to be one area where future growth can be anticipated.

Furthermore, the nature of the meridional coordination of pincers ligands, and along with this their ability to enforce a stereo-specific environment above and below the ML_3 plane, offers a strong opportunity to capitalize upon the potential for chiral synthesis. The ability of the chiral ligand BINAP and its derivatives has demonstrated the potential for such chelating C_2 -symmetric ligands, and chiral pincer ligands offer a similar, if not improved, opportunity for the development of chiral catalysts since the ‘business-end’ of the catalyst is even closer to the stereo-directing environment. As seen in this treatment, chiral enhancements can be observed in Diels-Alder and aldol reactions, dipolar additions to aldehydes, Michael additions, and reductions, leading to appreciable ee’s in the products. It is noteworthy that control of stereodirection in the metallocene single-site catalysts (C_2 vs C_s) has allowed for the efficient stereo-specific polymerization of propylene to give isotactic or syndiotactic polymer. Future developments in this area with pincer complexes are likely, with the ultimate discovery of a ligand with BINAP-type control appearing in the near future.

In summary, tridentate pincer ligands have shown a long period of development and an explosive period of exploitation. The future for further enhancements using this ligand scaffold is bright and lucrative. The ability to produce such a broad spectrum of ligand properties is unparalleled with other ligand systems. Pincer ligands are here to provide an anchor for the future of organometallic chemistry.

Index

- Abnormal NHC, 119
Acceptor, 163, 165, 167
Acceptorless, 163, 167
Acetylene, 157
1,2 addition, 321
Agostic C–C, 93, 101
Aldol condensation, 413, 414, 419, 439
Aldol reaction, 67, 68, 69, 70, 71
Alkene reduction, 73
Alkylation, 316
Alkylidene complexes, 266, 291
Alkyne dimerization, 298
Alkynes, 2, 3, 4, 5, 9, 21
Allenyl silanes, 36, 41
Allenylation, 64, 65
Allenylsilanes, 159
Allenylstannanes, 159
Allylation, 26, 27, 28, 29, 30, 31, 32, 34, 64, 65, 66
 asymmetric, 29, 41
 of electrophiles, 159
 of primary amines, 250
Allyl borates, 28
Allylboronates, 159
Allyl complex, 27, 30
N-allyl functionalized NHC ligands, 126
Allyl stannanes, 26, 27, 28, 30, 32, 34, 35, 41
Allylic alkylation, 158
Allylstannanes, 159
Amido, 287, 288, 300, 302, 306
Amine, 3, 12, 14
Amino acids, 410
Anchimerically, 7
Anthracene, 276
Anticancer, 139
Antimicrobial, 139, 140, 142, 144
 α -arylation of ketones, 158
Arylboronic acid, 155
Asymmetric allylation, 29, 41
Atmospheric pollution, 79
Au (Gold):
 oxidative addition, 225
 transition, 225–6
Axial chirality, 109
B–H activation, 87
Benzimidazolin-2-ylidene ligands, 125, 126, 128, 129, 130
Bimetallic, 313, 314, 326, 330, 332, 336–7, 338, 339
BINOL, 29
1,3-bis(dimethylphosphinomethyl)
 benzene, 275
Bis(iminophosphorane), 314
Bis(phosphinosulfides)phosphinines, 235
Bisligated, 325
Bond activation, 87–90, 92, 93, 95, 96, 97, 102, 103
Boronation, 33, 34, 41
Boronic esters, 250
Bridging carbene, 311, 313, 314, 326, 327, 341
C–C activation, 87, 88, 89, 90, 91, 92, 93, 95, 97, 101
C–C coupling, 153
C–H activation, 88, 89, 90, 91, 94, 95, 96, 97, 103, 173, 292, 304
C–O activation, 87, 101, 102, 103
C–S coupling, 175
C,C,C pincer, 109
C–H oxidative addition, 275
C $\equiv$ C bond, 4, 5
Carbaphosphazene, 335

- Carbene, 151, 171, 311–14, 317, 319, 320, 323, 324, 330, 332, 333, 334, 335, 338, 341, 347, 348, 349, 351
- Carbine, 235, 236, 240, 251, 263–7
- Carbodiphosphorane, 347, 348, 349
- Carbonyl, 158
- Catalysis, 1, 9
- Cationic, 7, 9
- CC triple bond, 3
- Cd (Cadmium), 226–7
- Chelate carbene, 332, 342
- Chelate, 311, 312, 313, 319, 320, 323, 324, 339, 347, 348, 349
- Chiral bisoxazoline pincer complexes, 51
- Chiral diamine pincer complexes, 51
- Chiral phosphine pincer complexes, 278
- Chloropalladation, 2, 3, 4, 5, 14, 16
- Chlorophosphine, 152, 156, 170
- Cisoid, 6
- Co (Cobalt):
- anion sensors, 194–5
 - arene complexes, 189
 - radicals, 194
 - transauration, 194–5
- Computation studies of Pd pincer complex decomposition, 394–6
- Coupling reactions, 304
- Cross coupling reaction, 82
- Cu (Copper):
- aggregates, 220
 - aromatic hydroxylation, 223
 - ate complexes, 220–1
 - C–H activation, 221–2, 223–4
 - cross-coupling with Grignard reagents, 188
 - electron deficient bonding, 220–1
 - electron transfer, 222
 - H/D exchange, 223–4
 - kinetic isotope effects, 222, 223–4
 - O₂ activation, 223
- 2+2 Cycloaddition, 320
- Cyclocarbonylation, 415–18
- Cycloheptatriene, 280, 282
- Cycloheptatrienyl carbene complex, 283
- Cyclometallation, 59, 60, 94, 251, 252
- Dehydrogenation, 153, 163, 165, 167, 169, 170
- Dendritic effects, 432
- DenPols, 413
- Density functional, 353
- Desulfurization, 80, 82, 83
- DFT:
- studies, 165
 - modeling, 30, 31, 37, 38, 39
- N,N'*-diallyl-benzimidazolin-2-ylidene ligand, 127
- Dianion, 235, 262, 264, 266
- Dicarbonylation, 93
- Diels-Alder reaction, 67, 68
- Dinitrogen, 165, 171
- Dinitrogen complexes, 171
- Diphosphine-functionalized benzimidazolin-2-ylidene ligand, 129
- Electrochemistry, dendrimers, 404
- Electrospray mass spectroscopy, 7
- α -Elimination, 171
- Endocyclic pincer carbenes, 278–80
- Enzyme, artificial, 434
- EPR, 241, 244
- ESI-MS, 7, 9
- Ethylene polymerization, 122
- Exaphenylcarbodiphosphorane, 274, 275
- Fe (Iron), 190
- Five-membered, 3, 4, 5, 9
- Fluorescent excimeric mission, 9
- Gas sensor, SO₂, 411–13
- Grafting, Au surfaces, 428
- Grignard reagents, 82
- H (Hydrogen):
- storage, 169
 - transfer, 172
- Halides, 3, 17, 18, 19
- Halobenzene, 155
- Hammett, 18
- Heck catalysis, 388, 392, 393, 394, 395
- Heck reaction, 111, 153, 155, 259, 415, 417
- Heck, 9, 12, 15, 16, 17, 18, 20
- Heck coupling, 12, 16, 20
- Herrmann's palladacycle, 12
- N*-heterocyclic carbene, 151, 171
- N*-heterocyclic carbene ligands, 107
- N*-heterocyclic carbene, 139
- Heterogenized system, 112, 113
- Hexaalkylditin, 34, 35
- Hg (Mercury):
- chiral ligands, 227–8
 - pyridine ligands, 227–8
 - transcyclometallation, 227
- Hydride, 163, 165, 168

- Hydrodesulfurization, 80, 85
Hydrogenation, 9, 118
Hyperbranched polymers, 421
Hypervalent compounds, 357
- iso*-propyl, 71, 73
Imine alkylation, 64
Iminophosphorane, 314, 315, 326, 334
Induction times, 392
Inter- and intramolecular, 275
Intermolecular, 4, 5
2-Iodoresorcinol, 155
IR, 4, 5
Ir (Iridium), 94, 95, 103, 153, 163, 165, 167, 168, 169, 170
 benzimidazole ligands, 206
 C–H activation, 204–206
 haptotropic rearrangement, 204–206
 kinetic isotope effects, 204–206
 luminescence, 206–207
 pyridine donors, 206
- Ketene, 313, 340, 341
Kharasch addition, 402, 404, 407, 408, 410, 411, 427
Kinetic studies of Heck catalysis, 392
Kinetics, 87, 88, 96, 97, 182, 184, 210, 212, 296, 411, 418
- Lanthanide, 266
Leaching studies, 390, 392
Leaching, 113
LEDs, 262
Lewis base, adducts, 319
Li (Lithium):
 heteroaggregates, 184–5
 synthesis, 183–4
Ligand:
 exchange, 3
 introduction route, 155
 synthesis, 288
Luminescence, 262
- Mass spectrometry, 7
Mechanistic studies, 193, 228
Mercury poisoning tests, 17
Mesoporous support, 391, 393
Metallacycle, 2, 6, 81, 85
Metallo-bioconjugates:
 amino acid Pd, 213–16
 amino acid Pt, 213–16
 cutinase-Pd, 212–13
 cutinase-Pt, 212–13
 enzyme-Pd, 212–13, 434
 enzyme-Pt, 212–13, 434
 saccharide-Pt, 216–17
- Metals:
 (other) Alkali metals (Na, K), 332
 Aluminum, Al, 322, 328, 330
 Chromium, Cr, 326
 Germanium, Ge, 332
 Hafnium, Hf, 316
 Lead, Pb, 3, 25, 31
 Lithium, Li, 316, 319, 339
 Palladium, Pd, 152, 153, 154, 158, 159, 161, 170
 Platinum, Pt, 332–6
 Rhodium, Rh, 336, 339, 341
 Samarium, Sm, 324
 Tin, Sn, 156, 359, 363, 364, 369, 373
 Titanium, Ti, 316
 Zinc, Zn, 322, 328, 331
 Zirconium, Zr, 317, 325
- The *trans*-metallating, 3
Methanediide, 311–14, 316, 317, 319, 320, 323, 324, 326, 330
Methanide, 314, 319, 322, 328, 330, 332, 339
Methylene transfer, 98, 99
Michael reaction, 71
Miyauracross-coupling
Mn (Manganese):
 1,4 addition, 188
 arene complexes, 189
 cross-coupling with Grignard reagents, 188
 cyclometalation, multiple, 189
 Li ate complexes, 188
Mo (Molybdenum), Imido ligands, 187
- N–H activation, 90
N,C,N pincer, 34, 36, 46, 110, 182, 185, 192
Nanofiltration, 400, 409, 427, 428, 431, 433
Negishi coupling, 157
Ni (Nickel), 90, 153, 175
 atom transfer radical addition (ATRA), 207
 atom transfer radical polymerization (ATRP), 207
 dendrimer, 402–410, 423, 427–428
 dendritic effects, 208
 Kharasch addition, 207
 Michael addition, 208
 PCP pincer compounds, 82
 phosphine compounds, 82, 85
Ni^{III}, radicals, 408

- NMR, 4, 5, 6, 18, 394
Non-covalent interactions,
 dendrimers, 418–20, 420–5, 427–31
Nucleophilic addition, 3, 5

Olefin, 167–8
 α -olefin, 153, 163, 167–8
Olefin metathesis, 167–8
Organoaluminium compounds, 376, 377
 preparation, 375
 reactivity, 376
 structure, 375
Organoantimony and organobismuth
 compounds, 377, 378, 378, 379
 preparation, 377
 structure, 378
Organosulfur compounds, 79, 80
Organotin compounds, 359, 361, 362, 364,
 366, 369, 370, 371, 373
 aryl transfer, 373, 377
 cyclization, 362
 fluorides, 371, 379
 hydrolysis, 370, 374
 ionization, 363, 365, 367, 372
 preparation, 359
 structure and reactivity, 361
Orthometallate, orthometalation, 274, 275,
 347, 348, 349, 351, 352, 335, 339,
 347, 348, 349, 351, 352
Os (Osmium), 90
Oxidative addition, 2, 3, 17, 18, 87, 88, 94,
 95, 96, 97, 101, 294, 296, 297, 298,
 301, 305

Palladacycles, 1–9, 12, 13, 14, 16, 17, 18, 20
Palladation, 3
Palladacycle, 1–7, 9, 12–21, 385, 388
PCP pincer, 151, 153, 154, 156, 161, 167,
 171, 173, 174, 175
 complexes, 276, 283, 386–95
Pd (Palladium), 152, 153, 154, 158, 159,
 161, 170
 black, 18
 chemoselective metalation, 209
 chiral ligands, 208
 dendrimer, 428
 heck coupling, 208
 ligand introduction route, 208
 main-chain reversible polymers, 210–212
 metalated compounds in
 synthesis, 209, 211
 non-covalent interactions, 210
 pincer complexes, 394
 selective metalation, 208
 single molecule force microscopy, 212
 Michael addition, 208
Pd(0)–Pd(II) catalytic cycle, 392
Pd(0)/Pd(II) catalytic cycle, 13
Pd(II)–Pd(IV) catalytic cycle, 394
Pd(II)/Pd(0) catalytic, 17
Pd(IV) species, 17
Petroleum composition, 79, 82
Pharmaceutical, 139, 140, 146, 147
Phenylboronic acid, 18
Phenylene-bridged dicarbene, 132
Phenylselenation, 159
 η^5 -phosphacyclohexadienyl complexes, 237
 λ^4 -phosphacyclohexadienyl anions, 236
Phosphine, 3, 14, 151, 152, 153, 154, 156,
 161, 162, 164, 165, 167, 170, 287,
 288, 290, 291, 292, 306
 λ^3 -phosphinines, 235, 248
Phosphine-free catalytic systems, 13
Phosphinite, 3, 16, 19, 152, 154, 155, 158,
 161, 162, 163, 165, 167, 168, 169,
 170, 171, 172, 173, 174
Phosphinito, 13, 18
Phosphino-sulfide, 235
Phosphite, 14, 19
Photoluminescence, 116
Pincer, 288
 carbene, 313, 318
 complex, 3, 6, 7, 9, 13, 16, 17, 18, 19, 21,
 151, 153, 155, 156, 158, 159, 161,
 162, 163, 165, 168, 169, 171, 172,
 173, 174
 compound, 51, 82, 83, 85
Pincer carbene complexes, 107–22, 278
(C,C,C) pincer, 312, 313
Pincer-type complexes, 128
 pincer carbene, 349, 351
PNP, 287–306
PNP pincer ligand, 277
Poisoning Studies, 390, 391, 393, 396
Poly(norbornene), 390, 391, 392, 393
Polymer support, 388
Polymerization, 186
Propargylamines, 3
Propargylation, 64, 65
Propargylic oxides, 35
Pt (Platinum), 153, 174349
 bimetallic complex, 219–20
 biomarkers, 216

- chemoselective metalation, 209
- dendrimer, 411–413, 423, 427
- electronic communication, 219–20
- gas diffusion kinetics, 210
- Hammett relation, 209
- luminescence, 217–19
- main chain reversible polymers, 210–212
- metalated compounds in
 - synthesis, 209, 211
- redox, 217
- SO₂ sensors, 210
- Surface plasmon resonance, 216–17
- Pyridine, 3, 5, 7, 9

- Re (Rhenium), 189
- Reactive aryl, 19
- Rearrangement, 349, 335
- Reduction of, 9
- Reductive elimination, 111
- Resorcinol, 152, 155, 170, 173
- Retro-chloropalladation, 3, 16
- Rh (Rhodium), 88, 92, 93, 94, 102, 139, 145, 153, 170
 - η^1 -arene, 203
 - agostic interactions, 201–202
 - allylation of aldehydes, 198
 - aziridination of imines, 202–204
 - benbox, 201–204
 - bimetallic complexes, 195
 - carbene coupling, 202–204
 - C–H activation, 195
 - conjugate reduction, 200
 - cyclopropanation of olefins, 202–204
 - Diels-Alder reactions, 198–9
 - enantioselective catalysis, 198–9
 - fischer carbene, 200
 - imine ligands, 197–8
 - ligand exchange, 194
 - Michael additions, 198–200
 - oxidative addition, 197
 - phebox ligands, 198–200
 - reductive aldol, 200
 - Rh(II), 201–202
 - transcyclometalation, 193
- Ring-opening metathesis polymerization (ROMP), 388
- Ru (Ruthenium), 90, 153, 171–3
 - arene complexes, 192–3
 - bimetallic complex, 219–20
 - diazonaphylene, 191
 - electronic communication, 190–2, 219–20
 - electron transfer, 190–2
 - metalated compounds in synthesis, 191
 - pyrazolyl donors, 192
 - transcyclometalation, 193
- S~P ligands, 250
- S–C–S, 235–69
- S–P–S, 250
- Schrock type catalyst, 167
- SCS pincer complexes, 386, 387, 390, 391, 392, 393, 394, 395
- Selenation, 37
- Self assembled monolayers, 428
- Shilov reaction
- Silver (Ag), 140, 141, 142, 144, 145, 146, 148, 149
- Silver-NHC complex, 109
- Silylation, 36, 37, 41
- Six-membered, 3
- Solid phase synthesis, 426
- Solid support, 390, 392
- Sonogashira coupling, 20–1
- Sonogashira reaction, 112
- Spectroelectrochemistry, 219
- Spirocyclic, spirocyclic, spirocyclic carbene, 313, 330
- Square-planar, 9
- Stability of pincer complexes, 17–18
- Stannanes, 156, 159
- Stannylation, 34, 35, 36, 37, 38
- Stereoselectivity, 28, 30
- Stille coupling, 156
- Styrene, 12, 13, 14, 17
- Supramolecular architectures, 210–212
- Suzuki-Miyaura coupling, 155
- Suzuki reaction, 112, 113
- Suzuki, 9, 12, 18, 19, 20
- Suzuki coupling, 250

- T*-butyl, 163, 165
- TADDOL, 29
- Tandem process, 167
- Thioether, 3, 235, 250, 254, 256, 268
- Thioketone, 235, 269
- Thiolation reaction, 175
- Three phase tests, 390, 391
- Ti (Titanium):
 - olefin polymerization, 186
 - Transauration, 186
 - triflate, bonding modes, 186

- Trans-chloropalladation, 2
- Trans-cinnamates, 16
- Trans*-dihydride iridium (III)
 complex, 283
- Transfer dehydrogenation, 163, 165
- Transmetalation, 1, 2, 3
- The trans-metallating, 3
- Transoid, 6, 7
- Triple carbene, 334
- Tripod, 116
- Tris-*o*-tolylphosphine, 9
- Tropylium ring, 282
- Twist angle, 162
- Vinyllic, 6
- W (Tungsten):
 - C-H activation, 187
 - imido ligands, 187
- X-ray, 162, 172, 174
- X-ray structures, 9, 266
- XAS, 394
- Ylides, 273, 278
- Zn (Zinc), in synthesis, 227