Available online at www.sciencedirect.com

SCIENCE DIRECT®

Coordination Chemistry Reviews 250 (2006) 1851–1888

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

Ortho-metallated transition metal complexes derived from tertiary phosphine and arsine ligands☆

Fabian Mohr[a,*], Steven H. Privér[b], Suresh K. Bhargava[b], Martin A. Bennett[b,c,*]

[a] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., Zaragoza 50009, Spain*
[b] *School of Applied Sciences (Applied Chemistry), RMIT University, GPO Box 2476V, Melbourne, Vic. 3001, Australia*
[c] *Research School of Chemistry, The Australian National University, Canberra, ACT 0200, Australia*

Received 29 June 2005; accepted 6 October 2005
Available online 14 February 2006

Contents

Abstract

This article reviews the synthesis, reactivity and structure of transition metal complexes containing *ortho*-metallated tertiary phosphines and arsines of the type $[2\text{-}R_2EC_6H_4]^-$ (E = P, As; R = various substituents). Available synthetic routes are summarized and some general spectroscopic and structural features are discussed. In subsequent sections, *ortho*-metallated complexes of this type are reviewed, arranged according to the triads of the d-block series. The literature has been covered to the end of 2004. The Appendix lists all known mononuclear, binuclear and trinuclear *ortho*-metallated transition metal complexes which have been structurally characterized by X-ray diffraction.

Keywords: *Ortho*-metallation; C—H activation; Triarylphosphine; Triarylarsine; Transition metal complexes

---

Abbreviations: acac, acetylacetonate; BHcat, catecholborane; Bz, benzyl; cod, 1,5-cyclooctadiene; coe, cyclooctene; Cp, cyclopentadienyl; Cp*, pentamethylcyclopentadienyl; Cy, cyclohexyl; cym, *p*-cymene; dba, dibenzylideneacetone; dmf, *N*,*N*′-dimethylformamide; dmso, dimethylsulfoxide; dppe, 1,2-bis(diphenylphosphino)ethane; dppm, bis(diphenylphosphino)methane; dppp, 1,3-bis(diphenylphosphino)propane; Fc, ferrocenyl; form, di-*p*-tolylformamidinate; mes, mesitylene; OAc, acetate; OBz, benzoate; OTf, trifluoromethanesulfonate (triflate); oq, 8-oxyquinolinate; py, pyridine; pz, pyrazolyl; succ, succinimidate; terpy, terpyridine; THF, tetrahydrofuran; tht, tetrahydrothiophene; tol, tolyl; tpzm, tris(1-pyrazolyl)methane

☆ *Note*: The alternative spellings “metalated” and “metallated” are common in the literature, the former being standard US usage. In this article, we use the latter spelling, with double l, which has the virtue of consistency with the normal spelling of adjectives derived from “metal”, e.g. “metallic” and “organometallic”.

* Corresponding authors. Tel.: +34 976761181/+61 26125 3639; fax: +34 976671187/+61 26125 3216.
E-mail addresses: fmohr@unizar.es (F. Mohr), bennett@rsc.anu.edu.au (M.A. Bennett).

0010-8545/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2005.10.003

1. Introduction

Cyclic organo-transition metal complexes containing a covalent metal–carbon σ-bond and a metal-donor atom bond (Fig. 1) have been a topic of continuing interest since the discovery in the 1960s of the nickel(II) complex **1** [1] and the chloro-bridged platinum and palladium complexes **2** [2] from the reactions of azobenzene with nickelocene and $[MCl_4]^{2-}$ (M = Pd, Pt), respectively. Complexes of this type were initially termed 'intramolecular coordination compounds' but are now more commonly called 'cyclometallated complexes' (Fig. 1A) or, in the case of compounds containing aryl carbon–metal σ-bonds, '*ortho*-metallated complexes' (Fig. 1B).

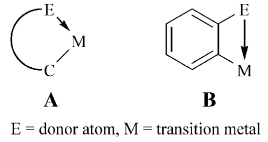
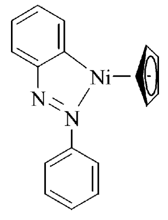
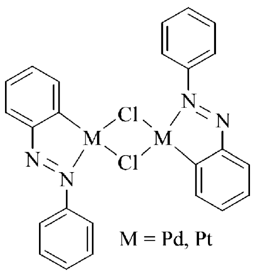


Fig. 1. Schematic representation of cyclometallated complexes.



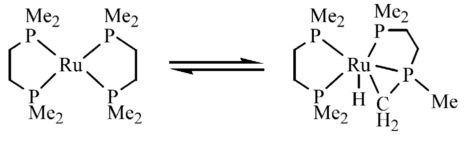
1



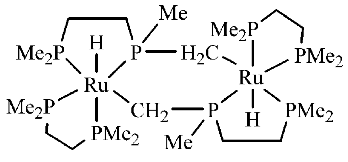
2

The first example of cyclometallation of a tertiary phosphine complex was observed by Chatt and Davidson [3], who showed by elegant deuterium-labelling experiments that the ruthenium(0) complex $[Ru\{Me_2P(CH_2)_2PMe_2\}_2]$ is in tautomeric equilibrium with a ruthenium(II) hydride formed by hydride abstraction from one of the methyl groups of the tertiary phosphine (Scheme 1).

Cotton and coworkers later showed by X-ray crystallography that, in the solid state, the ruthenium(II) complex is a dimer **3** derived by intermolecular cyclometallation [4,5]; whether monomer and dimer co-exist in solution has not been established.

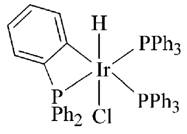


Scheme 1.

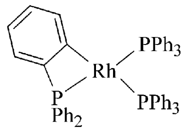


3

In the late 1960s, three groups demonstrated independently the *ortho*-metallation of triphenylphosphine in complexes of univalent cobalt, iridium and rhodium. Parshall observed that treatment of $[CoH(N_2)(PPh_3)_3]$ with deuterium gas exchanged 19 hydrogen atoms, i.e. the *ortho*-hydrogen atoms of the three PPh_3 ligands as well as the hydride ligand, and suggested that the process occurred via *ortho*-metallated species [6]. Bennett and Milner observed that heating of $[IrCl(PPh_3)_3]$ in inert organic solvents gives the colourless *ortho*-metallated hydrido–iridium(III) complex **4** [7], while Keim found that when $[RhMe(PPh_3)_3]$ is heated in solution, methane is eliminated and the orange *ortho*-metallated complex **5** is formed [8]. In the last two cases, it was established by use of the corresponding $P(C_6D_5)_3$ complexes that the abstracted hydrogen originates from the coordinated triphenylphosphine and not from the solvent.



4



5

Cyclometallation reactions represent examples of intramolecular, transition metal-mediated C–H bond activation, a process that is of considerable interest from a synthetic and industrial point of view as part of the quest for efficient methods of functionalizing hydrocarbon feedstocks into value-added products [9]. As a result of this interest, a vast number of cyclometallated compounds containing nitrogen, phosphorus, arsenic, oxygen and sulfur as the donor atoms with almost all the transition elements have now been reported and many have been structurally characterized. Ring sizes range from three to seven, five being the most common. As shown in Table 1, the topic has been reviewed extensively and was the subject of a monograph published in 1986 [10]. The mechanism of cyclometallation reactions, as examples of C–H bond activation, has also been reviewed [11].

Cyclometallated compounds, especially those containing five-membered rings, are finding increasing application as reagents or catalysts for important organic transformations. Cyclopalladated complexes containing N-donor atoms have been used in the synthesis of heterocyclic compounds (see review Refs. [12,14] in Table 1). Cyclopalladated P-donor complexes, such as $[Pd(\mu\text{-}OAc)\{CH_2C_6H_4P(o\text{-}tol)_2\}_2]$ and pincer complexes of the general type [PdX{1,3-

Table 1
Published reviews on cyclometallated complexes

Nature of donor atom (L)	Reference
N, S[a]	[12]
N, P	[13]
N, P, As, O, S	[14]
N, P, As, O, S, halogens	[10]
N, P, S[b]	[11]
N, P, O, S, Se	[15]
N, P, As, O, S	[16]
N, P, As, O, S	[17]
N, S (heterocyclic)	[18]
N	[19]
S	[20]
As	[21]
N, P, As, O, S	[22]
N, P[c]	[23]
N, P, O, S, Se, halogens[d]	[24]

[a] Heterocycle synthesis.
[b] Mechanisms of cyclometallation.
[c] Mainly cyclopalladated complexes.
[d] Five-membered ring complexes.

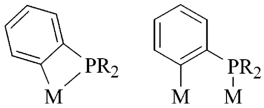


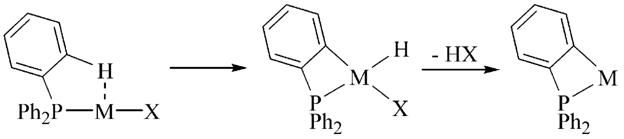
Fig. 2. Chelating (κ^2) and bridging (μ) coordination modes of $[2\text{-}R_2PC_6H_4]^-$.

$C_6H_3(CH_2PR_2)_2\}]$ (X = various anionic ligands; R = various substituents), are active, thermally robust catalyst precursors for carbon–carbon and carbon–heteroatom bond-forming reactions of the Mizoroki-Heck, Suzuki and Stille types [25–31], and iridium P–C–P pincer complexes catalyse alkane dehydrogenation, either in the presence or absence of a hydrogen acceptor [29,32–34].

In this review, we do not traverse this well-trodden ground but concentrate on the longer known *ortho*-metallated complexes of triphenylphosphine and other arylphosphines, containing the ligand system $[2\text{-}R_2PC_6H_4]^-$ and its derivatives, of which many more examples have been described since the publication of the reviews listed in Table 1. It has become evident that these systems can adopt both chelating (κ^2P,C) and bridging ($\mu_2\text{-}P,C$) coordination modes, as shown in Fig. 2; thus, in this respect, they resemble other ligands of small bite-angle such as dialkyldithiocarbamate, $[R_2NCS_2]^-$, bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$, and phosphorus bis(ylides), $[R_2P(CH_2)_2]^-$. In this review, we attempt to summarize the chemistry of complexes containing $[2\text{-}R_2PC_6H_4]^-$, including also the limited information available on their As and Sb analogues.

2. Synthetic methods

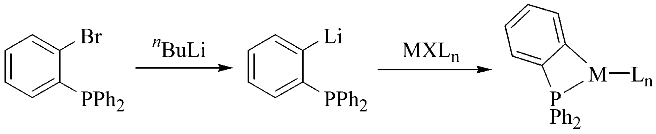
The simplest and most widely used procedure for the preparation of *ortho*-metallated complexes of triphenylphosphine is still the thermal or photochemical activation of the *ortho* C–H bond of the ligand (Scheme 2). In the first step, which can be regarded as an oxidative addition of the C–H bond, the *ortho*-hydrogen atom migrates to the metal atom, a step that may be assisted by a ground state agostic C–H interaction [35,36]. Although the resulting hydrido(aryl) can sometimes be isolated, as in the case of $[IrCl(PPh_3)_3]$, the hydride ligand most commonly undergoes reductive elimination with an anionic ligand, such as H, Me or Cl, as in the case of $[RhMe(PPh_3)_3]$. More generally, for tertiary phosphines R_2P(aryl), *ortho*-metallation is promoted both by the presence of bulky alkyl substituents R on phosphorus (e.g. *t*-butyl or cyclohexyl) and by steric bulk in the coordination sphere (e.g. three or more tertiary phosphines). A combination of enthalpic and entropic effects is likely to be responsible for this behaviour, as discussed by Shaw [37,38]. However, as summarized in the earlier reviews [10,14,16,17,21,22], if the substituent R is *o*-tolyl, metallation always occurs preferentially at the benzylic carbon atom, which leads to a thermodynamically favoured five-membered chelate ring.



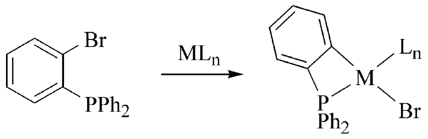
Scheme 2.

There are some examples of the generation of *ortho*-metallated complexes, especially of the early transition elements, by base-promoted removal of a proton from the *ortho*-position of a coordinated arylphosphine. For ligands such as PMe_2Ph, however, the possibility that the proton is abstracted preferentially from a methyl group must be borne in mind; see, for example, Ref. [39].

Especially for arylphosphine complexes of elements of the nickel triad, thermal or photochemical C–H activation is often not applicable because P–Ph bond cleavage either predominates over or occurs together with C–H bond cleavage [40,41]. Two alternative procedures have been developed. Transmetallation, which has been widely used to synthesize five- and six-membered metallacycles containing N- and P-donors [10,14,16–18,22], can also be employed to make complexes containing $2\text{-}C_6H_4PPh_2$, as shown in Scheme 3. This procedure, in which $2\text{-}LiC_6H_4PPh_2$ is generated from $2\text{-}BrC_6H_4PPh_2$, has been applied to Pt, Rh, Ir and Au (see Sections 4.4–4.6). In a complementary approach (Scheme 4), which avoids the lithiation step, the C–Br bond of $2\text{-}BrC_6H_4PPh_2$ undergoes oxidative addition to Pd(0) or Rh(I) (Sections 4.4 and 4.5).



Scheme 3.



Scheme 4.

3. General features

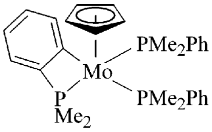
The formation of a four-membered chelate ring M(2-$C_6H_4PPh_2$) derived from PPh_3 is, of course, immediately evident from a single-crystal X-ray structural determination but spectroscopic data can often provide useful preliminary indications. In particular, the ^{31}P chemical shifts of four-membered, κ^2-$C_6H_4PR_2$ complexes are usually highly shielded relative to those of the corresponding monodentate tertiary phosphines or of chelate five-membered rings. This behaviour is normal for complexes containing three- or four-membered rings; see, for example, Refs. [42,43]. In contrast, the ^{31}P chemical shifts of μ-$C_6H_4PR_2$ complexes show no abnormal shielding. Additional bands also appear in the 1560, 1450 and 750 cm^{-1} regions of the IR spectra of 2-$C_6H_4PPh_2$ complexes compared with those of their PPh_3 precursors as a result of the change from mono-substitution to 1,2-disubstitution in the aromatic ring.

The numerous X-ray structures of κ^2-2-$C_6H_4PR_2$ complexes that are now available are listed in the Appendix. In all cases, the four-membered ring is almost flat and the angle subtended at the metal atom (the bite angle) is characteristically small, in the range 63–70°, indicative of strain. Further evidence for strain is obvious from the C–P–M angles as well as the angles subtended at the *ortho*-carbon atom of the *ortho*-metallated ring. The former range from ca. 82–87° (compared to ca. 111–122° in P-coordinated phosphines), whilst the latter fall in the range of 105–107° (compared to ca. 117–122° in non-*ortho*-metallated phosphines). Where comparisons are possible, the M–P and M–C distances generally seem to be in the normal ranges for the particular element and oxidation state. The P–C distances in the cyclometallated rings are sometimes, but not invariably, shorter than those of the other aryl groups.

4. *Ortho*-metallated transition metal complexes

4.1. Sc–Ta, Cr, Mo, W

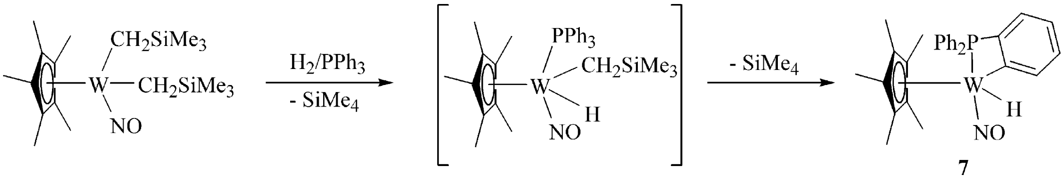
For these elements, only molybdenum and tungsten are so far known to form *ortho*-metallated complexes derived from arylphosphines. The only well-characterized example of a 2-$C_6H_4PPh_2$ complex of molybdenum appears to be the monomeric, diamagnetic, half-sandwich complex **6**, which was isolated in 24% yield from the reaction of $[MoCl_2(Cp)(PMe_2Ph)_2]$ with methyllithium in the presence of one equivalent of PMe_2Ph [44].



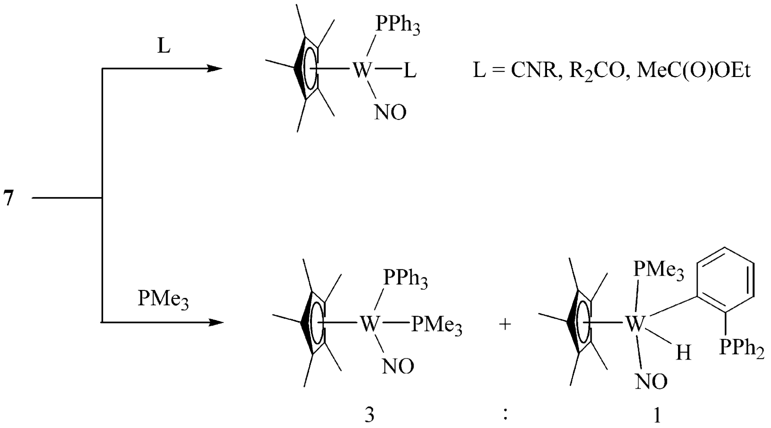
6

The σ-alkyl groups of $[W(Cp^*)(NO)(CH_2SiMe_3)_2]$ are cleaved by dihydrogen at room temperature in the presence of PPh_3 to yield complex **7** as bright yellow, thermally stable crystals (Scheme 5) [45,46]. The reaction probably proceeds stepwise via a 16-electron intermediate $[W(Cp^*)(NO)H(CH_2SiMe_3)]$, which is trapped by PPh_3. The hydride and aryl groups in **7** are mutually *cis* and readily undergo reductive elimination when the complex is treated with a variety of ligands (Scheme 6). Unusually, trimethylphosphine gives not only the expected adduct but, in a competitive reaction, displaces the P-donor end of the 2-$C_6H_4PPh_2$ ligand.

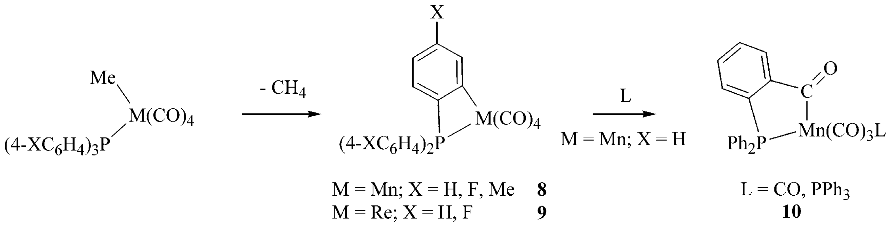
Base-promoted deprotonation of PMe_2Ph has also been used to prepare *ortho*-metallated hydrido-tungsten complexes. Treatment of $[WH_2Cl_2(PMe_2Ph)_4]$ with one and two



Scheme 5.



Scheme 6.



Scheme 7.

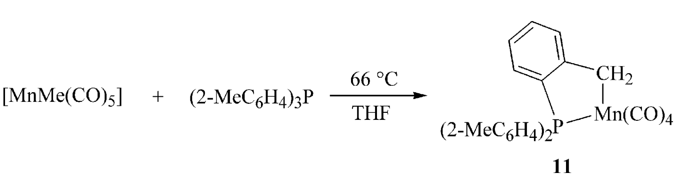
equivalents of strong bases, such as $K[N(SiMe_3)_2]$, ^tBuLi, $^tBuCH_2Li$, MeLi and $LiNMe_2$, gives, respectively, $[WH_2Cl(\kappa^2\text{-}2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3]$ (thermally unstable, yellow crystals) and $[WH_3(\kappa^2\text{-}2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3]$ (orange crystals) [47]. The latter was shown by X-ray crystallography to have a dodecahedral structure; both compounds are remarkable for being non-fluxional eight-coordinate species. The hydride ligands appear to be derived by α- or γ-elimination processes in the anion used in the preparation.

4.2. Mn, Tc, Re

When solutions of *cis*-$[MnMe(CO)_4\{P(4\text{-}XC_6H_4)_3\}]$ (X = H, F, Me) are heated under reflux in toluene, methane is eliminated. The main products are the *ortho*-metallated complexes **8**, which can be isolated after chromatographic separation of by-products in ca. 50% yield (Scheme 7) [48,49]. The distorted octahedral structure of the complex with X = Me has been established by X-ray crystallography [50]. The corresponding rhenium compounds **9** (X = H, F) are obtained similarly from *cis*-$[ReMe(CO)_4\{P(4\text{-}XC_6H_4)_3\}]$ (X = H, F) in refluxing xylene [51]. The less sterically hindered manganese complexes *cis*-$[MnMe(CO)_4L]$ (L = PMe_2Ph, PEt_2Ph) are not metallated in refluxing toluene [49].

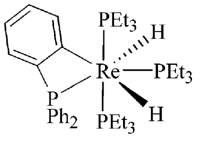
The *ortho*-metallated complex $[Mn(CO)_4(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)]$ **8** (X = H) readily undergoes intramolecular insertion of CO to form the five-membered ring acyl complex **10** on treatment with CO or PPh_3 (Scheme 7) [49]. In contrast to normal behaviour, this reaction cannot easily be reversed, thus indicating the greater stability of the five-membered ring relative to that of its four-membered ring precursor. The same feature is also evident from the exclusive manganation of tri-*o*-tolylphosphine at a methyl group to give the chelate benzyl complex **11** (Scheme 8) [49].

The by-products in the formation of the mononuclear complexes **8** are a mixture of binuclear complexes **12a–c**, which can be formed independently by direct reaction of **8** with their precursors *cis*-$[MnMe(CO)_4\{P(4\text{-}XC_6H_4)_3\}]$ (Scheme 9) [51,52]. Similar complexes having L = L′ = CO result from heating either **8** or the derived acyls **10** with $[MMe(CO)_5]$ (M = Mn, Re) [52]. Tested syntheses of complexes **8** (X = H), **10** (L = CO) and **12** (X = H; L = L′ = CO) have been provided [53].



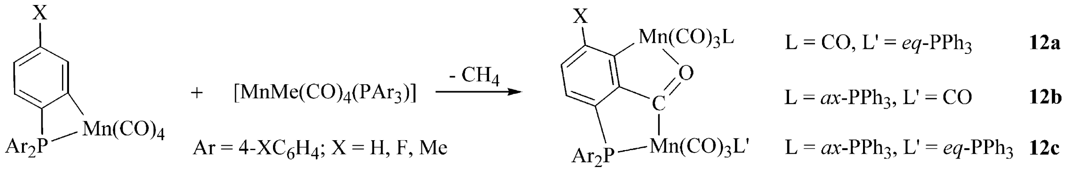
Scheme 8.

The *ortho*-metallated complex $[Re(CO)_3(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(PPh_3)]$ has been mentioned without details as a minor product from the reaction of $[Re_2(CO)_{10}]$ with PPh_3 [54]. Some triphenylphosphine rhenium hydride complexes have been observed to undergo cyclometallation. In an attempt to prepare $[ReH(PEt_3)_5]$ by heating $[ReH_3(\eta^4\text{-}C_5H_6)(PPh_3)_2]$ with an excess of PEt_3, the *ortho*-metallated complex $[ReH_2(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(PEt_3)_3]$ **13** was isolated [55]. The complex is a distorted pentagonal bipyramid with two axial PEt_3 ligands; the latter are replaced by PMe_3 at 80 °C. Spin-saturation transfer experiments show that magnetization is transferred between the hydride ligands even at −20 °C; however, there is no transfer between the hydrides and the *ortho*-proton on the metallated ring, nor between the latter and the *ortho*-protons on the remaining phenyl groups. The octahedral complex $[Re(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(PMe_3)_4]$ **14** has been obtained by treatment of the thioallyl complex $[ReH_2(\eta^3\text{-}C_4H_4S\text{-}\kappa S)(PPh_3)_2]$ with PMe_3 (Scheme 10) [56].

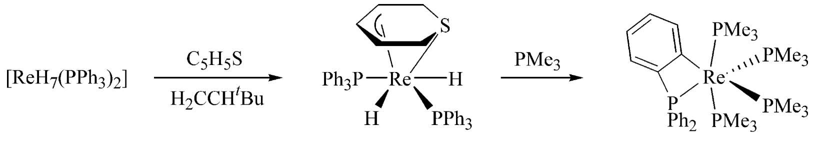


13

In the presence of a large excess of *t*-butylethene, which irreversibly removes hydride ligands, UV-irradiation of $[ReH_5(PMe_2Ph)_3]$ in benzene under dinitrogen affords both a benzene complex $[Re(CH_2CH_2CMe_3)(\eta^6\text{-}C_6H_6)(PMe_2Ph)_2]$ and the *ortho*-metallated complex **15**, which was identified by X-ray crystallography [57].

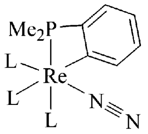


Scheme 9.



14

Scheme 10.



L = PMe$_2$Ph

15

An unusual mode of coordination for an *ortho*-metallated arylphosphine is observed in the dirhenium complex [Re_2Cl_3\{μ-($Ph_2PC_5H_4N$-κ*P*κ*N*)\}$_2$\{μ-$C_6H_4PPh(C_5H_4N)$-κ*P*κ*N*κ*C*\}], which is obtained from the reaction of [$Re_2Cl_6(P^nBu_3)_2$] with diphenyl-2-pyridylphosphine in refluxing methanol [58,59]. In this complex, a phenyl group of one of the three P,N-bridging ligands has lost a hydrogen atom and behaves additionally as a P,C-bridging group (Fig. 3).

No *ortho*-metallated tertiary phosphine and arsine complexes of technetium have been reported.

4.3. Fe, Ru, Os

Zerovalent iron complexes containing 1,2-bis(diphenylphosphino)ethane readily undergo *ortho*-metallation. Photolysis or thermolysis of the etheneiron(0) complex [Fe(η^2-C_2H_4)(dppe)$_2$], or photolysis of the dihydrido-iron(II) complex [FeH_2(dppe)$_2$], gives the *ortho*-metallated hydrido-iron(II) complex **16** (Scheme 11) [60–62], both reactions being readily reversible.

The reversibility of the phenyl ring-to-metal hydrogen transfer is shown by the fact that treatment of **16** with DCl gives a 4:1 mixture of [FeDCl(dppe)$_2$] and [FeHCl\{(2-C_6H_4D)(Ph)$PCH_2CH_2PPh_2$\}(dppe)] [60]. Complex **16** thus acts a source of the iron(0) unit Fe(dppe)$_2$; it is readily protonated by HBF_4 under N_2 to give [FeH(N_2)(dppe)$_2$]BF_4 and decarbonylates aldehydes with formation of [Fe(CO)(dppe)$_2$] [62]. The σ-methyl analogue of **16**, [FeMe\{(2-C_6H_4)(Ph)$PCH_2CH_2PPh_2$\}(dppe)] is made by photolysis of [$FeMe_2$(dppe)$_2$], which induces with loss of methane [63].

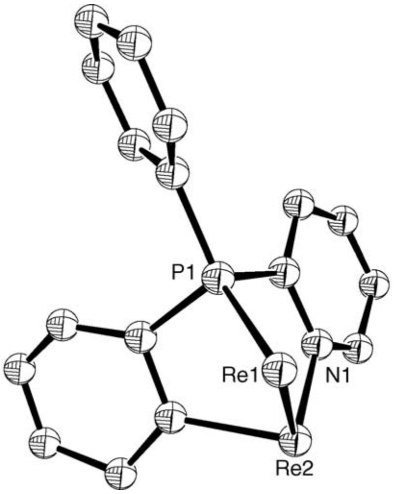
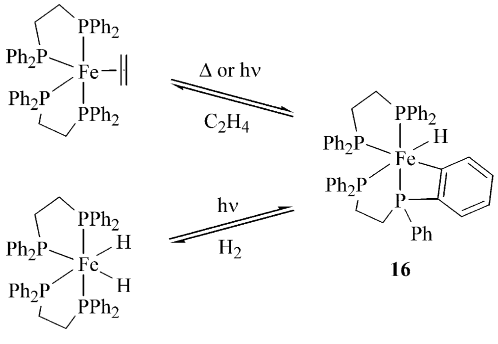


Fig. 3. Central core of [Re_2Cl_3\{μ-($Ph_2PC_5H_4N$-κ*P*κ*N*)\}$_2$\{μ-C_6H_4PPh (C_5H_4N)-κ*P*κ*N*κ*C*\}] showing the unusual coordination mode of the unique diphenyl-2-pyridylphosphine ligand. The other two bridging $NC_5H_4PPh_2$ ligands as well as the three Cl atoms have been omitted for clarity.

The iron(II) complex [$FeH_2(N_2)(PEtPh_2)_3$] has also been briefly reported to undergo spontaneous *ortho*-metallation in daylight, with loss of dihydrogen, but there are no characterizing data for the product [62,64,65]. Irradiation (450 W) of σ-silyl complexes [Fe(Cp)(SiR_3)(CO)$_2$] [$R_3 = MePh_2$, Me_3, MePh(1-$C_{10}H_7$)] with $AsPh_3$ in the presence of Me_3NO is reported [66] to give rare examples of mononuclear *ortho*-metallated complexes derived from triphenylarsine, viz., [Fe(Cp)(CO)(κ^2-2-$C_6H_4AsPh_2$)], but these were not isolated or characterized spectroscopically; the conclusion was based only on the detection of the eliminated silane (R_3SiH) in 85% yield.

Although the crystal structures of both [$RuCl_2(PPh_3)_3$] [67] and [$RuHCl(PPh_3)_3$] [68] show the presence of a weak metal–*ortho*-hydrogen interaction, only the latter compound gives evidence for facile *ortho*-metallation. It behaves similarly to [$CoH(N_2)(PPh_3)_3$] (see Section 1) in its slow reaction with D_2 to give finally [RuDCl\{P(2,6-$D_2C_6H_3$)$_3$\}] [69,70]; a catalytic version of this reaction can be used to prepare fully *ortho*-deuterated PPh_3 [70]. The dinitrogen complex [$RuH_2(N_2)(PPh_3)_3$] behaves similarly. Various reactions based either on zerovalent metal complexes, or on hydrido- and alkyl-complexes of the divalent metals, have been employed to synthesize a range of Ru(II) and Os(II) complexes of 2-$C_6H_4PPh_2$, as discussed below.

Electrophilic olefins, such as dimethyl maleate, are reported to be hydrogenated stoichiometrically by [$RuHCl(PPh_3)_3$], as shown in Scheme 12 [71].



16

Scheme 11.

$$[\mathrm{RuHCl(PPh_3)_3}] + \underset{\mathrm{R = CO_2Me}}{\mathrm{RCH{=}CHR}} \longrightarrow \underset{\mathbf{17}}{[\mathrm{RuCl}(\kappa^2\text{-}2\text{-}\mathrm{C_6H_4PPh_2})(\mathrm{PPh_3})]} + \mathrm{PPh_3} + \mathrm{RCH_2CH_2R}$$

Scheme 12.

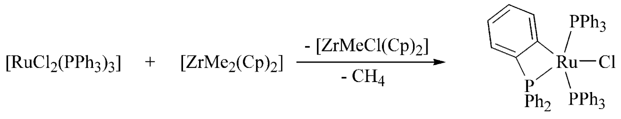
$$[\mathrm{RuDCl(PPh_3)_3}\text{-}d_1] \rightleftharpoons [\mathrm{RuHCl(PPh_3)_3}\text{-}d_2]$$

Scheme 13.

In the solid state, the structure of $[\mathrm{RuCl}(\kappa^2\text{-}2\text{-}\mathrm{C_6H_4PPh_2})(\mathrm{PPh_3})]$ **17** is unknown, but in dioxane it is monomeric and in benzene there is a monomer–dimer equilibrium. It reacts with H_2 and, in the presence of $\mathrm{PPh_3}$, $[\mathrm{RuHCl(PPh_3)_3}]$ is re-formed. It also reacts with CO giving $[\mathrm{RuCl(CO)}(\kappa^2\text{-}2\text{-}\mathrm{C_6H_4PPh_2})(\mathrm{PPh_3})]$; there is no insertion into the Ru–C σ-bond under these conditions.

A somewhat similar stoichiometric hydrogenation occurs in the reaction between $[\mathrm{RuHCl(PPh_3)_3}]$ and 2-hexyne, 3-hexyne or diphenylacetylene, but the main ruthenium-containing product in this case is formulated as $[\mathrm{RuCl}(\kappa^2\text{-}2\text{-}\mathrm{C_6H_4PPh_2})(\mathrm{PPh_3})_2]\cdot\mathrm{CH_2Cl_2}$ **18** [72]. Deuterium gas cleaves the Ru–C σ-bond of **18** but, at least initially, deuterium appears almost exclusively on the aryl carbon, indicating that there is rapid intermolecular equilibration of D and H between the *ortho*-phenyl and hydride sites. The equilibrium shown in Scheme 13 is shifted strongly to the right by zero-point energy differences, thus also accounting for the reported, apparently slow exchange of D_2 with the Ru–H bond of $[\mathrm{RuHCl(PPh_3)_3}]$. The results reported in ref. [72] also explain the different mechanisms for alkyne and alkene hydrogenation catalysed by $[\mathrm{RuHCl(PPh_3)_3}]$.

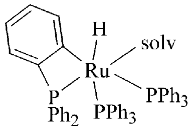
Complex **18** (without $\mathrm{CH_2Cl_2}$ of solvation) has also been obtained from the reaction of $[\mathrm{RuCl_2(PPh_3)_3}]$ with $[\mathrm{ZrMe_2(Cp)_2}]$ (Scheme 14) [73,74], while the corresponding iodo-derivative is formed by the action of methyl iodide on $[\mathrm{RuH}(\kappa^2\text{-}2\text{-}\mathrm{C_6H_4PPh_2})(\mathrm{PPh_3})(\mathrm{OEt_2})]$ (see below) [75]. The ^{31}P NMR spectra of $[\mathrm{RuX}(\kappa^2\text{-}2\text{-}\mathrm{C_6H_4PPh_2})(\mathrm{PPh_3})_2]$ (X = Cl, I) are consistent with a trigonal bipyramidal structure **18**, in which the phosphorus atom of the four-membered ring is *cis* to equivalent $\mathrm{PPh_3}$ ligands.



18

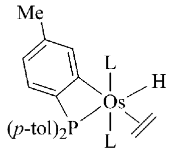
Scheme 14.

The complexes $[\mathrm{RuH}(\kappa^2\text{-}2\text{-}\mathrm{C_6H_4PPh_2})(\mathrm{PPh_3})_2(\mathrm{solv})]$ (solv = $\mathrm{Et_2O}$, THF) **19** are formed, via intermediate hydrido-alkyls containing Ru and Li, from the reaction of an excess of MeLi or $\mathrm{Me_3SiCH_2Li}$ with $[\mathrm{RuHCl(PPh_3)_3}]$ [76]. Ethene reacts with $[\mathrm{RuH_2(PPh_3)_4}]$, $[\mathrm{RuH_4(PPh_3)_3}]$ or complex **19** to give a colourless complex in which the solvent molecule of **19** has been replaced by ethene [75]; there is spectroscopic evidence for the existence of two isomers but the ligand dispositions are not known with certainty. An osmium complex obtained similarly from $[\mathrm{OsH_4\{P(}p\text{-}\mathrm{tol)_3\}_3}]$ and ethene has been assigned structure **20** [77].



solv = $\mathrm{Et_2O}$, THF

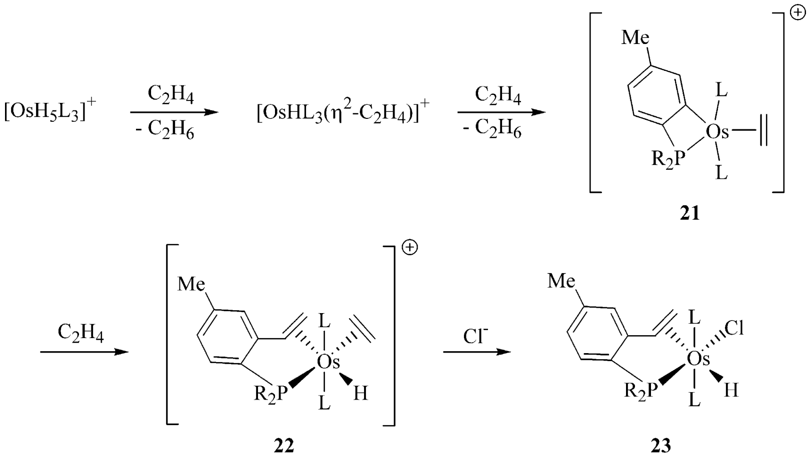
19



L = P(*p*-tol)$_3$

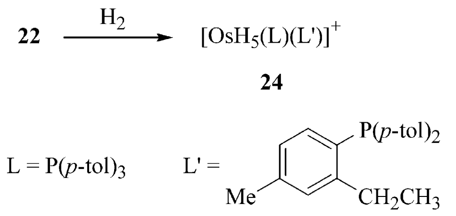
20

The cationic hydride $[\mathrm{OsH_5L_3}]^+$ [L = P(*p*-tol)$_3$], which is generated by protonation of $[\mathrm{OsH_4L_3}]$, undergoes an interesting sequence of reactions with ethene (Scheme 15) [77]. The first



L = P(*p*-tol)$_3$ R = *p*-tol

Scheme 15.

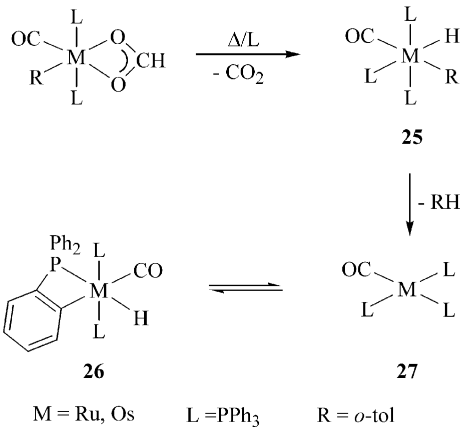


Scheme 16.

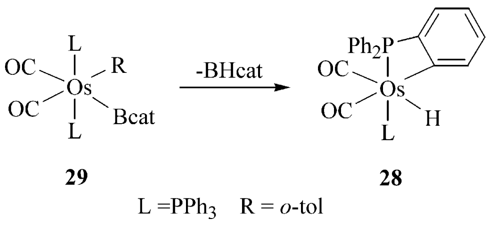
product is the coordinately unsaturated complex $[OsHL_3(\eta^2\text{-}C_2H_4)]^+$, which eliminates ethane above −20 °C to give the *ortho*-metallated complex **21**; the latter undergoes slow insertion of ethene into the Os–C σ-bond to give complex **22** containing the chelate ligand (2-vinyl-4-tolyl)di-4-tolylphosphine. Chloride ion displaces ethene from **22** to give the neutral complex **23**; dihydrogen adds to the vinyl group of **22** to give complex **24** containing (2-ethyl-4-tolyl)di-4-tolylphosphine (Scheme 16).

The six-coordinate formato complexes $[M(o\text{-tol})(\kappa^2\text{-}O_2CH)(CO)(PPh_3)_2]$ (M = Ru, Os) lose CO on heating in the presence of PPh_3 to give initially the *cis*-hydrido(*o*-tolyl) complexes **25** (Scheme 17), which can be isolated in the case of osmium. For ruthenium, the corresponding product immediately eliminates toluene to give the *ortho*-metallated ruthenium(II) complex **26**, many of whose reactions indicate that it is in tautomeric equilibrium with the ruthenium(0) complex **27**. The same type of process occurs, more slowly, when the osmium complex **25** is heated in toluene [78].

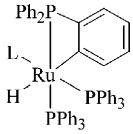
Complex **28** (Scheme 18) is the cyclometallated tautomer of the osmium(0) fragment $Os(CO)_2(PPh_3)_2$, which is generated by heating either the osmium(0) complexes $[Os(CO)_2(PPh_3)_2(L)]$ (L = CH_2O, C_2H_4) in alcoholic solvents [79] or by elimination of catecholborane from the *cis*-(aryl)(boryl) complex **29** in benzene at room temperature [80]. The second method has been used to prepare an isomeric mixture of complexes in which one CO ligand of **28** is replaced by *p*-tolylisocyanide. The X-ray structure of **28** shows that the Os–P distances to PPh_3 and in the four-membered ring differ only slightly [2.3637(7), 2.3512(7) Å, respectively] [80].



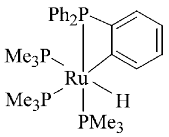
Scheme 17.



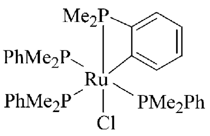
Scheme 18.



L = py **30**, MeCN **31**



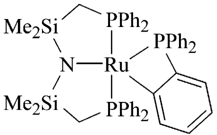
32



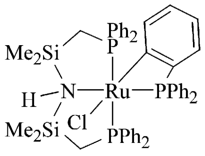
33

Reduction of $[RuCl_2(PPh_3)_n]$ (n = 3, 4) with sodium–amalgam in THF in the presence of pyridine or acetonitrile affords the *ortho*-metallated complexes **30** and **31** in which the hydride ligand is *trans* to the aryl carbon [81], whereas similar reduction of $[RuCl_2(PMe_3)_4]$ in the presence of PPh_3 gives complex **32** in which the hydride ligand is *cis* to the aryl carbon [82]. An X-ray crystal structure of the bromo-derivative of **31** shows the Ru–P distances in the four-membered ring [2.298(2) Å] to be significantly less than those for the unmetallated ligands [2.355(2) and 2.359(2) Å]. Treatment of **32** with methyl iodide replaces hydride by iodide, the final stable isomer of the product having a *mer*-arrangement of PMe_3 ligands. Reaction of the Grignard reagent $[MgCl(2\text{-}CH_2C_6H_4C_6H_4CH_3\text{-}2')]$ with *trans*-$[RuCl_2(PMe_2Ph)_4]$ causes *ortho*-metallation of one of the PMe_2Ph ligands, complex **33** being isolated in 41% yield [83].

Coordinated triphenylphosphine in the five-coordinate amido-phosphine complex $[RuCl(PPh_3)\{N(SiMe_2CH_2PPh_2)_2\text{-}\kappa N\kappa^2 P\}]$ readily undergoes *ortho*-metallation, with loss of HCl, on reaction with MeLi, Me_3SiCH_2Li or C_3H_5MgBr, to give $[Ru(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)\{N(SiMe_2CH_2PPh_2)_2\}]$ **33a**. The same precursor also isomerizes, either on recrystallization or on treatment with PEt_3, to give the octahedral complex **33b**, as a result of hydrogen transfer from PPh_3 to the amido nitrogen atom. The X-ray structure of **33b** shows the presence of a hydrogen bond between the N–H group and the chlorine atom. The four-membered ring in **33a** is cleaved irreversibly by H_2 (1 bar) to give $[RuH(PPh_3)\{N(SiMe_2CH_2PPh_2)_2\}]$ [83a].



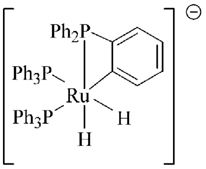
33a



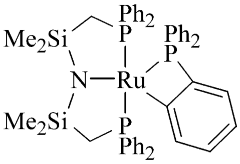
33b

The anionic bis(hydrido) *ortho*-metallated complex K[$RuH_2(\kappa^2$-2-$C_6H_4PPh_2)(PPh_3)_2$], solvated with ether and naphthalene, has been isolated from the reduction of [$RuHCl(PPh_3)_3$] with $KC_{10}H_8$ and structurally characterized [84]. The hydride ligands in the distorted octahedral anion **34** were not located directly but their positions can be inferred to be as shown. Two molecules of the anion are bridged by potassium ions. The Ru–P distances (2-$C_6H_4PPh_2$, PPh_3) that are *trans* to hydride in the independent molecules are similar (2.34–2.35 Å) and slightly greater than the Ru–P distances *trans* to the aryl carbon (2.30–2.32 Å). The complex has been investigated and patented as a catalyst for the homogeneous hydrogenation of aldehydes, ketones, carboxylic acid esters and nitriles [85–87].

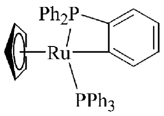
Reaction of Li[*fac*-$RuH_3(PPh_3)$] with [IrCl(cod)]$_2$ in a 2:1 molar ratio gives as the kinetic product the binuclear tri-μ-hydrido complex [(cod)Ir(μ-H)$_3$RuH($PPh_3)_3$], which isomerizes to the structurally characterized di-μ-hydrido complex [(cod)Ir(μ-H)$_2$RuH($PPh_3)_2$]. This loses H_2 reversibly to give an *ortho*-metallated complex formulated as [(cod)Ir(μ-H)RuH(κ^2-2-$C_6H_4PPh_2)(PPh_3)_2$] **34a**, in which the aromatic ring of the *ortho*-metallated unit may be attached through its π-electrons to the adjacent iridium atom [87a].



34



34a

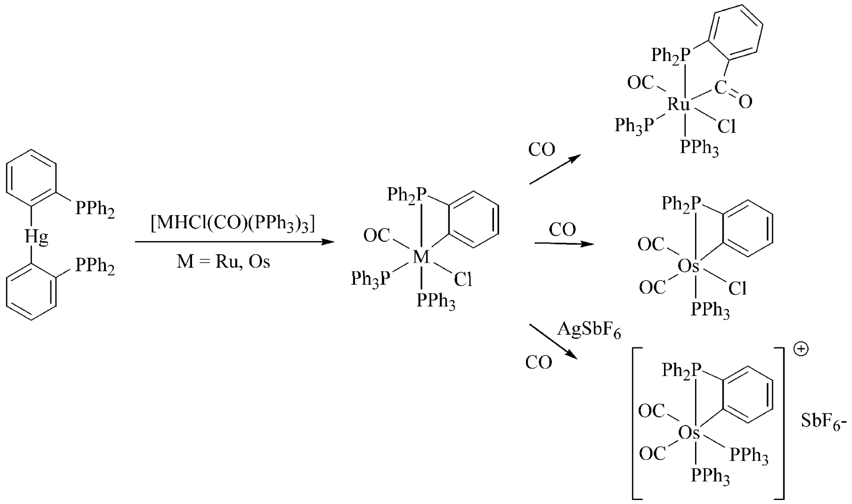


35

Although most 2-$C_6H_4PPh_2$ complexes of ruthenium and osmium can be derived conveniently from precursors containing coordinated PPh_3, the transmetallation reaction between the organomercury compound [Hg(κC-2-$C_6H_4PPh_2)_2$] and [MHCl(CO)($PPh_3)_3$] (M = Ru, Os) has been used to synthesize a variety of compounds, as shown in Scheme 19 [88].

Half-sandwich η^5-cyclopentadienyl or η^6-arene complexes of Ru and Os provide an excellent demonstration of the importance of steric effects in promoting *ortho*-metallation of triphenylphosphine. The complex [Ru(κ^2-2-$C_6H_4PPh_2$)(Cp)(PPh_3)] **35** is obtained by elimination of methane from the methyl compound [RuMe(Cp)($PPh_3)_2$] in refluxing decalin, whereas the corresponding $PMePh_2$ and PMe_2Ph methyl complexes do not undergo *ortho*-metallation below their decomposition points [89–91]. Complex **35** is also obtained directly from the reaction of [RuCl(Cp)($PPh_3)_2$] with Me_3CCH_2MgBr in ethylcyclohexane at 60–80 °C [92].

The more crowded compound [RuMe(Cp^*)($PPh_3)_2$] cannot be detected, even at room temperature, owing to its spontaneous *ortho*-metallation [93]. Thermolysis of [RuMe(Cp^*)($PMe_2Ph)_2$] in benzene at 120 °C for 48 h gives the phenyl derivative [RuPh(Cp^*)($PMe_2Ph)_2$]; when the temperature is raised to 140 °C this complex loses benzene giving the *ortho*-metallated product [Ru(κ^2-2-$C_6H_4PPh_2$)(Cp^*)($PMe_2Ph)_2$] [94], which is also obtained directly from [RuMe(Cp^*)($PMe_2Ph)_2$] in toluene at 100 °C [93].

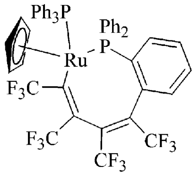


Scheme 19.

Lehmkuhl and co-workers [92,93] have adduced evidence for a 16-electron intermediate Ru(κ^2-2-$C_6H_4PR_2$)(Cp) in the reactions of cyclopentadienyl ruthenium(II) alkyls. Thus, whereas the neopentyl complex [Ru(CH_2CMe_3)(Cp*)(PMe_3)$_2$] reacts with C_6D_6 to give [Ru(C_6D_5)(Cp*)(PMe_3)$_2$] and d_1-neopentane, the complex [Ru(CH_2CMe_3)(Cp)($PMePh_2$)$_2$] reacts with C_6D_6 give the corresponding C_6D_5 complex and undeuterated neopentane. Likewise, the reaction of [RuCl(Cp)(PPh_3)$_2$] with Me_3CCH_2MgBr and subsequently C_6D_6 gives [Ru(C_6D_5)(Cp)(PPh_3)$_2$] and undeuterated neopentane. The last two results appear to be consistent with initial loss of neopentane to give an intermediate Ru(κ^2-2-$C_6H_4PR_2$)(Cp), which adds C_6D_6. Whether deuterium is present in the *ortho*-position of the arylphosphines was apparently not investigated, though it is implied by the mechanism. These results are not consistent with those of Diversi et al. [94] in the Cp* series, which demonstrate that the phenyl derivative is formed *before* the *ortho*-metallated complex. Moreover, according to DFT calculations [94], although the transformation from the neopentyl to the *ortho*-metallated complex is exothermic (−27.9 kcal/mol), the formation of the phenyl complex from the latter is endothermic (+3.2 kcal/mol). A re-examination of the experimental results is clearly warranted.

Treatment of the σ-alkyls [RuR(Cp)(PPh_3)$_2$] (R = Me, Et, ^{n}Pr) with ethene (5–8 bar) gives the (2-vinylphenyl)diphenylphosphine hydrido complex [RuH(2-CH_2=$CHC_6H_4PPh_2$)(Cp)], which is presumed to result from insertion of ethene into the Ru–C_{aryl} bond of an *ortho*-metallated intermediate, as shown in Scheme 20 [95] (cf. Scheme 15).

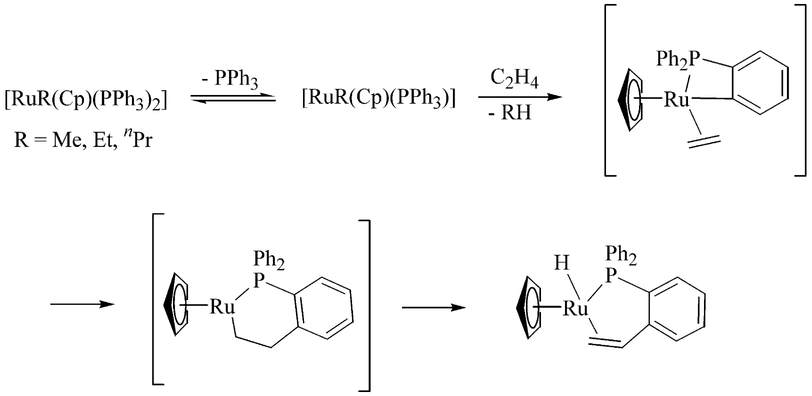
Under 50 bar ethene, however, the product is [RuR(Cp)(PPh_3)(η^2-C_2H_4)], because the intermediate RuR(Cp)(PPh_3) binds ethene more rapidly than it undergoes *ortho*-metallation. The metallacycle **36** is obtained in poor yield by double insertion of hexafluoro-2-butyne into the Ru–C_{aryl} bond of [Ru(κ^2-2-$C_6H_4PPh_2$)(Cp)(PPh_3)] **35** [90].



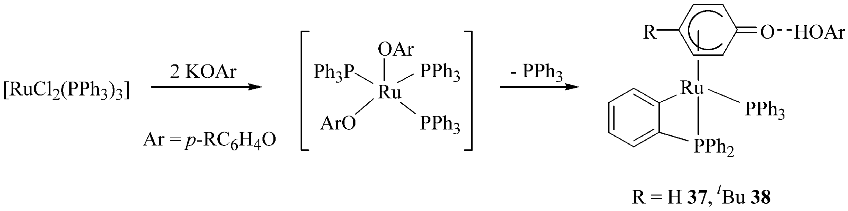
36

The η^5-cyclooctadienyl complex [Ru(κ^2-2-$C_6H_4PPh_2$)(η^5-C_8H_{11})(PPh_3)] is obtained by heating [$RuH_2(PPh_3)_4$], [$RuH_4(PPh_3)_3$] or [RuH(κ^2-2-$C_6H_4PPh_2$)(PPh_3)$_2$(OEt_2)] with 1,5-cyclooctadiene [75] and the η^5-oxacyclohexadienyl complexes **37** and **38** are obtained from the reaction of [$RuCl_2(PPh_3)_3$] with two equivalents of potassium aryloxide at room temperature (Scheme 21) [96]. These complexes, which are probably formed by loss of PPh_3 from a Ru(OAr)$_2$(PPh_3)$_3$ intermediate and subsequent *ortho*-metallation, contain one or more molecules of the phenol hydrogen-bonded to the keto group of the η^5-ArO unit.

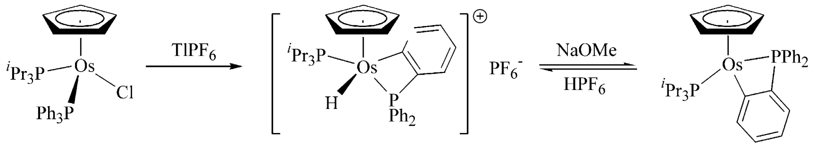
Spontaneous *ortho*-metallation of PPh_3 is induced by abstraction of Cl^- from [OsCl(Cp)(PPh_3)(P^iPr_3)] with $TlPF_6$, as shown in Scheme 22 [97]. The resulting hydrido–osmium(IV) cation **39** is deprotonated reversibly by NaOMe to give the neutral osmium(II) complex **40**. There is no competing hydride abstraction from P^iPr_3 in the $TlPF_6$ reaction, indicative of the greater stability of metal–aryl versus metal–alkyl bonds. In **39**, the hydride is transoid to the phenyl carbon atom and is cisoid to both phosphorus atoms, the Os–H distances in independent molecules being 1.50(6) and 1.49(7) Å. The Os–C bond in **39** is cleaved by methanol to give [OsH(Cp)(PPh_3)(P^iPr_3)].



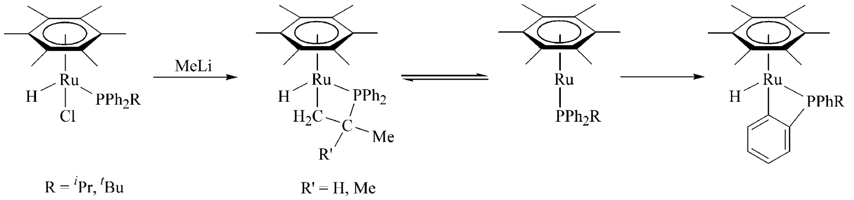
Scheme 20.



Scheme 21.



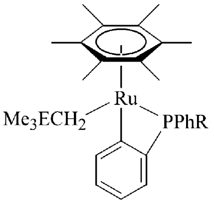
Scheme 22.



Scheme 23.

Treatment of [RuHCl(η^6-C_6Me_6)(L)] (L = PPh_3, P^iPrPh_2, P^tBuPh_2) with MeLi, PhLi or Red-Al gives, as the final products, *ortho*-metallated hydrido-ruthenium(II) complexes, which are probably formed by intramolecular C–H oxidative addition in ruthenium(0) intermediates Ru(η^6-C_6Me_6)(L) [98]. In the cases of L = P^iPrPh_2, P^tBuPh_2, the first products isolated are derived by C–H activation of the isopropyl or *t*-butyl groups; they subsequently isomerize to the thermodynamically more stable aryl complexes via reversible hydride migration in Ru(η^6-C_6Me_6)(L). The process is illustrated in Scheme 23.

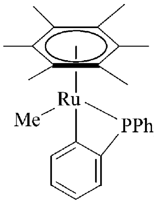
Reaction of [$RuCl_2$(η^6-C_6Me_6)(L)] (L = PPh_3, $PMePh_2$) with an excess of Me_3SiCH_2MgCl in pentane gives *ortho*-metallated complexes **41** and **42** in ca. 20% yield; the lithium reagent Me_3SiCH_2Li gives no product. The diastereomers of **42** can be separated by chromatography [99].



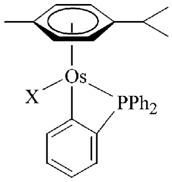
R = Ph; E = Si **41**
R = Me; E = Si **42**
R = Ph; E = C **43**
R = Me; E = C **44**

The corresponding reactions with Me_3CCH_2MgCl give the neopentyl analogues **43** and **44** (only the *R*,*S*:*S*,*R* diastereomer), together with 2,2-dimethylruthenacyclobutanes, which do not survive chromatography [100]; on elution with $CHCl_3$ the latter are transformed into *ortho*-metallated chloro-complexes (Scheme 24) [101].

In the presence of [Fe(Cp)$_2$]PF_6 as an electron-transfer catalyst, the dimethyl compound [$RuMe_2$(η^6-C_6Me_6)(PPh_3)] in benzene undergoes *ortho*-metallation, with loss of methane, to give complex **45** [102]. Similar reactions occur with the corresponding, less bulky, $PMePh_2$ and PMe_2Ph derivatives, but with increasing competition from intermolecular C–H bond activation of benzene.



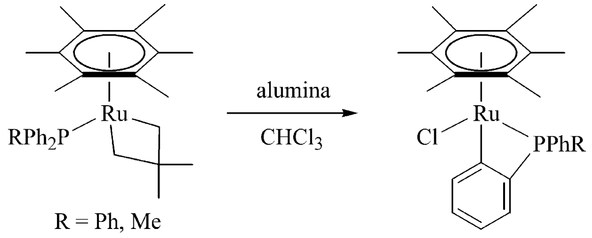
45



X = Me **46**
X = Cl **47**

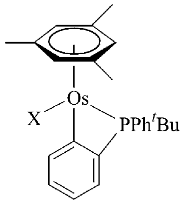
The salt [RuMe(η^2-C_2H_4)(η^6-C_6Me_6)(PPh_3)]BF_4 decomposes in CH_2Cl_2 over a 12 h period to give the (2-vinylphenyl) diphenylphosphine complex [RuH(2-CH_2=$CHC_6H_4PPh_2$)(η^6-C_6Me_6)]BF_4, probably by insertion of ethene into an *ortho*-metallated intermediate [Ru(κ^2-2-$C_6H_4PPh_2$)(η^6-C_6Me_6)]$^+$ [103] (cf. Schemes 15 and 21).

The *ortho*-metallated osmium(II) *p*-cymene complexes **46** and **47** have been isolated from the prolonged reaction of [$OsCl_2$(η^6-cym)(PPh_3)] with Al_2Me_6 [104]. On heating in 2-propanol/Na_2CO_3, the η^6-mesitylene complex [$OsCl_2$(η^6-mes)(PPh_3)] is converted first into [OsHCl(η^6-mes)(PPh_3)] and then into the mesitylene analogue of **47**. The mesitylene $PPh_2{}^tBu$ complex undergoes *ortho*-metallation more rapidly under the same conditions, giving a mixture of the chloro- and hydrido-



Scheme 24.

complexes, **48** and **49**, respectively, each as a pair of diastereomers; the chloro-complexes were separated by chromatography [105]. The corresponding ruthenium complexes do not undergo *ortho*-metallation on reaction with 2-propanol/Na_2CO_3. The hydrido(methyl) and hydrido(phenyl) complexes $[OsH(R)(\eta^6\text{-mes})(PPh_3)]$ (R = Me, Ph) undergo *ortho*-metallation in benzene, toluene or cyclohexane in the presence of alumina or silica, giving $[OsH(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(\eta^6\text{-mes})]$; in the aromatic solvents, there is competing intermolecular C–H activation (ca. 20%) giving $[OsH(R)(\eta^6\text{-mes})(PPh_3)]$ (R = Ph, tol) [105].



X = Cl **48**
X = H **49**

Although there are far fewer complexes of Ru and Os containing $\mu\text{-}2\text{-}C_6H_4PPh_2$ than $\kappa^2\text{-}2\text{-}C_6H_4PPh_2$, amongst the nine complexes that have been isolated from the thermolysis of a 1:2 mixture of $[Os_3(CO)_{12}]$ and PPh_3 in xylene are various triosmium complexes containing the $2\text{-}C_6H_4PPh_2$ unit. $[Os_3(CO)_9(PPh_3)(\mu\text{-H})(\mu_2\text{-}2\text{-}C_6H_4PPh_2)]$ (Fig. 4I) contains a $2\text{-}C_6H_4PPh_2$ group bridging two osmium atoms [106]. In $[Os_3(CO)_8(\mu_2\text{-}PPh_2)(\mu\text{-Ph})(\mu_3\text{-}2\text{-}C_6H_4PPh)]$ (Fig. 4II) there is a bridging phosphido group, $2\text{-}C_6H_4PPh$, and the cleaved phenyl group is bridging two metal atoms in the cluster. $[Os_3(CO)_8(\mu_3\text{-}2\text{-}C_6H_4PPh_2)(\mu\text{-H})(PPh_3)]$ (Fig. 4III) contains a bridging $2\text{-}C_6H_4PPh_2$ group, but in this case the *ortho*-carbon atom of the substituted phenyl ring also bridges two osmium atoms in an asymmetrical fashion leading to significantly different Os–C distances to the bridging aryl carbon [2.16, 2.34 Å]. A further complex, $[Os_3H(CO)_7(\mu_2\text{-}PPh_2)(\mu_3\text{-}2\text{-}C_6H_3C_6H_4PPh_2)]$ (Fig. 4IV) contains a unit derived by formal insertion of a C_6H_3 fragment into a $\kappa^2\text{-}2\text{-}C_6H_4PPh_2$ group [107,108]. More recently, the triosmium complex $[Os_3(\mu\text{-H})_2(CO)_9(\mu_3\text{-}2\text{-}C_6H_4PPh)]$ (Fig. 4V), in which the phosphorus atom of the $2\text{-}C_6H_4PPh$ group bridges two osmium atoms, has been formed in high yields by refluxing $[Os_3(\mu\text{-H})(CO)_{10}(\mu_2\text{-}PPh_2)]$ in *n*-octane [109].

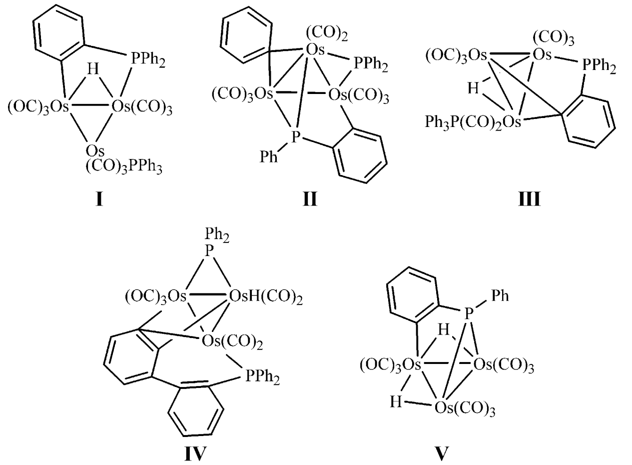


Fig. 4. Triosmium clusters containing $2\text{-}C_6H_4PPh_2$ in various coordination modes [106–109].

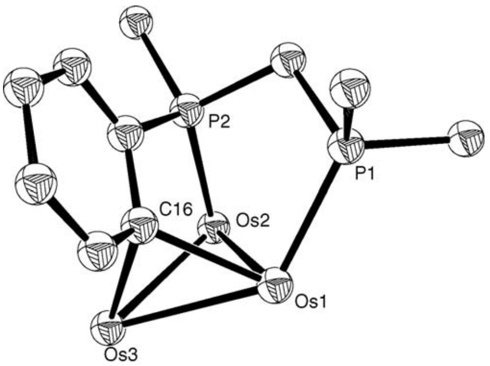


Fig. 5. Central core of the metallated complex derived from $[Os_3(CO)_{10}(\mu\text{-dppm})]$ [110]. The CO ligands as well as the bridging hydride have been omitted for clarity. Only the ipso-carbon atoms of one the PPh_2 phenyl groups are shown.

Metallation at a phenyl group occurs when $[Os_3(CO)_{10}(\mu\text{-dppm})]$ is heated in toluene to give $[Os_3H(CO)_8\{\mu\text{-}\kappa P,P\text{-}\mu_2\text{-}\kappa C\text{-}C_6H_4P(Ph)CH_2PPh_2\}]$ [110]. The phenyl group bridges a pair of osmium atoms, as shown in Fig. 5. The complex is electronically unsaturated, as demonstrated by the reversible uptake of CO accompanied by transfer of hydride from a bridging to terminal position [110].

A binuclear complex formulated as $[Os_2(CO)_6(\mu\text{-}2\text{-}C_6H_4PMe_2)(\mu_2\text{-}PMe_2)]$ has been isolated from the reaction of $[Os_3(CO)_7(\mu_3\text{-}C_6H_4)(\mu_2\text{-}PMe_2)_2]$ in refluxing nonane [111], and $[Ru_2(CO)_6(\mu_2\text{-}C_6H_4PPh_2)_2]$ has been obtained in 10% yield from the thermolysis of $[Ru_3(CO)_9(PPh_3)_3]$ in decalin [112], though in both cases X-ray structural confirmation is lacking.

The trinuclear cluster $[Os_3(\mu\text{-H})(\mu_2\text{-}SbPh_2)(\mu_3\text{-}\eta_2\text{-}C_6H_4)(CO)_9]$ forms an adduct with PPh_3, which loses CO at ambient temperature and, in the presence of an excess PPh_3, gives an *ortho*-metallated product $[Os_3(\mu_2\text{-}SbPh_2)(\mu\text{-}2\text{-}C_6H_4PPh_2)(CO)_8(PPh_3)_2]$. The corresponding complex $[Os_3(\mu_2\text{-}SbPh_2)\{\mu\text{-}2\text{-}C_6H_3\text{-}5\text{-}MeP(p\text{-tol})_2\}(CO)_8(PPh_3)_2]$ is obtained from the adduct of the original cluster with tri-*p*-tolylphosphine, after treatment with PPh_3 [112a].

Cotton and co-workers have prepared black, dinuclear osmium(III) ($5d^5$–$5d^5$) complexes $[Os_2Cl_2(\mu\text{-}O_2CR)_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ (R = Me **50**, Et) in ca. 25% yield from $[Os_2Cl_2(\mu\text{-}O_2CR)_4]$ and PPh_3 in refluxing acetic acid [113,114]. As shown in Fig. 6, complex **50** contains two bridging cisoid acetate groups and two cisoid $\mu\text{-}C_6H_4PPh_2$ groups. The carboxylate groups can be removed by reaction of the complex with Me_3SiCl to give brown $[Os_2Cl_4(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ **51** in 88% yield [115]. The coordination geometry about each osmium atom is trigonal bipyramidal, with cisoid $2\text{-}C_6H_4PPh_2$ groups; unusually, the trigonal bipyramids are mutually perpendicular. The carboxylate complexes are essentially diamagnetic and all are believed to contain a triple bond between the osmium atoms. The metal–metal bond lengths [2.271(2), 2.272(1) Å in the car-

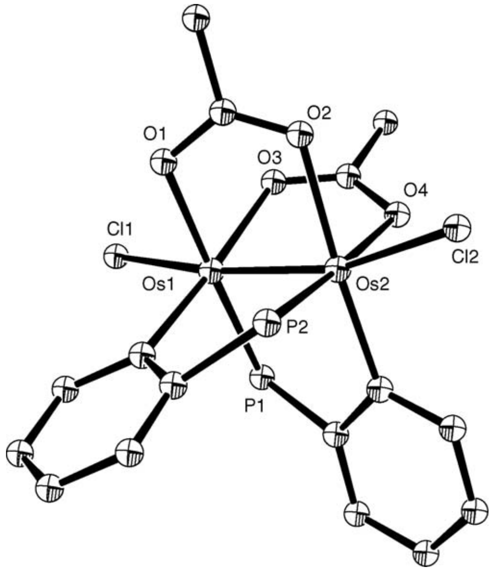
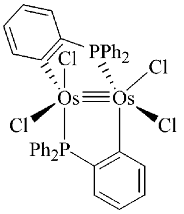


Fig. 6. Structure of $[Os_2Cl_2(\mu\text{-}O_2CCH_3)_2(\mu\text{-}2\text{-}C_6H_4PC_6H_5)_2]$ **50** (Ph_2 groups omitted for clarity).

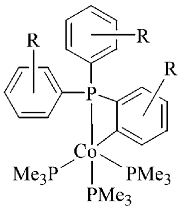
boxylates, 2.231(1) Å in the chloride] are among the shortest known for Os≡Os compounds.



51

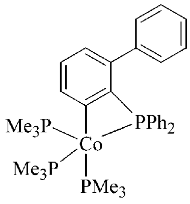
4.4. Co, Rh, Ir

In addition to the *ortho*-deuteration of $[CoH(N_2)(PPh_3)_3]$ reported in 1968 [6] (see Section 1), the reaction of this compound with styrene was reported in 1973 to give a brown compound formulated as the *ortho*-metallated species $[Co(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(PhCH{=}CH_2)(PPh_3)_2]$, which has two unpaired electrons; the other products were dinitrogen and ethylbenzene [116]. Methane is the predominant gaseous product of thermolysis of $[CoMe(PPh_3)_3]$ at 135 °C but the cobalt-containing products have not been identified [117]. Well-defined *ortho*-metallated complexes of cobalt have been isolated only recently. The reaction of $[CoMe(PMe_3)_4]$ with triarylphosphines $(n\text{-}RC_6H_4)_3P$ ($n = 4$, R = H, Me; $n = 2$, R = NMe_2, CH_2NMe_2, CN, Et and ^{i}Pr) gives methane and the black, crystalline *ortho*-metallated complexes **52** in high yields [118,119]. X-ray structural determinations of $[Co(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(PMe_3)_3]$ [118] and $[Co(\kappa^2\text{-}2\text{-}C_6H_3\text{-}3\text{-}EtPPh_2)(PMe_3)_3]$ [119] show the complexes to be distorted trigonal bipyramidal, with the Co–C σ-bond in an axial position. In the cases cited above, for $n = 2$, the exclusive formation of the metal–carbon bond *ortho* to the substituent shows that the *ortho*-metallation process is controlled by steric rather than electronic factors. However, when R = Me (in contrast to R = Et), hydrogen is abstracted from the aliphatic substituent to give a five-membered ring complex $[Co(\kappa^2\text{-}2\text{-}CH_2C_6H_4PPh_2)(PMe_3)_3]$. Similarly, when the substituent at the 3-position is conformationally restricted, as in (1-naphthyl)diphenylphosphine and (5,6,7,8-tetrahydronaphthalene-1-yl)diphenylphosphine, hydrogen is abstracted preferentially from the 8-position to give the corresponding five-membered cobaltacycles. By contrast, when R = Ph, a substituent which is capable of free rotation, *ortho*-metallation is again preferred, complex **53** being formed from $[CoMe(PPh_3)_4]$ and (2-biphenylyl)diphenylphosphine [120]. The sterically hindered Schiff-base $2\text{-}RN{=}CHC_6H_4PPh_2$ (R = ^{t}Bu) reacts with $[CoMe(PMe_3)_4]$ to give the *ortho*-metallated complex **54**; when R = Et, ^{i}Pr or Cy, however, hydrogen is eliminated preferentially from the imino group to give five-membered ring iminoacyls $[Co(\kappa P,C\text{-}2\text{-}RN{=}CC_6H_4PPh_2)(PMe_3)_3]$ [121].

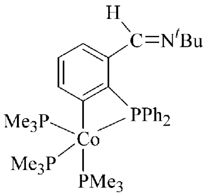


R = H, Me, Et, ^{i}Pr, CN, NMe_2, CH_2NMe_2

52

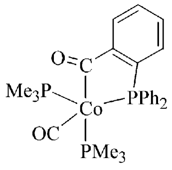


53

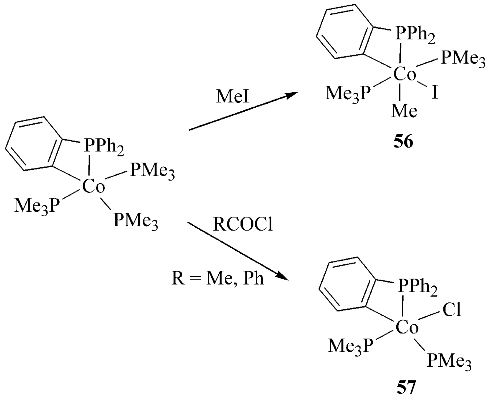


54

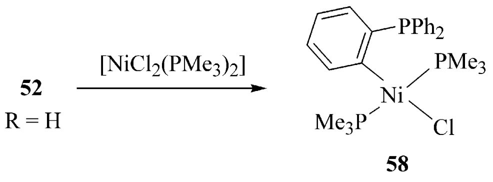
Complexes **52**–**54** react readily with two equivalents of CO by insertion into the Co–C σ-bond and replacement of one of the PMe_3 ligands to give acyls such as **55**, whereas ethene fails to insert and only replaces one of the equatorial PMe_3 ligands [118,120,121]. The Co–C σ-bond in **52** (R = H) is rapidly cleaved by H_2 giving initially $[CoH(PPh_3)(PMe_3)_3]$ but these *ortho*-metallated cobalt complexes are generally poor hydrogenation catalysts. However, they undergo oxidations with retention of the four-membered ring (Scheme 25).



55



Scheme 25.



Scheme 26.

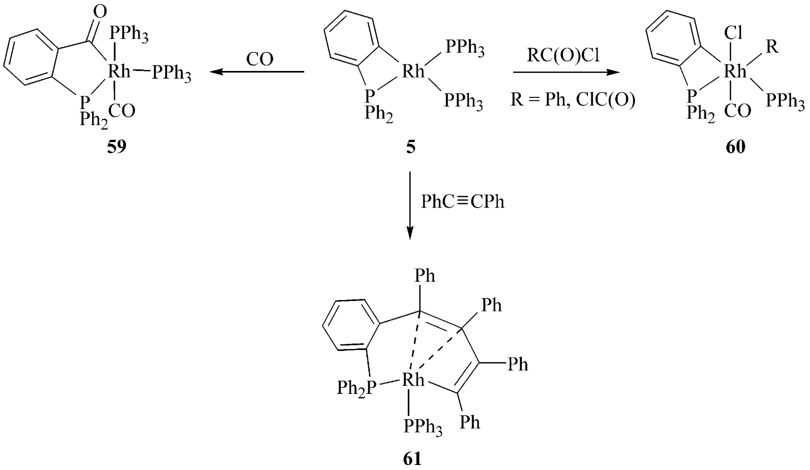
For example, complex **52** (R = H) oxidatively adds methyl iodide to give the distorted octahedral cobalt(III) complex **56** and reacts with acyl chlorides to give the brown, paramagnetic, approximately trigonal bipyramidal cobalt(II) complex **57** [118]. Cobalt is thus unique among the d-block elements in forming mononuclear *ortho*-metallated PPh_3 complexes in three oxidation states.

In a so far unique reaction, the 2-$C_6H_4PPh_2$ group can be transferred from complex **52** (R = H) to $[NiCl_2(PMe_3)_2]$ giving a 55% yield of complex **58**, in which the phosphorus atom of 2-$C_6H_4PPh_2$ is not coordinated [118] (Scheme 26). If this type of reaction could be generalized, it might provide a useful alternative synthesis of *ortho*-metallated complexes of elements such as platinum, palladium and gold (Sections 4.5 and 4.6) directly from triphenylphosphine, thus avoiding the preparation of (2-halogeno)diphenylphosphines as precursors.

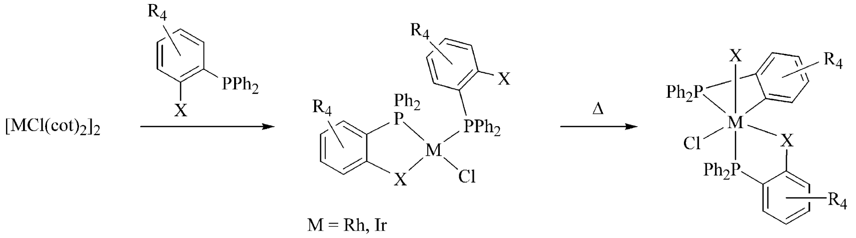
The first rhodium(I) *ortho*-metallated phosphine complex $[Rh(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(PPh_3)_2]$ **5** (see Section 1), obtained during attempted recrystallization of $[RhMe(PPh_3)_3]$, was reported by Keim in 1968 and was characterized by elemental analysis as well as IR and UV spectroscopy [8]. The same complex can also be prepared by heating the rhodium aryloxide complexes $[Rh(OAr)(PPh_3)_3]$ (Ar = Ph, 4-MeC_6H_4, 2-MeC_6H_4 and 4-$MeOC_6H_4$) in toluene [122]. The reactivity of complex **5** with deuterium, CO, diolefins and alkynes as well as benzoyl chloride and oxalyl chloride has been studied by Keim. Treatment of a solution of **5** with deuterium gas, and subsequent oxidation of the resulting product with H_2O_2, gives *ortho*-deuterated Ph_3PO [123]. These observations are similar to those made by Parshall with $[CoH(N_2)(PPh_3)_3]$ (see Section 1). Complex **5** reacts with CO to give the insertion–addition product **59**, while benzoyl chloride or oxalyl choride undergo three-fragment oxidative addition to **5** giving **60** (Scheme 27) [123]. Complex **5** also reacts with diolefins, including 1,3-butadiene, 1,5-cyclooctadiene and norbornadiene to give pentacoordinated, diamagnetic rhodium(I) complexes containing the olefins π-coordinated to the metal [124]. Diphenylacetylene and $CF_3C{\equiv}CCF_3$ react with **5** to give complexes formulated by Keim as rhodiacyclopentadienes formed by coupling of two alkyne units [124]. An X-ray structural determination of the diphenylacetylene derivative **61** has shown, however, that the coupled alkyne units have inserted into the Rh–C_{aryl} bond, the metal atom being coordinated by an alkene and vinyl-carbon σ-bond [125].

The triply *ortho*-metallated rhodium(III) complex **62** was prepared in low yield by the reaction of *mer*-$[RhCl_3(SEt_2)_3]$ with 2-$LiC_6H_4PPh_2$ and was structurally characterized by X-ray crystallography [126]. The Rh–C σ-bonds in **62** are remarkably stable towards insertion by CO or ^{t}BuNC and are only slowly cleaved even by a large excess of CF_3CO_2H.

Lahuerta and co-workers have studied in detail the chemistry of rhodium and iridium complexes containing 2-haloarylphosphine ligands of the type 2-$XC_6R_4PPh_2$, where X = Br, R = F and X = Cl, R = H. $[Rh(CO)_2(acac)]$ reacts with 8-hydroxyquinoline and 2-$BrC_6F_4PPh_2$ to give the yellow complex $[Rh(oq)(CO)(\kappa P\text{-}2\text{-}BrC_6F_4PPh_2)]$ [127]. On refluxing this



Scheme 27.

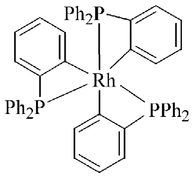


M = Rh, Ir
X = Br, R = F; X = Cl, R = H

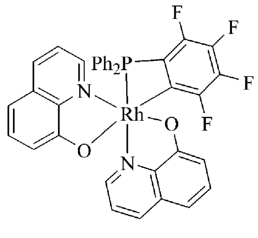
66

Scheme 28.

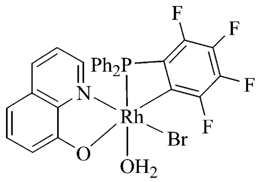
complex in toluene, a complex mixture is obtained from which the *ortho*-metallated complexes **63** and **64** have been isolated and structurally characterized by X-ray crystallography [127,128]. However, if [Rh(oq)(CO)(κ*P*-2-Br$C_6F_4PPh_2$)] is refluxed in toluene in the presence of excess Et_4NBr (acting as a source of bromide) complex **64** can be prepared almost free from side products in 87% yield [129]. In the solid state complex **64** forms a dimer through hydrogen bonding between the coordinated water molecule and the oxygen atom of the hydroxyquinoline. The weakly coordinated water ligand in complex **64** can easily be replaced by other P-donor ligands to give the *ortho*-metallated derivatives **65** [128,129].



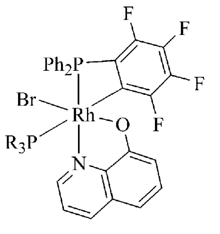
62



63



64

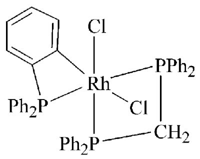


R = Ph, 4-MeC_6H_4, 4-FC_6H_4, 4-MeOC_6H_4, OMe, OPh,

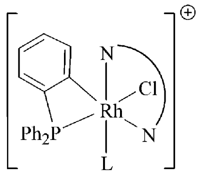
65

The 2-haloarylphosphines 2-X$C_6R_4PPh_2$ (X = Br, R = F; X = Cl, R = H) react with [MCl(coe)$_2$]$_2$ (M = Rh, Ir) to give complexes [MCl(2-X$C_6R_4PPh_2$)$_2$] [130–132]. Structural and spectroscopic studies have shown that in these compounds one of the phosphine ligands is coordinated to the metal through both the halogen and phosphorus atom whilst the other phosphine acts as a monodentate P-donor ligand (Scheme 28). On heating, these complexes undergo intramolecular oxidative addition reaction of the C–X bond to the metal giving *ortho*-metallated species **66** (Scheme 28). The bidentate 2-Cl$C_6H_4PPh_2$ ligand in **66** (M = Rh, X = Cl, R = H) is replaced by bidentate ditertiary phosphines with formation of [RhCl_2(κ^2-2-$C_6H_4PPh_2$)(L–L)] (L–L = dppm, dppe) [133]. The complexes [IrX_2(κ^2-2-$C_6F_4PPh_2$)(κ^2-*P*,*Br*-2-Br$C_6F_4PPh_2$)] (X = Cl, Br) and [RhCl_2(κ^2-2-$C_6F_4PPh_2$)(dppm)] **67** have been structurally characterized.

Complex **67** is also formed by thermally induced intramolecular oxidative addition of the C–Cl bond to the rhodium atom in [RhCl(κ*P*-2-Cl$C_6H_4PPh_2$)(κ^2-dppm)] in ethanol or by heating a THF solution of [Rh_2(HO_2CCH_3)$_2$(μ-2-$C_6H_4PPh_2$)$_2$(μ-O_2CCH_3)$_2$] in the presence of dppm and Me_3SiCl [133]. One of the chloride ligands in complex **67** can be abstracted using $AgSbF_6$ resulting in formation of the cationic complex [RhCl(κ*P*-2-Cl$C_6H_4PPh_2$)(κ^2-dppm)]SbF_6. Similar cationic complexes **68** can be prepared by treating [RhCl_2(κ^2-2-$C_6H_4PPh_2$)(κ^2-*P*,*Cl*-2-Cl$C_6H_4PPh_2$)] with 1,10-phenanthroline or 2,2′-bipyridine in the presence of $AgSbF_6$ [133].

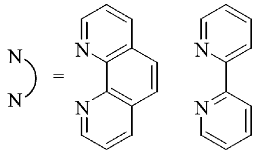


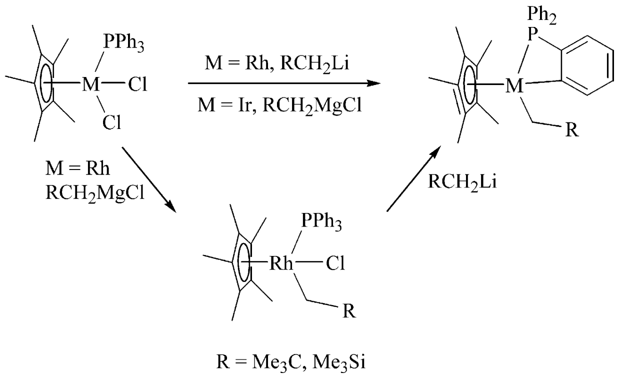
67



68

L = 2-Cl$C_6H_4PPh_2$



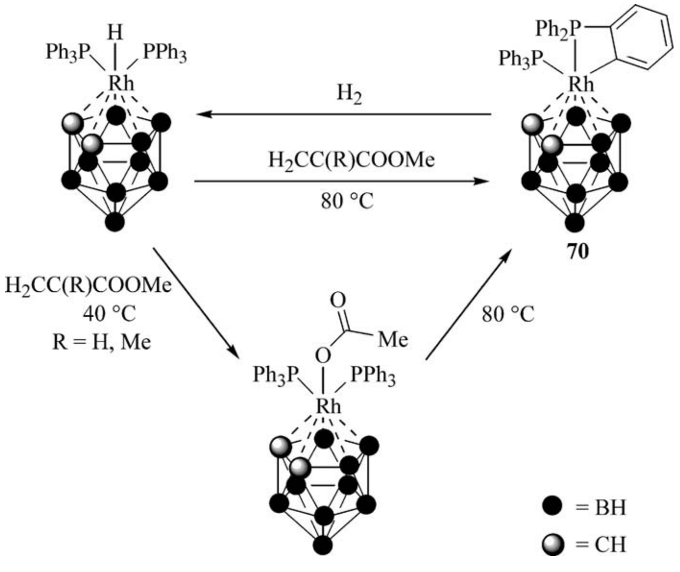


Scheme 29.

Diversi and co-workers have shown that *ortho*-metallation of triphenylphosphine can occur in the reactions of $[MCl_2(Cp^*)(PPh_3)]$ (M = Rh, Ir) with RCH_2MgCl or RCH_2Li ($R = Me_3C$, Me_3Si) (Scheme 29). Thus, the *ortho*-metallated complex **69** (M = Rh) is formed in low yield from the reaction of RCH_2Li with $[RhCl_2(Cp^*)(PPh_3)]$ [134,135], whereas RCH_2MgCl gives the non-cyclometallated species $[RhCl(CH_2R)(Cp^*)(PPh_3)]$ in higher yield. Treatment of the latter with RCH_2Li gives **69**, hence these differences in behaviour must arise from the higher basicity of the organolithium reagent. Surprisingly, however, whereas RCH_2Li reacts with $[IrCl_2(Cp^*)(PPh_3)]$ to give a complex mixture of products, RCH_2MgCl gives the *ortho*-metallated complex **69** (M = Ir); the X-ray crystal structure of the complex having $R = Me_3Si$ has been reported [135]. Similarly, treatment of $[IrCl_2(Cp^*)(PMePh_2)]$ with Me_3CCH_2MgCl gives the *ortho*-metallated complex $[Ir(CH_2CMe_3)(Cp^*)(\kappa^2\text{-}2\text{-}C_6H_4PMePh)]$, only the *R*,*R*:*S*,*S* diastereomer being formed [136] [cf. exclusive formation of the *R*,*S*:*S*,*R* diastereomer in the $Ru(\eta^6\text{-}C_6Me_6)$ case (see Section 4.3)].

In the iridium series, *ortho*-metallation can also be induced by electron-transfer catalysis (cf. Ru, Section 4.3). For example, on treatment with 10–15 mol% of the one-electron oxidants $[Fe(Cp)_2]PF_6$, $AgBF_4$ or $[Ph_3C]BF_4$, $[IrMe_2(Cp^*)(PPh_3)]$ in benzene or CH_2Cl_2 loses methane and, after 2 h, $[IrMe(Cp^*)(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)]$ can be isolated in 92% yield. In benzene, this *ortho*-metallated complex reacts further over 16 h in the presence of $[Fe(Cp)_2]PF_6$ to give $[IrMePh(Cp^*)(PPh_3)]$ [137,138]. Addition of $[Fe(Cp)_2]^+$ to $[IrMe_2(Cp^*)L]$ ($L = PMePh_2$, PMe_2Ph) in benzene induces intermolecular C–H activation to give $[IrMePh(Cp^*)L]$, but in CD_2Cl_2, $[IrMe_2(Cp^*)(PMePh_2)]$ gives the *ortho*-metallated product $[IrMe(Cp^*)(\kappa^2\text{-}2\text{-}C_6H_4PMePh)]$ as a 1:1 mixture of diastereomers. These reactions proceed via transient, red-violet iridium(IV) species, which have been detected by ESR spectroscopy [136].

Photolysis of $[IrH_2(Cp^*)(PPh_3)]$ in benzene causes elimination of H_2 and formation of the products of intermolecular and intramolecular C–H activation, $[IrHPh(Cp^*)(PPh_3)]$ and $[IrH(Cp^*)(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)]$, respectively, in a ratio of 47:53. In acetonitrile, the *ortho*-metallated complex is the main product, while in cyclohexane ca. 30% of the intermolecular C–H activation product, $[IrH(C_6H_{11})(Cp^*)(PPh_3)]$, is also formed [139,140]. Intramolecular C–H activation of arylphosphines seems generally to be less favoured in $Ir(Cp^*)$ systems than in the isolobal $Ru(\eta^6\text{-arene})$ or $Os(\eta^6\text{-arene})$ systems.



Scheme 30.

In their studies of rhodacarboranes Hawthorne and co-workers found that heating *closo*-$[3,3\text{-}(PPh_3)_2\text{-}3H\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$ with isopropenyl acetate or vinyl acetate in refluxing benzene formed the *ortho*-metallated rhodacarborane **70** in high yield [141]. The crystal structure of this complex has also been reported [142]. The same compound can also be produced by heating solutions of the bis(triphenylphosphine)(acetato)rhodacarborane, produced by the reaction of isopropenyl acetate or vinyl acetate with *closo*-$[3,3\text{-}(PPh_3)_2\text{-}3H\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$ at 40 °C (Scheme 30). This *ortho*-metallation process is reversible, albeit slow; thus, when heated solutions of **70** are exposed to dihydrogen gas, the initial bis(triphenylphosphine)hydridorhodacarborane is slowly reformed (Scheme 30) [141].

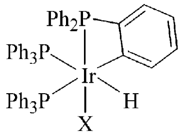
As mentioned in Section 1, the iridium(III) complex $[IrHCl(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(PPh_3)_2]$ **4** was one of the first *ortho*-metallated arylphosphine complexes to be reported [7]. In general, complexes of the type $[IrClL_3]$ [$L = PPh_3$, $P(4\text{-}RC_6H_4)_3$, $AsPh_3$, $SbPh_3$; R = F, Me, OMe] undergo *ortho*-metallation on heating to give the corresponding hydrido complexes analogous to **4**, the process being slower for $L = AsPh_3$, $SbPh_3$ than for the arylphosphines [143]. Experiments using deuterated solvents and either $P(C_6D_5)_3$ or $P(2\text{-}DC_6H_4)_3$ have confirmed that an *ortho*-hydrogen atom is transferred to iridium. The X-ray structure of the bromo-analogue of **4** [144] shows that coordination about iridium is distorted considerably from the usual octahedral arrangement, probably as a consequence of the presence both of the strained four-membered ring and the hydride. Tested syntheses of $[IrCl(PPh_3)_3]$ and **4** are available [145].

Although the isolation of $[IrMe(PPh_3)_3]$ from the reaction of $[IrCl(PPh_3)_3]$ with methyllithium has been claimed [146], the compound appears to undergo rapid *ortho*-metallation and subsequent reactions in solution. In general, the reaction of $[IrCl(PPh_3)_3]$ with an excess of organolithium reagents

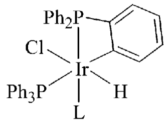
(RLi) gives rise to a number of compounds derived from the initial product $[\mathrm{IrR(PPh_3)_3}]$, many of which cannot be isolated but can be detected by NMR (^{1}H, ^{31}P) spectroscopy [147]. In the case of R = Me, the initially formed $[\mathrm{IrMe(PPh_3)_3}]$ is rapidly transformed into an equilibrium mixture derived by reversible dissociation of $\mathrm{PPh_3}$ and *ortho*-metallation, *viz.*, *cis*-$[\mathrm{IrH(Me)(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(PPh_3)}]$ and *fac*-$[\mathrm{IrH(Me)(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(PPh_3)_2}]$, whereas for R = $\mathrm{CH_2CMe_3}$ and $\mathrm{CH_2SiMe_3}$, the first detectable products are the alkylidene complexes $[\mathrm{Ir(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(CHEMe_3)(PPh_3)_2}]$ (E = C, Si) **71**, which react immediately with $\mathrm{PPh_3}$ or CO giving the *ortho*-metallated iridium(I) complexes $[\mathrm{Ir(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(PPh_3)_2}]$ **72** and $[\mathrm{Ir(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(CO)(PPh_3)}]$ **73**, respectively. Complex **72**, which can be detected in all aged $[\mathrm{IrCl(PPh_3)_3}]$/RLi reaction mixtures, has been isolated as bright orange crystals from the reaction of $[\mathrm{IrCl(PPh_3)_3}]$ with the carboranyllithium reagents 1-Li-2-R-1,2-$\mathrm{B_{10}C_2H_{10}}$ (R = Me, Ph) [148]. Less bulky reagents Li(carb) [carb = 2-H-1,2-$\mathrm{B_{10}C_2H_{10}}$ and 7-R-1,7-$\mathrm{B_{10}C_2H_{10}}$ (R = H, Me, Ph)] react with $[\mathrm{IrCl(PPh_3)_3}]$ to give only **4** [149], and this also occurs if $[\mathrm{IrCl(PPh_3)_3}]$ is treated with any organolithium reagent in a 1:1 molar ratio [147]. Evidently, isomerization of $[\mathrm{IrCl(PPh_3)_3}]$ outweighs the unfavourable equilibrium between $[\mathrm{IrCl(PPh_3)_3}]$ and the organolithium reagent.

Some reactions of complex **72** are summarized in Scheme 31. It reacts with CO to give successively mono- and di-carbonyl complexes, **73** and **74**, respectively [150]. The X-ray structure of the latter compound, made by a different procedure (see below), has been reported [151]. The Ir–C bond in **72** is cleaved by dihydrogen or by methanol to give *fac*- and *mer*-$[\mathrm{IrH_3(PPh_3)_3}]$, respectively [150]. Brief heating of complex **72** in toluene causes *ortho*-metallation of a second $\mathrm{PPh_3}$ ligand and formation of cream-coloured *cis*-$[\mathrm{IrH(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)_2(PPh_3)}]$ **75** [147]. The X-ray structure of complex **75** has also been reported, although it was not specified how the compound had been made [152]. Treatment of $[\mathrm{IrH_5(PPh_3)_2}]$ with ethene in benzene at 45 °C gives the *ortho*-metallated, bis(ethene) iridium(I) complex $[\mathrm{Ir(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(PPh_3)(C_2H_4)_2}]$, which reacts with CO to give the corresponding dicarbonyl $[\mathrm{Ir(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(CO)_2(PPh_3)}]$ [153]. The latter is probably identical with that prepared in Ref. [150], as judged by the cited ν(CO) data. The X-ray structure of the bis(ethene) complex has been reported [151].

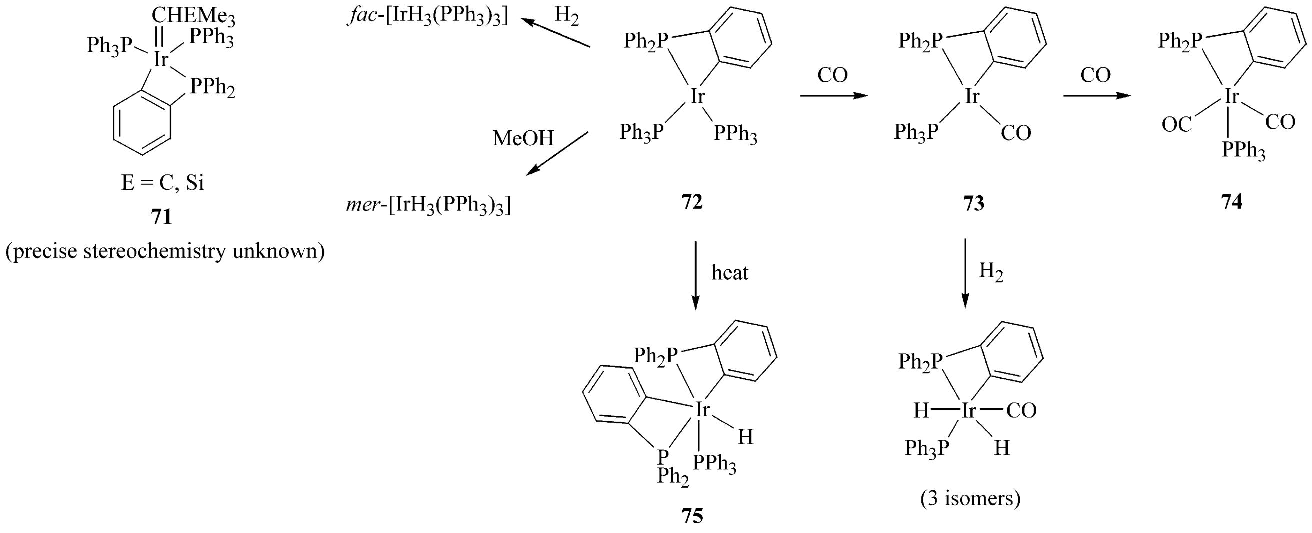
The iridium(III) hydrido complexes $[\mathrm{IrClH_2(PPh_3)_3}]$ and $[\mathrm{IrH_3(PPh_3)_3}]$ readily eliminate dihydrogen on UV-irradiation to give the *ortho*-metallated complexes **76a** and **76b**, respectively [154], the former being an isomer of **4**. The iridium(I) dinitrogen complex $[\mathrm{IrCl(N_2)(PPh_3)_2}]$ undergoes *ortho*-metallation in dmso to give a hydrido complex **77a**, whose probable stereochemistry is as shown. The coordinated dmso is readily displaced by CO to give a mixture of iridium(III) carbonyl complexes, probably **77b** and **77c**. These are *ortho*-metallated isomers of Vaska's complex, $[\mathrm{IrCl(CO)(PPh_3)_2}]$, to which they revert on heating in benzene [155]. Complex **77c** has been structurally characterized, having been isolated in small quantities by treatment of $[\mathrm{IrCl(PPh_3)_3}]$ with the phosphavinyl Grignard reagent [CyP=C(^{t}Bu)MgCl] and subsequent carbonylation of the reaction mixture [156]. It should be noted that Vaska's complex, unlike $[\mathrm{IrCl(PPh_3)_3}]$, does not spontaneously undergo *ortho*-metallation, contrary to the assumption made in Ref. [156].



X = Cl **76a**
X = H **76b**



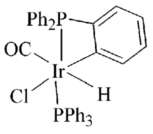
L = dmso **77a**
L = CO **77b**



(precise stereochemistry unknown)

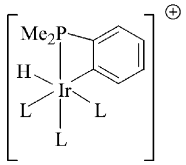
(3 isomers)

Scheme 31.



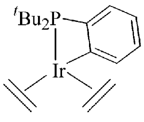
77c

The reaction of $[IrCl(cod)]_2$ with PMe_2Ph in acetonitrile generates $[Ir(PMe_2Ph)_4]^+$, which on prolonged heating undergoes *ortho*-metallation to give the hydrido–iridium(III) cation **78**, the PF_6 salt of which has been structurally characterized [157].



L = PMe_2Ph

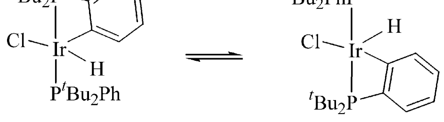
78



79

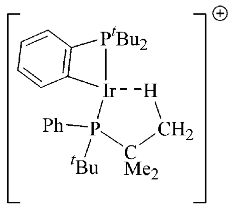
In the presence of an excess of ethene, the iridium(III) hydride $[IrH_2(OCH_2CF_3)(P^tBu_2Ph)_2]$ undergoes *ortho*-metallation to give the iridium(I) bis(ethene) complex **79** [158]. Spontaneous *ortho*-metallation also occurs when $[IrCl(coe)_2]_2$ is treated with P^tBu_2Ph to give the deep-red, five-coordinate iridium(III) hydride $[IrHCl(\kappa^2\text{-}2\text{-}C_6H_4P^tBu_2)(P^tBu_2Ph)]$ **80**, which catalyses the isomerization of allylbenzene to *cis*- and *trans*-propenylbenzene by reversible addition of Ir–H to the C=C bond. The presence of small, spectroscopically undetectable, amounts of **80** in samples of $[IrH_2Cl(P^tBu_2Ph)_2]$ is responsible for the irreproducible behaviour of the latter compound in the same catalytic process. The catalytically active species is formed by dissociation of P^tBu_2Ph from **80**. Variable temperature ^{31}P NMR spectroscopy shows that the metallated and non-metallated P^tBu_2Ph ligands exchange (Scheme 32) [159].

Treatment of **80** with $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ generates the orange, formally four-coordinate cation $[IrH(\kappa^2\text{-}2\text{-}C_6H_4P^tBu_2)(P^tBu_2Ph)]^+$ **81** [160]. Although its variable temperature NMR spectrum in CD_2Cl_2 gives no evidence for agostic interactions, there is an agostic interaction in the crystalline solid to a *t*-butyl hydrogen atom of the ligand *trans* to the *ortho*-metallated ligand. The resulting Ir–C distance [2.745 Å] is ca. 0.16–0.19 Å shorter than that in the non-*ortho*-metallated salt $[IrH_2(P^tBu_2Ph)_2][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$. Similar *ortho*-metallated complexes are not obtained with smaller substituents, such as cyclohexyl, on phosphorus.



80

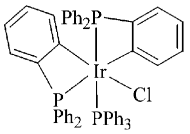
Scheme 32.



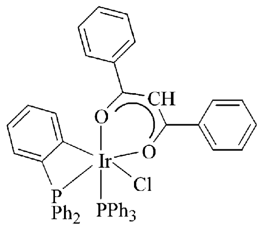
81

Treatment of *mer*-$[IrCl_3(SEt_2)_3]$ with an excess of 2-$LiC_6H_4PPh_2$ gives, as the main isolated product, the doubly *ortho*-metallated complex **82** (the chloro-analogue of **75**), which must be formed by cleavage of a metal–carbon σ-bond during the reaction; only a small amount of the expected iridium(III) analogue of **62** could be detected by ^{31}P NMR spectroscopy [126].

The reaction of dibenzoyldiazomethane with *trans*-$[IrCl(N_2)(PPh_3)_2]$ forms the complex $[IrCl\{N_2C(C(O)Ph)_2\}(PPh_3)_2]$, which on heating in toluene undergoes decomposition with loss of N_2 to produce the iridium(III) β-diketonato complex **83** incorporating a four-membered cyclometallated ring [161]. By carrying out the same reaction using *trans*-$[IrCl(N_2)\{P(C_6D_5)_3\}_2]$ it was shown that the hydrogen atom on the carbene fragment originates from the phenyl group that forms the *ortho*-metallated ring.

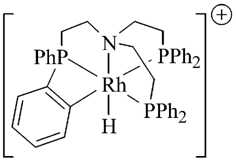


82



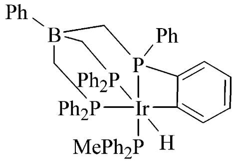
83

Most of the *ortho*-metallated complexes of Rh and Ir discussed so far are derived from PPh_3, but there are two examples in which the PPh_2 group of a multidentate ligand undergoes *ortho*-metallation. On treatment with methyl triflate, the trigonal bipyramidal hydrido-rhodium(I) complex $[RhH\{N(CH_2CH_2PPh_2)_3\text{-}\kappa N\kappa^3 P\}]$ forms initially a hydrido(methyl)rhodium(III) cation, which subsequently looses methane to give the rhodium(III) *ortho*-metallated complex **83a** [161a]. The four-membered ring is cleaved by benzene at 5 °C to give $[RhH(Ph)\{N(CH_2CH_2PPh_2)_3]^+$, but this reaction is reversed when the solution is heated. There is no *ortho*-metallation in the corresponding $P(CH_2CH_2PPh_2)_3$ system.

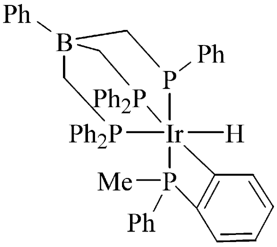


83a

Ortho-metallation in the iridium(III) complexes of the anionic ligand $[PhB(CH_2PPh_2)_3]^-$ has also been observed. Treatment of the cyclooctenyl complex $[IrH(\eta^3\text{-}C_8H_3)\{PhB(CH_2PPh_2)_3\text{-}\kappa^3P\}]$ with $PMePh_2$ gives initially the dihydride $[IrH_2(\eta^3\text{-}C_8H_3)\{PhB(CH_2PPh_2)_3\text{-}\kappa^3P\}(PMePh_2)]$. On photolysis, this eliminates H_2 and undergoes competitive *ortho*-metallation at the phenyl groups of the anionic ligand and $PMePh_2$, giving complexes **83b** and **83c** in a ratio of 7:3. Treatment of the cyclooctenyl complex with PMe_3 gives directly the PMe_3 analogue of **83b** [161b].



83b



83c

In 1984, Cotton and Chakravarty reported that rhodium acetate reacts with PPh_3 in refluxing acetic acid to form the binuclear rhodium(II) complex $[Rh_2(MeCO_2H)_2(\mu\text{-}O_2CMe)_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ (Fig. 7) containing two bridging $2\text{-}C_6H_4PPh_2$ groups [162]. The bridging acetate groups can be replaced by bridging chloride groups by treatment with Me_3SiCl in the presence of tertiary phosphine ligands; the X-ray structures of $[Rh_2(L)_2(\mu\text{-}Cl)_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ (L = PMe_3, PPh_3) have been reported [163].

Since these initial discoveries, the structures, reactivity and catalytic properties of numerous *ortho*-metallated binuclear rhodium complexes have been studied in depth, mainly by Lahuerta and co-workers. A detailed account of their work has appeared in a recent monograph [164], so only a brief summary will be given here.

A variety of tertiary phosphines, including PPh_3, PMe_2Ph, $PMePh_2$, $2\text{-}XC_6R_4PPh_2$ (X = Cl, R = H; X = Br, R = F), $P(4\text{-}RC_6H_4)_3$ (R = ^{t}Bu, Me_3Si, OMe, Me, Cl, Br, F) and $P(3\text{-}RC_6H_4)_3$ (R = Me, OMe, Cl), react with $[Rh_2(\mu\text{-}O_2CMe)_4]$ in acetic acid to yield doubly *ortho*-metallated dirhodium complexes of the type $[Rh_2L_2(\mu\text{-}P,C)_2(\mu\text{-}O_2CR)_2]$, where P,C = bridging phosphine, R = Me, CF_3 and L = acetic acid, H_2O, py, many of which have been structurally characterized (see Table A.2 in Appendix) [165–178]. However, if the same reaction is carried out in toluene, only singly *ortho*-metallated complexes are formed (Scheme 33) [179–187]. The singly *ortho*-metallated complexes can be converted into the doubly metallated species by treatment with more phosphine [172,185,188,189]. Various intermediate complexes containing axial or equatorial coordinated phosphine ligands formed during conversion of singly *ortho*-metallated into doubly metallated species have been detected spectroscopically or isolated and structurally characterized [190,191].

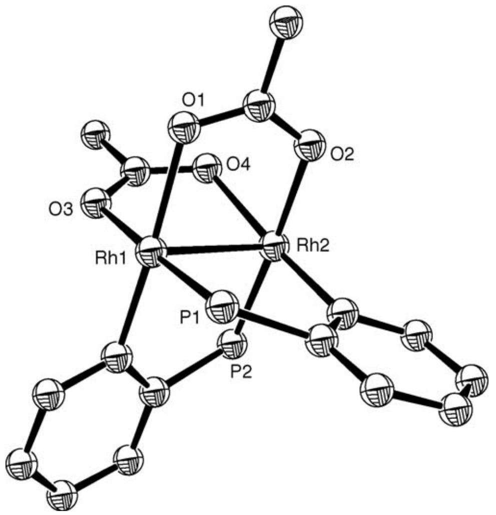
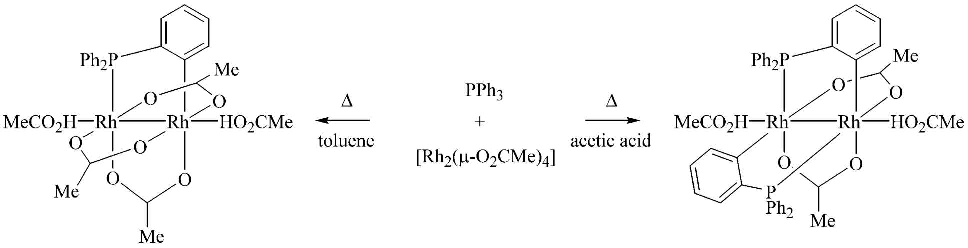
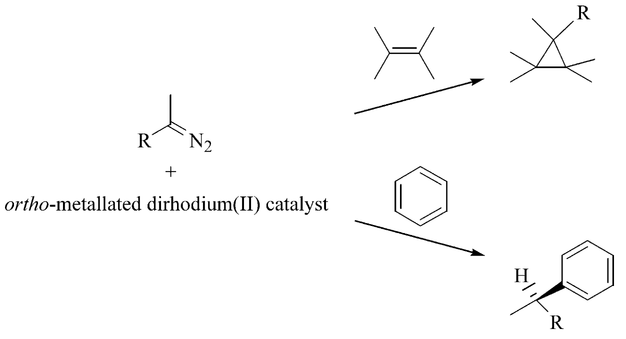


Fig. 7. Structure of $[Rh_2(MeCO_2H)_2(\mu\text{-}O_2CMe)_2(\mu\text{-}C_6H_4PC_6H_5)_2]\cdot 2CH_3CO_2H$. ($Ph_2$ groups and coordinated acetic acid omitted for clarity).

The mechanism [192,193] and kinetics [194,195] of this cyclometallation reaction have also been investigated in detail. Both the axial acetic acid ligands and the bridging acetate groups in binuclear singly *ortho*-metallated rhodium complexes undergo exchange reactions with CD_3CO_2D or CF_3CO_2H in a two step process. Initially, rapid exchange of the two axial acetic acid molecules and the acetate group *trans* to the metallated phosphine occurs. In the second step the acetate groups *cis* to the metallated phosphine are exchanged [183,196]. In the presence of trifluoroacetic acid the deuterated rhodium complex $[Rh_2(\mu\text{-}O_2CCF_3)_2\{\mu\text{-}2\text{-}C_6D_4P(C_6D_5)_2\}_2]$ undergoes D/H exchange at the *ortho* positions of the phenyl rings of the phosphine. It was shown that this reaction occurred by electrophilic attack at the Rh–C bond by the acid and demetallation followed by a reverse metallation

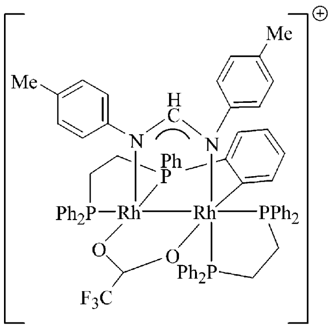


Scheme 33.



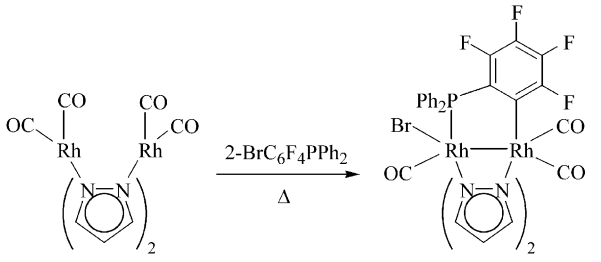
Scheme 34.

reaction [183,196]. The doubly *ortho*-metallated complexes are inherently chiral and pure enantiomers can be obtained by replacing the bridging acetate groups with chiral carboxylates and subsequent chromatographic separation of the diastereoisomers [197]. Alternatively, chiral *ortho*-metallated dirhodium complexes can be prepared by the reaction of rhodium acetate with a chiral phosphine [198]. The bridging acetate groups in $[Rh_2(MeCO_2H)_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2(\mu\text{-}O_2CMe)_2]$ can be replaced by succinimidate by refluxing the rhodium complex with succinimide in toluene, thus producing $[Rh_2(succH)(H_2O)(\mu\text{-}2\text{-}C_6H_4PPh_2)_2(\mu\text{-}succ)_2]$ in which the bridging succ ligands are in a head-to-head configuration. A less stable isomer in which they are arranged head-to-tail has also been prepared [199]. Similarly, dppm can displace the acetate bridges in $[Rh_2(MeCO_2H)_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2(\mu\text{-}O_2CMe)_2]$ to form $[Rh_2Cl_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2(\mu\text{-}dppm)_2]$ in high yield [200,201]. The axial acetic acid ligands are replaced by chloride ligands when the reaction is carried out in the presence of Me_3SiCl. Doubly *ortho*-metallated dirhodium(II) compounds have found use as active catalysts in various transformations of α-diazo compounds, including cyclopropanation, C–H insertion reactions and aromatic substitution (Scheme 34) [173,199,202–205].



84

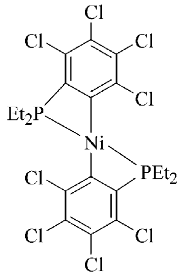
Other dirhodium(II) complexes containing *ortho*-metallated phosphines are formed in moderate yields when the pyrazolyl bridged dirhodium compound $[Rh_2(CO)_2(\mu\text{-}pz)]_2$ is treated with $2\text{-}BrC_6F_4PPh_2$ in refluxing toluene (Scheme 35) [206,207] This cyclometallation involves a two-centre-two-electron oxidative addition process along with cleavage of the C–Br bond of the phosphine.



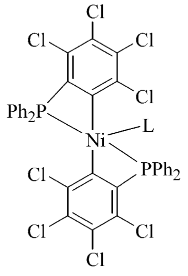
Scheme 35.

Recently, Cotton and co-workers reported the structures of some organometallic triangles built up from three dirhodium complexes containing two *ortho*-metallated $C_6H_4PPh_2$ ligands, bridged by dicarboxylates [208].

Other workers have reported *ortho*-metallation of $Ph_2P(CH_2)_2PPh_2$ in binuclear rhodium complexes containing bridging formamidinate ligands. $[Rh_2(H_2O)_2(\mu\text{-form})_2(\mu\text{-}O_2CCF_3)_2]$ reacts with dppe in diethyl ether at room temperature to produce the cationic complex **84**, in which one trifluoroacetate and one formamidinate ligand have been replaced by dppe units. Furthermore, one of the dppe ligands has undergone *ortho*-metallation to form a five membered ring; thus dppe acts as a tridentate ligand in this complex [209,210].

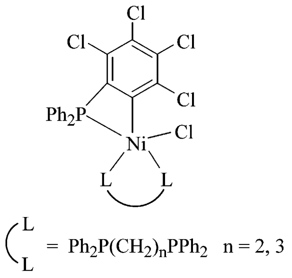


85



L = PEt_3, PMe_2Ph

86



87

4.5. Ni, Pd, Pt

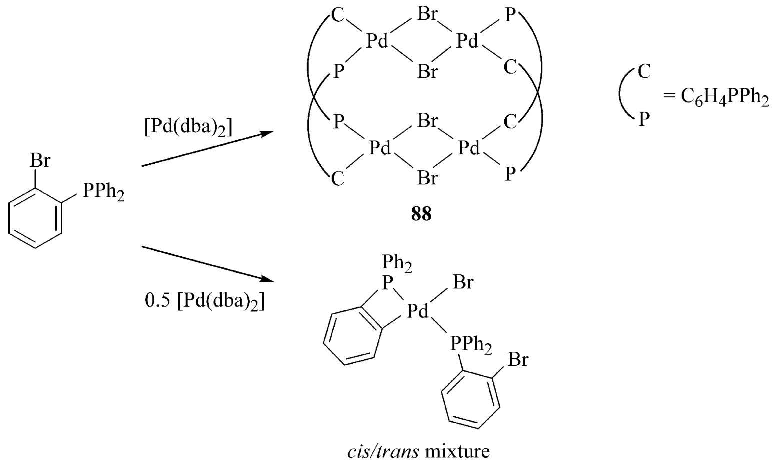
Although the nickel complex **1** [1] was the first cyclometallated complex to be isolated (see Section 1), most of the *ortho*-metallated arylphosphine complexes in this triad belong to platinum(II) and, to a lesser extent, palladium(II). The only well established examples for nickel(II) have been obtained by the oxidative addition of a C–Cl bond of tertiary phosphines containing a C_6Cl_5 group to nickel(0) [211]. Treatment of $[Ni(cod)_2]$ with $2\text{-}C_6Cl_5PR_2$ (R = Et, Ph) gives complexes $[Ni(\kappa^2\text{-}2\text{-}C_6Cl_4PR_2)_2]$ which, in the case of R = Et, has a planar-coordinated structure **85**. The insoluble derivative having R = Ph shows irreproducible ferromagnetic behaviour and may have a polymeric, ring opened, Ni–P–C–Ni structure in the solid state. Nevertheless, neutral, monodentate ligands L (PEt_3, PMe_2Ph) react with $[Ni(\kappa^2\text{-}2\text{-}C_6Cl_4PPh_2)_2]$ to give monomeric, five-coordinate adducts $[Ni(\kappa^2\text{-}2\text{-}C_6Cl_4PPh_2)_2L]$ **86**; the PEt_3 derivative has been shown to be a distorted trigonal bipyramid in the solid state and to contain chelating $2\text{-}C_6Cl_4PPh_2$ groups. If the oxidative addition of $2\text{-}C_6Cl_5PR_2$ to $[Ni(cod)_2]$ is carried out in the presence of the bidentate ligands dppe or dppp, five-coordinate complexes $[NiCl(\kappa^2\text{-}2\text{-}C_6Cl_4PPh_2)(L\text{-}L)]$ **87** are obtained. Similar compounds containing monodentate tertiary phosphines, $[NiCl(\kappa^2\text{-}2\text{-}C_6Cl_4PR_2)L_2]$ [R = Ph, L = PMe_2Ph, PEt_3, $P(CH_2Ph)_3$, PPh_3; R = Et, L = $P(CH_2Ph)_3$] can also be made and converted into salts of the type $[Ni(\kappa^2\text{-}2\text{-}C_6Cl_4PR_2)L_2]BF_4$ in which the cation contains planar-coordinated nickel(II). The X-ray structure of $[NiCl(2\text{-}C_6Cl_4PPh_2)(PEt_3)_2]$ shows the $2\text{-}C_6Cl_4PPh_2$ group to be bound only through carbon, with only a weak Ni–P interaction; the coordination about nickel is distorted square planar.

Carbon monoxide reacts reversibly with $[Ni(\kappa^2\text{-}2\text{-}C_6Cl_4PPh_2)_2]$, probably forming a five-coordinate adduct; it does not insert into the Ni–C σ-bonds. The apparent stability of the four-membered chelate rings in these complexes has been attributed to the steric bulk and electron-deficient nature of the $2\text{-}C_6Cl_4PPh_2$ ligands [211].

The formation of the ditertiary phosphine 2,2′-$Ph_2PC_6H_4C_6H_4PPh_2$ from $[Ni(cod)_2]$ and $[Hg(2\text{-}C_6H_4PPh_2)_2]$ may proceed by reductive elimination of Ni–C σ-bonds from an undetected intermediate $[Ni(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)_2]$ [212].

Lahuerta and co-workers have isolated an extensive series of *ortho*-palladated complexes of triphenylphosphine from the oxidative addition of the C–Br bond of $2\text{-}BrC_6H_4PPh_2$ to the labile palladium(0) complex $[Pd(dba)_2]$ [213,214]. Reaction in a 1:1 molar ratio gives a structurally characterized tetranuclear species $[PdBr(2\text{-}C_6H_4PPh_2)]_4$ **88** in which two $[Pd_2(\mu\text{-}Br)_2]$ units are linked by a pair of bridging $2\text{-}C_6H_4PPh_2$ groups, as shown in Scheme 36. This compound is converted into the corresponding chloro-derivative by refluxing with an excess of $[Bu_4N]Cl$. Reaction of $2\text{-}BrC_6H_4PPh_2$ with $[Pd(dba)_2]$ in a 2:1 molar ratio gives a mononuclear complex $[PdBr(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(\kappa P\text{-}2\text{-}BrC_6H_4PPh_2)]$ **89**, as a mixture of *cis*- and *trans*-isomers, in which the $2\text{-}C_6H_4PPh_2$ group adopts a chelating rather than bridging mode of coordination. The X-ray structure of *trans*-**89** confirms the presence of the four-membered chelate ring with a "bite" angle of 69°; the coordination geometry is distorted square planar [214]. The bromo bridges of **88** are cleaved by tertiary phosphines, as shown in Scheme 37. Ligands of small cone angle, such as PMe_3 or PMe_2Ph, give binuclear complexes **90** in which $2\text{-}C_6H_4PPh_2$ bridges a pair of palladium atoms, whereas bulkier ligands such as triarylphosphines or PCy_3 give mononuclear complexes **91**, usually as a *cis*/*trans* mixture of isomers. The ligand $PMePh_2$ gives an equilibrium mixture of dimeric and monomeric derivatives [214].

Complex **88** also reacts with silver carboxylates to give dinuclear complexes **92** containing $\mu\text{-}2\text{-}C_6H_4PPh_2$ and $\mu\text{-}O_2CR$ (R = Me, CF_3) groups and with $AgBF_4$ to give labile dinuclear solvento-cations **93** (solvent = THF, MeCN) which retain the bridging $2\text{-}C_6H_4PPh_2$ arrangement (Scheme 37). The solvent molecules are readily replaced by tertiary phosphines, the resulting stable cationic species again being either dinuclear or mononuclear depending on the size of the tertiary phosphine [214]. Both in the solid state and solution, complex **91** (L = PPh_3) undergoes a slow coupling of the metallated ring with a PPh_2

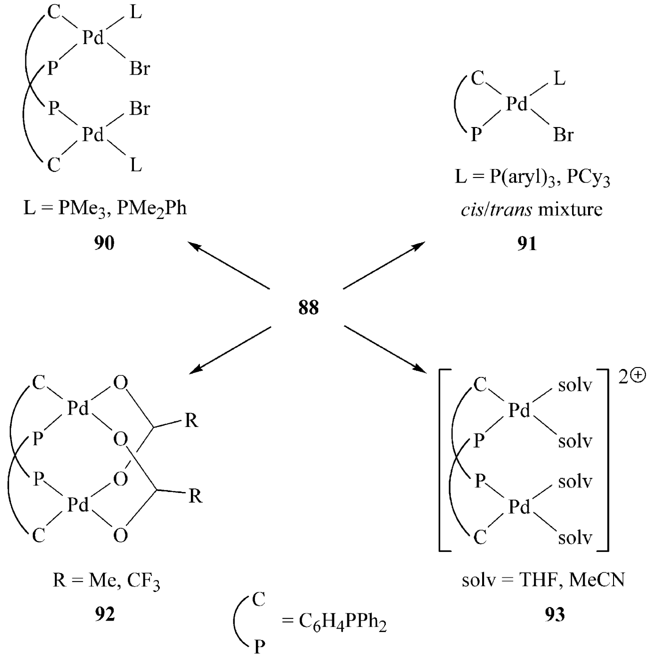


88

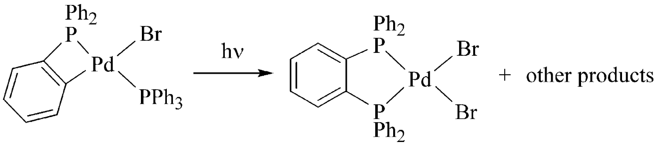
cis/trans mixture

89

Scheme 36.

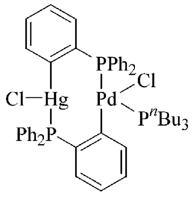


Scheme 37.



Scheme 38.

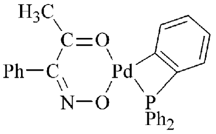
group derived from PPh_3 to give, among unidentified species, $[PdBr_2\{1,2\text{-}C_6H_4(PPh_2)_2\}]$, as shown in Scheme 38 [215].



94

The organomercury compound $[Hg(2\text{-}C_6H_4PPh_2)_2]$ reacts with $[PdCl_2(P^nBu_3)_2]$ in refluxing toluene to give complex **94** in which palladium and mercury are bridged by a pair of 2-$C_6H_4PPh_2$ groups [212].

Other, less well-characterized *ortho*-palladated complexes derived from PPh_3 have been claimed although the decisive ^{31}P NMR data in support of the formulations are lacking. Treatment of $[PdCl_2(PPh_3)_2]$ in dmf with aqueous lithium acetate is stated to give $[PdCl(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(PPh_3)]$ [216]. Reaction of 1-oximino-1-phenylpropan-2-one with $[Pd(PPh_3)_4]$, subsequent oxidation with molecular oxygen, and pyrolysis of the product gives a pale green-yellow complex formulated as **95** [217].

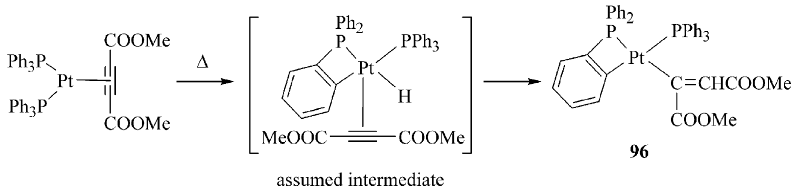


95

In the early 1970s Shaw and co-workers reported the cyclometallation of a series of platinum complexes containing bulky tertiary phosphine ligands [218,219]. Thus, heating solutions of *trans*-$[PtCl_2(P^tBuPh_2)_2]$ slowly gives the *ortho*-metallated complex *trans*-$[PtCl(2\text{-}C_6H_4PPh^tBu)(P^tBuPh_2)]$ in low yield, the main product being *trans*-$[PtHCl(P^tBuPh_2)_2]$; the analogous complex containing two *t*-butyl groups is metallated much more readily and in higher yield as a result of the relief of steric crowding. Metallation occurs more readily in the corresponding bromo- and especially iodo-derivatives, and is also promoted by the addition of weak bases, such as sodium acetate, by the presence of nitrate or methyl in the coordination sphere, or by the use of weakly basic solvents such as 2-methoxyethanol [218–221]. The structure of the nitrato complex *trans*-$[Pt(ONO_2)(\kappa^2\text{-}2\text{-}C_6H_4P^tBu_2)(P^tBu_2Ph)]$ has been confirmed by X-ray crystallography [222]. *p*-Tolylphosphines metallate much more readily than phenylphosphines. The combination of steric and electronic effects that must be responsible for all these effects has not been fully unravelled. There is no evidence for *ortho*-metallation of the less sterically crowded complex *trans*-$[PtCl_2(P^iBuPh_2)_2]$ [223]. The complexes *trans*-$[PtCl_2(P^tBu_2\{o\text{-tolyl}\})_2]$ and *trans*-$[PtCl_2(P^tBu\{o\text{-tolyl}\}_2)_2]$ metallate at the *o*-tolyl-methyl carbon atoms in preference to an *ortho*-aryl carbon atom, thus forming a chelate five-membered ring [221]. The same is true for the analogous tertiary arsine complexes [224], but there are no reports of the formation of a four-membered, *ortho*-platinated tertiary arsine complex by this method.

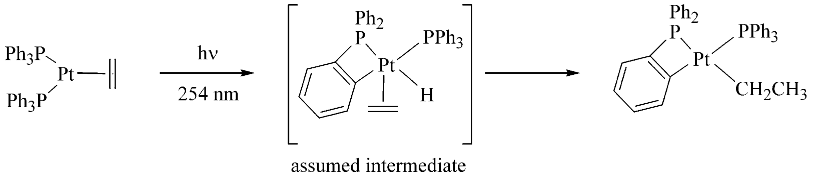
Heating a toluene solution of the dimethyl acetylenedicarboxylate platinum(0) complex $[Pt(MeO_2CC{\equiv}CCO_2Me)(PPh_3)_2]$ for 24 h gives an *ortho*-platinated complex of triphenylphosphine **96**, as shown in Scheme 39 [225]. The structure of **96** has been conformed by X-ray crystallography [226]. The complex is presumably formed by insertion of the alkyne into the Pt–H bond generated in the initial *ortho*-metallation of PPh_3.

A similar process occurs in the ultraviolet irradiation of the platinum(0) complex $[Pt(C_2H_4)(PPh_3)_2]$ in CH_2Cl_2 at

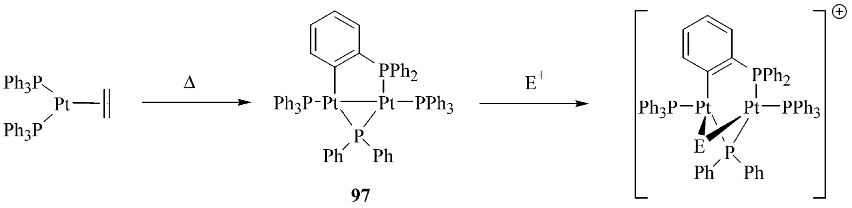


96

Scheme 39.



Scheme 40.



E = H, $Cu(PPh_3)$, $Ag(PPh_3)$, $Au(PPh_3)$

Scheme 41.

254 nm, which gives the *ortho*-metallated complex $[PtEt(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(PPh_3)]$, as shown in Scheme 40 [227,228].

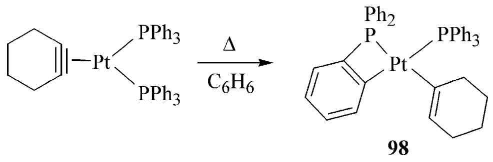
The products of this irradiation are, however, sensitive to the conditions. At 280 nm in $CHCl_3$ the product isolated is the hydrido complex $[PtHCl(PPh_3)_2]$, while in ethanol a white product that turns red on standing or heating is obtained. Similar species have been reported to form when nitrogen is passed through $[Pt(C_2H_4)(PPh_3)_2]$ in *o*-xylene for 24 h [229] and on photolysis of the oxalato complex $[Pt(\kappa^2\text{-}C_2O_4)(PPh_3)_2]$ [230,231]. They may all be identical with the dinuclear platinum(I) complex $[Pt_2(\mu\text{-}PPh_2)(\mu\text{-}2\text{-}C_6H_4PPh_2)(PPh_3)]$ **97**, which has been isolated from the controlled thermolysis of $[Pt(C_2H_4)(PPh_3)_2]$ in toluene [40] or 2-methoxyethanol [41], and has been structurally characterized (Scheme 41).

The electrophiles H^+ and $[M(PPh_3)]^+$ (M = Cu, Ag, Au) add across the Pt–Pt bond of **97** to give cationic A-frame type complexes [41,232]; the structure of the $Cu(PPh_3)$ derivative has been confirmed by X-ray crystallography.

Like their dimethyl acetylenedicarboxylate analogue, complexes of the type $Pt(alkyne)(PPh_3)_2$ containing the highly strained cyclic alkynes cyclohexyne ($1,2\text{-}C_6H_8$) and benzyne ($1,2\text{-}C_6H_4$) undergo spontaneous *ortho*-metallation of PPh_3. Thus, on heating in benzene for 18 days, $[Pt(\eta^2\text{-}C_6H_8)(PPh_3)_2]$ gives the isomeric η^1-cyclohexenyl complex **98** (Scheme 42) [233].

The much less stable benzyne complex $[Pt(\eta^2\text{-}C_6H_4)(PPh_3)_2]$ decomposes at room temperature to give the corresponding η^1-phenyl complex **99** (Scheme 43) [233].

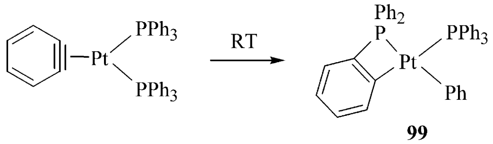
A similar process occurs when the 2,2′-biphenylyl complex **100** is heated in C_6D_6 at 80 °C (Scheme 44). The resulting *ortho*-metallated complex **101** exists in solution as a pair of enantiomers, as shown by ^{31}P NMR spectroscopy [234].



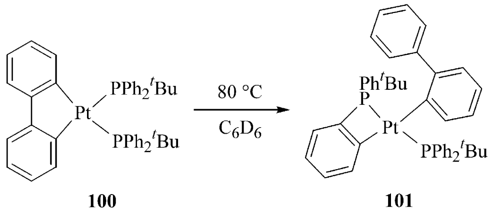
Scheme 42.

The tris(1-pyrazolyl)methane (tpzm) complex **102**, which is obtained from $[PtMe_2(tpzm)]$ and PPh_3, undergoes *ortho*-metallation of PPh_3 on heating slowly in vacuo to 185 °C (Scheme 45) [235,236]. Although the monomeric formulation of the product **103** seems most probable, confirmatory ^{31}P NMR spectroscopic or X-ray structural evidence was not given.

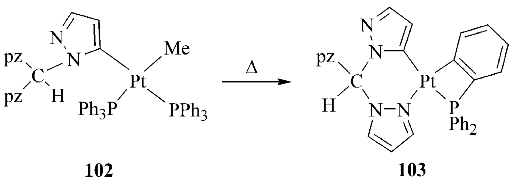
A product formulated tentatively as **104** has been isolated from the reaction of the bromotrifluoroethene complex $[Pt(\eta^2\text{-}CF_2{=}CFBr)(PMePh_2)_2]$ with CO [237].



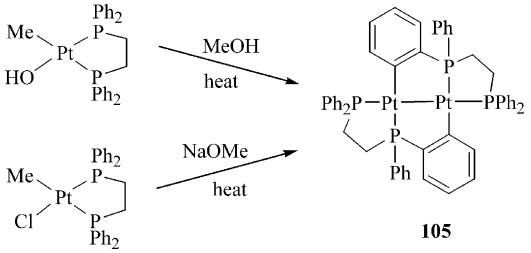
Scheme 43.



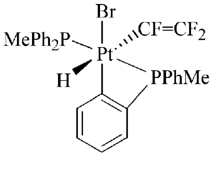
Scheme 44.



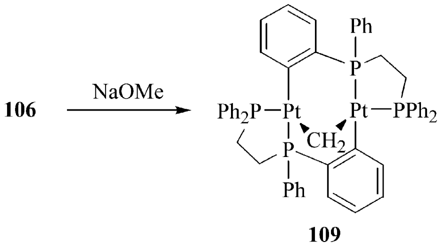
Scheme 45.



Scheme 46.



104



Scheme 48.

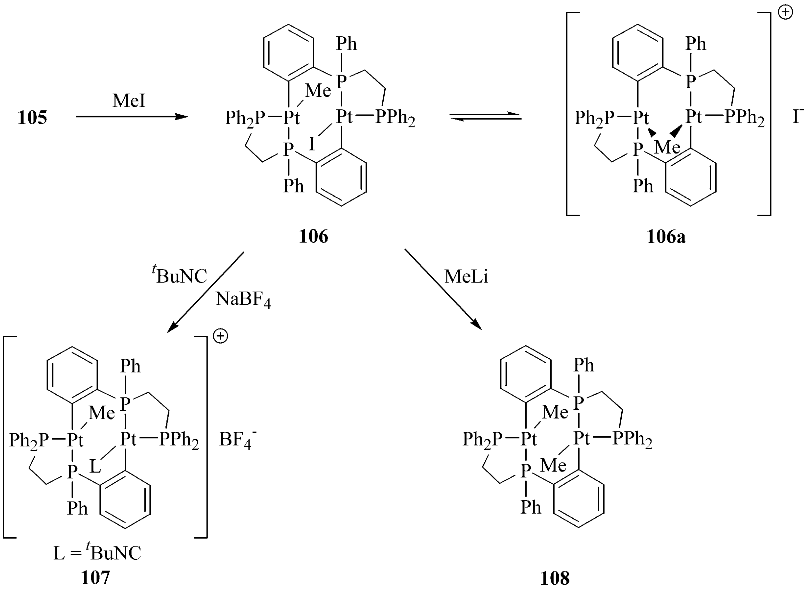
Ortho-metallation of dppe is induced by heating the hydroxo-complex [Pt(OH)(Me)(dppe)] in methanol or by heating [PtCl(Me)(dppe)] with NaOMe. The orange product **105** (Scheme 46) contains two platinum(I) ($5d^9$) centers held together by a metal–metal bond [r(Pt–Pt) = 2.628(1) Å] and a pair of bridging, *ortho*-metallated dppe ligands [238]. The same complex is formed in low yield (ca. 25%) during the decomposition of [$Pt(OMe)_2$(dppe)] in CD_2Cl_2 at room temperature or on prolonged heating of [$PtCl_2$(dppe)] in methanolic NaOMe [238,239].

Complex **105** undergoes oxidative addition of electrophiles to the Pt–Pt bond to give diplatinum(II) complexes. Of particular interest is the methyl iodide adduct **106**, in which the methyl group appears to migrate rapidly on the NMR timescale between the platinum atoms, even below −100 °C, owing to reversible ionization of iodide ion and formation of a μ-methyl cation **106a** (Scheme 47) [240]. Treatment of **106** with *t*-butyl isocyanide in the presence of $NaBF_4$ 'fixes' the methyl group on one platinum atom to give the non-fluxional cation **107**. The iodide ligand in **106** can also be replaced by a second methyl group to give a neutral dimethyl complex **108** [r(Pt···Pt) = 3.010(1) Å] in which the methyl groups are almost eclipsed and the coordination geometry about each platinum atom is strongly distorted from planarity.

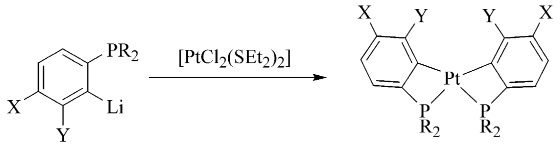
Complex **106** is deprotonated by NaOMe to give a neutral μ-methylene complex **109** with an A-frame structure [r(Pt···Pt) = 2.915(1) Å] (Scheme 48) [241].

Complex **109** can be re-protonated to regenerate **106**, and also reacts with [Me_3O]PF_6 to give the μ-ethyl analogue of **106a**. Complex **105** and its dppp analogue have also been shown to add metal-based electrophiles such as [$Au(PPh_3)$]$^+$ [242], $Ag(O_2CCF_3)$, $HgCl_2$ and $Hg(O_2CCF_3)_2$ [243] to give triangular clusters. From the reaction of **105** with $AgBF_4$, the μ-hydroxo analogue of **109** has been isolated and structurally characterized [244].

Probably because of the ready formation of μ-PPh_2 complexes such as **97** (see above), analogues of **105** containing bridging *ortho*-metallated arylphosphines cannot be obtained by heating [$Pt(OH)(Me)(PPh_3)_2$] in methanol. However, Bennett and co-workers have obtained a range of such complexes by making use of transmetallation. Treatment of [$PtCl_2(SEt_2)_2$] with 2-$LiC_6H_4PPh_2$ gives the complex *cis*-[$Pt(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)_2$] **110**, which contains two four-membered chelate rings, as shown by ^{31}P NMR spectroscopy and X-ray crystallography; a small

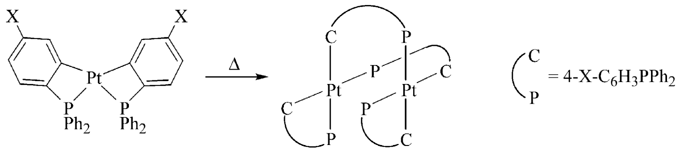


Scheme 47.



X = Y = H; R = Ph **110**
X = Me; Y = H; R = Ph **111**
X = H; Y = Me; R = Ph **112**
X = Y = H; R = ^{i}Pr **113**

Scheme 49.



X = H **110**
X = Me **111**

Scheme 50.

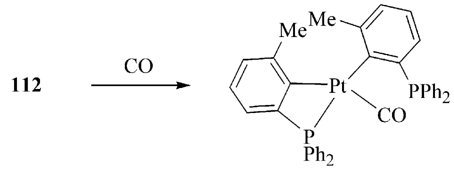
amount of the *trans*-isomer is also formed and can be detected by ^{31}P NMR spectroscopy (Scheme 49) [126,245]. The analogous methyl-substituted complexes [Pt(κ^2-2-C_6H_3-5-MePPh$_2$)$_2$] **111** and [Pt(κ^2-2-C_6H_3-6-MePPh$_2$)$_2$] **112**, and the ^{i}Pr analogue of **110**, complex **113**, have been prepared similarly [246,247].

Complexes **110** and **111** dimerize on heating in toluene to give stable complexes containing two bridging and two chelating arylphosphine ligands (Scheme 50) [246,248], whereas complex **112** forms only traces of dimer, and **113** is unchanged, illustrating once again the effect of bulky substituents, either on the phosphorus or in the σ-bonded aryl group, in stabilizing the four-membered cyclometallated rings.

Dimerization of **110** and **111** is also promoted by CO (1 bar) at room temperature; a second product of this reaction is an insoluble polymer or oligomer which appears to contain both bridging and chelating P,C groups as indicated by solid-state ^{31}P NMR. The catalytic effect of CO presumably derives from its ability to coordinate to Pt(II), thus promoting opening of the P,C-chelate rings (no insertion into the Pt–C σ-bonds is observed). In agreement with this suggestion, complex **112** forms an adduct **114** containing terminally bound CO in which one of the phosphorus atoms has been displaced (Scheme 51) [246].

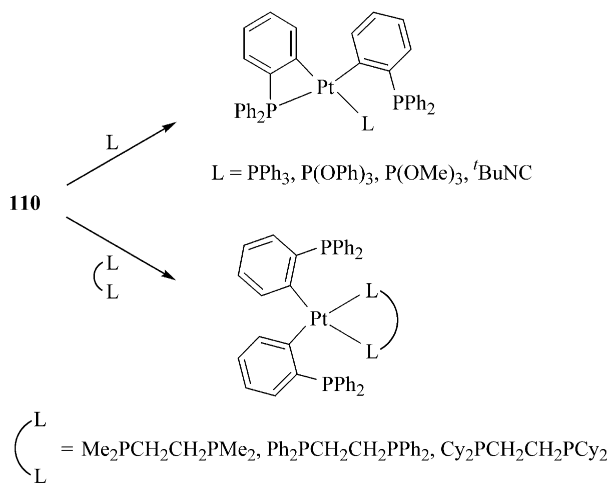
Facile ring-opening by displacement of coordinated phosphorus is also evident in the reactions of complexes **110** and **111** with monodentate and bidentate Group 15 donors and with *t*-butyl isocyanide (Scheme 52) [126,246].

Complexes **110** and **111** undergo oxidative addition reactions with halogens and with a range of alkyl halides to give the expected platinum(IV) complexes, e.g. the methyl iodide adduct **115**, but in some cases ring-opening interferes. For example, reaction of **110** with bromine gives finally the chelate σ-aryl phosphine oxide complex **116**, presumably resulting from addition of the halogen to both metal and phosphorus and subsequent hydrolysis of the resulting dibromophosphorane [126].

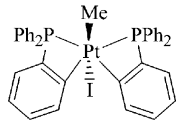


114

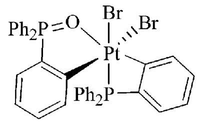
Scheme 51.



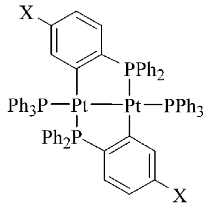
Scheme 52.



115

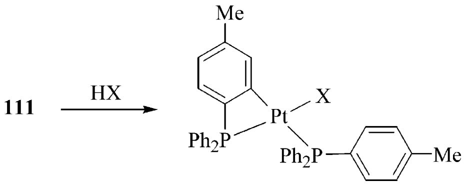


116

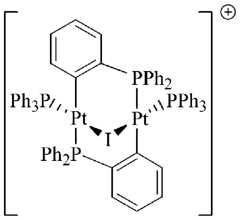


X = H **117**
X = Me **118**

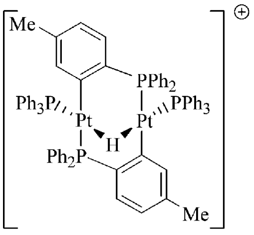
Comproportionation of complexes **110** or **111** with [Pt(PPh$_3$)$_3$] or [Pt(η^2-C_2H_4)(PPh$_3$)$_2$] in refluxing toluene gives the corresponding diplatinum(I) complexes [Pt$_2$(PPh$_3$)$_2$(μ-C_6H_3-5-R-2-PPh$_2$)$_2$] (R = H **117**, Me **118**), which are structurally and chemically analogous to the dppe-derived complex **105** [245,246]. Like **105**, they react with electrophiles, e.g. **117** with iodine gives the iodide salt of the cationic A-frame species **119** [r(Pt···Pt) = 2.931(2) Å] [245]; reaction of **118** with HPF$_6$ gives the μ-hydrido cation **120** whose X-ray structure shows unexpectedly that the 5-methyl substituent of the μ-2-C_6H_3-5-MePPh$_2$ group is disordered between the σ-bonded aryl and the 'phenyl' groups of the *ortho*-PPh$_2$ substituent [246]. This can only occur if the hydride migrates reversibly between the Pt–Pt center and the Pt–C σ-bond, i.e., a reversible reductive elimination.



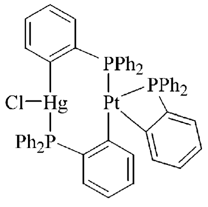
Scheme 53.



119



120

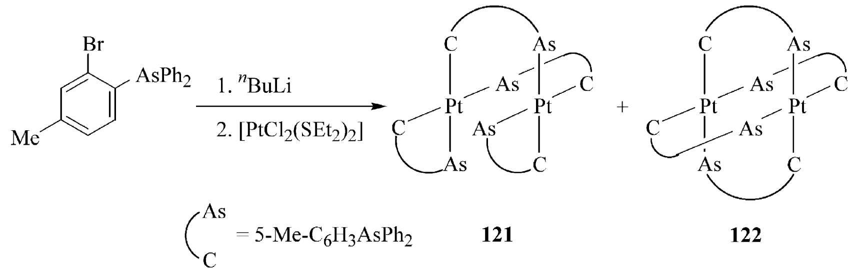


123

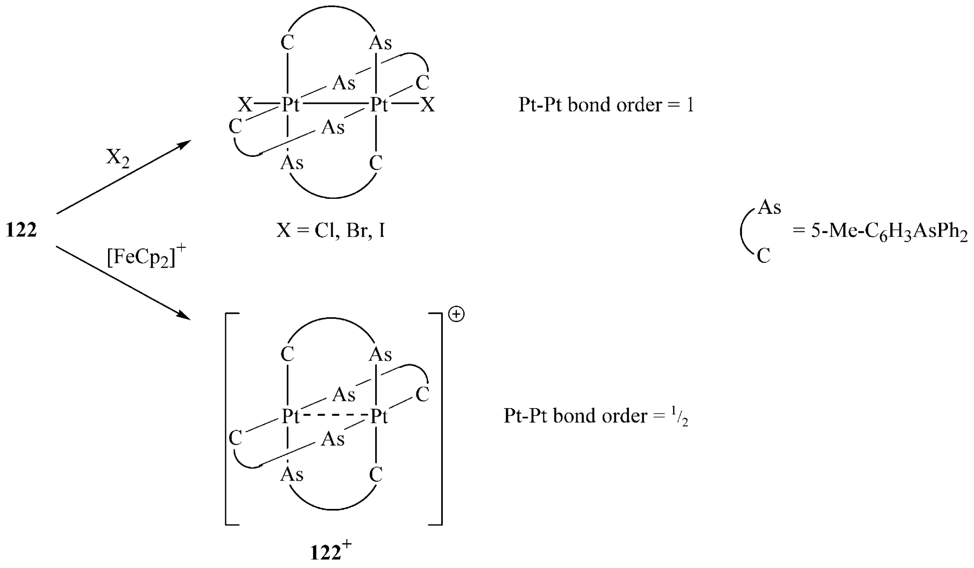
Treatment of complex **111** with one equivalent of a mineral acid results in the selective cleavage of one Pt–C σ-bond, giving mono-chelate complexes *cis*-[PtX(κ^2-2-C_6H_3-5-$MePPh_2$)(κP-4-$MeC_6H_4PPh_2$)] (X = Cl, Br, ONO_2, $OCOCF_3$) (Scheme 53), which isomerize slowly to the corresponding *trans*-isomers. The compounds having X = I, F, CN, OH, OAc, OBz, NCO, SCN, NCS, SeCN, NO_2 and N_3 have been made from the chloro-compound by standard anation reactions. Carbon-bonded derivatives have been prepared by reaction of the appropriate organolithium reagent with either the chloro compound (X = Me, Ph) or the trifluoroacetato compound (X = C_6F_5); cationic complexes *cis*-[Pt(L)(κ^2-2-C_6H_3-5-$MePPh_2$)(κP-4-$MeC_6H_4PPh_2$)]$^+$ have been either prepared or generated in situ by reaction of the chloro-compound with $AgBF_4$ and addition of a neutral ligand [L = 4-$MeC_6H_4PPh_2$, EPh_3 (E = As, Sb), CO, NH_3, NEt_3, py, $PhNH_2$, *o*-, *m*- and *p*-toluidine, R_2S (R = Ph, Me, Et), THF, tht, dmso, $EPPh_3$ (E = O, S, Se), $P(OR)_3$ (R = Me, Ph), ^{t}BuNC and RC≡CR (R = Me, Ph)]. The Pt-P coupling constants of this series have been used to develop the most extensive NMR *trans*-influence series currently available [246]. The mono-chelate cation [Pt(κ^2-2-$C_6H_4PPh_2$)$(PPh_3)_2$]$^+$ has also been prepared by abstraction of Cl^- from [PtCl$(PPh_3)_3$]Cl with Ag^+ [249] and by slow hydrolysis of [PtF$(PPh_3)_3$]SbF_6 in CD_2Cl_2 [250]; the X-ray structure of the SbF_6 salt has been determined.

Transmetallation has also been used to prepare the first *ortho*-metallated complexes derived from triphenylarsine, which show interesting differences from the tertiary phosphine systems discussed above. Reaction of (2-LiC_6H_3-4-Me)$AsPh_2$ with [$PtCl_2(SEt_2)_2$] does not give the expected arsine analogue of **111** [Pt(κ^2-2-C_6H_3-5-$MeAsPh_2$)$_2$] (Scheme 49); rather, a ca. 1:1 mixture of two, isomeric dinuclear complexes **121** and **122** is formed, as shown in Scheme 54 [251]. Isomer **121** contains two bridging and two chelating (2-C_6H_3-5-Me)$AsPh_2$ ligands and is structurally similar to the phosphorus compound obtained by heating **111** (Scheme 50); isomer **122** contains four bridging $MeC_6H_3AsPh_2$ ligands in a lantern arrangement. Heating in toluene converts **121** quantitatively into **122**, a process that has not been achieved in the corresponding phosphorus system. Evidently the bridging mode of coordination is favored over chelating for the arsenic ligands.

Oxidative addition of chlorine, bromine and iodine, either to pure **122**, or to the isomeric mixture of **121** and **122**, gives metal-metal bonded diplatinum(III) ($5d^7$–$5d^7$) complexes [Pt_2X_2(μ-2-C_6H_3-5-$MeAsPh_2$)$_4$] (X = Cl, Br, I) in which the lantern structure is retained (Scheme 55). The corresponding cyano, N-bonded thiocyanato, cyanato and fluoro complexes have been prepared from the chloro-derivative by appropriate metathetical reactions [251]. Zinc dust reduction of the dihalo complexes gives pure **122**, free from **121**. The Pt–Pt bond lengths in the series range from 2.6530(4), 2.6524(4) Å for X = F (values for two independent molecules) to 2.7910(2) Å for X = CN, being in all cases less than the Pt···Pt separation of 2.8955(4) Å in **122** owing to the formation of the metal-metal bond. Complex **122** undergoes a reversible, one-electron oxidation at $E_{1/2} = -0.165$ V (versus FcH/FcH$^+$) by cyclic voltammetry, and is oxidized quantitatively by ferrocenium salts to a paramagnetic $5d^7$–$5d^8$ mono-cation [Pt_2(μ-2-C_6H_3-5-$MeAsPh_2$)$_4$]$^+$ **122$^+$** (Scheme 55) [r(Pt–Pt) = 2.7069(3) Å in the BF_4 salt] [252].



Scheme 54.



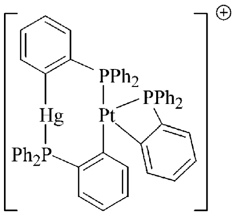
Scheme 55.

According to ESR data and theoretical calculations, the unpaired electron is localized in a predominantly $5d_{z}{}^{2}$ orbital between the two platinum atoms; the formal Pt–Pt bond order is 1/2.

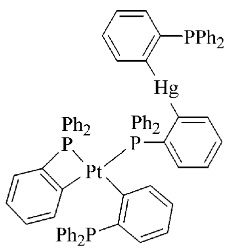
The reagent $[Hg(2\text{-}C_6H_4PPh_2)_2]$ has been used to prepared mixed platinum-mercury complexes containing *ortho*-metallated triphenylphosphine [212]. When heated in toluene with $[PtCl_2(cod)]$, the initially formed P-donor complex *cis*-$[PtCl_2\{Hg(2\text{-}C_6H_4PPh_2)_2\}]$ is converted into complex **123**, which has been shown to contain one κ^2-2-$C_6H_4PPh_2$ group and two μ-2-$C_6H_4PPh_2$ groups. The cation **124** is obtained by treatment of **123** with $AgPF_6$. Reaction of $[Hg(2\text{-}C_6H_4PPh_2)_2]$ with the zerovalent complexes $[Pt(dba)_2]$ or $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ gives ca. 20% yield of a complex formulated as **125** on the basis of multinuclear NMR spectroscopy; it contains monodentate P-bonded $Hg(2\text{-}C_6H_4PPh_2)_2$, κ^2-2-$C_6H_4PPh_2$, and κ-C-2-$C_6H_4Ph_2$ [212].

4.6. Cu, Ag, Au

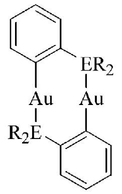
No *ortho*-metallated complexes of copper or silver containing either P- or As-donor atoms are known, although the X-ray structure of the $[Cu(PPh_3)]^+$ adduct of complex **97** (Scheme 41) shows that the σ-bonded carbon of μ-2-$C_6H_4PPh_2$ interacts weakly with the copper atom [222]. Bennett, Bhargava and co-workers have prepared a large number of dinuclear gold(I) complexes of general formula $[Au_2(\mu\text{-}2\text{-}C_6H_4ER_2)_2]$ (E = P, $R_2 = Ph_2$, Et_2, ${}^iPr_2$, PhEt; E = As, R = Ph, Me) **126** from the reaction of $[AuBr(PEt_3)]$ with the appropriate organolithium reagent and have made a detailed study of their chemistry [247,253–255]. Analogous complexes in which the cyclometallated aromatic ring bears methyl substituents at the 5- or 6-positions have been obtained similarly [256,257]. This transmetallation procedure was first used by Abicht and Issleib [258] to prepare the dinuclear gold(I) complex $[Au_2(\mu\text{-}2\text{-}C_6H_4CH_2PPh_2)_2]$ from $[AuBr(PEt_3)]$ and $2\text{-}LiC_6H_4CH_2PPh_2$ [258]. The intermediate **127** has been isolated serendipitously as a by-product from the reaction of $[AuBr(AsPh_3)]$ with $2\text{-}LiC_6H_3\text{-}3\text{-}MePPh_2$ and identified by X-ray crystallography [259].



124



125



E = P; $R_2 = Ph_2$, Et_2, ${}^iPr_2$, PhEt

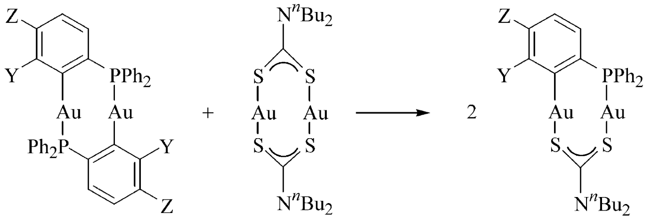
E = As; $R_2 = Ph_2$, Et_2

126

The X-ray structures of the digold(I) complexes **126** feature a pair of linearly coordinated gold atoms, separated by ca. 2.85 Å (E = P) or 2.95 Å (E = As) (Table 2) in an eight-membered ring of chair conformation; the Au···Au separation in the tertiary phosphine derivatives is close to that in metallic gold (2.88 Å) [260]. In the 10-membered ring complex $[Au_2(\mu\text{-}2\text{-}C_6H_4CH_2PPh_2)_2]$

Table 2
Gold–gold distances in binuclear *ortho*-metallated digold(I) and digold(II) complexes

	Au···Au (Å)	Reference
$[Au_2(\mu\text{-}2\text{-}C_6H_4P^iPr_2)_2]$	2.8647(3)	[247]
$[Au_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$	2.8594(3)	[253]
$[Au_2(\mu\text{-}2\text{-}C_6H_4PEt_2)_2]$	2.8617(6)	[253]
$[Au_2(\mu\text{-}2\text{-}C_6H_4AsPh_2)_2]$	2.9358(5)	[253]
meso-$[Au_2(\mu\text{-}2\text{-}C_6H_4PPhEt)_2]$	2.859(1)	[255]
$[Au_2(\mu\text{-}2\text{-}C_6H_3\text{-}6\text{-}MePPh_2)_2]$	2.861(2)	[256]
$[Au_2(\mu\text{-}2\text{-}C_6H_3\text{-}6\text{-}MeAsPh_2)_2]$	2.954(3)	[257]
$[Au_2(\mu\text{-}2\text{-}SO_2C_6H_4PPh_2)_2]$	2.9498(2)	[266]
$[Au_2(OBz)_2(\mu\text{-}2\text{-}C_6H_4PEt_2)_2]$	2.5243(7)	[254]
meso-$[Au_2Cl_2(\mu\text{-}2\text{-}C_6H_4PEtPh)_2]$	2.5528(2)	[255]
$[Au_2Cl_2(\mu\text{-}2\text{-}C_6H_3\text{-}5\text{-}MeAsPh_2)_2]$	2.5526(3)	[257]
$[Au_2Br_2(\mu\text{-}2\text{-}C_6H_3\text{-}5\text{-}MeAsPh_2)_2]$	2.5651(3)	[257]
$[Au_2I_2(\mu\text{-}2\text{-}C_6H_3\text{-}5\text{-}MeAsPh_2)_2]$	2.5880(3)	[257]
$[Au_2I_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$	2.5898(6)	[267]
$[Au_2(C_6F_5)_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$	2.6139(4)	[268]

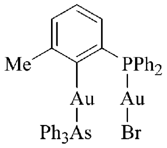


Y = H; Z = Me
Y = Me; Z = H

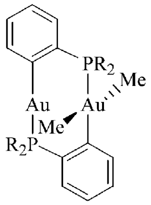
Scheme 56.

the Au···Au separation is increased to 3.0035(9) Å [261]. It is worth noting that the structures of **126**, and some aspects of the chemistry of these compounds, discussed below, resemble those of other digold(I) complexes containing bridging 1,3-dipolar ligands, particularly the phosphine bis(ylide) derivatives [262–264].

Although they are stable in the solid-state, the digold(I) complexes are labile in solution. Thus, mixtures of $[Au_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ and $[Au_2(\mu\text{-}2\text{-}C_6H_4PEt_2)_2]$ scramble the bridging groups over a period of hours in solution (contrary to an earlier statement [254]), and on mixing solutions of $[Au_2(\mu\text{-}2\text{-}C_6H_3\text{-}n\text{-}Me\text{-}PPh_2)_2]$ ($n = 5, 6$) with either $[Au_2(\mu\text{-}S_2CN^nBu)_2]$ or $[Au_2Cl_2(\mu\text{-}dppm)_2]/NH_4PF_6$, hetero-bridged species are formed, as shown in Schemes 56 and 57 [265].

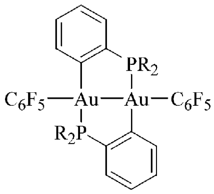


127



R = Ph, Et

129

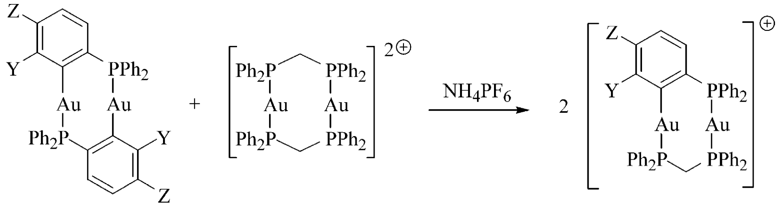


R = Ph, Et

130

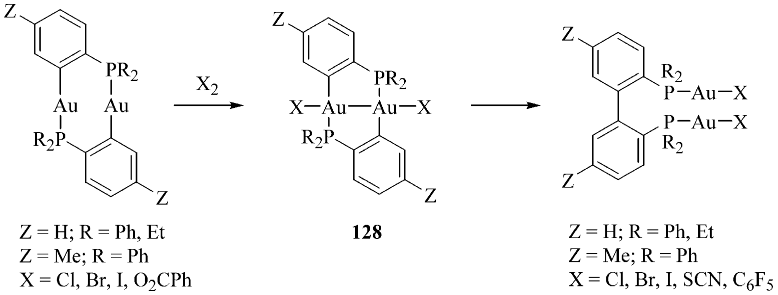
The digold(I) complexes $[Au_2(\mu\text{-}2\text{-}C_6H_4PR_2)_2]$ ($R_2 = Ph_2$, Et_2, ${}^iPr_2$ and PhEt) and $[Au_2(\mu\text{-}2\text{-}C_6H_3\text{-}5\text{-}MePPh_2)_2]$ undergo oxidative additions of halogens and dibenzoyl peroxide to the gold-gold unit to give digold(II) complexes **128** in which each gold atom is planar coordinated (Scheme 58) [247,254–257]. The presence of a metal-metal bond between the $5d^9$ metal centres is confirmed by the observed Au–Au separations of 2.55–2.61 Å (Table 2), which are ca. 0.2 Å shorter than in the parent digold(I) compounds. The complexes are, therefore, direct analogues of the diplatinum(I) complexes **105**, **117** and **118** (Section 4.5).

The diiodo complex **128** (X = I, Z = H) is also the main product of reaction of $[Au_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ with methyl iodide, although the asymmetrical (iodo)methyl species has been detected by ^{31}P NMR spectroscopy [254]. The axial halide ligands in **128** undergo typical metatheses with silver acetate, benzoate or nitrate. Although the dihalo complexes are reduced by methyllithium to the parent digold(I) species, the bis(benzoato) complexes $[Au_2(OBz)_2(\mu\text{-}2\text{-}C_6H_4PR_2)_2]$ (R = Ph, Et) react with dimethylmagnesium to give dimethyl gold(I)–gold(III) complexes **129**, which are probably formed by rearrangement



Y = H; Z = Me
Y = Me; Z = H

Scheme 57.

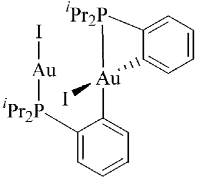


Scheme 58.

of a dimethydigold(II) intermediate. The corresponding reactions with C_6F_5Li give the expected digold(II) complexes $[Au_2(C_6F_5)_2(\mu\text{-}2\text{-}C_6H_4PR_2)_2]$ **130** [268].

The digold(II) complexes $[Au_2X_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ ($X = Cl, Br, I, SCN, C_6F_5$) and $[Au_2X_2(\mu\text{-}2\text{-}C_6H_3\text{-}5\text{-}MePPh_2)_2]$ ($X = Cl$, Br, I) rearrange slowly and irreversibly in solution by intramolecular reductive elimination of the Au–C bonds, and formation of one C–C bond, to give digold(I) complexes of the corresponding (2,2′-biphenylyl)diphenylphosphines (Scheme 58) [254,256,267]. The digold(II) complexes containing axial *O*-donor anions, such as benzoate or acetate, do not behave similarly. In contrast, the dihalodigold(II) complexes formed by addition of halogens to $[Au_2(\mu\text{-}2\text{-}C_6H_3\text{-}6\text{-}MePPh_2)_2]$ at −70 °C rearrange rapidly in solution, even at −20 °C, to give heterovalent gold(I)–gold(III) complexes **131** in which the bonding mode of one of the $2\text{-}C_6H_3\text{-}6\text{-}MePPh_2$ groups has changed from bridging to chelating (Scheme 59).

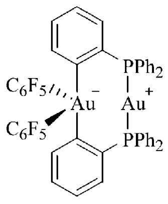
The structure of **131** ($X = I$) has been confirmed by X-ray crystallography, the Au(I)· · ·Au(III) separation being 3.4692(7) Å [256]. These complexes do not rearrange further by C–C coupling, probably due to steric hindrance by the 6-methyl substituents to the reductive elimination process. There is, nevertheless, good evidence that analogous complexes are intermediates in the C–C coupling reaction of Scheme 58. First, in the rearrangements of $[Au_2X_2(\mu\text{-}2\text{-}C_6H_4PR_2)_2]$ ($X = C_6F_5$, SCN; R = Ph, Et) **130**, species whose ^{31}P NMR spectra resemble those of **131** can be detected, though not isolated [268]. Second, whereas chlorination of $[Au_2(\mu\text{-}2\text{-}C_6H_4P^iPr_2)_2]$ gives a symmetrical digold(II) complex, analogous to **128**, iodination gives a gold(I)-gold(III) complex **132**, whose ^{31}P NMR spectrum and X-ray structure resemble that of **131**; bromination gives a mixture of both forms. In this system, heating induces internal C–C bond formation to give finally the digold(I) complexes of 2,2′-$^iPr_2PC_6H_4C_6H_4P^iPr_2$ [247].



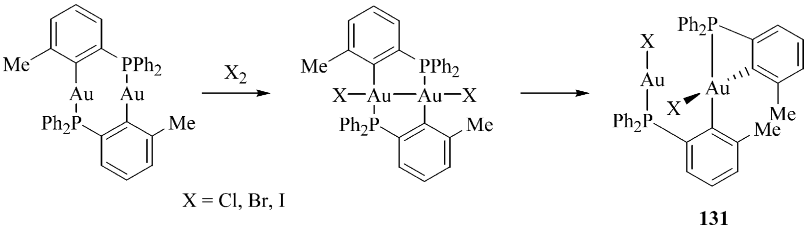
132

Ab-initio calculations [269] confirm that the main steps leading to the C–C coupled products are, first, a σ-aryl migration of one of the bridging ligands in the digold(II) complex to give its heterovalent isomer A and, second, a reductive elimination at the resulting gold(III) centre via the transition state B, giving the coupled product C, as shown in Scheme 60. The presence of strongly electron-withdrawing axial ligands, such as benzoate or acetate, in the digold(II) complex evidently destabilizes the heterovalent relative to the homovalent isomer; when the axial ligand is strongly electron-donating, such as methyl or phenyl, it migrates in preference to the aryl of the bridging ligands to give the heterovalent species D, thus preventing coupling of the bridging ligands.

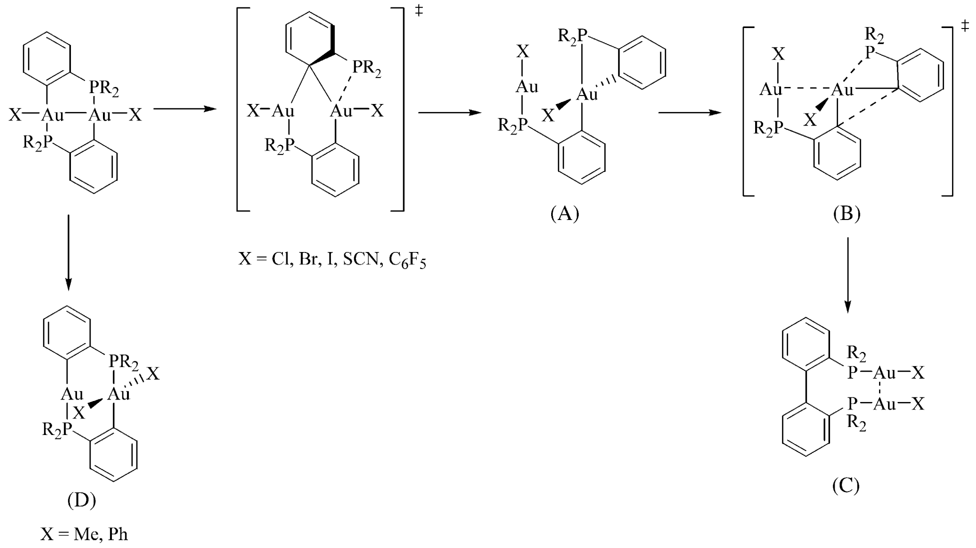
An additional complication in this chemistry whose consequences remain to be explored is the existence of heterovalent gold complexes in which the bridging ligands are arranged head-to-head rather than head-to-tail. Isomerization of the bis(pentafluorophenyl)digold(II) complex **130** ($R = Ph$) gives, in addition to the C–C coupled product, an isomer **133** in which one of the bridging $2\text{-}C_6H_4PPh_2$ groups has turned through 180° [268].



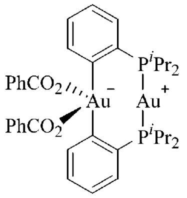
133



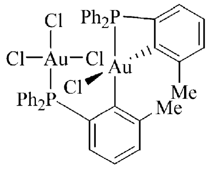
Scheme 59.



Scheme 60.

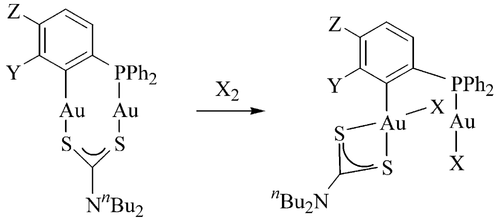


134



135

This complex can be regarded as a zwitterion containing one cationic gold(I) and one anionic gold(III) centre, the separation between them being 2.931(1) Å [cf. 2.6139(4) Å in the homovalent isomer **129**]. Complex **133** must arise by an alternative rearrangement of intermediate A in Scheme 60 in which a phosphorus atom and one X^- group migrate from one gold atom to its neighbour. A similar zwitterion **134** is formed by treatment of the gold(I)–gold(III) complex **132** with silver benzoate [247]. In the light of these results, it is surprising that reaction of complex **131** (X = I) with silver benzoate and then with C_6F_5Li gives a structurally similar compound in which iodide has simply been replaced by C_6F_5 [270].



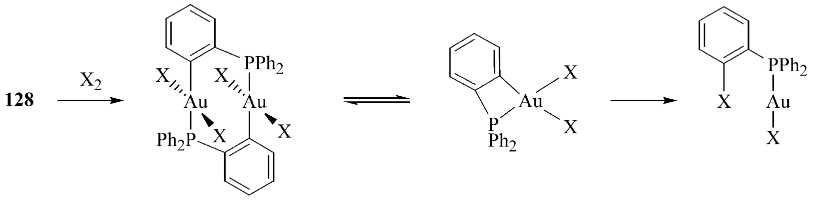
X = Cl, Br, I; Y = Me; Z = H
X = Cl, I; Y = H; Z = Me

Scheme 61.

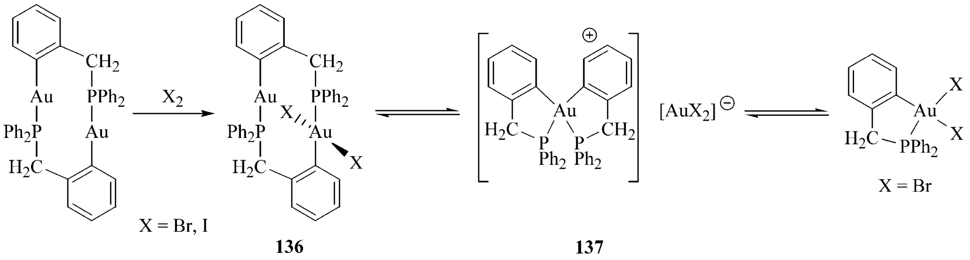
Halogenation of the hetero-bridged digold(I) complexes containing a bridging P,C unit and bridging dithiocarbamate (Scheme 61) gives gold(I)–gold(III) complexes in which dithiocarbamate becomes chelating while the P,C group remains bridging (Scheme 61) [265].

The metal–metal bond in the digold(II) complexes **128** (Scheme 58) is cleaved by an excess of halogen. Thus, **128** (X = Br, I; Z = H) with an excess of bromine or iodine gives an equilibrium mixture of binuclear and mononuclear dihalogold(III) complexes, identified by ^{31}P NMR spectroscopy, which finally undergo electrophilic cleavage of the Au–C σ-bond to form the gold(I) complexes [AuX(2-$XC_6H_4PPh_2$)] as shown in Scheme 62 [254,256].

Treatment of the gold(I)–gold(III) complex **131** (X = Cl) (Scheme 59) with one molar equivalent of $PhICl_2$, or of [Au_2Cl_2(μ-C_6H_3-6-Me-2-PPh_2)$_2$] with two molar equivalents of $PhICl_2$, gives an almost insoluble yellow digold(III) complex **135** derived by addition of chlorine to the gold(I) centre [256].



Scheme 62.



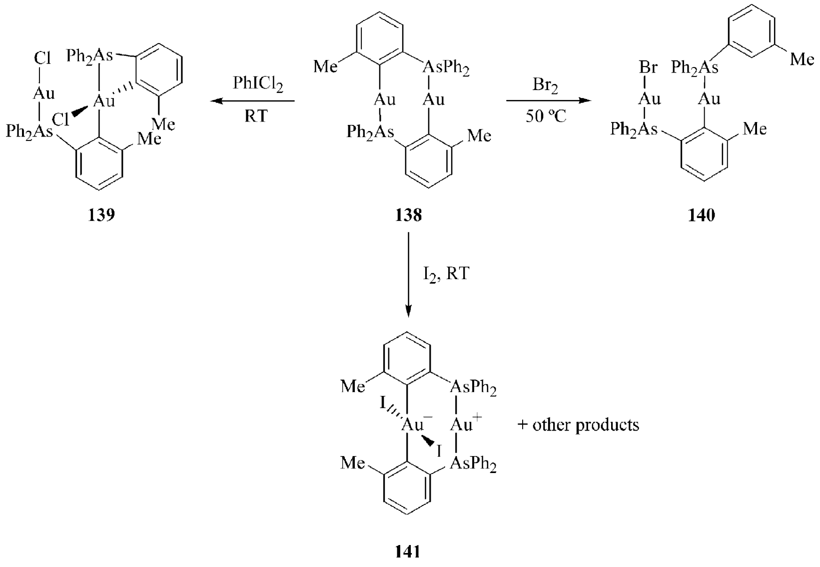
Scheme 63.

Studies of the ^{197}Au Mössbauer spectra [271,272] and X-ray photoelectron spectra [273,274] of many of the *ortho*-aurated complexes have been carried out. They enable the +1, +2 and +3 oxidation states to be distinguished and confirm the formulations based on X-ray crystallography and NMR spectroscopy. These techniques are especially useful in cases such as the poorly soluble complex **135** for which X-ray quality single crystals could not be obtained.

The addition of bromine or iodine to the 10-membered ring complex [$Au_2(\mu$-2-$C_6H_4CH_2PPh_2)_2$] takes a somewhat different course from that of the eight-membered ring *ortho*-aurated complex. Probably because of the greater separation between the metal atoms, the halogens add initially to only one gold atom to give gold(I)–gold(III) complexes **136**, which are in equilibrium with the salts [$Au(\kappa^2$-2-$C_6H_4CH_2PPh_2)_2$][AuX_2] (X = Br, I) **137** (Scheme 63) [261]. The stability of the five-membered chelate rings is probably responsible for the existence of the planar cation and for the failure to undergo C–C coupling. An excess of bromine gives the neutral five-membered ring complex [$AuBr_2(\kappa^2$-2-$C_6H_4CH_2PPh_2)$].

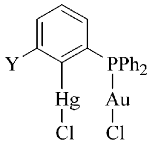
Preliminary studies indicate that the digold(I) *ortho*-metallated tertiary arsine complexes undergo oxidative additions with halogens (X_2) similarly to the phosphine analogues, e.g. [$Au_2(\mu$-C_6H_3-5-Me-2-$AsPh_2)_2$] gives the expected digold(II) complexes [$Au_2X_2(\mu$-2-C_6H_3-5-$MeAsPh_2)_2$], which undergo internal reductive elimination by heating to give the digold(I) complexes [$Au_2X_2\{\mu$-$C_6H_3C_6H_3$-5,5′-Me_2-2,2′-$(AsPh_2)_2\}$] [257]. However, there are some unexpected differences, especially in the case of [$Au_2(\mu$-2-C_6H_3-6-$MeAsPh_2)_2$] **138** (Scheme 64). The latter reacts with $PhICl_2$ to give **139**, which is the arsenic analogue of **131** (X = Cl) (Scheme 59), but with bromine at 50 °C is the monobromo-digold(I) complex **140**, the source of the added hydrogen atom and the fate of the lost bromine atom have not been determined. Surprisingly, one product isolated from the reaction of **138** with iodine is the zwitterionic gold(I)–gold(III) complex **141**, which is similar to complexes **133** and **134** in the phosphine series [257].

A few other reactions of the binuclear *ortho*-aurated complexes have been investigated. Treatment of the digold(I) complexes [$Au_2(\mu$-2-$C_6H_4PPh_2)_2$] and [$Au_2(\mu$-2-C_6H_3-6-$MePPh_2)_2$] with $HgCl_2$ causes electrophilic cleavage of the Au–C σ-bonds and formation of complexes **142** in which the *ortho*-metallated units bridge gold and mercury [253,259]. Sulfur dioxide inserts into the Au–C σ-bonds of [$Au_2(\mu$-2-$C_6H_4PPh_2)_2$] giving [$Au_2(\mu$-2-$SO_2C_6H_4PPh_2)_2$], the dimeric unit being retained intact [266]. From the reaction of [$Au_2Cl_2(\mu$-2-C_6H_3-5-$MeAsPh_2)_2$] with ethynylferrocene in the presence of base the mononuclear gold(I) alkynyl complex **143** has been isolated and structurally characterized [257]. This complex may be formed by reductive elimination from the gold(III) centre of an intermediate gold(I)–gold(III) bis(acetylide) [$Au^I(\mu$-2-C_6H_3-5-$MeAsPh_2)_2Au^{III}(C{\equiv}CR)_2$] (R = Fc), analogous to the dimethyl



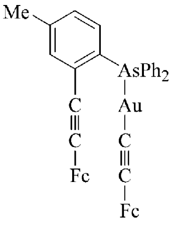
Scheme 64.

complex **129**. Though this intermediate has not been detected, a structurally similar complex containing a bridging ylide, μ-$Ph_2P(CH_2)_2$, has been reported recently [275].



Y = H, Me

142



143

The reaction of $[Au_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ with methyl triflate, which was expected to undergo binuclear oxidative addition along the Au· · ·Au axis, gives in fact the triflate salt of a pentanuclear cation $[Au_5(\mu\text{-}2\text{-}C_6H_4PPh_2)_4]^+$ **144** (Fig. 8) [276]. There are other unidentified products of this reaction, and the sequence that leads to **144** remains unclear, though the first step appears to be electrophilic attack on the Au–C bond. The same complex is obtained by use of $[Au(OTf)(PPh_3)]$ in place of methyl triflate. The cation contains a butterfly arrangement of four gold atoms on the two-fold axis of which a unique gold atom is located. The latter is bound only to a pair of carbon atoms from two of the four bridging $2\text{-}C_6H_4PPh_2$ units. Each of these carbon atoms engages in a Au–C_{ipso}–Au interaction similar to those in the cations $[Au_2(PPh_3)_2(\mu\text{-}R)]^+$ (R = Fc derivatives), which are formed on protonation of $[AuR(PPh_3)]$ [277].

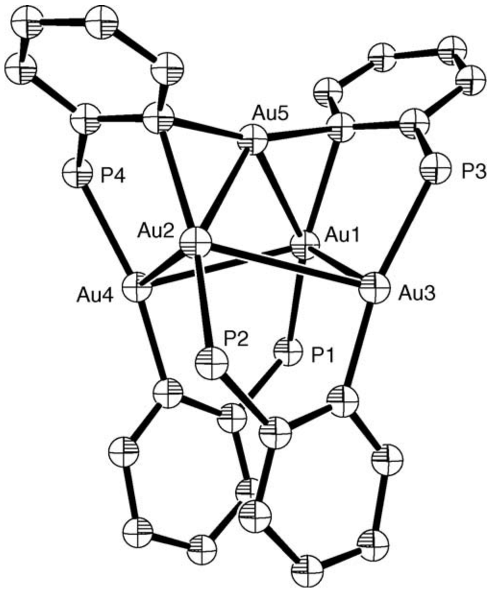
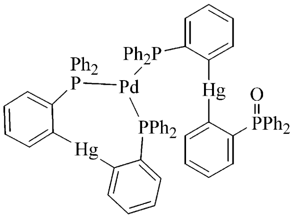


Fig. 8. Structure of the cation $[Au_5(\mu\text{-}2\text{-}C_6H_4PPh_2)_4]^+$ **144** (C_6H_5 groups omitted for clarity).

4.7. Zn, Cd, Hg

There are no examples in this group of *ortho*-metallated complexes in which phosphorus or arsenic and the aromatic carbon are both attached to the metal. In $[Hg(\kappa C\text{-}2\text{-}C_6H_4PPh_2)_2]$, which is made from $HgCl_2$ and $2\text{-}LiC_6H_4PPh_2$, the phosphorus atoms are not coordinated to the metal atom and the compound can be converted into the corresponding bis(oxide), bis(sulfide), and bis(borane) adducts [212,278]. It has been used to transfer $2\text{-}C_6H_4PPh_2$, either completely or partially, to certain d-block elements (Sections 4.3 and 4.5) and behaves as a bidentate P-donor ligand of variable bite angle to Hg^{II}, Pd^{II} and Pt^{II} halides. Its reaction with $[Pd(dba)_2]$ gives an orange, P-coordinated palladium(0) complex $[Pd\{(2\text{-}Ph_2PC_6H_4)_2Hg\}_2]$ [212]. On exposure to air, a P=O derivative **145** is formed which has been shown to contain trigonally coordinated Pd(0) by X-ray crystallography [278]. The complex $[Pd\{(2\text{-}Ph_2PC_6H_4)_2Hg\}_2]$ decomposes in refluxing toluene to give 2,2′-$Ph_2PC_6H_4C_6H_4PPh_2$ with elimination of metallic Pd and Hg, possibly via undetected *ortho*-palladated intermediates.



145

5. Conclusions and outlook

Since the discovery of the spontaneous *ortho*-metallation of coordinated triphenylphosphine 37 years ago, *ortho*-metallated complexes derived from arylphosphines have been discovered for almost all the elements in the Mn, Fe, Co and Ni triads of the Periodic Table (technetium is the only exception). In contrast, only molybdenum and tungsten of the early transition elements, and gold of the copper triad, have so far given well-characterized *ortho*-metallated complexes. Although spontaneous *ortho*-metallation of an arylphosphine remains the most common preparative method, three others have proved useful in particular cases: (1) base-promoted deprotonation at the *ortho*-site of a coordinated arylphosphine; (2) transmetallation from a suitable main group derivative, such as $2\text{-}LiC_6H_4PPh_2$; (3) oxidative addition of a suitable aryl bromide, such as $2\text{-}BrC_6H_4PPh_2$. These procedures may prove to be applicable also to the preparation of the less extensively studied *ortho*-metallated tertiary arsine complexes, because coordinated tertiary arsines seem to be less prone than their phosphorus analogues to undergo spontaneous *ortho*-metallation.

Like other chelate ligands of small bite angle, the $2\text{-}C_6H_4PR_2$ group adopts two common bonding modes, chelating, $\kappa^2 P,C$, and bridging, ligands $\mu^2\text{-}P,C$. A third possible mode, κC, has been observed but is rare, and there are several examples of tridentate behaviour in which the carbon atom bridges two metal atoms. The limited information currently available, mainly with platinum, indicates that the bridging mode may be favoured for $2-C_6H_4AsPh_2$. Facile interconversion between chelate and bridging modes has been established in complexes of palladium, platinum and gold. In principle, there seems to be no reason why a range of multiply metal–metal bonded complexes of the early transition elements containing bridging $2-C_6H_4ER_2$ groups (E = P, As) should not be accessible, provided suitable synthetic procedures can be devised. For both coordination modes, it is clear that *ortho*-metallated complexes of the 5d- and 4d-elements greatly outnumber those of the 3d-elements, probably because metal-ligand and metal-carbon σ-bonds are generally stronger for the heavier d-block elements and also because complexes of the 4d- and 5d-elements are usually less kinetically labile than those of their 3d-congeners.

With the exception of CO insertion into the metal-carbon bond forming five-membered ring acyls, $2-Ph_2PC_6H_4COM$, few studies have been made of the insertion of unsaturated organic compounds into the M–C bond of *ortho*-metallated tertiary phosphine complexes. Also, apart from Lahuerta's work with dirhodium(II) complexes, almost no attention has been paid to the catalytic properties of *ortho*-metallated complexes, despite the possibility of varying catalytic activity by introducing a metal-carbon σ-bond into the coordination sphere of a tertiary phosphine complex. We hope that this review has demonstrated that there is plenty of potential in this rich field to keep organometallic chemists inspired for many years to come.

Appendix A

The following Tables A.1 and A.2 list of all the *ortho*-metallated compounds containing tertiary phosphines and arsines that have been characterized by X-ray crystallography.

Table A.1
Cyclometallated complexes containing a four-membered ring

Compound	Reference
$[Mo(Cp)(\kappa^2-2-C_6H_4PMe_2)(PMe_2Ph)]$	[44]
$[WH(Cp^*)(NO)(\kappa^2-2-C_6H_4PPh_2)]$	[46]
$[WH_3(\kappa^2-2-C_6H_4PMe_2)(PMe_2Ph)_3]$	[47]
$[Mn(CO)_4\{\kappa^2-2-(4-MeC_6H_3)P(4-MeC_6H_4)_2\}]$	[50]
$[ReH_2(\kappa^2-2-C_6H_4PPh_2)(PEt_3)_2]$	[55]
$[Re(\kappa^2-2-C_6H_4PPh_2)(PMe_3)_4]$	[56]
$[Re(\kappa^2-2-C_6H_4PMe_2)(N_2)(PMe_2Ph)_3]$	[57]
$[OsH(CO)_2(\kappa^2-2-C_6H_4PPh_2)(PPh_3)]$	[80]
$[RuBr(\kappa^2-2-C_6H_4PMe_2)(PMe_2Ph)_3]$	[83]
$[Ru(\kappa^2-2-C_6H_4PPh_2)\{N(SiMe_2CH_2PPh_2)-\kappa N\kappa^2 P\}]$	[83a]
$[RuCl(\kappa^2-2-C_6H_4PPh_2)\{N(SiMe_2CH_2PPh_2)-\kappa N\kappa^2 P\}]$	[83a]
$K[RuH_2(\kappa^2-2-C_6H_4PPh_2)(PPh_3)_2]$	[84]
$[OsCl(CO)(\kappa^2-2-C_6H_4PPh_2)(PPh_3)_2]$	[88]
$[Ru(Cp)(\kappa^2-2-C_6H_4PPh_2)(PPh_3)]$	[91]
$[Ru(\eta^6-C_6H_5O)(\kappa^2-2-C_6H_4PPh_2)(PPh_3)]$	[96]
$[Ru(\eta^6-4-{}^tBuC_6H_4O)(\kappa^2-2-C_6H_4PPh_2)(PPh_3)]$	[96]
$[OsH(Cp)(\kappa^2-2-C_6H_4PPh_2)(P^iPr_3)]PF_6$	[97]
$[Ru(CH_2SiMe_3)(\eta^6-C_6Me_6)(\kappa^2-2-C_6H_4PPh_2)]$	[99]
$[Ru(CH_2SiMe_3)(\eta^6-C_6Me_6)(\kappa^2-2-C_6H_4PMePh)]$	[99]
$[Ru(CH_2SiMe_3)(\eta^6-C_6Me_6)(\kappa^2-2-C_6H_4PMe_2)]$	[99]
$[Ru(CH_2{}^tBu)(\eta^6-C_6Me_6)(\kappa^2-2-C_6H_4PPh_2)]$	[100]
$[Ru(CH_2{}^tBu)(\eta^6-C_6Me_6)(\kappa^2-2-C_6H_4PMePh)]$	[100]
$[Ru(CH_2{}^tBu)(\eta^6-C_6Me_6)(\kappa^2-2-C_6H_4PMe_2)]$	[100]
$[RuCl(\eta^6-C_6Me_6)(\kappa^2-2-C_6H_4PMePh)]$	[101]
$[Co(\kappa^2-2-C_6H_4PPh_2)_2(PMe_3)_3]$	[118]
$[CoI(Me)(\kappa^2-2-C_6H_4PPh_2)_2(PMe_3)_2]$	[118]
$[CoCl(\kappa^2-2-C_6H_4PPh_2)_2(PMe_3)_2]$	[118]
$[Co(\kappa^2-2-C_6H_3-3-EtPPh_2)(PMe_3)_3]$	[119]
$[Co\{\kappa^2-P,C-3-({}^tBuNCH)C_6H_3PPh_2\}(PMe_3)_3]$	[121]
$[Rh(\kappa^2-2-C_6F_4PPh_2)(oq)_2]$	[127]
$[RhBr(\kappa^2-2-C_6F_4PPh_2)(oq)(H_2O)]$	[128]
$[RhBr(\kappa^2-2-C_6F_4PPh_2)(oq)(PPh_3)]$	[129]
$[IrCl_2(\kappa^2-2-C_6F_4PPh_2)(\kappa^2-P,Br-2-BrC_6F_4PPh_2)]$	[130]
$[IrBr_2(\kappa^2-2-C_6F_4PPh_2)(\kappa^2-P,Br-2-BrC_6F_4PPh_2)]$	[130]
$[RhCl_2(\kappa^2-2-C_6H_4PPh_2)(\kappa^2-P,Cl-2-ClC_6H_4PPh_2)]$	[132]
$[RhCl_2(\kappa^2-2-C_6H_4PPh_2)(dppm)]$	[133]
$[RhCl_2(\kappa^2-2-C_6H_4PPh_2)\{PPh_2(2-ClC_6H_4)\}(terpy)]SbF_6$	[133]
$[Ir(Cp^*)(CH_2SiMe_3)(\kappa^2-2-C_6H_4PPh_2)]$	[135]
$[Rh(\kappa^2-2-C_6H_4PPh_2)(PPh_3)(C_2B_9H_{11})]$	[142]
$[IrH(Br)(\kappa^2-2-C_6H_4PPh_2)(PPh_3)_2]$	[144]
$[Ir(CO)_2(\kappa^2-2-C_6H_4PPh_2)]$	[151]
$[Ir(\eta^2-CH_2CH_2)_2(\kappa^2-2-C_6H_4PPh_2)(PPh_3)]$	[151]
$[Ir(\eta^2-CH_2CH_2)_2(\kappa^2-2-C_6H_4P^iPr_2)(P^iPr_2Ph)]$	[151]
$[IrH(\kappa^2-2-C_6H_4PPh_2)_2(PPh_3)]$	[152]
$[IrHCl(\kappa^2-2-C_6H_4PPh_2)(CO)(PPh_3)]$	[156]
$[IrH(\kappa^2-2-C_6H_4PPh_2)(PMe_2Ph)]PF_6$	[157]
$[IrH(\kappa^2-2-C_6H_4P^tBu_2)(P^tBu_2Ph)][B\{3,5-(CF_3)_2C_6H_3\}_4]$	[160]
$[IrCl(\kappa^2-2-C_6H_4PPh_2)(PPh_3)\{PhC(O)CHC(O)Ph\}]$	[161]
$[RhI\{C_6H_4P(Ph)CH_2CH_2N(CH_2CH_2PPh_2)_2-\kappa C\kappa N\kappa^3 P\}]BPh_4$	[161a]
$[Ni(\kappa^2-2-C_6Cl_4PEt_2)_2]$	[211]
$[Ni(\kappa^2-2-C_6Cl_4PPh_2)_2(PEt_3)]$	[211]
$[NiCl(\kappa C-2-C_6Cl_4PPh_2)(PEt_3)_2]$	[211]
$[PtI(Me)(\kappa^2-2-C_6H_4PPh_2)_2]$	[126]
$[(\kappa^2-2-C_6H_4PPh_2)Pt(\mu-C_6H_4PPh_2)_2HgCl]$	[212]
$[PdBr(\kappa^2-2-C_6H_4PPh_2)(\kappa P-2-BrC_6H_4PPh_2)]$	[214]
$[Pt(ONO_2)(\kappa^2-2-C_6H_4P^tBu_2)(P^tBu_2Ph)]$	[222]
$[Pt\{C(COOMe)=CH(COOMe)(\kappa^2-2-C_6H_4PPh_2)(PPh_3)]$	[226]
$[PtPh(\kappa^2-2-C_6H_4PPh_2)(PPh_3)]$	[233]
$[Pt(\eta^1-C_6H_9)(\kappa^2-2-C_6H_4PPh_2)(PPh_3)]$	[233]
$[Pt(\kappa^2-2-C_6H_4PPh_2)_2]$	[245]
$[Pt(\kappa^2-2-C_6H_3-5-MePPh_2)_2]$	[246]
$[Pt(\kappa^2-2-C_6H_3-6-MePPh_2)_2]$	[246]
$[PtCl(\kappa^2-2-C_6H_3-5-MePPh_2)(4-MeC_6H_4PPh_2)]$	[246]
$[PtMe(\kappa^2-2-C_6H_3-5-MePPh_2)(4-MeC_6H_4PPh_2)]$	[246]
$[PtCN(\kappa^2-2-C_6H_3-5-MePPh_2)_2]$	[246]
$[Pt(C_6F_5)(\kappa^2-2-C_6H_3-5-MePPh_2)(4-MeC_6H_4PPh_2)]$	[246]
$[Pt(\kappa^2-2-C_6H_3-5-MePPh_2)(4-MeC_6H_4PPh_2)_2]BF_4$	[246]
$[Pt(\kappa O-O_2CCF_3)(\kappa^2-2-C_6H_3-5-MePPh_2)(4-MeC_6H_4PPh_2)]$	[246]
$[Pt(\kappa^2-2-C_6H_4PPh_2)(PPh_3)_2]SbF_6$	[250]
$[IAu(\mu-2-C_6H_3-6-MePPh_2)AuI(\kappa^2-2-C_6H_3-6-MePPh_2)]$	[256]
$[(C_6F_5)Au(\mu-2-C_6H_3-6-MePPh_2)Au(C_6F_5)(\kappa^2-2-C_6H_3-6-MePPh_2)]$	[270]

Table A.2
Complexes containing cyclometallated bridging ligands

Compound	Reference
$[ClPt(PPh_3)(\mu-2-C_6H_4PPh_2)(\mu-PPh_2)PtCl]$	[41]
$[Pt_2(\mu-2-C_6H_4PPh_2)(\mu-PPh_2)(PPh_3)_2]$	[40,41]
$[Re_2Cl_3\{\mu-(Ph_2PC_5H_4N-\kappa P\kappa N\}_2\{\mu-C_6H_4PPh(C_6H_4N)-\kappa P\kappa N\kappa C\}]$	[58]
$[Os_3(\mu-H)(CO)_7(\mu_2-PPh_2)(\mu_3-2-C_6H_3C_6H_4PPh_2)]$	[107]
$[Os_3(\mu-H)(CO)_9(PPh_3)(\mu_2-2-C_6H_4PPh_2)]$	[108]
$[Os_3(CO)_8(\mu-Ph)(\mu_2-PPh_2)(\mu_3-2-C_6H_4PPh)]$	[108]
$[Os_3(\mu-H)(CO)_8(PPh_3)(\mu_3-2-C_6H_4PPh_2)]$	[108]
$[Os_3(\mu-H)_2(CO)_9(\mu_3-2-C_6H_4PPh)]$	[109]

Table A.2 (*Continued*)

Compound	Reference
$[Os_3(CO)_{10}\{Ph_2PCH_2P(Ph)C_6H_4-2\}]$	[110]
$[Os_3(\mu_2-SbPh_2)(\mu-2-C_6H_4PPh_2)(CO)_8(PPh_3)_2]$	[112a]
$[Os_3(\mu_2-SbPh_2)\{\mu-2-C_6H_3-5-MeP(p-tol)_2\}(CO)_8(PPh_3)_2]$	[112a]
$[Os_2Cl_2(\mu-O_2CMe)_2(\mu-2-C_6H_4PPh_2)_2]$	[113]
$[Rh_2(MeCO_2H)_2(\mu-O_2CMe)_2(\mu-2-C_6H_4PPh_2)_2]$	[113]
$[Os_2Cl_2(\mu-O_2CCH_2Me)_2(\mu-2-C_6H_4PPh_2)_2]$	[114]
$[Os_2Cl_4(\mu-2-C_6H_4PPh_2)_2]$	[115]
$[Rh_2(py)_2(\mu-O_2CMe)_2(\mu-2-C_6H_4PPh_2)_2]$	[162]
$[Rh_2(PPh_3)_2(\mu-Cl)_2(\mu-2-C_6H_4PPh_2)_2]$	[163]
$[Rh_2(PMe_3)_2(\mu-Cl)_2(\mu-2-C_6H_4PPh_2)_2]$	[163]
$[Rh(\kappa^2-O_2CMe)(\mu-O_2CMe)_2\{\mu-2-C_6H_4PPh(2-BrC_6F_4)\}Rh(\kappa^2-P,Br-2-BrC_6F_4PPh_2)]$	[165]
$[Rh(H_2O)(\mu-O_2CMe)_2\{\mu-2-C_6H_4PPh(2-BrC_6F_4)\}Rh(\kappa^2-P,Br-2-BrC_6F_4PPh_2)]$	[166]
$[Rh_2(\mu-O_2CMe)_2\{\mu-2-C_6H_4PPh(2-BrC_6F_4)\}_2]$	[166]
$[Rh_2(py)_2(\mu-O_2C^tBu)_2(\mu-2-C_6H_4PMePh)_2]$	[167]
$[Rh_2(H_2O)_2(\mu-O_2C^tBu)_2(\mu-2-C_6H_4PMe_2)_2]$	[168]
$[Rh(PPh_3)(\mu-O_2CMe)_2(\mu-2-C_6H_4PPh_2)(\mu-CH_2PPh_2)Rh]$	[171]
$[Rh(PPh_3)(\mu-O_2CMe)_2(\mu-2-C_6H_4PPh_2)\{\mu-C_6H_4PPh(2-ClC_6H_4)\}Rh]$	[172]
$[Rh_2(H_2O)_2(\mu-O_2CMe)_2\{\mu-4-Me_3SiC_6H_3P(4-Me_3SiC_6H_4)_2\}_2]$	[173]
$[Rh_2(MeCO_2H)_2(\mu-O_2CMe)_3\{\mu-4-MeOC_6H_3P(4-MeOC_6H_4)_2\}]$	[174]
$[Rh_2(py)_2(\mu-O_2CCPh_3)_2(\mu-2-C_6H_4PPh_2)_2]$	[175]
$[Rh_2(MeCO_2H)_2(\mu-O_2CMe)_2\{\mu-3-MeC_6H_3P(3-MeC_6H_4)_2\}_2]$	[176]
$[Rh_2(PPh_3)_2(\mu-O_2CCF_3)_2(\mu-2-C_6H_4PPh_2)_2]$	[177]
$[Rh_2(H_2O)(MeCO_2H)(\mu-O_2CMe_3)_2\{\mu-4-MeOC_6H_3P(4-MeOC_6H_4)_2\}_2]$	[178]
$[Rh_2(MeCO_2H)_2(\mu-O_2CMe)_3(\mu-2-C_6H_4PPh_2)]$	[179]
$[Rh_2(H_2O)_2(\mu-O_2CMe)_3(\mu-2-ClC_6H_3PPh_2)]$	[180]
$[Rh_2(MeCO_2H)_2(\mu-O_2CMe)_3\{\mu-C_6H_4PPh(2-ClC_6H_4)\}]$	[181]
$[Rh_2(CF_3CO_2H)_2(\mu-O_2CCF_3)_3(\mu-2-C_6H_4PPh_2)]$	[182]
$[Rh(PCy_3)(\mu-O_2CMe)_3\{\mu-C_6H_4PPh(2-BrC_6H_4)\}Rh]$	[184]
$[Rh_2(MeCO_2H)_2(\mu-O_2CMe)_2[\{C_6H_4PhP(C_5H_4)\}_2Fe]]$	[185]
$[Rh(MeCO_2H)(\mu-O_2CMe)_2\{\mu-C_6H_4PPh(Fc)_2\}_2Rh]$	[185]
$[Rh_2(MeCO_2H)_2(\mu-O_2CMe)_3\{\mu-C_6H_4PPh(2-BrC_6H_4)\}]$	[186]
$[Rh(\kappa^2-O_2CMe)(\mu-O_2CMe)_2(\mu-2-C_6H_4PPh_2)Rh(\kappa^2-P,Cl-2-ClC_6H_4PPh_2)]$	[187]
$[Rh_2(MeCO_2H)_2(\mu-O_2CMe)_2(\mu-2-C_6H_4PPh_2)\{\mu-4-ClC_6H_3P(4-ClC_6H_4)_2\}]$	[188]
$[Rh_2(MeCO_2H)_2(\mu-O_2CMe)_2(\mu-2-C_6H_4PPh_2)_2]$	[189]
$[Rh_2(MeCO_2H)_2(\mu-O_2CMe)_2\{\mu-4-ClC_6H_3P(4-ClC_6H_4)_2\}_2]$	[189]
$[Rh_2(py)_2(\mu-O_2CCF_3)_2(\mu-2-C_6H_4PPh_2)_2]$	[197]
$[Rh_2(CF_3CO_2H)_2(\mu-O_2CCF_3)_2(\mu-2-C_6H_4PPh_2)_2]$	[197]
$[Rh_2(MeCO_2H)_2(\mu-O_2CMe)_2\{\mu-C_6H_4P(2,5-Me_2C_4H_6)\}_2]$	[198]
$[Rh(H_2O)(\mu-succ)_2(\mu-2-C_6H_4PPh_2)_2Rh(succH)]$	[199]
$[Rh_2(H_2O)_2(\mu-succ)_2(\mu-2-C_6H_4PPh_2)_2]$	[199]
$[Rh_2Cl_2(\mu-2-C_6H_4PPh_2)_2(\mu-dppm)_2]$	[200]
$[Rh_2(MeCO_2H)_2(\mu-O_2CMe)_2\{\mu-4-FC_6H_3P(4-FC_6H_4)_2\}_2]$	[202]
$[Rh_2(H_2O)_2(\mu-O_2CMe)_2\{\mu-C_6H_4PPh(C_6F_5)\}_2]$	[204]
$[Rh_2(H_2O)_2\{\mu-O_2C(CF_2)_2CF_3\}_2\{\mu-C_6H_4PPh(C_6F_5)\}_2]$	[204]
$[RhBr(CO)(\mu-pz)_2(\mu-2-C_6F_4PPh_2)Rh(\kappa^2-P,Br-2-BrC_6F_4PPh_2)]$	[206]
$[RhBr(CO)(\mu-2,4-Me_2pz)_2(\mu-2-C_6F_4PPh_2)Rh(\kappa^2-P,Br-2-BrC_6F_4PPh_2)]$	[207]
$[Rh_2(MeCN)_6(\mu-2-C_6H_4PPh_2)_2](BF_4)_2$	[208]
$[\{Rh_2(py)_2(\mu-2-C_6H_4PPh_2)_2\}_3(\mu-O_2CCO_2)_3]$	[208]
$[\{Rh_2(dmf)_2(\mu-2-C_6H_4PPh_2)_2\}_3(\mu-O_2CC_6H_4CO_2)_3]$	[208]
$[Rh\{\mu-C_6H_4PPh(CH_2)_2PPh_2\}(\mu-O_2CCF_3)\{\mu-(4-MeC_6H_4N)CH\}Rh(\kappa^2-dppe)]O_2CCF_3$	[209]
$[Rh\{\mu-C_6H_4PPh(CH_2)_2PPh_2\}(\mu-O_2CCF_3)\{\mu-(4-MeC_6H_4N)CH\}Rh(4-MeC_6H_4NH)(O_2CCF_3)]$	[210]
$[(\kappa^2-2-C_6H_4PPh_2)Pt(\mu-2-C_6H_4PPh_2)_2HgCl]$	[212]
$[Pt_2(\mu-CuPPh_3)(\mu-2-C_6H_4PPh_2)(\mu-PPh_2)(PPh_3)_2]PF_6$	[232]
$[Pt_2\{\mu-C_6H_4P(Ph)CH_2CH_2PPh_2\}_2]$	[238]
$[Pt_2Me_2\{\mu-C_6H_4P(Ph)CH_2CH_2PPh_2\}_2]$	[241]
$[Pt_2(\mu-CH_2)\{\mu-C_6H_4P(Ph)CH_2CH_2PPh_2\}_2]$	[241]
$[Pt_2(\mu-AuPPh_3)\{\mu-C_6H_4P(Ph)CH_2CH_2PPh_2\}_2]BF_4$	[242]
$[Pt_2\{\mu-C_6H_4P(Ph)CH_2CH_2CH_2PPh_2\}_2]$	[243]
$[Pt_2\{\mu-Hg(OOCCF_3)_2\}\{\mu-C_6H_4P(Ph)CH_2CH_2CH_2PPh_2\}_2]$	[243]
$[Pt_2(\mu-OH)\{\mu-C_6H_4P(Ph)CH_2CH_2CH_2PPh_2\}_2]BF_4$	[244]
$[Pt_2(\mu-2-C_6H_4PPh_2)_2(PPh_3)_2]$	[245]
$[Pt_2(\mu-I)(\mu-2-C_6H_4PPh_2)_2(PPh_3)_2]I$	[245]
$[Pt_2(\mu-5-MeC_6H_3PPh_2)_2(\kappa^2-5-MeC_6H_3PPh_2)_2]$	[246]
$[Pt_2(\mu-H)(\mu-5-MeC_6H_3PPh_2)_2\{PPh_2(4-MeC_6H_4)\}_2]PF_6$	[246]
$[Au_2(\mu-2-C_6H_4P^iPr_2)_2]$	[247]
$[(BzO)Au(\mu-2-C_6H_4P^iPr_2)_2Au]$	[247]
$[Au_2Cl_2(\mu-2-C_6H_4P^iPr_2)_2]$	[247]
$[IAu(\mu-2-C_6H_4P^iPr_2)_2Au(\kappa^2-2-C_6H_4P^iPr_2)]$	[247]
$[Pt_2(\mu-5-MeC_6H_3AsPh_2)_4]$	[251]
$[Pt_2(\kappa^2-5-MeC_6H_3AsPh_2)_2(\mu-5-MeC_6H_3AsPh_2)_2]$	[251]
$[Pt_2F_2(\mu-5-MeC_6H_3AsPh_2)_4]$	[251]
$[Pt_2Cl_2(\mu-5-MeC_6H_3AsPh_2)_4]$	[251]
$[Pt_2Br_2(\mu-5-MeC_6H_3AsPh_2)_4]$	[251]
$[Pt_2I_2(\mu-5-MeC_6H_3AsPh_2)_4]$	[251]
$[Pt_2(CN)_2(\mu-5-MeC_6H_3AsPh_2)_4]$	[251]
$[Pt_2(NCS)_2(\mu-5-MeC_6H_3AsPh_2)_4]$	[251]
$[Pt_2(NCO)_2(\mu-5-MeC_6H_3AsPh_2)_4]$	[251]
$[Pt_2(\mu-5-MeC_6H_3AsPh_2)_4]BF_4$	[252]
$[Au_2(\mu-2-C_6H_4PPh_2)_2]$	[253]
$[Au_2(\mu-2-C_6H_4AsPh_2)_2]$	[253]
$[HgCl(\mu-2-C_6H_4PPh_2)AuCl]$	[253]
$[Au_2(\mu-2-C_6H_4PEt_2)_2]$	[254]
$[Au_2(OBz)_2(\mu-2-C_6H_4PEt_2)_2]$	[254]
$[Au_2(\mu-2-C_6H_4PEtPh)_2]$	[255]
meso-$[Au_2Cl_2(\mu-2-C_6H_4PEtPh_2)_2]$	[255]
$[Au_2(\mu-6-MeC_6H_3PPh_2)_2]$	[256]
$[Au_2(\mu-4-MeC_6H_3PPh_2)_2]$	[256]
$[IAu(\mu-4-MeC_6H_3PPh_2)_2AuI(\kappa^2-4-MeC_6H_4PPh_2)]$	[256]
$[Au_2Br_2(\mu-5-MeC_6H_3AsPh_2)_2]$	[257]
$[Au_2I_2(\mu-5-MeC_6H_3AsPh_2)_2]$	[257]
$[Au_2Cl_2(\mu-5-MeC_6H_3AsPh_2)_2]$	[257]
$[Au_2(\mu-6-MeC_6H_3AsPh_2)_2]$	[257]
$[AuI_2(\mu-6-MeC_6H_3AsPh_2)_2Au]$	[257]
$[HgCl(\mu-3-MeC_6H_3PPh_2)AuCl]$	[259]
$[AuBr(\mu-3-MeC_6H_3PPh_2)Au(AsPh_3)]$	[259]
$[Au_2(\mu-2-C_6H_4CH_2PPh_2)_2]$	[261]
$[Au_2(\mu-4-MeC_6H_3PPh_2)(\mu-S_2CN^nBu_2)]$	[265]
$[AuI(\mu-4-MeC_6H_3PPh_2)AuI(\kappa^2-S,S-S_2CN^nBu_2)]$	[265]
$[Au_2I_2(\mu-2-C_6H_4PPh_2)_2]$	[267]
$[Au(Me)_2(\mu-2-C_6H_4PPh_2)_2Au]$	[268]
$[(C_6F_5)_2Au(\mu-2-C_6H_4PPh_2)_2Au]$	[268]
$[Au_2(C_6F_5)_2(\mu-2-C_6H_4PPh_2)_2]$	[268]
$[(C_6F_5)Au(\mu-4-MeC_6H_3PPh_2)_2Au(C_6F_5)(\kappa-P-4-MeC_6H_3PPh_2)]$	[270]
$[Au_2(\mu-2-SO_2C_6H_4PPh_2)_2]$	[266]
$[Au_5(\mu-2-C_6H_4PPh_2)_4]OTf$	[276]

References

[1] J.P. Kleiman, M. Dubeck, J. Am. Chem. Soc. 85 (1963) 1544.

[2] A.C. Cope, R.W. Siekman, J. Am. Chem. Soc. 87 (1965) 3272.

[3] J. Chatt, J.M. Davidson, J. Chem. Soc. (1965) 843.

[4] F.A. Cotton, B.A. Frenz, D.L. Hunter, J. Chem. Soc., Chem. Commun. (1974) 755.

[5] F.A. Cotton, D.L. Hunter, B.A. Frenz, Inorg. Chim. Acta 15 (1975) 155.
[6] G.W. Parshall, J. Am. Chem. Soc. 90 (1968) 1669.
[7] M.A. Bennett, D.L. Milner, Chem. Commun. (1967) 581.
[8] W. Keim, J. Organomet. Chem. 14 (1968) 179.
[9] A.E. Shilov, G.B. Shul'pin, Chem. Rev. 97 (1997) 2879.
[10] I. Omae, Organometallic Intramolecular Coordination Compounds, Elsevier, Amsterdam, 1986.
[11] A.D. Ryabov, Chem. Rev. 90 (1990) 403.
[12] J. Spencer, M. Pfeffer, Adv. Met.-Org. Chem. 6 (1998) 103.
[13] G.W. Parshall, Acc. Chem. Res. 3 (1970) 139.
[14] J. Dehand, M. Pfeffer, Coord. Chem. Rev. 18 (1976) 327.
[15] H.P. Abicht, K. Issleib, Z. Chem. 17 (1977) 1.
[16] M.I. Bruce, Angew. Chem. Int. Ed. Engl. 16 (1977) 73.
[17] I. Omae, Coord. Chem. Rev. 32 (1979) 235.
[18] E.C. Constable, Polyhedron 3 (1984) 1037.
[19] G.R. Newkome, W.E. Puckett, V.K. Gupta, G.E. Kiefer, Chem. Rev. 86 (1986) 451.
[20] I. Omae, Coord. Chem. Rev. 28 (1979) 97.
[21] I. Omae, Coord. Chem. Rev. 42 (1982) 245.
[22] I. Omae, Coord. Chem. Rev. 83 (1988) 137.
[23] V.V. Dunina, O.A. Zalevskaya, V.M. Potapov, Russ. Chem. Rev. 57 (1988) 250.
[24] I. Omae, Coord. Chem. Rev. 248 (2004) 995.
[25] W.A. Herrmann, V.P.W. Böhm, C.P. Reisinger, J. Organomet. Chem. 576 (1999) 23.
[26] I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009.
[27] N.J. Whitcombe, K.K. Hii, S.E. Gibson, Tetrahedron 57 (2001) 7449.
[28] R.B. Bedford, J. Chem. Soc., Chem. Commun. (2003) 1787.
[29] M.E. van der Boom, D. Milstein, Chem. Rev. 103 (2003) 1759.
[30] J.T. Singleton, Tetrahedron 59 (2003) 1837.
[31] R.B. Bedford, C.S.J. Cazin, D. Holder, Coord. Chem. Rev. 248 (2004) 2283.
[32] C.M. Jensen, Chem. Commun. (1999) 2443.
[33] I. Göttker-Schnetmann, P. White, M. Brookhart, J. Am. Chem. Soc. 126 (2004) 1804 (and references cited therein).
[34] K. Zhu, P.D. Achord, X. Zhang, K. Krogh-Jespersen, A.S. Goldman, J. Am. Chem. Soc. 126 (2004) 13044 (and references cited therein).
[35] M. Brookhart, M.L.H. Green, L.L. Wong, Prog. Inorg. Chem. 36 (1988) 1.
[36] R.H. Crabtree, D.G. Hamilton, Adv. Organomet. Chem. 28 (1988) 299.
[37] B.L. Shaw, J. Am. Chem. Soc. 97 (1975) 3856.
[38] B.L. Shaw, J. Organomet. Chem. 200 (1980) 307.
[39] S. Al-Fibori, C. Crocker, W.S. McDonald, B.L. Shaw, J. Chem. Soc., Dalton Trans. (1981) 1572.
[40] M.A. Bennett, D.H. Berry, T. Dirnberger, D.C.R. Hockless, E. Wenger, J. Chem. Soc., Dalton Trans. (1998) 2367.
[41] R. Bender, S.E. Bouaoud, P. Braunstein, Y. Dusausoy, N. Merabet, J. Raya, D. Rouag, J. Chem. Soc., Dalton Trans. (1999) 735.
[42] T.G. Appleton, M.A. Bennett, I.B. Tomkins, J. Chem. Soc., Dalton Trans. (1976) 439.
[43] P.E. Garrou, Chem. Rev. 81 (1981) 229.
[44] R. Poli, S.T. Krueger, F. Abugideiri, B.S. Haggerty, A.L. Rheingold, Organometallics 10 (1991) 3041.
[45] J.D. Debad, P. Legzdins, S.A. Lumb, R.J. Batchelor, F.W.B. Einstein, Organometallics 14 (1995) 2543.
[46] D.J. Burkey, J.D. Debad, P. Legzdins, J. Am. Chem. Soc. 119 (1997) 1139.
[47] H. Rothfuss, J.C. Huffman, K.G. Caulton, Inorg. Chem. 33 (1994) 2946.
[48] R. Hoxmeier, B. Deubzer, H.D. Kaesz, J. Am. Chem. Soc. 93 (1971) 536.
[49] R.J. McKinney, R. Hoxmeier, H.D. Kaesz, J. Am. Chem. Soc. 97 (1975) 3059.
[50] R.J. McKinney, C.B. Knobler, B.T. Huie, H.D. Kaesz, J. Am. Chem. Soc. 99 (1977) 2988.
[51] R.J. McKinney, H.D. Kaesz, J. Am. Chem. Soc. 97 (1975) 3066.
[52] R.J. McKinney, B.T. Huie, C.B. Knobler, H.D. Kaesz, J. Am. Chem. Soc. 95 (1973) 633.
[53] R.J. McKinney, S.S. Crawford, Inorg. Synth. 26 (1989) 155.
[54] D.J. Cox, R. Davis, J. Organomet. Chem. 186 (1980) 347.
[55] W.D. Jones, J.A. Maguire, Organometallics 6 (1987) 1728.
[56] G.P. Rosini, W.D. Jones, J. Am. Chem. Soc. 114 (1992) 10767.
[57] M.A. Green, J.C. Huffman, K.G. Caulton, W.K. Rybak, J.J. Ziółkówski, J. Organomet. Chem. 218 (1981) C39.
[58] T.J. Barder, S.M. Tetrick, R.A. Walton, F.A. Cotton, G.L. Powell, J. Am. Chem. Soc. 105 (1983) 4090.
[59] T.J. Barder, F.A. Cotton, G.L. Powell, S.M. Tetrick, R.A. Walton, J. Am. Chem. Soc. 106 (1984) 1323.
[60] G. Hata, H. Kondo, A. Miyake, J. Am. Chem. Soc. 90 (1968) 2278.
[61] S.D. Ittel, C.A. Tolman, P.J. Krusic, A.D. English, J.P. Jesson, Inorg. Chem. 17 (1978) 3432.
[62] H. Azizian, R.H. Morris, Inorg. Chem. 22 (1983) 6.
[63] T. Ikariya, A. Yamamoto, J. Organomet. Chem. 118 (1976) 65.
[64] A. Sacco, M. Aresta, J. Chem. Soc., Chem. Commun. (1968) 1223.
[65] E. Koerner von Gustorf, I. Fischler, J. Leitich, H. Dreeskamp, Angew. Chem., Int. Ed. Engl. 11 (1972) 1088.
[66] G. Cerveau, G. Chauviere, E. Colomer, R.J.P. Corriu, J. Organomet. Chem. 210 (1981) 343.
[67] S.J. La Placa, J.A. Ibers, Inorg. Chem. 4 (1965) 778.
[68] A.C. Skapski, P.G.H. Troughton, J. Chem. Soc., Chem. Commun. (1968) 1230.
[69] P.S. Hallman, B.R. McGarvey, G. Wilkinson, J. Chem. Soc. (1968) 3143.
[70] G.W. Parshall, W.H. Knoth, R.A. Schunn, J. Am. Chem. Soc. 91 (1969) 4990.
[71] B.R. James, L.D. Markham, D.K.W. Wang, J. Chem. Soc., Chem. Commun. (1974) 439.
[72] A.M. Stolzenberg, E.L. Muetterties, Organometallics 4 (1985) 1739.
[73] S. Sabo, B. Chaudret, D. Gervais, R. Poilblanc, Nouv. J. Chim. 5 (1981) 597.
[74] S. Sabo, B. Chaudret, D. Gervais, Nouv. J. Chim. 7 (1983) 181.
[75] D.J. Cole-Hamilton, G. Wilkinson, Nouv. J. Chim. 1 (1977) 141.
[76] D.J. Cole-Hamilton, G. Wilkinson, J. Chem. Soc. Dalton (1977) 797.
[77] P.J. Desrosiers, L. Cai, J. Halpern, J. Am. Chem. Soc. 111 (1989) 8513.
[78] W.R. Roper, L.J. Wright, J. Organomet. Chem. 234 (1982) C5.
[79] G.R. Clark, C.E.L. Headford, K. Marsden, W.R. Roper, J. Organomet. Chem. 231 (1982) 335.
[80] C.E.F. Rickard, W.R. Roper, A. Williamson, L.J. Wright, Organometallics 19 (2000) 4344.
[81] D.J. Cole-Hamilton, G. Wilkinson, J. Chem. Soc., Dalton Trans. (1979) 1283.
[82] H. Werner, J. Gotzig, J. Organomet. Chem. 284 (1985) 73.
[83] S.D. Chappell, L.M. Engelhardt, A.H. White, C.L. Raston, J. Organomet. Chem. 462 (1993) 295;
(a) M.D. Fryzuk, C.D. Montgomery, S.J. Rettig, Organometallics 10 (1991) 467.
[84] G.P. Pez, R.A. Grey, J. Corsi, J. Am. Chem. Soc. 103 (1981) 7528.
[85] R.A. Grey, G.P. Pez, A. Wallo, J. Corsi, J. Chem. Soc., Chem. Commun. (1980) 783.
[86] R.A. Grey, G.P. Pez, A. Wallo, J. Am. Chem. Soc. 103 (1981) 7536.
[87] G.P. Pez, R.A. Grey, U.S. Patent 4,268,454, (assigned to Allied Chemical Corp.) 1981;
(a) J.T. Poulton, K. Folting, K.G. Caulton, Organometallics 11 (1992) 1364.
[88] M.A. Bennett, A.M. Clark, M. Contel, C.E.F. Rickard, W.R. Roper, L.J. Wright, J. Organomet. Chem. 601 (2000) 299.
[89] M.I. Bruce, R.C.F. Gardner, F.G.A. Stone, J. Organomet. Chem. 40 (1972) C39.
[90] M.I. Bruce, R.C.F. Gardner, F.G.A. Stone, J. Chem. Soc., Dalton Trans. (1976) 81.
[91] M.I. Bruce, M.P. Cifuentes, M.A. Humphrey, E. Poczman, M.R. Snow, E.R.T. Tiekink, J. Organomet. Chem. 338 (1988) 237.

[92] H. Lehmkuhl, M. Bellenbaum, J. Grundke, J. Organomet. Chem. 330 (1987) C23.

[93] H. Lehmkuhl, M. Bellenbaum, J. Grundke, H. Mauermann, C. Krüger, Chem. Ber. 121 (1988) 1719.

[94] P. Diversi, M. Fuligni, F. Marchetti, C. Pinzino, J. Organomet. Chem. 690 (2005) 605.

[95] H. Lehmkuhl, J. Grundke, G. Schroth, R. Benn, Z. Naturforsch. B. 39 (1984) 1050.

[96] J.L. Snelgrove, J.C. Conrad, G.P.A. Yap, D.E. Fogg, Inorg. Chim. Acta 345 (2003) 268.

[97] M. Esteruelas, E. Gutiérrez-Puebla, A.M. López, E. Oñate, J.I. Tolosa, Organometallics 19 (2000) 275.

[98] M.A. Bennett, T.N. Huang, J.L. Latten, J. Organomet. Chem. 272 (1984) 189.

[99] P. Diversi, G. Ingrosso, A. Lucherini, F. Marchetti, V. Adovasio, M. Nardelli, J. Chem. Soc., Dalton Trans. (1990) 1779.

[100] P. Diversi, G. Ingrosso, A. Lucherini, F. Marchetti, V. Adovasio, M. Nardelli, J. Chem. Soc., Dalton Trans. (1991) 203.

[101] V. Adovasio, P. Diversi, G. Ingrosso, A. Lucherini, F. Marchetti, M. Nardelli, J. Chem. Soc., Dalton Trans. (1992) 3385.

[102] A. Ceccanti, P. Diversi, G. Ingrosso, F. Laschi, A. Lucherini, S. Magagna, P. Zanello, J. Organomet. Chem. 526 (1996) 251.

[103] H. Kletzin, H. Werner, J. Organomet. Chem. 291 (1985) 213.

[104] J.A. Cabeza, P.M. Maitlis, J. Chem. Soc., Dalton Trans. (1985) 573.

[105] M.A. Bennett, A.M.M. Weerasuria, J. Organomet. Chem. 394 (1990) 481.

[106] C.W. Bradford, R.S. Nyholm, G.J. Gainsford, J.M. Guss, P.R. Ireland, R. Mason, J. Chem. Soc., Chem. Commun. (1972) 87.

[107] G.J. Gainsford, J.M. Guss, P.R. Ireland, R. Mason, C.W. Bradford, R.S. Nyholm, J. Organomet. Chem. 40 (1972) C70.

[108] C.W. Bradford, R.S. Nyholm, J. Chem. Soc., Dalton Trans. (1973) 529.

[109] S.B. Colbran, P.T. Irele, B.F.G. Johnson, F.J. Lahoz, J. Lewis, P.R. Raithby, J. Chem. Soc., Dalton Trans. (1989) 2023.

[110] J.A. Clucas, D.F. Foster, M.M. Harding, A.K. Smith, J. Chem. Soc., Chem. Commun. (1984) 949.

[111] A.J. Deeming, R.E. Kimber, M. Underhill, J. Chem. Soc., Dalton Trans. (1973) 2589.

[112] M.I. Bruce, G. Shaw, F.G.A. Stone, J. Chem. Soc., Dalton Trans. (1972) 2094;
[112a] G. Chen, M. Deng, C.K. Lee, W.K. Leong, Organometallics 21 (2002) 1227.

[113] A.R. Chakravarty, F.A. Cotton, D.A. Tocher, J. Chem. Soc., Chem. Commun. (1984) 501.

[114] A.R. Chakravarty, F.A. Cotton, D.A. Tocher, Inorg. Chem. 23 (1984) 4697.

[115] F.A. Cotton, K.R. Dunbar, J. Am. Chem. Soc. 109 (1987) 2199.

[116] Y. Kubo, A. Yamamoto, S. Ikeda, J. Organomet. Chem. 59 (1973) 353.

[117] A. Yamamoto, S. Kitazume, L.S. Pu, S. Ikeda, J. Am. Chem. Soc. 93 (1971) 371.

[118] H.F. Klein, S. Schneider, M. He, U. Flörke, H.J. Haupt, Eur. J. Inorg. Chem. (2000) 2295.

[119] H.F. Klein, R. Beck, U. Flörke, H.J. Haupt, Eur. J. Inorg. Chem. (2003) 853.

[120] H.F. Klein, R. Beck, U. Flörke, H.J. Haupt, Eur. J. Inorg. Chem. (2003) 1380.

[121] H.F. Klein, R. Beck, U. Flörke, H.J. Haupt, Eur. J. Inorg. Chem. (2002) 3305.

[122] V.F. Kuznetsov, G.P.A. Yap, C. Bensimon, H. Alper, Inorg. Chim. Acta 280 (1998) 172.

[123] W. Keim, J. Organomet. Chem. 19 (1969) 161.

[124] W. Keim, J. Organomet. Chem. 16 (1969) 191.

[125] J.S. Ricci, J.A. Ibers, J. Organomet. Chem. 27 (1971) 261.

[126] M.A. Bennett, S.K. Bhargava, M. Ke, A.C. Willis, J. Chem. Soc., Dalton Trans. (2000) 3537.

[127] F.L. Barceló, J.C. Besteiro, P. Lahuerta, C. Foces-Foces, F.H. Cano, M. Martinez-Ripoll, J. Organomet. Chem. 270 (1984) 343.

[128] F.L. Barceló, P. Lahuerta, M.A. Ubeda, C. Foces-Foces, F.H. Cano, M. Martinez-Ripoll, J. Organomet. Chem. 301 (1986) 375.

[129] F.L. Barceló, P. Lahuerta, M.A. Ubeda, A. Cantarero, F. Sanz, J. Organomet. Chem. 309 (1986) 199.

[130] J.C. Besteiro, P. Lahuerta, M. Sanaú, I. Solana, F.A. Cotton, R. Llusar, W. Schwotzer, Polyhedron 7 (1988) 87.

[131] P. Lahuerta, J. Latorre, R. Martínez-Máñez, F. Sanz, J. Organomet. Chem. 356 (1988) 355.

[132] P. Lahuerta, R. Martínez, F. Sanz, A. Cantarero, F. Torrens, J. Chem. Res. (S) (1988) 22.

[133] P. Lahuerta, J. Latorre, R. Martínez-Máñez, J. Payá, A. Tiripicchio, M.T. Camellini, Inorg. Chim. Acta 209 (1993) 177.

[134] P. Diversi, G. Ingrosso, A. Lucherini, D. Fasce, J. Chem. Soc., Chem. Commun. (1982) 945.

[135] L. Andreucci, P. Diversi, G. Ingrosso, A. Lucherini, F. Marchetti, V. Adovasio, M. Nardelli, J. Chem. Soc., Dalton Trans. (1986) 803.

[136] P. Diversi, A. Ferrarini, G. Ingrosso, A. Lucherini, G. Uccello-Barretta, C. Pinzino, F. de Biani Fabrizi, F. Laschi, P. Zanello, Gazz. Chim. Ital. 126 (1996) 391.

[137] P. Diversi, S. Iacoponi, G. Ingrosso, F. Laschi, A. Lucherini, P. Zanello, J. Chem. Soc., Dalton Trans. (1993) 351.

[138] P. Diversi, S. Iacoponi, G. Ingrosso, F. Laschi, A. Lucherini, C. Pinzino, G. Uccello-Barretta, P. Zanello, Organometallics 14 (1995) 3275.

[139] A.H. Janowicz, R.G. Bergman, J. Am. Chem. Soc. 104 (1982) 352.

[140] A.H. Janowicz, R.G. Bergman, J. Am. Chem. Soc. 105 (1983) 3929.

[141] R.E. King III, D.C. Busby, M.F. Hawthorne, J. Organomet. Chem. 279 (1985) 103.

[142] C.B. Knobler, R.E. King III, M.F. Hawthorne, Acta Cryst. 42C (1986) 159.

[143] M.A. Bennett, D.L. Milner, J. Am. Chem. Soc. 91 (1969) 6983.

[144] K. von Deuten, L. Dahlenburg, Cryst. Struct. Commun. 9 (1980) 421.

[145] M.A. Bennett, J.L. Latten, Inorg. Synth. 26 (1989) 200.

[146] J. Schwartz, J.B. Cannon, J. Am. Chem. Soc. 94 (1972) 6226.

[147] L. Dahlenburg, J. Organomet. Chem. 251 (1983) 347.

[148] B. Longato, F. Morandini, S. Bresadola, J. Organomet. Chem. 88 (1975) C7.

[149] S. Bresadola, B. Longato, F. Morandini, Inorg. Chim. Acta 25 (1977) L135.

[150] F. Morandini, B. Longato, S. Bresadola, J. Organomet. Chem. 132 (1977) 291.

[151] G. Perego, G. Del Piero, M. Cesari, M.G. Clerici, E. Perrotti, J. Organomet. Chem. 54 (1973) C51.

[152] G. Del Piero, G. Perego, A. Zazzetta, M. Cesari, Cryst. Struct. Commun. 3 (1974) 725.

[153] M.G. Clerici, S. Di Gioacchino, F. Maspero, E. Perrotti, A. Zanobi, J. Organomet. Chem. 84 (1975) 379.

[154] G.L. Geoffroy, R. Pierantozzi, J. Am. Chem. Soc. 98 (1976) 8054.

[155] J.S. Valentine, J. Chem. Soc., Chem. Commun. (1973) 857.

[156] M. Brym, C. Jones, Transition Met. Chem. 28 (2003) 595.

[157] R.H. Crabtree, J.M. Quirk, J. Organomet. Chem. 187 (1980) C32.

[158] B. Hauger, K.G. Caulton, J. Organomet. Chem. 450 (1993) 253.

[159] A.C. Cooper, K.G. Caulton, Inorg. Chim. Acta 251 (1996) 41.

[160] A.C. Cooper, E. Clot, J.C. Huffman, W.E. Streib, F. Maseras, O. Eisenstein, K.G. Caulton, J. Am. Chem. Soc. 121 (1999) 97.

[161] M. Cowie, I.R. McKeer, S.J. Loeb, M.D. Gauthier, Organometallics 5 (1986) 860;
[161a] C. Bianchini, D. Masi, A. Meli, M. Peruzzini, F. Zanobini, J. Am. Chem. Soc. 110 (1988) 6411;
[161b] J.D. Feldman, J.C. Peters, T.D. Tilley, Organometallics 21 (2002) 4050.

[162] A.R. Chakravarty, F.A. Cotton, D.A. Tocher, J.H. Tocher, Organometallics 4 (1985) 8.

[163] F.A. Cotton, K.R. Dunbar, C.T. Eagle, Inorg. Chem. 26 (1987) 4127.

[164] P. Lahuerta, F. Estevan, in: P. Braunstein, L.A. Oro, P.R. Raithby (Eds.), Metal Clusters in Chemistry, vol. II, Wiley-VCH, Weinheim, 1999, p. 678 (and references therein).

[165] F.L. Barceló, F.A. Cotton, P. Lahuerta, R. Llusar, M. Sanaú, W. Schwotzer, M.A. Ubeda, Organometallics 5 (1986) 808.

[166] F.L. Barceló, F.A. Cotton, P. Lahuerta, M. Sanaú, W. Schwotzer, M.A. Ubeda, Organometallics 6 (1987) 1105.
[167] E.C. Morrison, D.A. Tocher, Inorg. Chim. Acta 157 (1989) 139.
[168] E.C. Morrison, D.A. Tocher, J. Organomet. Chem. 408 (1991) 105.
[169] M.V. Borrachero, F. Estevan, P. Lahuerta, J. Payá, E. Peris, Polyhedron 12 (1993) 1715.
[170] F. Estevan, S. García-Granda, P. Lahuerta, J. Latorre, E. Peris, M. Sanaú, Inorg. Chim. Acta 229 (1995) 365.
[171] M.V. Borrachero, F. Estevan, S. García-Granda, P. Lahuerta, J. Latorre, E. Peris, M. Sanaú, J. Chem. Soc., Chem. Commun. (1993) 1864.
[172] F.A. Cotton, F.L. Barceló, P. Lahuerta, R. Llusar, J. Payá, M.A. Ubeda, Inorg. Chem. 27 (1988) 1010.
[173] F. Estevan, P. Lahuerta, J. Lloret, M. Sanaú, M.A. Ubeda, J. Vila, J. Chem. Soc., Chem. Commun. (2004) 2408.
[174] F.P. Pruchnik, R. Starosta, T. Lis, P. Lahuerta, J. Organomet. Chem. 568 (1998) 177.
[175] M. Barberis, P. Lahuerta, J. Pérez-Prieto, M. Sanaú, J. Chem. Soc., Chem. Commun. (2001) 439.
[176] P. Lahuerta, R. Martínez-Máñez, J. Paya, E. Peris, Inorg. Chim. Acta 173 (1990) 99.
[177] F. Estevan, P. Lahuerta, E. Peris, M.A. Ubeda, S. García-Granda, F. Gómez-Beltrán, E. Pérez-Carreño, G. González, M. Martínez, Inorg. Chim. Acta 218 (1994) 189.
[178] F.P. Pruchnik, R. Starosta, Z. Ciunik, A. Opolski, J. Wietrzyk, E. Wojdat, D. Dus, Can. J. Chem. 79 (2001) 868.
[179] P. Lahuerta, J. Payá, E. Peris, M.A. Pellinghelli, A. Tiripicchio, J. Organomet. Chem. 373 (1989) C5.
[180] P. Lahuerta, J. Payá, S. García-Granda, F. Gómez-Beltrán, A. Anillo, J. Organomet. Chem. 443 (1993) C14.
[181] P. Lahuerta, J. Payá, X. Solans, M.A. Ubeda, Inorg. Chem. 31 (1992) 385.
[182] P. Lahuerta, E. Peris, M.A. Ubeda, S. García-Granda, F. Gómez-Beltrán, M.R. Diaz, J. Organomet. Chem. 455 (1993) C10.
[183] S. García-Granda, P. Lahuerta, J. Latorre, M. Martínez, E. Peris, M. Sanaú, M.A. Ubeda, J. Chem. Soc., Dalton Trans. (1994) 539.
[184] S. García-Granda, M.R. Diaz, F. Gómez-Beltrán, E. Peris, P. Lahuerta, Acta Cryst. C50 (1994) 691.
[185] F. Estevan, P. Lahuerta, J. Latorre, E. Peris, S. García-Granda, F. Gómez-Beltrán, C.J. Aguirre, M.A. Salvadó, J. Chem. Soc., Dalton Trans. (1993) 1681.
[186] P. Lahuerta, J. Latorre, E. Peris, M. Sanau, S. García-Granda, J. Organomet. Chem. 456 (1993) 279.
[187] A. Garcia-Bernabé, P. Lahuerta, M.A. Ubeda, S. García-Granda, P. Peritierra, Inorg. Chim. Acta 229 (1995) 203.
[188] P. Lahuerta, J. Payá, E. Peris, C.J. Aguirre, S. García-Granda, F. Gómez-Beltrán, Inorg. Chim. Acta 192 (1992) 43.
[189] P. Lahuerta, J. Payá, M.A. Pellinghelli, A. Tiripicchio, Inorg. Chem. 31 (1992) 1224.
[190] C.J. Alarcón, P. Lahuerta, E. Peris, M.A. Ubeda, C.J. Aguirre, S. García-Granda, F. Gómez-Beltrán, Inorg. Chim. Acta 254 (1997) 177.
[191] C.J. Alarcón, F. Estevan, P. Lahuerta, M.A. Ubeda, G. González, M. Martínez, S.E. Stiriba, Inorg. Chim. Acta 278 (1998) 61.
[192] G. González, P. Lahuerta, M. Martínez, E. Peris, M. Sanaú, J. Chem. Soc., Dalton Trans. (1994) 545.
[193] F. Estevan, G. González, P. Lahuerta, M. Martínez, E. Peris, R. van Eldik, J. Chem. Soc., Dalton Trans. (1996) 1045.
[194] P. Lahuerta, J. Payá, A. Bianchi, Inorg. Chem. 31 (1992) 5336.
[195] G. González, M. Martínez, F. Estevan, A. García-Bernabé, P. Lahuerta, E. Peris, M.A. Ubeda, M.R. Diaz, S. García-Granda, B. Tejerina, New J. Chem. 20 (1996) 83.
[196] P. Lahuerta, E. Peris, Inorg. Chem. 31 (1992) 4547.
[197] D.F. Taber, S.C. Malcolm, K. Bieger, P. Lahuerta, M. Sanaú, S.E. Stiriba, J. Pérez-Prieto, M.A. Monge, J. Am. Chem. Soc. 121 (1999) 860.
[198] F. Estevan, P. Krueger, P. Lahuerta, E. Moreno, J. Pérez-Prieto, M. Sanaú, H. Werner, Eur. J. Inorg. Chem. (2001) 105.
[199] M. Barberis, F. Estevan, P. Lahuerta, J. Pérez-Prieto, M. Sanaú, Inorg. Chem. 40 (2001) 4226.
[200] F.A. Cotton, K.R. Dunbar, J. Am. Chem. Soc. 109 (1987) 3142.
[201] F.A. Cotton, K.R. Dunbar, M.G. Verbruggen, J. Am. Chem. Soc. 109 (1987) 5498.
[202] F. Estevan, P. Lahuerta, J. Pérez-Prieto, M. Sanaú, S.E. Stiriba, M.A. Ubeda, Organometallics 16 (1997) 880.
[203] F. Estevan, P. Lahuerta, J. Pérez-Prieto, I. Pereira, S.E. Stiriba, Organometallics 17 (1998) 3442.
[204] P. Lahuerta, I. Pereira, J. Pérez-Prieto, M. Sanaú, S.E. Stiriba, D.F. Taber, J. Organomet. Chem. 612 (2000) 36.
[205] M. Barberis, J. Pérez-Prieto, K. Herbst, P. Lahuerta, Organometallics 21 (2002) 1667.
[206] F.L. Barceló, P. Lahuerta, M.A. Ubeda, C. Foces-Foces, F.H. Cano, M. Martinez-Ripoll, J. Chem. Soc., Chem. Commun. (1985) 43.
[207] F.L. Barceló, P. Lahuerta, M.A. Ubeda, C. Foces-Foces, F.H. Cano, M. Martinez-Ripoll, Organometallics 7 (1988) 584.
[208] F.A. Cotton, C.A. Murillo, X. Wang, R. Yu, Inorg. Chem. 43 (2004) 8394.
[209] G. Bruno, G. De Munno, G. Tresoldi, S. Lo Schiavo, P. Piraino, Inorg. Chem. 31 (1992) 1538.
[210] G. Tresoldi, G. De Munno, F. Nicolo, S. Lo Schiavo, P. Piraino, Inorg. Chem. 35 (1996) 1377.
[211] M. Font-Bardía, J. González-Platas, G. Muller, D. Panyella, M. Rocamora, X. Solans, J. Chem. Soc., Dalton Trans. (1994) 3075.
[212] M.A. Bennett, M. Contel, D.C.R. Hockless, L.L. Welling, A.C. Willis, Inorg. Chem. 41 (2002) 844.
[213] A.M. Aarif, F. Estevan, A. Garcia-Bernabé, P. Lahuerta, M. Sanaú, M.A. Ubeda, Inorg. Chem. 36 (1997) 6472.
[214] F. Estevan, A. García-Bernabé, P. Lahuerta, M. Sanaú, M.A. Ubeda, M.C. Ramírez-Arellano, Inorg. Chem. 39 (2000) 5964.
[215] F. Estevan, A. García-Bernabé, P. Lahuerta, M. Sanaú, M.A. Ubeda, J.R. Galán-Mascarós, J. Organomet. Chem. 596 (2000) 248.
[216] D.M. Fenton, J. Org. Chem. 38 (1973) 3192.
[217] K. Maeda, I. Moritani, T. Hosokawa, S.-I. Murahashi, J. Chem. Soc., Chem. Commun. (1975) 689.
[218] A.J. Cheney, B.E. Mann, B.L. Shaw, R.M. Slade, J. Chem. Soc., Chem. Commun. (1970) 1176.
[219] A.J. Cheney, B.E. Mann, B.L. Shaw, R.M. Slade, J. Chem. Soc. A (1971) 3833.
[220] J.M. Duff, B.L. Shaw, J. Chem. Soc., Dalton Trans. (1972) 2219.
[221] A.J. Cheney, B.L. Shaw, J. Chem. Soc., Dalton Trans. (1972) 754.
[222] R. Countryman, W.S. McDonald, Acta Cryst. B33 (1977) 3580.
[223] A.R.H. Bottomley, C. Crocker, B.L. Shaw, J. Organomet. Chem. 250 (1983) 617.
[224] B.L. Shaw, R.E. Stainbank, J. Chem. Soc., Dalton Trans. (1973) 2394.
[225] H.C. Clark, K.E. Hine, J. Organomet. Chem. 105 (1976) C32.
[226] N.C. Rice, J.D. Oliver, J. Organomet. Chem. 145 (1978) 121.
[227] S. Sostero, O. Traverso, M. Lenarda, M. Graziani, J. Organomet. Chem. 134 (1977) 259.
[228] R. Boaretto, S. Sostero, O. Traverso, Inorg. Chim. Acta 330 (2002) 59.
[229] F. Glockling, T. McBride, R.J.I. Pollock, J. Chem. Soc., Chem. Commun. (1973) 650.
[230] D.M. Blake, C.J. Nyman, J. Chem. Soc., Chem. Commun. (1969) 483.
[231] D.M. Blake, C.J. Nyman, J. Am. Chem. Soc. 92 (1970) 5359.
[232] C. Archambault, R. Bender, P. Braunstein, Y. Dusausoy, J. Chem. Soc., Dalton Trans. (2002) 4084.
[233] M.A. Bennett, T. Dirnberger, D.C.R. Hockless, E. Wenger, A.C. Willis, J. Chem. Soc., Dalton Trans. (1998) 271.
[234] N. Simhai, C.N. Iverson, B.L. Edelbach, W.D. Jones, Organometallics 20 (2001) 2759.
[235] A.J. Canty, N.J. Minchin, J. Organomet. Chem. 226 (1982) C14.
[236] A.J. Canty, N.J. Minchin, J.M. Patrick, A.H. White, J. Chem. Soc., Dalton Trans. (1983) 1253.
[237] A.J. Mukhedkar, M. Green, F.G.A. Stone, J. Chem. Soc. A (1970) 947.
[238] D.P. Arnold, M.A. Bennett, M.S. Bilton, G.B. Robertson, J. Chem. Soc. Chem. Commun. (1982) 115.
[239] H.E. Bryndza, J.C. Calabrese, M. Marsi, D.C. Roe, W. Tam, J.E. Bercaw, J. Am. Chem. Soc. 108 (1986) 4805.

[240] D.P. Arnold, M.A. Bennett, G.M. McLaughlin, G.B. Robertson, M.J. Whittaker, J. Chem. Soc., Chem. Commun. (1983) 32.

[241] D.P. Arnold, M.A. Bennett, G.M. McLaughlin, G.B. Robertson, J. Chem. Soc., Chem. Commun. (1983) 34.

[242] M.A. Bennett, D.E. Berry, K.A. Beveridge, Inorg. Chem. 29 (1990) 4148.

[243] G.P.C.M. Dekker, C.J. Elsevier, S.N. Poelsma, K. Vrieze, P.W.N.M. van Leeuwen, W.J.J. Smeets, A.L. Spek, Inorg. Chim. Acta 195 (1992) 203.

[244] M.A. Bennett, D.E. Berry, K.A. Beveridge, J. Browning, M.P. Russow, Acta Cryst. C49 (1993) 1320.

[245] M.A. Bennett, D.E. Berry, S.K. Bhargava, E.J. Ditzel, G.B. Robertson, A.C. Willis, J. Chem. Soc., Chem. Commun. (1987) 1613.

[246] S.H. Privér, PhD Thesis, Department of Applied Chemistry, RMIT University, 2004.

[247] M.A. Bennett, H. Neumann, L.L. Welling, A.C. Willis, unpublished results.

[248] M.A. Bennett, S.K. Bhargava, J. Messelhäuser, S.H. Privér, L.L. Welling, A.C. Willis, unpublished results.

[249] C. Scheffknecht, A. Rhomberg, E.P. Müller, P. Peringer, J. Organomet. Chem. 463 (1993) 245.

[250] H.C.S. Clark, J. Fawcett, J.H. Holloway, E.G. Hope, L.A. Peck, D.R. Russell, J. Chem. Soc., Dalton Trans. (1998) 1249.

[251] M.A. Bennett, S.K. Bhargava, A.M. Bond, A.J. Edwards, S.-X. Guo, S.H. Privér, A.D. Rae, A.C. Willis, Inorg. Chem. 43 (2004) 7752.

[252] M.A. Bennett, S.K. Bhargava, J.F. Boas, R.T. Boeré, A.M. Bond, A.J. Edwards, S.-X. Guo, A. Hammerl, J.P. Pilbrow, S.H. Privér, P. Schwerdtfeger, Inorg. Chem. 44 (2005) 2472.

[253] M.A. Bennett, S.K. Bhargava, K.D. Griffiths, G.B. Robertson, W.A. Wickramsinghe, A.C. Willis, Angew. Chem. Int. Ed. Engl. 26 (1987) 258.

[254] M.A. Bennett, S.K. Bhargava, D.C.R. Hockless, L.L. Welling, A.C. Willis, J. Am. Chem. Soc. 118 (1996) 10469.

[255] M.A. Bennett, N. Evans, L.L. Welling, A.C. Willis, unpublished results.

[256] S.K. Bhargava, F. Mohr, M.A. Bennett, L.L. Welling, A.C. Willis, Organometallics 19 (2000) 5628.

[257] K. Kitadai, M. Takahashi, M. Takeda, S.K. Bhargava, S.H. Priver, M.A. Bennett, J. Chem. Soc., Dalton Transactions (2006), in press.

[258] H.P. Abicht, K. Issleib, J. Organomet. Chem. 149 (1978) 209.

[259] S.K. Bhargava, F. Mohr, A.C. Willis, Inorg. Chim. Acta 352 (2003) 19.

[260] R.J. Puddephatt, The Chemistry of Gold, Elsevier Scientific Publishing Co., New York, 1978, p. 6.

[261] M.A. Bennett, S.K. Bhargava, D.C.R. Hockless, F. Mohr, K. Watts, L.L. Welling, A.C. Willis, Z. Naturforsch. 59b (2004) 1563.

[262] A. Grohmann, H. Schmidbaur, in: J. Wardell, E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 3, Pergamon, Oxford, 1995, p. 1.

[263] H. Schmidbaur, A. Grohmann, M.E. Olmos, in: H. Schmidbaur (Ed.), Gold Progress in Chemistry, Biochemistry and Technology, Wiley, Chichester, 1999, p. 647.

[264] A. Laguna, M. Laguna, Coord. Chem. Rev. 193–195 (1999) 837.

[265] S.K. Bhargava, F. Mohr, M.A. Bennett, L.L. Welling, A.C. Willis, Inorg. Chem. 40 (2001) 4271.

[266] M.A. Bennett, O.P. Karunaratne, L.L. Welling, A.C. Willis, unpublished results.

[267] M.A. Bennett, S.K. Bhargava, K.D. Griffiths, G.B. Robertson, Angew. Chem. Int. Ed. Engl. 26 (1987) 260.

[268] M.A. Bennett, D.C.R. Hockless, A.D. Rae, L.L. Welling, A.C. Willis, Organometallics 20 (2001) 79.

[269] H.H. Hermann, P. Schwerdtfeger, S.K. Bhargava, F. Mohr, Organometallics 22 (2003) 2373.

[270] M.A. Bennett, S.K. Bhargava, F. Mohr, L.L. Welling, A.C. Willis, Aust. J. Chem. 55 (2002) 267.

[271] M. Takeda, M. Takahashi, Y. Ito, T. Takano, M.A. Bennett, S.K. Bhargava, Chem. Lett. (1990) 543.

[272] S.K. Bhargava, F. Mohr, M. Takahashi, M. Takeda, Bull. Chem. Soc. Jpn. 74 (2001) 1051.

[273] C.S. Gopinath, R. Muthukumaran, L.L. Welling, M.A. Bennett, P.T. Manoharan, Chem. Phys. Lett. 296 (1998) 566.

[274] S.K. Bhargava, F. Mohr, J.D. Gorman, J. Organomet. Chem. 607 (2000) 93.

[275] L.A. Méndez, J. Jiménez, E. Cerrada, F. Mohr, M. Laguna, J. Am. Chem. Soc. 127 (2005) 852.

[276] M.A. Bennett, L.L. Welling, A.C. Willis, Inorg. Chem. 36 (1997) 5670.

[277] A.N. Nesmeyanov, E.G. Perevalova, K.I. Grandberg, D.A. Lemenovskii, T.V. Baukova, O.B. Afanassava, J. Organomet. Chem. 65 (1974) 131.

[278] M.A. Bennett, M. Contel, D.C.R. Hockless, L.L. Welling, J. Chem. Soc., Chem. Commun. (1998) 2401.