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BISDIPHENYLPHOSPHINOMETHANE IN DINUCLEAR COMPLEXES

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CONTENTS

A. INTRODUCTION

The idea that two metals kept in close proximity could react cooperatively with substrate molecules led to a very broad development of ligand systems able to lock two metals in such a position [1].

As far as the chemistry of low oxidation state transition metals is concerned, tertiary phosphines have been the most commonly employed ligands and have played a major role in the development of this chemistry. It seemed therefore sensible that a four-electron-donor diphosphine would be a

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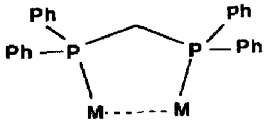
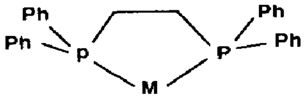
good candidate for bridging two low oxidation state transition metal complexes.

Among the diphosphines $R_2P(CH_2)_nPR_2$, it appeared that those containing only one central atom ($n = 1$) such as dppm ($Ph_2PCH_2PPh_2$) are very efficient bridging ligands, probably as a consequence of their geometric ability to form closed (in the case of metal–metal bonded species) or open five-membered rings. For the same geometrical reason, bisphenylphosphinoethane (dppe, $n = 2$) is an excellent chelating ligand. This observation resulted in an extensive chemistry of dppm-containing dinuclear complexes, and more specifically Rh and Pt-complexes (vide infra).





In 1983, an excellent review by Puddephatt [2] covering the chemistry of dppm appeared, but since then, a large amount of work has been done in this field and a number of new research objectives have appeared or developed, as will be described in the text.

The present review is a survey of the coordination of dppm with the different elements along the periodic table with special emphasis on the reactivity of the complexes and of dppm itself.

We have largely focused on dinuclear complexes, omitting almost completely the large field of dppm-stabilized clusters and including mononuclear compounds only when they show interesting relevant reactivity. Special attention is given to the chemistry of hydrido derivatives. As far as possible the present work is limited to references not included in the review of Puddephatt [2].

Finally, we mention some relevant examples of the chemistry of ligands similar to dppm, i.e. containing a single linkage atom between two tertiary phosphine groups. Special attention is devoted to dmpm which is increasingly used in dinuclear complexes.

B. DPPM AND THE PERIODIC TABLE *. SURVEY OF DINUCLEAR HOMOBIMETALLIC AND SOME MONONUCLEAR COMPLEXES ACCORDING TO THE METAL

(i) Group 1

It has long been known that strong bases such as MeLi (vide infra) could deprotonate either free or coordinated dppm. However, the crystal structure

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* The notation used in this review follows IUPAC recommendations.

of $(Ph_2PCHPPh_2)Li \cdot TMEDA$ was reported in 1983 [3] and shows that lithium is only coordinated to the phosphorus atoms.

(ii) Group 5

Cotton and co-workers have recently attempted the preparation of dinuclear metal–metal multiply-bonded complexes of vanadium and niobium containing a bridging diphosphine. They obtained in low yield the complex $[V(\mu\text{-}Cl)(\mu\text{-dppm})(BH_4)]_2$ shown to contain two bridging dppm ligands [4], whereas the niobium complex $Nb_2Cl_6(\eta^2\text{-dppm})_2$ contained chelating dppm ligands [5]. Nevertheless, when changing to dmpm $(Me_2PCH_2PMe_2)$, these authors isolated the corresponding non-metal–metal bonded $[V(\mu\text{-}Cl)(\mu\text{-dmpm})(BH_4)]_2$ in low yield while they obtained $Nb_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-dmpm})_2$ containing two bridging dmpm groups and a double metal–metal bond in high yield [6].

The analogous $Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-dmpm})_2$ complex, also containing a double (Ta=Ta) bond, has been prepared and studied crystallographically as part of a general study of a series of $M_2Cl_6(P_2)_2$ complexes (M = Ta, Mo, Ru; P_2 = bridging diphosphine) [7].

(iii) Group 6

Whereas this group offers only few examples of dppm complexes, most of them mononuclear, it shows probably the best example of studies on the intrinsic chemistry of the ligand itself.

Interaction of zerovalent carbonyl complexes of group 6 with dppm usually gave rise to mononuclear complexes (see ref. 2), but analogous reactions with dmpm have been shown to produce, in addition to the expected mononuclear derivatives, dinuclear complexes of the type *fac*-$(\mu\text{-dmpm})_3M_2(CO)_6$ (M = Cr, Mo, W) [8]. Analogous dmpm dinuclear derivatives of Mn, Re, Fe and Ni have also been prepared in the same way [8].

When bis(di-*o*-tolyl)phosphinomethane (bdtom) is used, in addition to the $M(CO)_4(bdtom)$ complexes (M = Cr, Mo), mononuclear derivatives containing an η^6-coordinated tolyl ring, $M(CO)_2(bdtom)$, were isolated [9].

An interesting hydrido-bridged dinuclear anion, $[(\mu\text{-}H)(\mu\text{-dppm})Mo_2(CO)_8]^-$, has been prepared by Darensbourg et al. from $[(\mu\text{-}H)Mo_2(CO)_{10}]^-$ and dppm [10]. The protonation of this compound in the presence of dppe afforded $(\mu\text{-dppm})(\mu\text{-dppe})Mo_2(CO)_8$.

Finally, the quadruply metal–metal bonded $Mo_2X_4(dppm)_2$ complexes (X = Cl [11], Br [12]) have been prepared by Cotton and co-workers. These authors also determined the structure of $Mo_2Cl_6(dppm)_2$ [7] which had been prepared by Wilkinson and co-workers [13] using a different method.

Two electrochemical studies of mononuclear complexes have appeared recently. The complex *mer*-$Cr(CO)_3(\eta^2\text{-dppm})(\eta^1\text{-dppm})$ has been prepared from $Cr(CO)_3(C_7H_8)$ and dppm. Interestingly, this complex can be oxidized electrochemically into $[Cr(CO)_3(\eta^2\text{-dppm})(\eta^1\text{-dppm})]^+$ which can either disproportionate into the corresponding Cr(0) and Cr(II) complexes or eliminate CO to give $[Cr(CO)_2(\eta^2\text{-dppm})]^+$ [14].

A bis dinitrogen complex, $W(N_2)_2(dppm)_2$, has been prepared by Richards and co-workers from reduction of WCl_6 with Mg in THF under N_2. Reaction with CO affords $W(CO)_2(dppm)_2$ and the complex undergoes a reversible one-electron oxidation in THF [15].

Dppm molecules chelated to group 6 metal carbonyl complexes exhibit rich reactivity, as demonstrated by Al-Jibori and Shaw [16]. Thus, deprotonation by LiBu or LiMe occurs readily at the central carbon atom to give carbanions or lithio derivatives which can be subsequently alkylated by RX (X = halogen, R = Me, Et, $PhCH_2$, $CH_2{=}CHCH_2$ or Me_3Si) to give $M(CO)_4(Ph_2PCHRPPh_2)$.

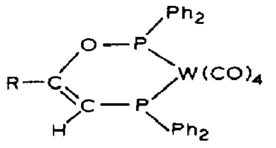
In the presence of excess MeLi and MeI, $M(CO)_4[Ph_2PC(Me)_2PPh_2]$ is obtained. Similar chemistry has been obtained with $MX_2(Ph_2PCH_2PPh_2)$ (M = Pd, X = I; M = Pt, X = Cl, Br, I) [16] but then a non-coordinated base ($LiN(SiMe_3)_2$) was employed for deprotonation.

The anion $[M(CO)_4(Ph_2PCHPPh_2)]^-$ (M = W, Cr) reacts with CH_3OCH_2Cl at 20 °C in THF to yield $M(CO)_4[Ph_2P(CH_3OCH_2)CHPPh_2]$ whereas at 80 °C in benzene a new vinylidene diphosphine complex, $M(CO)_4[Ph_2PC({=}CH_2)PPh_2]$, is obtained in high yield. The latter complex undergoes Michael-type additions with a large range of amines including optically active ones, hydrazines, acetylides and dichlorocarbene [17,18].

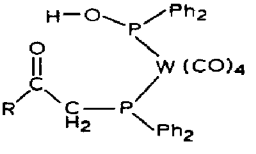
Similar reactions can be performed with Pd and Pt complexes (see group 10).

$M(CO)_4(dppm)$ (M = Cr, Mo, W), subsequent to deprotonation by Li(n-Bu) and acylation produces $M(CO)_4[Ph_2PCH(COR)PPh_2]$ [19]. These complexes react reversibly with NaOMe and with RCOCl in the presence of pyridine to give $M(CO)_4[Ph_2PC({=}COR)PPh_2]$ and $M(CO)_4[Ph_2P)_2C{=}CR(OCOR)]$, respectively.

An interesting rearrangement reaction of $W(CO)_4[Ph_2PCH(COPh)PPh_2]$ is photochemically induced. The six-membered ring containing the complex $W(CO)_4[Ph_2POC(Ph){=}CHPPh_2]$, **I**, is first obtained. In the presence of traces of water, it is converted into $W(CO)_4(PPh_2OH)(PPh_2CH_2COPh)$, **II**.



I



II

Finally, addition of PPh_2Cl after deprotonation of $M(CO)_4dppm$ yields $M(CO)_4[(Ph_2P)_3CH]$ [20] which can react further with K_2PtCl_4 or $PtCl_2L_2$ to give $PtCl_2[M(CO)_4((Ph_2P)_3CH)]_2$ and $PtCl_2L[M(CO)_4(Ph_2P)_3CH)]$, respectively.

(iv) Group 7

Mononuclear dppm manganese complexes are known [21] and their chemistry with CN or SCN has recently been described [22]. However the dppm manganese chemistry of the dinuclear species has been very popular since the discovery of a novel mode of coordination of carbon monoxide in $Mn_2(\mu\text{-}CO)(CO)_4(dppm)_2$. Thus, it was found that one carbon monoxide ligand was bound in a μ-η^2 way and thus would act as a 4-electron ligand [23,24]. The molecular dynamics of this complex as well as that of $Mn_2(CO)_6(dppm)_2$ [25] have been studied. Addition of diazomethane on the pentacarbonyl derivatives produced $Mn_2(CO)_4[\mu\text{-}C(O)CH_2N_2](\mu\text{-}dppm)$ [26,27]. Addition of other small molecules ($L = SO_2$, CS_2, BF_3) leads to $Mn_2(CO)_5(\mu\text{-}L)(dppm)_2$ [26]. Protonation was readily achieved to give $[Mn_2H(CO)_6(dppm)_2]X$ if X is a non-coordinating anion ($X = CF_3CO_2$, BF_4, BPh_4, SO_3F) [26,28] or $Mn_2HX(CO)_5(dppm)_2$ ($X = CF_3CO_2$, Cl) [28]. However, an interesting study by Deeming and Donovan-Mtunzi [29] has shown that protonation affords first at −80 °C $[Mn_2H(\mu\text{-}\eta^2\text{-}CO)(CO)_4(dppm)_2]BF_4$, which gives above −60 °C $[Mn_2H(CO)_6(dppm)_2]BF_4$ by destabilization of the μ-η^2 bridging carbonyl group.

$Mn_2H(CN)(CO)_4(dppm)_2$ has been shown to contain a similar μ-η^2 four-electron bridging cyano group [30]. Addition of $HBF_4 \cdot Et_2O$ to this complex and to $Mn_2H(CN)(CO)_5(dppm)_2$ produces $[Mn_2H(\mu\text{-}\eta^2\text{-}CNH)(CO)_4(dppm)_2]BF_4$ and $[Mn_2H(CNH)(CO)_5(dppm)_2]BF_4$, respectively. The terminal cyano ligand is more easily protonated and the protonation of the bridging cyano group destabilizes the compound which gives $[Mn_2H(CNH)(CO)_5(dppm)_2]^+$ above −20 °C [31]. The dihydride $Mn_2(\mu\text{-}H)_2(CO)_4(dppm)_2$ is prepared from $Mn_2HBr(CO)_5(dppm)_2$ after decarbonylation with Me_3NO and reduction with $LiAlH_4$. The compound inserts MeCHO or MeCN whereas addition of CO, $(POMe)_3$ or H^+/CO results in the displacement of H_2 [32] (see Fig. 1).

Finally, analogous complexes of the type $Mn_2(CO)_5(L_2)_2$ ($L_2 = (C_2H_5)_2PCH_2P(C_2H_5)_2$, $(c\text{-}C_6H_{11})_2PCH_2P(c\text{-}C_6H_{11})_2$ have been obtained from the reaction of $Mn_2(CO)_{10}$ with L_2 in refluxing decane [33]. Carbonylation of these compounds affords $Mn_2(CO)_6(L_2)_2$ [33]. A similar complex, $Mn_2(CO)_6(Me_2PCH_2PMe_2)_2$, is the first example of a *cis-trans* dmpm diphosphine-bridged complex [34]. It can be photochemically isomerized [34] into the symmetrical *trans-trans* complex [8].

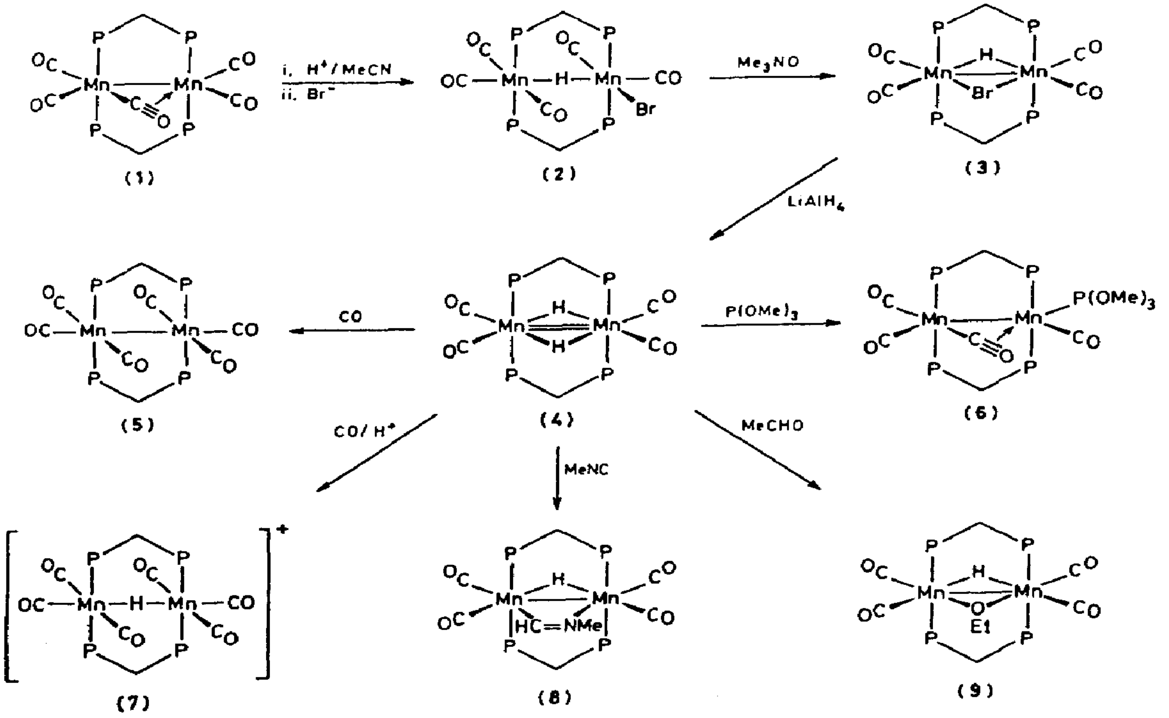


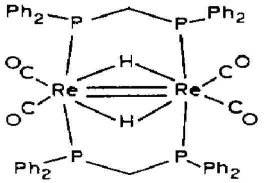
Fig. 1. Reactions of the dihydride $Mn(\mu\text{-}H)_2(CO)_4(dppm)_2$ [32]. (Reproduced with permission of the Royal Society of Chemistry.)

Surprisingly, it is only very recently that analogous rhenium derivatives have been prepared, mainly by two groups using two very different approaches: (i) photochemical reactions of rhenium carbonyl derivatives or (ii) preparation of high-valent halogeno compounds.

The complexes $Re_2(CO)_8(\mu\text{-}L_2)$ (L_2 = dppm, dmpm, dppe, dmpe) are formed upon addition of L_2 to $(\mu\text{-}H)(\mu\text{-}CH{=}CHC_4H_9)Re_2(CO)_8$ [35] and, subsequent to photochemical activation, they are able to oxidatively add water or methanol to give $Re_2(\mu\text{-}H)(\mu\text{-}OH)(CO)_6L_2$, $Re_2(\mu\text{-}OH)_2(CO)_6L_2$, $Re_2(\mu\text{-}H)(\mu\text{-}OR)(CO)_6L_2$, and $Re_2(\mu\text{-}OR)_2(CO)_6L_2$ [35]. This is a rare example of water oxidative addition by metal carbonyls and the products are remarkably stable when compared to similar unbridged derivatives (Fig. 2).

The photochemical reactions of $Re_2(CO)_8(\mu\text{-}L_2)$ with alkenes [36] (L_2 = dmpm, dppe, dmpe) and alkynes [37] (L_2 = dppm, dmpm) have also been investigated. With alkenes, a fluxional alkenyl-bridged complex $(\mu\text{-}H)(\mu\text{-}CH{=}CHR)(\mu\text{-}L_2)Re_2(CO)_6$ is formed whereas with alkynes four products are successively obtained after CO loss.

The bis diphosphine-bridged complexes, $Re_2(CO)_6(L_2)_2$ (L_2 = dppm, dmpm; $(L_2)_2$ = (dppm)(dmpm)), were synthesized by thermal or photochemical reaction of $Re_2(CO)_8(L_2)$ with excess diphosphines [38].



Again the complexes show a very rich reactivity. They react with water, methanol or alkynes to give $(\mu\text{-H})(\mu\text{-OR})(\mu\text{-L}_2)_2\text{Re}_2(\text{CO})_4$ (R = H, Me) and $(\mu\text{-H})(\mu\text{-C}{\equiv}\text{CR})(\mu\text{-L}_2)_2\text{Re}_2(\text{CO})_4$, respectively. Of special interest is the observation that refluxing $\text{Re}_2(\text{CO})_6(\text{L}_2)_2$ in 1,2,4-trimethylbenzene alone or in the presence of a good hydrogen atom donor (9,10-dihydroanthracene or decalin) or in the presence of H_2 leads to the dihydrido-bridged complex $(\mu\text{-H})_2\text{Re}_2(\text{CO})_4(\text{L}_2)_2$ thought to contain a double metal–metal bond [38].

The dihydrides $\text{Re}_2(\mu\text{-H})_2(\text{CO})_6\text{L}_2$ ($\text{L}_2 = (\text{EtO})_2\text{POP}(\text{OEt})_2$, dppm) have been prepared from the reaction of $\text{Re}_3\text{H}_3(\text{CO})_{12}$ in octane [39]. Very interestingly, $\text{Re}_2(\mu\text{-H})_2(\text{CO})_6\text{dppm}$ reacts with CH_3CN to yield $\text{Re}_2(\mu\text{-H})(\text{CO})_6\text{L}_2(\mu\text{-NC(H)Me})$; with RNC, $\text{Re}_2(\mu\text{-H})(\text{CO})_6(\text{L}_2)(\mu\text{-HNR})$ complexes are obtained (R = t-Bu, n-Bu, $p\text{-MeOC}_6\text{H}_4$) or $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{CH}_2$) [40].

The analogous paramagnetic complex $\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})^-$ has recently been prepared and studied by ESR [41].

Another series of dppm-bridged dirhenium complexes has been extensively studied by Walton and co-workers [42]. They recently reexamined the crystal structure of $\text{Re}_2^{\text{III}}\text{Cl}_6(\text{dppm})_2$ and have shown that the complex

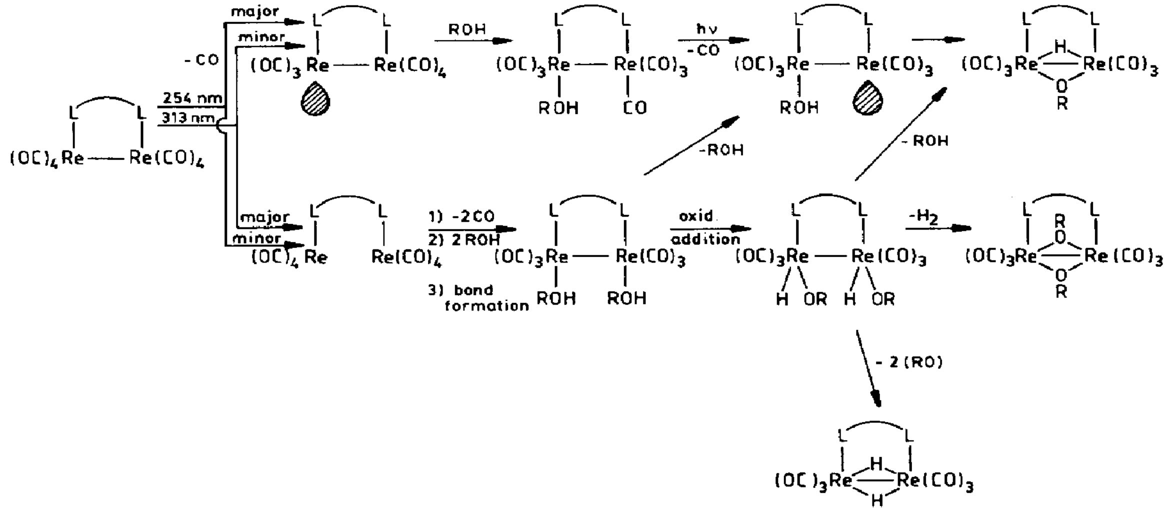


Fig. 2. The two pathways proposed for the photochemical reactions of $\text{Re}_2(\text{CO})_8(\text{L–L})$ with water or methanol [35]. (Reproduced with permission of the American Chemical Society.)

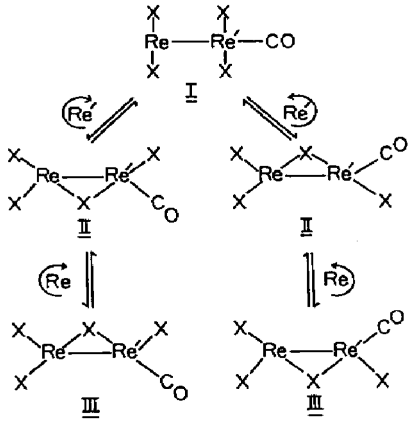


Fig. 3. A proposed mechanism for the interconversion of three possible isomers (I, II and III) of $Re_2X_4(dppm)_2CO$ [46]. Dppm ligands have been omitted for clarity. They lie above and under the $Re_2X_4(CO)$ plane. (Reproduced with permission of the American Chemical Society.)

contains two bridging chlorides. Also of great interest is the electrochemical study on the "$Re_2Cl_x(dppm)_2$" system ($x = 4, 5, 6$) where they could show that these three complexes can be readily interconverted by oxidation ($x = 4 \rightarrow x = 5 \rightarrow x = 6$) or reduction.

The chemical oxidation and reduction of $Re_2Cl_6(dppm)_2$ using respectively $NOPF_6$ and $CoCp_2$ give paramagnetic ions which possess previously unknown metal–metal bond orders of 1.5 [43,44]. The crystal structure of $[Re_2Cl_6(dppm)_2]^+$ has been solved and the most noticeable feature is an Re–Re distance (2.6823 (6) Å) notably longer than in the neutral starting material (2.626(1) Å) [43,44]. Also prepared were the paramagnetic dications $[Re_2(\mu\text{-dppm})_2Cl_3(NCR)_2](PF_6)_2$ from the monocationic precursors [44].

The structural characterizations of $Re_2^{II}Cl_4(L_2)_2$ (L_2 = dppm, dmpe) show the complexes to contain triple metal–metal bonds (Re–Re = 2.234(3) Å and 2.264(1) Å, respectively) [45]. Upon reaction with CO (L_2 = dppm), two complexes are produced successively, $Re_2Cl_4(\mu\text{-dppm})_2(CO)$ (see Fig. 3) and $Cl_2Re(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2ReClCO$ [47]. The electronic configuration of this dicarbonyl compound suggests the presence of a double metal–metal bond as for $Re_2Cl_6(dppm)_2$ which is confirmed by X-ray crystallography (Re–Re = 2.584(1) Å).

When two equivalents of t-butyl isocyanide are added to $Re_2Cl_4(dppm)_2$, the novel paramagnetic μ-iminyldirhenium(II), (III) complex, $[Re_2(\mu\text{-Cl})(\mu\text{-C=NH-t-Bu})(\mu\text{-dppm})_2Cl_2(CN\text{-t-Bu})_2]PF_6$, is formed (Re–Re = 2.7039(6) Å) [48]. $Re_2Cl_4(dppm)_2$ also reacts with nitriles to afford the cations $[Re_2Cl_3(dppm)_2NCR]X$ (X = Cl, PF_6; R = CH_3, C_2H_5, C_6H_5, 4Ph-C_6H_4)

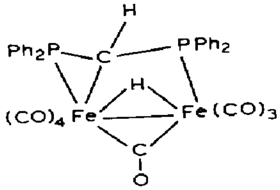
[49]. The monocarbonyl compound $Re_2Cl_4(dppm)_2CO$ reacts further with the isocyanide CNR (R = i-Pr, t-Bu, xylyl or mesityl) to produce $Re_2Cl_4(dppm)_2(CO)(CNR)$ [46]. With t-butyl isocyanide, $Re_2Cl_4(dppm)_2$ (CN-t-Bu) and $[Re_2Cl_3(dppm)_2$ $(CN\text{-}t\text{-}Bu)_2]PF_6$ are formed [50].

The dicarbonyl complex $Re_2Cl_4(dppm)_2(CO)_2$ also reacts with isocyanides and nitriles (L), in the presence of $TlPF_6$ to yield $[Re_2Cl_3(dppm)_2$ $(CO)_2L]PF_6$. The reduction of this complex with cobaltocene affords the paramagnetic neutral derivative $Re_2Cl_3(dppm)_2(CO)_2L$, the first example of a multiply-bonded dirhenium complex that possesses the Re_2^{3+} core [51]. Finally, $Re_2Cl_4(PMe_3)_2(\mu\text{-dppm})$ has recently been prepared by phosphine exchange from $Re_2Cl_4(PMe_3)_4$ [52].

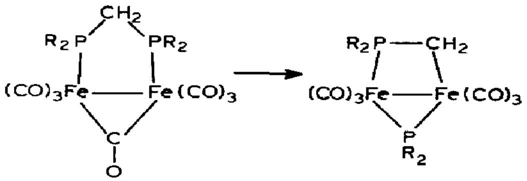
(v) Group 8

In the field of iron carbonyl chemistry, the stabilization of the $Fe_2(CO)_9$ core has been achieved by using various diphosphines and the complexes $Fe_2(CO)_7L_2$ and $Fe_2(CO)_5(L_2)_2$ (L_2 = various diphosphines including dppm and dmpm) [53] are known. The dmpm complexes have been prepared at the same time by King and Raghuveer [8] and Wilkinson and co-workers [54]. From the latter paper, the crystal structure of $Fe_2(CO)_4(\mu\text{-CO})(dmpm)_2$ showed the presence of a single metal–metal bond. These authors also studied the interaction of iron(II) acetate with a series of Grignard reagents where mononuclear derivatives were obtained [55].

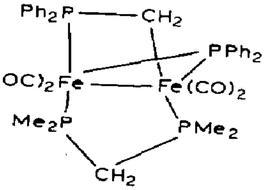
However, $Fe_2(\mu\text{-CO})(CO)_6(\mu\text{-dppm})$ is deprotonated by methyl lithium to form an ionic species which affords the dinuclear complex shown below [56] upon protonation.



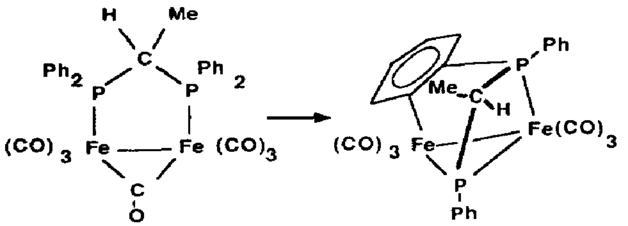
When refluxed in THF, $Fe_2(CO)_7(L_2$ (L_2 = dppm, dmpm) undergoes a phosphorus–carbon bond cleavage after CO loss [47]



A similar reaction is observed when $Fe_2(CO)_5$(dppm)(dmpm) is heated in toluene to afford the complex [57]:



Finally, substitution of a hydrogen by a methyl group on the methylene carbon of dppm prevents the $Ph_2P\text{–}CH_2$ bond cleavage and instead an orthometallation together with P–Ph bond cleavage are observed [57]:



Cyclopentadienyl carbonyl iron derivatives

The reaction of $Cp_2Fe_2(\mu\text{-}CH_2)(\mu\text{-}CO)CO_2$ with dppm affords $Cp_2Fe_2(\mu\text{-}CH_2)(\mu\text{-}CO)(\mu\text{-}dppm)$ which upon protonation with HPF_6 produces $[Fe_2(\mu\text{-}CH_3)(\mu\text{-}CO)(\mu\text{-}dppm)Cp_2]PF_6$, a complex containing an asymmetrical bridging methyl group attached to one iron atom via a C–Fe σ bond and to the other via an η^2C–H (agostic) interaction [58]. The dinuclear and tetranuclear complexes $Me_2Si[(\eta^5\text{-}C_5H_4)_2(CO)Fe(\mu\text{-}CO)_2Fe(\eta^1\text{-}dppm)]$ [59], $Me_2Si[\eta^5\text{-}C_5H_4Fe(CO)]_2(dppm)$ [60] and $[Me_2Si[(\eta^5\text{-}C_5H_4)_2Fe_2(CO)_3]]_2(dppm)$ [60] have been prepared and studied by Mössbauer spectroscopy [59].

Dppm chemistry of ruthenium

Surprisingly the dppm chemistry of ruthenium has been rarely studied, probably because of the lack of easily available starting material. It is mainly limited to mononuclear derivatives.

In fact, the only bis (dppm) bridged ruthenium derivatives have been obtained by Lehmann and Wilkinson [61], through the reaction of $[Ru_3O(O_2CMe)(MeOH)_3]O_2CMe$ with zinc amalgam and dppm. $Ru_2(O_2CMe)_4(dppm)_2$ was produced in two isomeric forms: other compounds containing chelating dppm acetato complex were also prepared [61].

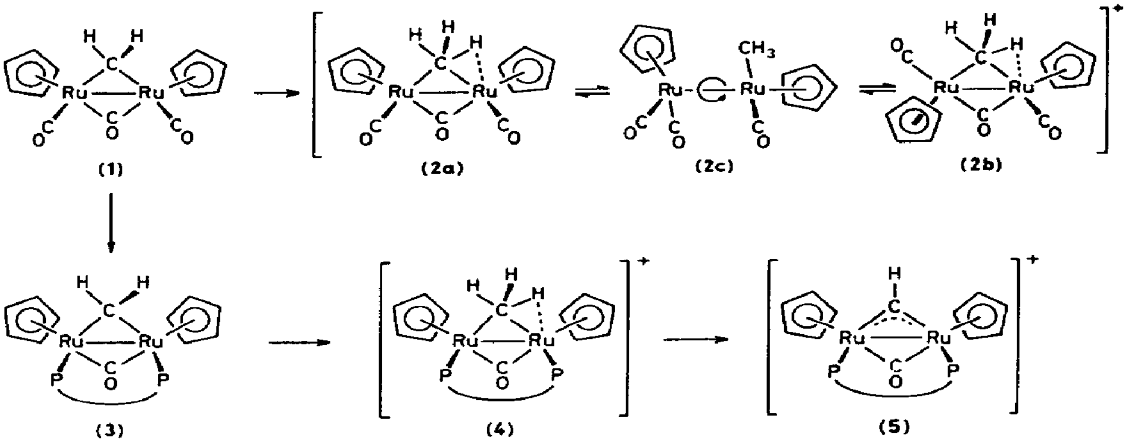


Fig. 4. Methyl group mobility and conversion into methyne at a diruthenium center [64]. (Reproduced with permission of the Royal Society of Chemistry.)

The only similar complexes structurally characterized are $Ru_2(\mu\text{-}CO)(CO)_4(\mu L_2)_2$ ($L_2 = (MeO)_2PN(Et)P(OMe)_2$) obtained by reaction of $Ru_3(CO)_{10}L_2$ with excess ligand on irradiation [53], $[Ru_2Cl(Me_2PCH_2PMe_2)(PhNPy)_2]BPh_4$ formed upon reaction of $Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNH\ py)$ with dmpm [62] and $Ru_2Cl_6(dmpm)_2$ recently prepared by Cotton and co-workers [7] from $Ru_2Cl(O_2CCH_3)_2(mhp)_2$ with Me_3SiCl and dmpm.

A small number of mono(dppm) bridged dinuclear derivatives are also known. The complex $[(bipy)_2RuCl]_2(\mu\text{-}dppm)X_2$ ($X = ClO_4$, PF_6) can be prepared from $RuCl_2(bipy)_2$ and dppm; it can be oxidized into the Ru^{II}, Ru^{III} and Ru^{III}, Ru^{III} form [63].

Knox and co-workers [64] have prepared the μ-compound $(CpRu)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\mu\text{-}dppm)$ by photochemical carbonyl substitution from $(CpRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$. It is protonated by $HBF_4 \cdot Et_2O$ into a μ-methyl complex which slowly loses H_2 to give a μ-methyne derivative [64] as shown in Fig. 4.

Oxidation of the μ-methylene complex by $FeCp_2^+$ leads to the direct formation of the μ-methyne complex which can add H_2 (150 atm, 100 °C) to give again the μ-methyl derivative, or be alkylated by CH_3Li or reduced by $NaBH_4$ [65].

$Ru_2(CO)_4(\mu\text{-}PPh_2)(\mu\text{-}dppm)$ has been isolated in low yield from the reaction of $Ru_3(CO)_{12}$ with $HC(PPh_2)_3$ in refluxing benzene [66]. As part of an extensive study of the preparation and reactivity of dppm-ruthenium clusters Bonnet and co-workers [67] have studied the reaction of $Ru_3(CO)_8(dppm)_2$ with I_2 and obtained $RuI_2(CO)_2(dppm)$ together with the dinuclear complex $Ru_2(\mu\text{-}I)_2(CO)_4(\mu\text{-}dppm)$ which has been structurally characterized [68]. A dinuclear dppm bridged oxoallyl complex $Ru_2(CO)_5(\mu,\eta^4\text{-}CH_2C(O)CH_2)(dppm)$ has been obtained by Shapley and co-workers [69] upon reaction of the ketone complex $Ru_3(CO)_7(\mu_3,\eta^3\text{-}CH_2C(O)CH_2)$ $(\mu\text{-}CH_2)(dppm)$ with CO [69].

The most popular mononuclear ruthenium dppm complex is certainly $RuCl_2(dppm)_2$, first obtained directly from $RuCl_3 \cdot 2H_2O$ as the *trans* isomer by Chatt and Hayter [70]. The *cis* isomer can be prepared using $RuCl_2(DMSO)_4$ as the starting material [71,72] or from $K_4Ru_2OCl_{10}$ [73]. The interconversion of the two isomers has been studied [74]; a tris dppm complex $[Ru(dppm)_3ClO_4]ClO_4$ has also been reported [75].

Cole-Hamilton and co-workers [76] have prepared interesting dicationic, dicarbonyl complexes $[Ru(CO)_2(dppm)_2]^{2+}$ by reacting $RuCl_2(dppm)_2$ with various silver salts under CO. Interestingly they reported some of the first dppm-bridged heterobimetallic complexes, namely *cis*-$[Ru(CO)_2(dppm)_2AgX]Y_2$ ($X = BF(OH)_3$, $Y = BF_4$; $X = ClO_4$, $Y = ClO_4$; $X = Cl$, $Y = AsF_6$). Hydride reduction of the dicarbonyl dicationic species afforded the first isolable formyl derivative of ruthenium $[Ru(CHO)(CO)(dppm)_2]X$ [77] whose reactivity has been studied [78,79]. Analogous osmium derivatives were obtained by a similar procedure [80].

The ruthenium(0) olefin derivative $Ru(C_8H_8)(dppm)_2$ has been obtained from $Ru(C_8H_8)_2(PPh_3)_2$ and dppm [81] whereas the reaction of CpRuH(COD) with dppm produces a structurally characterized [82] σ alkenyl derivative $CpRu(dppm)(C_8H_{13})$.

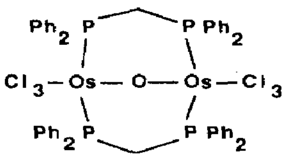
Other examples of mononuclear dppm complexes involve the ruthenium(0) derivative $Ru(COD)(dppm)_2$ which reacts with molecular hydrogen to give $RuH_2(dppm)_2$ [71]. This dihydride exists in solution as a mixture of the *cis* and the *trans* isomers. However, it reacts with $CHCl_3$ or $HBF_4 \cdot H_2O$ to give only the *trans* isomers of $RuHCl(dppm)_2$ and $[RuH(dppm)_2OH_2]BF_4$ [71]. It is worth noting that $Ru(COD)(dppm)_2$ and $RuH_2(dppm)_2$ are good starting materials for preparing heterobimetallic complexes (vide infra).

$RuH_2(dppm)_2$ was also prepared from *trans*-$Ru(O_2CR)_2(dppm)_2$ and $NaBH_4$ [83]. A number of other mononuclear dppm complexes such as $Ru(O_2CR)_2(dppm)_2$, $[Ru(O_2CR)(dppm)_2]BPh_4$, $Ru(O_2CR)_2(CO)_2(dppm)_2$ and $RuH_2(CO)(dppm)_2$ have also been reported [83]. A phenyl ruthenium complex $RuCl(Ph)(CO)(PPh_3)(dppm)$ is also known [84].

Finally, some related mononuclear dmpm ruthenium derivatives are also known, namely $Ru(dmpm)_3X_2$ ($X = Cl$, PF_6) and $[RuH(dmpm)_3]PF_6$ [85].

Dppm chemistry of osmium

To our knowledge the dppm bridged dinuclear chemistry of osmium is limited to the preparation of $Os_2O(dppm)_2Cl_6$, a compound containing two bridging dppm ligands as well as a linear μ-oxo bridge [86]. This interesting,



quite stable, compound exemplifies the potential of dppm to accommodate a large metal–metal distance (3.584(1) Å), the P–C–P angle reaching for this purpose a value of 124.6(7)°.

(vi) Group 9

In this group, the most salient feature is, compared to a very important development of the dppm chemistry of rhodium and iridium, a very limited one for cobalt.

Dppm chemistry of cobalt

Part of this cobalt chemistry derives from $Co_2(CO)_6(\mu\text{-dppm})$ which is prepared from $Co_2(CO)_8$ and dppm [87]. This compound reacts with H_2 to give $Co_2(CO)_4(\mu\text{-H})(\mu\text{-PPh}_2)(\mu\text{-dppm})$ in low yield and is oxidized by I_2 to

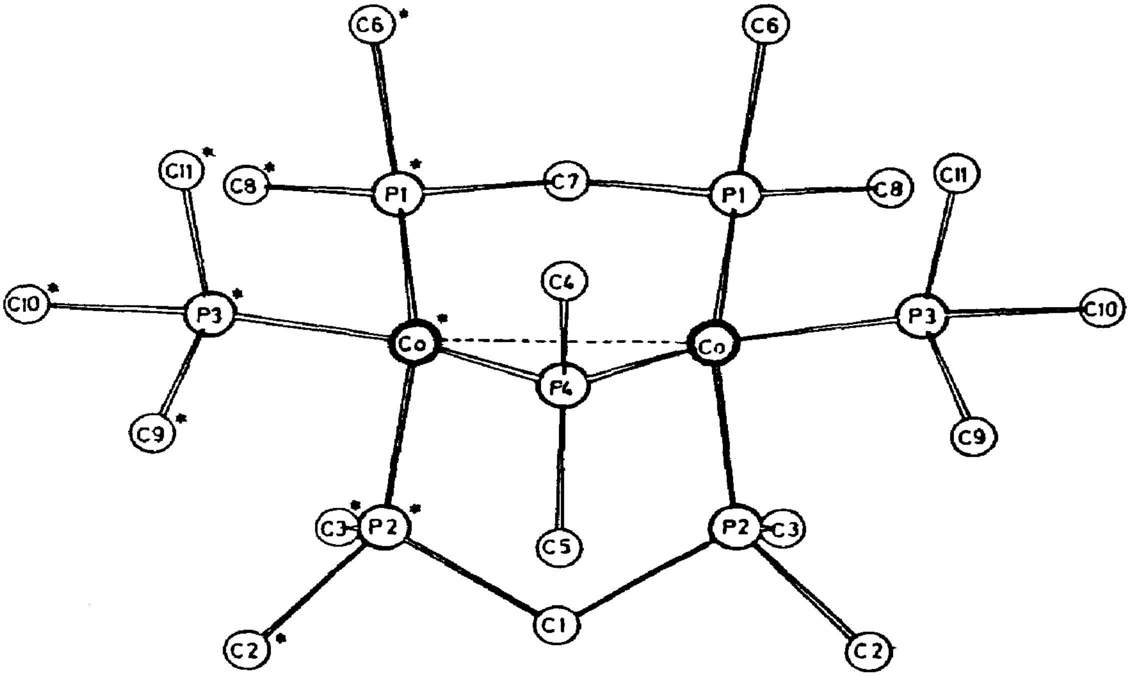


Fig. 5. Molecular structure of $[(PMe_3)(\mu\text{-dmpm})Co]_2PMe_2$ [93]. (Reproduced with permission of the American Chemical Society.)

give the bis dppm bridged $Co_2(dppm)_2(CO)_3I_2$ [87]. Its reaction with alkynes, yielding $Co_2(CO)_6(\mu$-dppm)(μ-alkyne) [88], and its solution structure and dynamics [89] have also been studied. Finally, displacement of the bridging carbonyl groups or reaction with $CHRN_2$ yields the μ-alkylidene complexes $Co_2(CO)_4(\mu\text{-}CH_2)(\mu$-CHR) ($\mu$-dppm) (R = H, CO_2Et) [90]. It could be shown that these products undergo rapid bridging to terminal methylene transformations. The related mononuclear complex $[Co(CO)(dppm)_2]ClO_4$ has also recently been reported [91].

The reaction of $CoCl_2$ with $NaBH_4$ in the presence of dppm is believed to give first a binuclear Co(I)–Co(II) mixed oxidation state product, finally leading to $CoHCl_2(dppm)_2$ and $CoCl(dppm)_3$. Other hydrido complexes, $[CoHCl(dppm)_2]BPh_4$ and $[CoH(BH_3CN)(dppm)_2]ClO_4$, have also been prepared [92].

Finally, using the similar ligand dmpm, Karsch et al. [93] recently reported an interesting paramagnetic dinuclear complex, $Co_2(\mu\text{-}PMe_2)(\mu\text{-}dmpm)_2(PMe_3)_2$ (see Fig. 5).

Dppm chemistry of rhodium

In contrast with dppm cobalt chemistry, rhodium chemistry has known much important development. This can be explained by the fact that the first dppm-bridged dinuclear complex was $[RhCl(CO)(dppm)]_2$, a very attractive starting material first prepared by Mague and Mitchener in 1969 [94] and structurally characterized by Cowie and Dwight [95] in 1980. The physical properties of such dinuclear complexes, $[MCl(CO)L_2]_2$ (M = Rh, Ir; L_2 = dppm, dpam), are a matter of constant interest, as shown by the recent study of their luminescence properties [96].

Importantly, $[RhCl(CO)(dppm)]_2$ readily loses CO in refluxing toluene to give $Rh_2Cl_2(CO)(dppm)_2$ [70] whose structure has recently been determined by X-ray crystallography [97]. The chemistry of both complexes has been extensively studied, particularly by Cowie and co-workers. Thus, both compounds react with the activated acetylenes DMA and HFB (DMA = $CH_3O_2CC_2CO_2CH_3$; HBF = $CF_3C_2CF_3$) to yield $Rh_2Cl_2(\mu\text{-}CO)(\mu$-acetylene)$(dppm)_2$ [98]. The bromo and iodo analogues are also known. A similar complex containing a bridging methylene group $Rh_2Cl_2(\mu\text{-}CH_2)(\mu$-HFB)$(dppm)_2$ (HFB = $CF_3C_2CF_3$) was obtained from $Rh_2Cl_2(dppm)_2(\mu$-HFB) and diazomethane [99].

$Rh_2X_2(\mu$-acetylene)$(dppm)_2$ (X = Cl, I) reacts with CO or SO_2(L) to yield $Rh_2X_2(\mu$-L)(μ-acetylene)$(dppm)_2$ [100]. With methyl isocyanide, $Rh_2X_2(CNMe)(\mu$-acetylene)$(dppm)_2$, $Rh_2X_2(CNMe)_2(\mu$-acetylene)$(dppm)_2$ or $[Rh_2X(CNMe)_2(\mu\text{-acetylene})(dppm)_2]X$ and finally $[Rh_2(CNMe)_4(\mu\text{-acetylene})(dppm)_2]X_2$ can be successively prepared [100].

Protonation of the A-frame complex, $Rh_2Cl_2(CO)(dppm)_2$, with HA affords $\mathrm{Rh_2Cl_2(\mu\text{-}H)(\mu\text{-}CO)(dppm)_2(A)}$ ($\mathrm{A = Cl, SO_3C_6H_4CH_3, BF_4}$) in which the proton inserts into the Rh–Rh bond and $\mathrm{A^-}$ coordinates on one Rh center [101].

Oxidative addition of $\mathrm{SC(Cl)NMe_2}$ to $\mathrm{Rh_2Cl_2(\mu\text{-}CO)(dppm)_2}$ yields $\mathrm{Rh_2Cl_3(CO)(SCNMe_2)(dppm)_2}$ or $\mathrm{[Rh_2Cl_2(CO)(SCNMe_2)(dppm)_2]BF_4}$ in the presence of $\mathrm{BF_4^-}$ [102]. Noteworthy is the reaction of $\mathrm{BH_4^-}$ with the latter cation producing the very air-sensitive $\mathrm{[Rh_2(CO)(\mu\text{-}SCNMe_2)(solvent)(dppm)_2]BF_4}$ (solvent = THF, MeCN) which, in the presence of CO, produces $\mathrm{Rh_2(CO)_2(\mu\text{-}SCNMe)(dppm)_2]BF_4}$. The reactions of $\mathrm{Rh_2Cl_2(CO)(dppm)_2}$ with isocyanides have also been investigated [103]. With isothiocyanates, examples of bridging thiocyanate coordination, of subsequent condensation and rearrangement reactions and of isocyanide formation, have been observed depending upon the nature of the isothiocyanate.

$\mathrm{[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]Cl}$ can insert into the Hg–Cl bond of $\mathrm{HgCl_2}$ to give $\mathrm{Rh_2Cl_3(\mu\text{-}HgCl)(CO)_2(\mu\text{-}dppm)_2}$ a complex containing an asymmetrical Rh–Hg–Rh bridge [104].

In a series of papers, Mague et al. [105–107] have studied the reactivity of binuclear cationic complexes of rhodium. They could show that the A-frame complex $\mathrm{[Rh_2(CO)_2(\mu\text{-}Cl)(dppm)_2]\ PF_6}$ reacts with silver carboxylates to yield $\mathrm{[Rh_2(CO)_2(\mu\text{-}O_2CMe)(dppm)_2]PF_6}$ [105]. This complex reacts further with activated acetylenes to give $\mathrm{[Rh_2(CO)(\mu\text{-}CO)(\mu\text{-}RC_2R)(O_2CMe)(dppm)_2]PF_6}$ ($\mathrm{R = CF_3, CO_2CH_3}$) from which CO is substituted by L ($\mathrm{L = CN^tBu, P(OMe)_3}$) to yield $\mathrm{(Rh_2L(\mu\text{-}CO)(\mu\text{-}RC_2R)(O_2CMe)(dppm)_2]\ PF_6}$. The crystal structures of $\mathrm{[Rh_2(P(OMe)_3)(\mu\text{-}CO)(\mu\text{-}MeO_2CC_2CO_2Me)(dppm)_2]PF_6}$ [106] and $\mathrm{[Rh_2(CNt\text{-}Bu)_4(\mu\text{-}F_3CC_2F_3)(dppm)_2](PF_6)_2}$ [107] have shown in both cases symmetrical binding of the acetylene as a dimetallated olefin.

Another type of acetylene coordination has been found when terminal acetylenes are reacted with the carboxylate A-frame complex $\mathrm{[Rh_2(\mu\text{-}O_2CR)(CO)_2(dppm)_2]ClO_4}$ ($\mathrm{R = CH_3, CF_3}$) yielding a μ-η^2 acetylide complex, $\mathrm{[Rh_2(\mu\text{-}\eta^2\text{-}C_2R')(CO)_2(dppm)_2]ClO_4}$ (R′ = H, Ph, t-Bu) [108]. The acetylide ligand is fluxional, exhibiting an oscillatory-type motion. Hydride reduction by $\mathrm{NaBH_4}$ or $\mathrm{LiBHEt_3}$ affords unstable bridging vinylidene complexes: $\mathrm{[Rh_2(\mu C{=}CHR')(CO)_2(dppm)_2]}$. Interestingly, when R′ = t-Bu, the complex undergoes a novel reoxidation process to give back $\mathrm{[Rh_2(\mu\text{-}\eta^2\text{-}C_2R)(CO)_2(dppm)_2]ClO_4}$ [108]. The crystal structure of this derivative has been confirmed by Cowie and Loeb [109] who showed that the overall geometry of the compound is that of an A-frame.

$\mathrm{[Rh_2(\mu\text{-}OR)(CO)_2(dppm)_2]ClO_4}$ ($\mathrm{R = H, CH_3, C_2H_5}$) has been prepared from $\mathrm{Rh_2Cl_2(CO)_2(dppm)_2}$, excess OR and $\mathrm{NaClO_4}$ in alcohol (R = Me, Et). The alkoxides are converted into hydroxide upon treatment with $\mathrm{HClO_4}$. Interestingly, a non conducting complex, $\mathrm{[Rh_2(\mu\text{-}OH\text{-}Cl)(CO)_2(dppm)_2]}$, is obtained from the reaction of $Rh_2Cl_2(CO)_2(dppm)_2$ with Na_2CO_3 in aqueous ethanol. These complexes have been shown to be synthetic precursors to a great variety of A-frame derivatives [110,111]. $Rh_2(\mu\text{-OH-Cl})(CO)_2(\mu\text{-dppm})_2]H_2O$ reacts with CO to yield $Rh_2Cl_2(CO)_2(dppm)_2$ whereas $[Rh_2(\mu\text{-X})(CO)_2(dppm)_2]ClO_4$ ($X = N_3$, NCS) gives $[Rh_2(\mu\text{-NCO})(CO)_2(dppm)_2]ClO_4$ and the complex of the σ, π bridging cyano ligand, $[Rh_2(\mu\text{-CN})(\mu\text{-CO})(CO)_2(dppm)_2]ClO_4$ [111]. The reactivity of the carboxylate complex $[Rh_2(\mu\text{-}O_2CR)(CO)_2(\mu\text{-dppm})_2]ClO_4$ was also studied: its treatment with CO followed by H_2 or H_2/CO mixture leads to $[Rh_2(\mu\text{-H})(\mu\text{-CO})(CO)_2(dppm)_2]ClO_4$ [112].

The alkoxide complexes also react under CO to give a 46-electron trinuclear cluster $[Rh_3(CO)_3(\mu\text{-CO})_3(\mu\text{-dppm})_2]ClO_4$ whose structure resembles that of an A-frame with a bridging "$Rh(CO)_3$" group [113].

Eisenberg and co-workers [114,115] have studied the chemistry of A-frame derivatives. They especially described in 1980 a very unstable deep purple rhodium(0) derivative, $Rh_2(CO)_2(dppm)_2$, obtained by reduction of $Rh_2Cl_2(CO)_2(dppm)_2$ with $NaBH_4$ [114]. Upon treatment with CO and H^+, this purple compound gave $Rh_2(\mu\text{-CO})(CO)_2(dppm)_2$ and $[Rh_2(\mu\text{-H})(CO)_2(dppm)_2]^+$, respectively, and was found to be a catalyst for water-gas shift and acetylene hydrogenation [114,115].

$Rh_2(\mu\text{-CO})(CO)_2(dppm)_2$ and $[Rh_2(\mu\text{-H})(\mu\text{-CO})(CO)_2(dppm)_2]^+$ both promote the decomposition of alkylnitrosoureas to give $Rh_2(NCO)_2(CO)_2(dppm)_2$ and $[Rh_2(\mu\text{-NCO})(CO)_2(dppm)_2]^+$, respectively [116]. Addition of CO to the hydrido-bridged cation results in the formation of $[Rh_2(\mu\text{-H})(\mu\text{-CO})(CO)_2(dppm)_2]^+$ whose structure has been determined by X-ray crystallography [114,115].

However, Woodcock and Eisenberg [117] recently reformulated the deep purple derivative as the dihydride $Rh_2(\mu\text{-H})_2(CO)_2(dppm)_2$ which readily

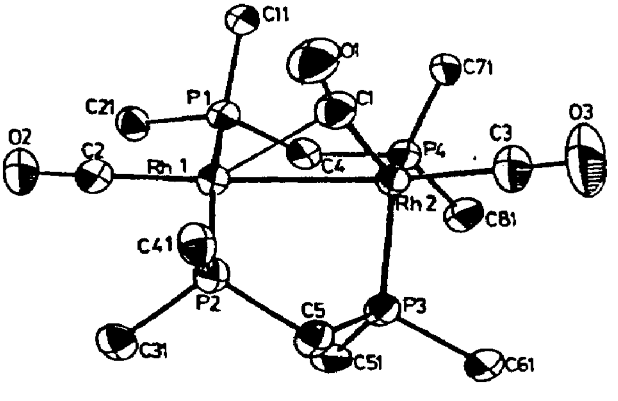
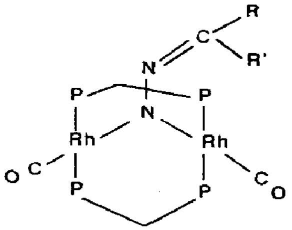


Fig. 6. The structure of $Rh_2(\mu\text{-CO})(CO)_2(dppm)_2$ [118]. (Reproduced with permission of the American Chemical Society.)

loses H_2 in vacuo or under N_2. The structure of $Rh_2(\mu\text{-}CO)(CO)_2(dppm)_2$ has shown that, surprisingly, this complex does not adopt an A-frame structure. Each rhodium center has a different coordination number (Rh(1), 4; Rh(2), 5) and the phosphines are *trans* on Rh(1) and *cis* on Rh(2) [118] (see Fig. 6). However, this complex undergoes a fluxional process in which the originally proposed A-frame structure could be an intermediate [118]. Reaction of the purple dihydride complex with acetylene affords a $\mu\text{-}\eta^2$ alkyne bridged derivative and the isomeric vinylidene derivative $Rh_2(\mu C{=}CHPh)(CO)_2(dppm)_2$ [119]. However, the mechanism of acetylene hydrogenation with the dihydride has recently been shown to proceed via a metal-centered radical-pair mechanism [120]. The dihydride also reacts with ethyl diazoacetate or diethyl diazocarbonate with elimination of H_2 and formation of the 1 : 1 A-frame adducts, $Rh_2(\mu\text{-}N_2CRCO_2Et)(CO)_2(dppm)_2$ (R = H, CO_2Et) [121].



Balch and co-workers [122–125] have very much contributed to the chemistry of such dppm bridged species. They have reported the preparation of the "redox-active" unsymmetrical derivative of tetrachloroanthraquinone, $Rh_2(dppm)_2(1\text{-}2\text{-}O_2C_6Cl_4)(CO)$, which can be reversibly electrochemically or chemically oxidized to the monocation $[Rh_2(\mu\text{-}dppm)_2(1{,}2\text{-}O_2C_6Cl_4)CO]^+$ [122]. However, recently these authors have been more interested in the preparation of trinuclear complexes containing a nearly linear array of metal centers and the study of their reactivity [123]. Heterometallic complexes could also be prepared in this way such as, for example, $Rh_2Pd(CO)_2Cl_3(\mu\text{-}Ph_2PCH_2As(Ph)CH_2PPh_2)_2][BPh_4]$ [124]. A particularly interesting recent result was the site-selective addition of hydrogen to a trirhodium derivative on the central rhodium atom to give the *cis* dihydride containing semi-bridging interactions with the other two rhodium centers [125] (see Fig. 7).

Electrochemical studies on tetrakis(isocyanide)rhodium(I) dimers have been carried out [126] and it was shown that nitrogenous Lewis bases could stabilize a rhodium(II) dimer after oxidation of the starting material [127].

A-frame pyrazolate bridged complexes $[Rh_2(\mu\text{-}pz)(CO)_2(dppm)_2]X$ (pz = pyrazolate, X = Cl, ClO_4, BPh_4) have been prepared by Oro et al. [128] from $Rh_2Cl_2(CO)_2(dppm)_2$, HL and KOH and have been shown to undergo transannular iodine oxidative addition to give $[Rh_2I_2(\mu\text{-}pz)(CO)_2(dppm)_2]X$

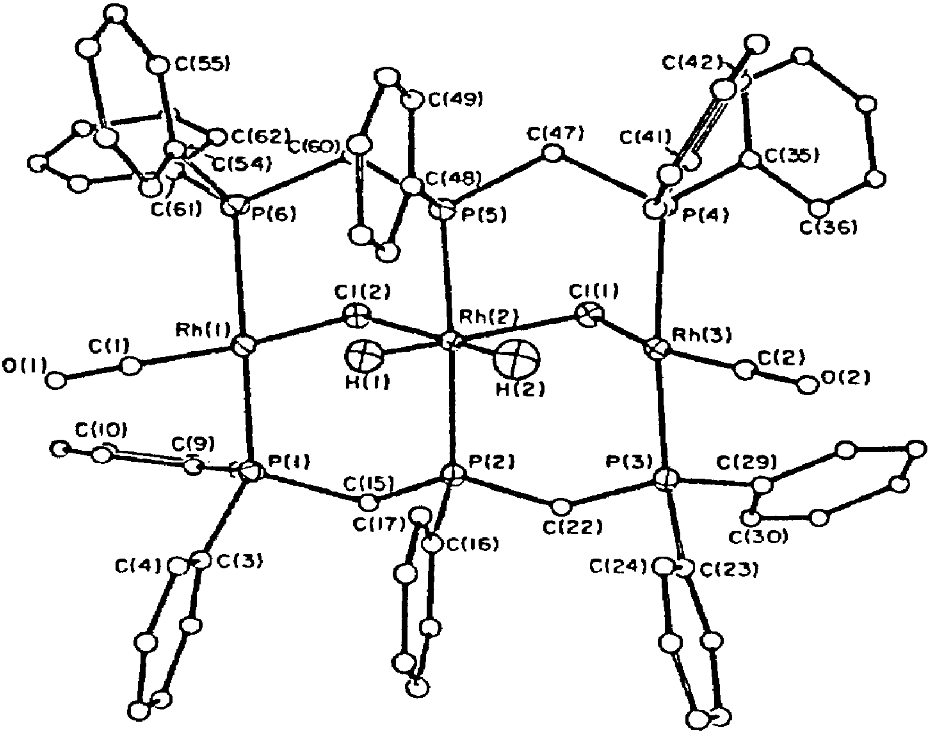


Fig. 7. Derivative of the bis((diphenylphosphino)methyl)phenylphosphine (dpmp): perspective view of the cation $[Rh_3(\mu\text{-dpmp})_2(H)_2(CO)_2(\mu\text{-Cl})_2]^+$. (Reproduced with permission of the American Chemical Society.)

[128]. A similar A-frame derivative $[Rh_2\{\mu\text{-CPh(NPh)}_2\}(\mu\text{-dppm})_2(CO)_2]ClO_4$ has been isolated upon addition of dppm on $Rh_2(\mu\text{-CPh)(NPh)}_2)(\mu\text{-dppm})_2(CO)_2]ClO_4$ [129].

$[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(dppm)]BPh_4$ in which dppm is monodentate has also been prepared recently by Oro et al. [130].

The complex $Rh_2(\mu\text{-pz})_2I_2(CO)_2(\mu\text{-dppm})$ has been prepared from $Rh_2(\mu\text{-pz})_2(CO)X$ by successive addition of iodine and dppm.

Another type of derivative which contains only one bridging dppm group and cyclopentadienyl rings or rhodium has been studied by Faraone et al. They first prepared RhCp(dppm)CO which contains a monodentate dppm group [131], but discovered that using $Rh_2Cp_2(\mu\text{-CO})(CO)_2$ as the starting material gave the dppm bridged $Rh_2Cp_2(\mu\text{-CO})(\mu\text{-dppm})$ [132] (Fig. 8). A number of reactions of this compound were undertaken and it was shown that CO could be replaced by SO_2, or pushed into a terminal position by Br_2 to be finally ejected whereas with $SnCl_2$ a (μ-carbonyl)(μ-$SnCl_2$) was isolated [132]. Oxidative addition of I_2 occurs at one center to give $CpRhCO(\mu\text{-dppm})RhCpI_2$. Lewis acids can attack the metal–metal bond to

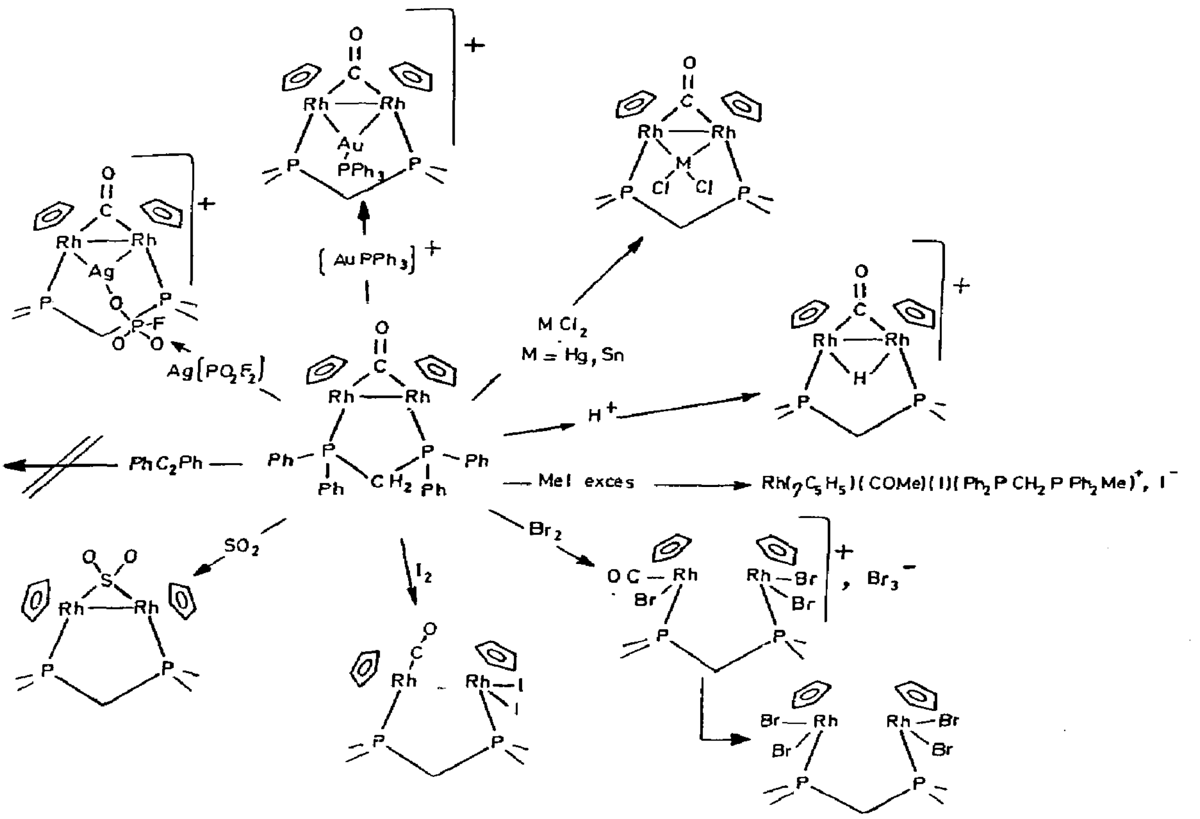


Fig. 8. Some additions to the electron-rich rhodium–rhodium bond of $(CpRh)_2(\mu\text{-dppm})(\mu\text{-CO})$.

yield Rh_2Hg and Rh_2Ag derivatives. $Rh_2Cp_2(\mu\text{-}HgCl_2)(\mu\text{-}CO)(\mu\text{-dppm})_2$ [133], $[Rh_2AgCp_2(\mu\text{-}CO)(\mu\text{-dppm})_2]X$ ($X = BF_4$, PF_6, ClO_4 or OPF_2O bonded directly to the bridging Ag atom) [134], $[Rh_2Cp_2(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-dppm})_2]X$ ($X = BF_4$, PF_6) [135] and $(Rh_2Cp_2(\mu\text{-}AuPPh_3)(\mu\text{-}CO)(\mu\text{-dppm})_2X$ ($X = BF_4$, PF_6) [135] are prepared in this way. With AgY, $Rh_2Cp_2(\mu\text{-}CO)(\mu\text{-}AgY)(\mu\text{-dppm})_2$ complexes ($Y = CH_3CO_2$, CF_3CO_2, $(C_2H_5)_2NCS_2$) [136].

$[Cp_2^*Rh_2(\mu\text{-}CH_2)(\mu\text{-dppm})]^{2+}$ ($Cp^* = CpMe_5$) was prepared by Maitlis and co-workers [137] who measured the Rh–Rh coupling constant to be 12.4 Hz.

The mononuclear complexes RhXLdppm ($X = Cl$, Me; $L = PMe_3$; PPh_3, dppm; $X = Cp$, $L = PMe_3$) and RhCpdppm have been prepared and studied by multinuclear NMR spectroscopy [138]. Substitution of COD by dppm in $Rh_2(\mu\text{-}PPh_2)_2(COD)_2$ affords $Rh_2(\mu\text{-}PPh_2)_2(COD)(dppm)$ and $Rh_2(\mu\text{-}PPh_2)_2(dppm)_2$ [139] in which dppm remains chelating.

Finally, dinuclear carbonyl complexes similar to the dppm ones described above but with various P–N–P or P–O–P bridging ligands are known [140].

Dppm chemistry of iridium

By comparison with that of rhodium, the dppm chemistry of iridium is much less developed. However, some very interesting studies have recently appeared in the literature.

Mague and De Vries who prepared the first cationic dppm bridged iridium complexes [141], recently studied their reactivity with acetylenes. They could thus obtain complexes such as [Ir$_2$(CO)$_2$LCl(μ-acetylene)(dppm)$_2$]A (A = BPh$_4$, ClO$_4$, PF$_6$; L = CO, P(OMe)$_3$; acetylene = H$_3$CO$_2$CC$_2$CO$_2$CH$_3$, HC$_2$CO$_2$CH$_3$). When A = BPh$_4$, an interesting reaction in boiling THF leads to [Ir(CO)$_2$(C$_6$H$_5$)(μ-H$_3$CO$_2$CC$_2$CO$_2$CH$_3$)(dppm)$_2$]BPh$_4$ through rupture of a B–C bond and transfer of a phenyl group to iridium [142].

Sutherland and Cowie undertook a systematic study of the preparation of dinuclear chlorocarbonyl complexes of iridium whether neutral or cationic [143]. By studying the reactivity of these products with acetylenes, they obtained some cationic derivatives analogous to those of Mague's but they also obtained neutral complexes such as Ir$_2$Cl$_2$(CO)$_2$(μ-CH$_3$OCC$_2$CO$_2$CH$_3$)(dppm)$_2$, whose structure showed the alkyne ligand to bridge to two iridium centers as a *cis*-dimetallated olefin [144]. These complexes lose CO in refluxing toluene to give Ir$_2$Cl$_2$(CO)(μ-CH$_3$O$_2$CC$_2$CO$_2$CH$_3$)(dppm)$_2$ which contains a terminal carbonyl group. Further addition of L produces

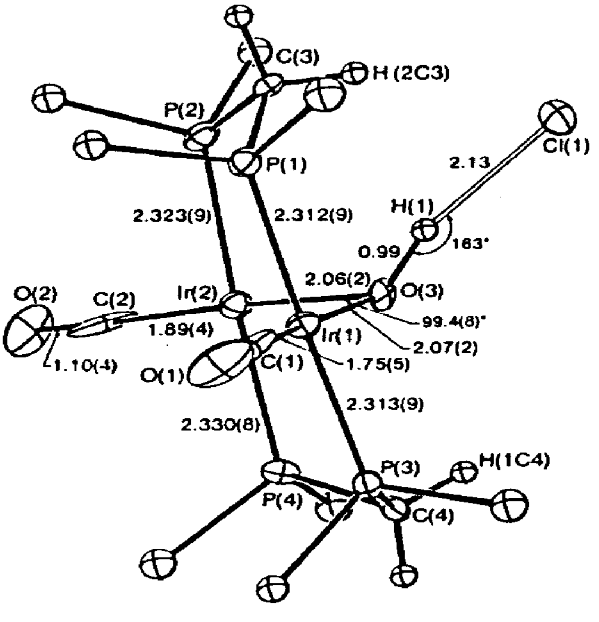


Fig. 9. The bridging hydroxo Ir$_2$(CO)(μ-OH-Cl)(dppm)$_2$ complex showing H···Cl interaction [145]. (Reproduced with permission of the American Chemical Society.)

$Ir_2Cl_2(CO)L(CH_3O_2CC_2CO_2CH_3)(dppm)_2$ in which both CO groups are terminal (L = CO) or in which the CO group bridges the two metals with no accompanying Ir–Ir bond (L = PMe_3, $P(OMe)_3$, MeCN) [146].

Reaction of $[(IrCl(CO)(dppm)]_2$ with NaOH results in the formation of a neutral bridging hydroxo $Ir_2(CO)_2(\mu\text{-OH-Cl})(dppm)_2$ complex (see Fig. 9) which shows a fascinating chemistry [145]. Thus, treatment with $HBF_4 \cdot Et_2O$ produces $[Ir_2(CO)_2(\mu\text{-OH})(dppm)_2]\ BF_4$ whereas reduction occurs in the presence of CO to give first $Ir_2(CO)_4(dppm)_2$ which, after flushing with N_2, yields $Ir_2(CO)_3(dppm)_2$.

The cationic bridging hydroxo derivative $[Ir_2(CO)_2(\mu\text{-OH})(dppm)_2]BF_4$ reacts with CO to give a bridging hydrido complex $[Ir_2(CO)_2(\mu\text{-H})(\mu\text{-CO})(dppm)_2]BF_4$ whose structure has been reported separately [147]. It can be protonated into a dicationic dihydride which is able to lose H_2 either after isomerisation or in the presence of acetonitrile. Similarly, the reverse reaction is possible and $[Ir_2(CO)_4(\mu\text{-CO})(dppm)_2](BF_4)_2$ reacts with OH^- to yield the bridging hydrido complex $[Ir_2(CO)_2(\mu\text{-H})(\mu\text{-CO})(dppm)_2]BF_4$. Obviously, these reaction sequences are related to the water-gas shift cycle, for which Sutherland and Cowie propose a model cycle [147].

They also studied the reactions of the neutral $[IrCl(CO)(\mu\text{-dppm})]_2$ and the cationic $[Ir_2(CO)_2(\mu\text{-Cl})(dppm)_2]BF_4$ with H_2 which produce respectively $Ir_2H_2Cl_2(CO)_2(dppm)_2$ and $[Ir_2H_4Cl(CO)_2(dppm)_2]BF_4$ which can lose H_2 to give $[Ir_2H_2(\mu\text{-Cl})(CO)_2(dppm)_2]BF_4$ [148].

Both the neutral and the cationic dihydrides react with $CH_3O_2CC_2CO_2CH_3$ to give, respectively, products resulting from mono or di-insertion of alkyne: $Ir_2HCl_2(CH_3O_2CC_2HCO_2CH_3)(CO)_2(dppm)_2$ and $Ir_2Cl_2(CO)_2(CH_3O_2CC_2CHCO_2CH_3)_2(dppm)_2$. In the latter case, the additional chloride group seems to come from the solvent (CH_2Cl_2) [148].

(vii) Group 10

This is perhaps the group in which the chemistry of dinuclear dppm bridged complexes has been the most intensively studied. However, similarly to group 9, one metal, i.e. platinum, has especially drawn attention while the chemistry of nickel is very new and little developed so far.

Nickel complexes

Kubiak and co-workers [149] reported the first dppm bridged dinickel derivative, $[Ni_2(\mu\text{-CNMe})(CNMe)_3(dppm)_2]PF_6$. The complex is asymmetrical and contains a dative metal–metal bond between the two metal atoms [149]. This compound can be reduced by Na/Hg into the binuclear complex of nickel(0), $Ni_2(CNMe)_3(dppm)_2$, shown to contain two *cis* bridging dppm ligands [150]. The bridging isocyanide ligand in the first complex can then be protonated or alkylated to yield $[Ni_2(\mu CNMeR)(CNMe_2)(dppm)_2]X$ ($R = H$, $X = PF_6$; $R = Me$, Et, $X = I$).

A similar carbonyl compound, $Ni_2(CO)_3(dppm)_2$, has also been recently reported [151], whereas the tetracarbonyl complex $Ni_2(CO)_4(dmpm)_2$ was obtained from $Ni(CO)_4$ and dmpm and was structurally characterized [152].

Palladium complexes

Palladium chemistry has been extensively developed by Balch and coworkers [153] who first observed the reversible coordination of CO in the bridging position of a dinuclear complex [154]. The kinetics and thermodynamics of this reaction have been studied recently [155]. Interestingly, the system shows high selectivity for binding of CO in the presence of H_2, C_2H_2, C_2H_4, CO_2, O_2 or air [155]. The scrambling of halogens between mononuclear or dinuclear palladium derivatives has been studied with complexes such as $Pd(dppm)X_2$ or $Pd_2(dppm)_2X_2$ (X = halogen) [156]. The thiocyanate ligand has been shown to bind either through sulfur or through nitrogen to dipalladium derivatives and the distribution of linkage isomers has been determined by ^{31}P NMR [157]. A related mononuclear complex containing two monodentate dppm ligands has been described and structurally characterized [158]. Addition of carbon monoxide or methyl isocyanide to the methyl derivatives $[Pd_2(dppm)_2(\mu\text{-}X)(CH_3)_2]X$ ($X = I^-$, Br^-) or $[Pd_2(dppm)_2(\mu\text{-}I)(CH_3)I]BF_4$ leads in each case to insertion products, e.g. $Pd_2(dppm)_2(\mu\text{-}X)(COCH_3)_2]X$, $[Pd_2(dppm)_2(\mu\text{-}I)(COCH_3)I]BF_4$ or $[Pd_2(dppm)_2\ (\mu CH_3C{=}NCH_3)(CNCH_3)_2]^+$. The reactivity of these species has been investigated and, for example, the reaction of the bis acetyl derivative with O_2 produces $Pd_2(dppm)_2I_2$ and acetic anhydride [159]. An interesting property of $Pd_2(dppm)_2X_2$ ($X = Cl$, Br, I) has been found recently. These compounds are able to abstract sulfur from H_2S and quantitatively produce dihydrogen together with $Pd_2X_2(\mu\text{-}S)(dppm)_2$ [160]. Oxidation with *m*-chloroperbenzoic acid produces a $\mu\text{-}SO_2$ species which spontaneously loses SO_2 to regenerate $Pd_2X_2(dppm)_2$.

The electrochemical properties of $Pd_2X_2(dppm)_2$ and of the mixed-metal derivative $PdPtX_2(dppm)_2$ have been investigated by Nemra et al. [161]. The complexes undergo irreversible one-electron oxidation and irreversible two-electron reduction. The complexes $PdMCl_2(dppm)_2$ have been found to be good precursors for heterometallic clusters [162].

The palladium(0) complex $Pd_2(dppm)_3$ has been shown to possess a long-lived excited state and can thus react under irradiation with CH_2Cl_2 to give the μ-methylene derivative $Pd_2(\mu\text{-}CH_2)(dppm)_2Cl_2$ [163].

$[Pd_2H(CH_3)(\mu\text{-}Cl)(dppm)_2]^+$ has been prepared in two steps from $Pd_2Cl_2(dppm)_2$ after treatment with $AlMe_3$ and the addition of methanol at $-78\,°C$. Upon warming, binuclear reductive elimination of methane occurs from the two adjacent palladium sites and $Pd_2Cl_2(dppm)_2$ [164] is obtained again.

The analogous dmpm complex $Pd_2Cl_2(dmpm)_2$ has been prepared recently [165,166]. It shows the remarkable property of being water-soluble and exists in solution at $pH > 4$ as $Pd_2(OH)_2(dmpm)_2$. The dinuclear complex reacts like its dppm analogue for a number of reactions and particularly adds a number of small molecules in the bridging position to give $Pd_2(\mu\text{-L})X(dmpm)_2$ ($L = CO, SO_2, CS_2$) [165,167]. The crystal structures of $Pd_2Br_2(dmpm)_2$ [166] and $Pd_2Cl_2(\mu\text{-CO})(dmpm)_2$ [165,167] have been determined. The reaction of $Pd(OAc)_2$ with $(dppm)_2$ under CO in the presence of CF_3COOH affords a trinuclear cluster, $[Pd_3(\mu_3\text{-CO})(dppm)_3]^{2+}$ [168] able to weakly coordinate halogen ion at a triply bridging site to give $[Pd_3(\mu^3\text{-X})(\mu_3\text{-CO})(dppm)_3]^+$ ($X = CF_3CO_2$, Cl, Br, I) [169]. The mechanism of formation of the dication has been studied and involves intermediate formation of $Pd_2X_2(dppm)_2$ and $Pd_2COX_2(dppm)_2$ followed by attack of "Pd (dppm)" [170].

During investigation of the mixture of isomers of the type $Pd_2(\mu\text{-CNR})(dppm)_2Cl_2$ formed from the labile isocyanide methyl-3(3′-isocyanocyclopent-2′-enylidene)propanoate, it was found that both Pd_2Cl_2 $(dppm)_2$ and the isocyanide adducts were light-sensitive [171]. The authors undertook a study of the degradation of both types of complex and determined the crystal structure of $Pd_2(\mu\text{-CNPh})Cl_2(dppm)_2$ which contains a large channel in the crystal lattice able to accommodate solvent molecules such as CH_2Cl_2 or C_6H_{12} [172].

The reaction of the complex $[Pd(\mu\text{-Cl})(P\text{–}C)]_2$ of the metallated ligand $P\text{-}C = Bu^t_2PCMe_2CH_2$ with dppm leads to $[PdCl(P\text{-}C)]_2(\mu\text{-dppm})$ [173].

Finally, as indicated above in this review coordinated dppm in $MX_2(dppm)$ ($M = Pd$, Pt) can be deprotonated by $LiN(SiMe_3)_2$ and alkylated [16,174].

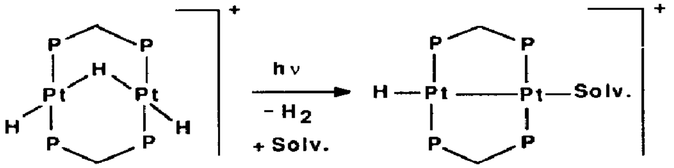
Platinum complexes

The interest for binuclear dppm-bridged platinum complexes is largely derived from the observation that during the reduction of $PtCl_2(dppm)_2$ into $Pt_2Cl_2(dppm)_2$ by $NaBH_4$ [175], a trihydride intermediate was formed which was characterized as $[Pt_2(\mu\text{-H})H_2(dppm)_2]X$ ($X = Cl$, PF_6) [176]. This electron-deficient complex has been shown to exhibit a very wide array of reactivity [2,177] and a number of similar derivatives of formula $[Pt_2H_nX_{3-n}(dppm)_2]^+$ have been prepared ($X = H$, Me, Cl...). We will report only the most recent reactions of these products.

The structures of $[Pt_2Me_3(dppm)_2]^+$ and of $[Pt_2(\mu\text{-H})Me_2(dppm)_2]^+$ [178] are known [179]. It is interesting to note that the former adopts an A-frame structure with a long metal–metal bond (2.933 Å) whereas the latter contains a *cis* phosphine coordination mode on one platinum as well as a short donor–acceptor metal–metal bond.

Ligand-induced binuclear reductive eliminations have been studied in the trihydride or analogous complexes (177) and their mechanism involving an intermediate of the type $[Pt_2H_2(\mu\text{-}H)L(dppm)_2]^+$ has been determined [180].

An interesting property of the trihydride is to readily lose H_2 upon photochemical irradiation, with high quantum yields [180,181]. However these reactions were carried out in polar solvents (acetonitrile, pyridine, THF, acetone) which coordinated to the platinum. The trihydride was also shown to react with CO and this reaction appears to be reversible [182]. Similarly, the displacement of CO by H_2, occurring in $[Pt_2H(CO)_2(dppm)_2]^+$ produces trihydride [182].



H_2 loss is observed also in the solid state to give a species with the rough formula $[Pt_2H(dppm)_2]^+$ but of unknown structure, in which the hydride ligand is probably terminal. Exposure of this material to CO produces $[Pt_2H(CO)(dppm)_2]^+$ [180].

A further reversible reaction of $[Pt_2H(CO)L_2]^+$ ($L_2 = $ dppm, $Et_2PCH_2PEt_2$) with CO yields $[HPt(\mu\text{-}L_2)_2Pt(CO)_2]^+$ and $[H(CO)Pt(\mu\text{-}L_2)_2Pt(CO)_2]^+$. This reaction involves disproportionation of the starting diplatinum(I) complex into platinum(0)-platinum(II) species [183].

The photochemistry of $[Pt_2(\mu\text{-}H)H(Me)(dppm)_2]^+$, $[Pt_2(\mu\text{-}H)Me_2(dppm)_2]^+$ and $[Pt_2(Me)_3(dppm)_2]^+$ leads to reductive elimination of H_2, CH_4 and C_2H_6 and formation of species such as $[Pt_2Me(solv)(dppm)_2]^+$. However, photolysis of $[Pt_2Me_3(dppm)_2]^+$ in pyridine yields the mononuclear complexes $PtMe_2(dppm)$ and $[PtMe(py)(dppm)]^+$ [184].

A somewhat surprising feature of the A-frame methyl cationic derivatives is that they are fluxional [185]. For example, in ^1H NMR, only one signal is very often observed for the methylene protons. A detailed study of the phenomenon has been undertaken in which the authors show that all the diplatinum complexes which undergo an "A-frame" inversion contain, or are capable of rearranging rapidly to, a complex with a bridging hydride. Thus, they propose in each case an intermediate containing a linear Pt–H–Pt bond as well as other intermediates in which donor–acceptor metal–metal bonds are involved. This kind of bond seems to be a dominant feature of the dinuclear chemistry [185].

The trihydride was found to be a good catalyst precursor for the water gas shift reaction at low CO pressure. The catalytic solutions were shown to contain the Pt_4 cluster, $Pt_4(\mu_2\text{-CO})_2(\mu_2\text{-dppm})_3(Ph_2PCH_2P(O)Ph_2)$ [186].

The reactivity of these dinuclear species has been studied in detail. With alkynes, the products depend on the solvent. Thus, reactions of the trihydride with CH_2Cl_2 produce $Pt_2Cl(\textit{cis}\text{-CR=CHR})(\mu\text{-RC}_2R)(\mu\text{-dppm})_2$ (R = CF_3, CO_2Me) with elimination of H_2, while in donor solvents S, $[Pt_2(H)S(\mu\text{-RC}_2R)(\mu\text{-dppm})_2]PF_6$ is obtained [187]. The complexes resemble those of Rh and Ir described previously in this review. With CF_3C_2H, the A-frame complex $Pt_2(C_2CF_3)_2(\mu\text{-CF}_3C_2H)(\mu\text{-dppm})_2$ containing two acetylide ligands is formed [187].

The similar A-frame complex $[PtHMe(\mu\text{-H})(\mu\text{-dppm})_2]SbF_6$ was obtained in a two-step reaction from $Pt_2Cl_2(\mu\text{-CH}_2)(\mu\text{-dppm})_2$ and successively $HSbF_6$ and $NaBH_4$ [188]. This complex was shown to undergo reductive elimination of the methane upon reaction with $CF_3C{\equiv}CCF_3$ to give $[Pt_2H(MeCN)(CF_3C_2CF_3)(dppm)_2]SbF_6$ as the major product [188].

$PtCl_2L_2$ (L_2 = dppm, depm, dipm) reacts with $MeC{\equiv}CH$ and NaOR in ROH to give the monomeric compounds $Pt(C{\equiv}CMe)_2L_2$ while the dimeric complex $Pt_2Cl_4(dmpm)_2$ gives *cis-cis*-$[Pt_2(C{\equiv}CMe)_4(dmpm)_2]$ [189]. Interestingly, $Pt(C{\equiv}CMe)_2(dppm)$ rearranges in solution in the presence of traces of dppm into the dimer *trans-trans*-$Pt_2(C{\equiv}CMe)_4(dppm)_2$ [189].

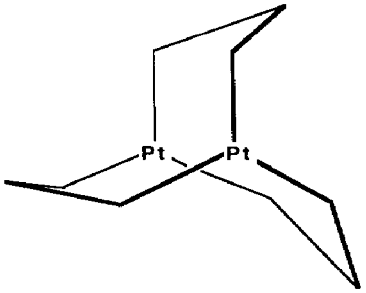
A series of ethyl platinum compounds has been prepared. The triethyl complex $[Pt_2Et_3(\mu\text{-dppm})_2]SbF_6$ reacts easily in solution to give $[Pt_2(\mu\text{-H})Et_2(\mu\text{-dppm})_2]SbF_6$ and ethylene through formally a binuclear elimination process [190]. A mixed oxidation state species has been obtained through reaction of depm ($Et_2PCH_2PEt_2$) with $[Pt_2(\mu\text{-H})H_2(\mu\text{-depm})_2]^+$ at −90 °C, similar to the reaction of $[Pt_2H(CO)L_2]^+$ with CO observed by the same authors (vide supra). After reductive elimination of hydrogen the complex $[Pt_2H(\mu\text{-depm})_3]^+$ is formed [191]. $[Pt_2HL(\mu\text{-dppm}_2)]PF_6$ reacts with excess CH_2N_2 to give the μ-methylene derivative $[Pt_2Me(\mu\text{-CH}_2)L(dppm)_2]PF_6$ (L = CO, PMe_2Ph). However, when L = PPh_3, $[Pt_2Me(\mu\text{-CH}_2)(CH_2PPh_3)(\mu\text{-dppm})_2]PF_6$ is obtained. This reacts further with CH_2Cl_2 to give $[Pt_2X(\mu\text{-CH}_2)(CH_2PPh_3)(\mu\text{-dppm})_2]PF_6$ [192].

The mechanism of methylene insertion into the platinum–platinum bond has been investigated for complexes of the type $Pt_2X_2(dppm)_2$ and it was shown that diazomethane acts as an electrophile towards the metal–metal bond [193]. The insertion of S_8 and SO_2 to give $Pt_2(\mu\text{-S})Cl_2(dppm)_2$ and $Pt_2(\mu\text{-SO}_2)(dppm)_2$ was also studied [194] whereas a detailed investigation of substitution reaction on a complex such as $[Pt_2L_2(dppm)_2]^{n+}$ (L = Cl, $n = 0$; L = PPh_3, $n = 2$) showed novel pathways including dissociation of one arm of a bridging dppm ligand and formation of an intermediate containing both a chelating and a bridging dppm group [195]. The crystal structure of the distorted complex $[Pt_2Cl(PPh_3(dppm)_2](PF_6)$ has been obtained [196].

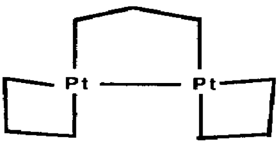
The mechanism of formation of A-frame compounds from the reaction of $[Pt_2(PPh_3)_2(dppm)_2](PF_6)_2$ with CH_2N_2, CO, SO_2, S_8 and HCl has also been determined [197].

Isocyanides can also be inserted into the platinum–platinum bond and products such as $Pt_2X_2(\mu\text{-}CNR)(dppm)_2$, $[Pt_2X(CNR)(dppm)_2]^+$, $[Pt_2(CNR)_2(dppm)_2]^{2+}$ and $[Pt_2(\mu\text{-}CNR)(CNR)_2(dppm)_2]^{2+}$ can be obtained [198].

A very interesting diplatinum(0) complex, $Pt_2(dppm)_3$ has been prepared [199,200] and shown by X-ray crystallography to adopt a "manxane"-like structure. The Pt–Pt distance is long (3.023(1) Å) and is indicative of little, if any, bonding interaction [200,201]. The corresponding dicationic species,



$[Pt_2(dppm)_3](PF_6)_2$, adopts a very different conformation as only one dppm ligand bridges a platinum–platinum bond (Pt–Pt = 2.646(1) Å) [202].



$Pt_2(dppm)_3$ oxidatively adds MeI in benzene to give $[Pt_2Me(\eta^1\text{-}dppm)(\mu\text{-}dppm)_2]PF_6$ after anion exchange. Further reaction produces $[Pt_2Me_2(\mu\text{-}I)(\mu\text{-}dppm)_2]PF_6$ [203]. Similarly, oxidative addition of RI produces $[Pt_2R(\mu\text{-}dppm)_2(\eta^1\text{-}dppm)]PF_6$ (R = Et, CO_3CH_2, Pr or Bu). Photochemical or thermal decomposition of the ethyl derivative involves β-elimination [204].

Addition of PPh_3 to $Pt_2(\mu\text{-}L_2)_3$ produces $Pt_2(\mu\text{-}L_2)_3PPh_3$ (L_2 = dmpm, depm) and $Pt_2(\mu\text{-}L_2)_3(PPh_3)_2$ (L_2 = dmpm, deopm) [205].

Protonation of $[Pt_2(\mu\text{-}R_2PCH_2PR_2)_3(PPh_3)_n]$ ($n = 0$, R = Ph or Et; $n = 1$, R = Me; $n = 2$, R = EtO) with NH_4PF_6 affords $[Pt_2H(\mu\text{-}dppm)_2(\eta^1\text{-}dppm)]^+$ (R = Ph) but double protonation occurs when smaller substituents are present on the phosphorus to give $[Pt_2H_2(\mu\text{-}R_2PCH_2PR_2)]^{2+}$ [206].

In order to vary the substituents at the phosphorus atom in the dinuclear diphosphine bridged derivatives, $PtCl_2(SMe_2)_2$ was reacted with a number of L_2 ligands (L_2 = dmpm, depm, dippm, dtbpm). Mononuclear $PtCl_2L_2$ (L_2 = depm, dippm) or dinuclear $Pt_2Cl_4(\mu\text{-}L_2)$ (L_2 = dmpm, dtbpm) were obtained according to the ligands [207].

The synthesis of a number of methyl derivatives of the type $PtMe_2(R_2PCH_2PR_2)$ (R = Ph, i-Pr) and $[Pt_2Me_4(\mu\text{-}R_2PCH_2PR_2)_2]$ (R = Me, Et, Ph) was achieved. It was concluded that increasing the bulk of substituents stabilizes the mononuclear complex with respect to the dinuclear one, determines primarily the ground-state conformations of the binuclear complexes and the activation energies for fluxionality, and decreases the reactivity of the complexes toward oxidative addition [208]. Thus, oxidative addition of MeI was found to be irreversible when R = Me to yield $Me_3IPt(\mu\text{-dmpm})_2PtMe_2$ and eventually $[Me_3Pt(\mu\text{-}I)(\mu\text{-dmpm})_2PtMe_3]I$. Its crystal structure shows a very large Pt–Pt separation (4.707(1) Å) [209]. When R = Et, the first oxidative addition was reversible and a further very slow reaction yielded $[Me_3Pt(\mu\text{-}I)(\mu\text{-depm})_2PtMe]I$. Finally, when R = Ph, no reaction occurred [209].

The reaction of $Pt_2Me_4(dmpm)_2$ with halogens gave the bridged Pt(IV)–Pt(II) derivatives $[Me_3Pt(\mu\text{-}X)(\mu\text{-dmpm})_2PtMe]Y$ (X = Cl, Y = Cl; X = Br, Y = Br, X = I, Y = I_3) and $[Me_3Pt(\mu\text{-}I)(\mu\text{-dmpm})_2Pt]I_3$ [210].

The preparations of *cis-cis*-$Pt_2Cl_2Me_2(dmpm)_2$, *trans-trans*-$Pt_2I_2Me_2(dmpm)_2$ and $[Pt_2(\mu\text{-}I)Me_2(dmpm)_2]PF_6$ have also been reported [211].

A diplatinum(IV) complex containing both a bridging *o*-xylylene and a bridging dppm group, $Pt_2Me_4(\mu\text{-}Br)_2(\mu\text{-}CH_2C_6H_4CH_2)(\mu\text{-dppm})$, has been prepared from $PtMe_2L_2$ upon treatment with *o*-xylylene dibromide and dppm [216]. The reaction of $[Pt_2Me_3(dppm)_2]BF_4$ with Ph_3CBF_4 in wet CH_2Cl_2 produces the dicationic $[Pt_2Me_2(dppm)_2]^{2+}$ which can react rapidly further with MeCN, CO, OH^-, Cl^- or MeOH to give $[Pt_2Me_2(MeCN)_2(dppm)_2](BF_4)_2$, $[Pt_2Me_2(\mu\text{-}CO)(dppm)_2](BF_4)_2$, $[Pt_2Me_2(CO)_2(dppm)_2](BF_4)_2$, $[Pt_2Me_2(\mu\text{-}OH)(dppm)_2]BF_4$, $[Pt_2Me_2(\mu\text{-}Cl)(dppm)_2]BF_4$, $[Pt_2Me_2(\mu\text{-}H)(dppm)_2]BF_4$, respectively [217].

The mononuclear alkyl complexes $PtR_2(dppm)$ (R = Me, CH_2Me, Et, CH_2Ph, Ph, C_6H_4Me, C_6H_4OMe-2, $C_6H_2Me_3$, 1-naphthyl, C_6F_5, C_6H_4Me-2) have been prepared from $PtCl_2(dppm)_2$. The complexes react with dppm to give $PtR_2(dppm)_2$. The equilibrium constant has been calculated and some reactions with MeI and HCl carried out [218].

The complexes $(Pt(\mu\text{-dppm})_2Pt(C_6F_5)]$ and $[LPt(\mu\text{-dppm})_2PtC_6F_5]^+$ (X = Cl, Br, SCN; L = PPh_3, $AsPh_3$, py, CO, t-BuNC) have been prepared from $PtCl_2(dppm)_2$ and shown to react with $Me_2OCC_2CO_2Me$, SO_2, $[N_2C_6H_4Me\text{-}p]^+$ and H^+ to give A-frame derivatives. With $SnCl_2$, insertion occurs into the Pt–Cl bond to give Pt–$SnCl_3$ derivatives [219].

A number of trichlorostanno derivatives of platinum have also been prepared from chloro precursors, namely $Pt_2X(SnCl_3)(dppm)_2$ ($X = Cl$, $SnCl_3$) and $Pt_2(SnCl_3)_2(dppm)_2(\mu\text{-}L)$ ($L = CH_2$, S) [212].

An interesting cluster similar to the Pd_3 one described above has been obtained from the interaction of $Pt(O_2CCF_3)$dppm with CO in aqueous methanol [213].

Examples of deprotonation of the dppm ligand also appear in platinum chemistry. The reaction of K_2PtCl_4, dppm and KOH in ethanol yields the first homoleptic bis diphenylphosphinomethanido complex, $Pt(Ph_2PCHPPh_2)_2$ [214]. A similar reaction carried out on the dinuclear cation $[Pt_2(PPh_3)_2(\mu\text{-dppm})_2](PF_6)_2$ leads to $[Pt_2(PPh_3)_2(\mu\text{-}Ph_2PCHPPh_2)(\mu\text{-dppm})]PF_6$ containing a four-membered Pt–C–P–Pt metallacycle [215].

Finally, the trinuclear derivative $[Pt_3(dppm)_2(RNC)_4](PF_6)_2$ ($R = Me_2C_6H_3$) can be regarded as an A-frame complex resulting from the insertion of the 14 electron fragment $Pt(RNC)_2$ into the metal–metal bond of $[Pt_2(dppm)_2(MeCN)_2](PF_6)_2$ [220].

(viii) Group 11

Although less employed than in the platinum metal chemistry, dppm has been found to be a good versatile ligand for group 11 metals, able to stabilize mono-, di- and polynuclear derivatives.

Copper derivatives have been known for a long time but recently dppm was employed to stabilize the products of the reaction between arylcopper(I) derivatives and CS_2 [221]. The main products of the reaction were $[(ArCS_2Cu)_2dppm]_2$ (Ar = phenyl, *o*-, *m*- and *p*-tolyl); the structure of the complex (Ar = *o*-tolyl) has been solved by X-ray diffraction [222]. Another product of the reaction is the tetranuclear complex $[Cu_4(dppm)_4(CS_3)_2]$ [223].

Bis dppm bridged disilver complexes are known and structurally characterized. $Ag_2(dppm)_2(NO_3)_2$ has been prepared directly from $AgNO_3$ and dppm in refluxing methanol and shown to contain a *trans*-$[Ag_2(dppm)_2]^{2+}$ structure. Interestingly, the complex can dimerize to give $[Ag_4(dppm)_4(NO_3)_2]$ consisting of two dinuclear units bridged by NO_3 ligands [224].

Numerous mixed heterobimetallic complexes containing silver are known (vide infra) but the mixed silver mercury complex was shown to be prepared as easily from $[Hg(\eta^1\text{-dppm})_2](O_3SCF_3)_2$ and AgO_3SCF_3 or from redistribution between $[Hg_2(dppm)_2]^{4+}$ and $[Ag_2(dppm)_2]^{2+}$ [225].

The gold dppm chemistry has been particularly developed although in many cases complexes containing deprotonated dppm are obtained. Thus, interaction of dppm with the gold clusters $[Au_{13}Cl_2(PMe_2Ph)_{10}](PF_6)_3$ or $[Au_{13}Br_4(PMePh_2)_8]Br$ leads to a mixture of $Au_2X_2(dppm)_2$ which had been prepared by a more conventional route [226] and $Au_2(Ph_2PCHPPh_2)_2$ [227].

Interaction of the mononuclear complex $[Au(C_6F_5)_2(dppm)]ClO_4$ [228] with NaH or Na_2CO_3 leads to the deprotonated complex $Au(C_6F_5)_2(Ph_2PCHPPh_2)$ which can react further with silver(I) or gold(I) salts to yield interesting bi- or trinuclear complexes bridged by diphenylphosphinomethanido groups, namely $(C_6F_5)_2Au[\mu\text{-}(Ph_2P)_2CH]AuC_6F_5$ and $[(C_6F_5)_2Au]_2[\mu(Ph_2P)_2CH]_2M$ (M = Ag, Au) [229]. $Au(C_6F_5)_2(Ph_2PCHPPh_2)$ reacts with AuXL (X = Cl, Br; L = tetrahydrothiophene (tht) or $AsPh_3$) to give the trinuclear complexes $X(C_6F_5)AuPh_2[PCH(AuL)PPh_2]AuX$ containing the tridentate $(Ph_2PCHPPh_2)^-$ ligand. Substitution of tht by PPh_3, py and 4-Mepy has also been carried out [230].

Similarly, the complex $Au_2(Ph_2PCHPPh_2)_2$ reacts with $Au(C_6F_5)(tht)$ (tht = tetrahydrothiophene) or $Ar(OClO_3)PPh_3$ to give the tetranuclear species $Au_2(Ph_2PCH(M)PPh_2)$ (M = AuC_6F_5 or $Ag(OClO_3)(PPh_3)$) [231].

The dinuclear $(AuBr)_2dppm$ and $[Au_2(dppm)_2](ClO_4)_2$ have also been prepared as part of a systematic study of coordination of gold(I) to biphosphine ligands [232].

A new diphosphine, namely the cyclopropylidenebisdiphenylphosphine, can stabilize, dinuclear gold(I) derivatives [233].

(ix) Group 12

As seen earlier [225], some mercury complexes containing the ligand dppm are known, such as $Hg(\eta^1\text{-dppm})_2(O_3SCF_3)_3$ [234] or the dinuclear $Hg_2(\mu\text{-dppm})_2(O_3SCF_3)_4$ [235].

(x) Group 13

A boron-dppm adduct, $B_5H_9 \cdot dppm$, has been described and characterized by X-ray crystallography [236].

Some aluminium and gallium-dppm complexes have recently been prepared by Schmidbaur et al. [237,238]. The aluminium and gallium alkyl MR_3 give monodentate 1 : 1 adducts $MR_3(\eta^1\text{-dppm})$ (M = Al, Ga; R_3 = Me_3, Me_2Cl) but, in the case of $AlEt_3$, the dinuclear complex $(AlEt_3)_2$ μ-dppm was observed [237]. The reaction of $Ph_2PCHLiPPh_2$ with two equivalents of R_2MCl (M = Ga, Al) produced the new compounds $R_2M(\mu\text{-}Cl)\mu[Ph_2P\text{–}CH(PPh_2)]$ in which the two aluminium atoms are bridged by a chloride and an $R_2P\text{–}CHR'$ group [238].

(xi) Lanthanum series

The dppm-lanthanide chemistry contains only one but very interesting example of a homoleptic complex with 3 π-allyl like coordinated diphosphinomethanide ligands [239].

C. DPPM AS A LIGAND FOR HETEROBIMETALLIC COMPLEXES

Examples of heterobimetallic complexes containing the dppm ligand now include many of the possible combinations of metals from group 6 to group 12.

Different methods have been used to prepare such complexes: (a) addition of dppm to preexisting dinuclear complexes; (b) reaction of complexes containing monohapto dppm groups with derivatives containing potential leaving ligands; (c) as for (b) but using a complex containing chelated dppm ligands able to perform a ring opening reaction; (d) reaction of an organometallic anion with a halogeno complex containing dppm (with or without ring opening); (c) transmetallation.

We shall try to note the kind of method each reaction involves. However, although general methods are known for the preparation of such complexes, only a few groups have systematically developed this chemistry. The main contribution to this field has been made by Shaw and co-workers who reported the first synthesis of a dppm-bridged heterobimetallic complex. A classification of the derivatives is difficult; we shall describe this chemistry chronologically according to the groups.

The first heterobimetallic complex containing bridging dppm groups was $PdPtX_2$ (μ-dppm)$_2$ (X = Cl, Br, I, SCN) which was prepared from $Pd(PPh_3)_4$, $PtCl_2(NC^tBu)_2$ and dppm [240,241]. Reaction of the complex (X = Cl) with the substrate L (L = SO_2, CO, $MeO_2CC{\equiv}CCO_2Me$, CS_2) affords ClPt(μ-L)(μ-dppm)$_2$PdCl. The reaction is reversible for L = SO_2, CO, CS_2 [241].

Treatment of $PtCl_2$(dppm) with lithium acetylides gives the diplatinum face-to-face complex $Pt_2(-C{\equiv}CR)_2(\mu\text{-dppm})_2$, but in the presence of excess dppm a mononuclear complex is obtained, $Pt(-C{\equiv}CR)_2(\eta^1\text{-dppm})_2$ containing two monodentate dppm groups [242,243]. An interesting reaction is observed between $[Pt(\eta^2\text{-dppm})_2]Cl_2$ and $Hg(C{\equiv}CR)_2$ which affords the bimetallic complex $(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2HgCl_2$ [291]. Addition of Na_2S affords selectively $Pt(C{\equiv}CR)_2(\eta^1\text{-dppm})_2$ whereas the similar reaction with AgOAc yields $(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgX$ (X = Cl, I). A number of related reactions have also been studied [244]. However, the mononuclear complex containing two monodentate dppm ligands has been rapidly found to be an excellent starting material for the synthesis of heterobimetallic complexes containing, together with platinum, elements as varied as W(0), [245], Rh(I) [245], Ir(I) [245], Ir(III) [245], Pt(I) [246], Cu [247], Ag(I) [247,248], Au(I) [247,248], Hg(II) [248] or Cd(II) [248] (see Fig. 10).

The bis acetylide complex reacts with silver salts or $[AgX(PPh_3)]_4$ to give $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2Ag]X$ (X = NO_3, PF_6) or $(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgX$ (X = Cl, I) [247]. Direct reaction of $[Pt(dppm)_2]Cl_2$ with one or two

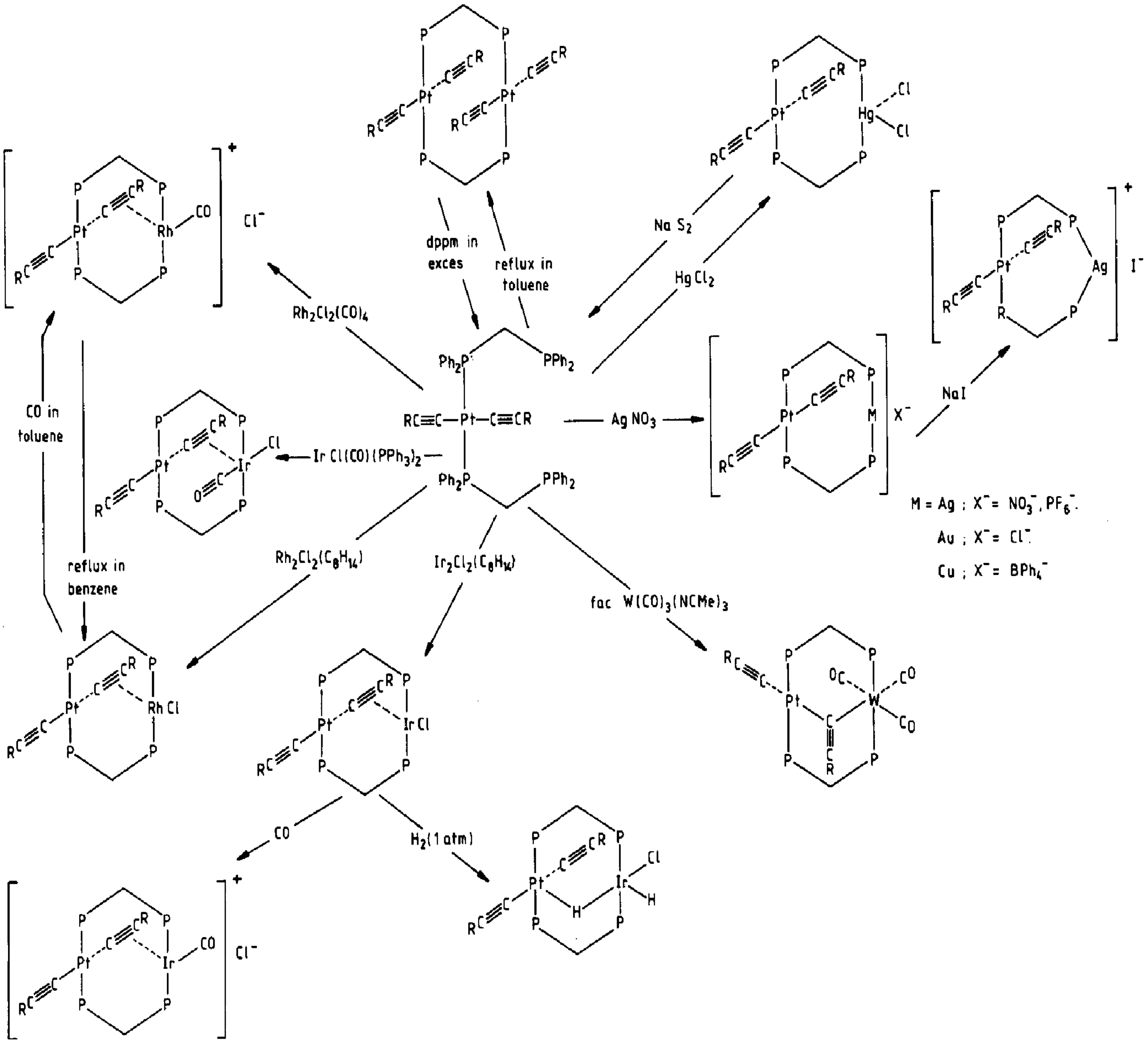


Fig. 10. Reactions of *trans*-Pt(C≡CR)$_2$(η^1-dppm)$_2$ as a starting material for heterobimetallic bridged complexes.

equivalent of AgOAc + RC≡CH also yields bimetallic derivatives. Similar copper and gold complexes, namely $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2M]X$ (M = Au, X = Cl; M = Cu, X = BPh_4) or $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2CuCl]$ [247], were also synthesized.

Diplatinum complexes are also prepared by this method using $Pt(RC{\equiv}CR)_2(dppm)$ and $PtHX(PPh_3)_2$ (X = Cl, Br). The symmetrical hydrido-bridged complex $[Pt_2(RC{\equiv}C)_2(\mu\text{-H})(\mu\text{-dppm})_2]$ is obtained in good yield. Upon deprotonation, $(RC{\equiv}C)Pt(\mu\text{-dppm})_2Pt(C{\equiv}CR)$ is obtained and further reactions with X = CS_2, $MeO_2CC{\equiv}CCO_2Me$, and SO_2 afford the A-frame complexes $(RC{\equiv}C)Pt(\mu\text{-X})(\mu\text{-dppm})_2Pt(C{\equiv}CR)$. The SO_2 complex is only observed in solution [246].

An interesting structural comparison was made between two simular complexes, $[Pt_2Me_2(\mu\text{-C}{\equiv}CMe)(\mu\text{-dppm})_2]BF_4$ and $[PtRhX(CO)(\mu\text{-C}{\equiv}CMe)(\mu\text{-dppm})_2]PF_6$ (X = Cl, C≡CMe), and it could be shown that whereas the diplatinum complex shows a symmetrically bonded acetylide ligand, in the platinum–rhodium complex, the acetylide is σ-bonded to the platinum and sideways-bonded to the rhodium [249,303].

The platinum–rhodium derivatives are prepared directly from $Pt(C{\equiv}CR)_2(dppm)_2$ and $Rh_2Cl_2(CO)_4$ or transmetallation using platinum–silver or platinum–mercury precursors [249]. Platinum–iridium complexes are obtained from the reaction of $Ir_2Cl_2(C_8H_{14})_4$ with $Pt(C{\equiv}CR)_2(dppm)_2$. $(RC{\equiv}C)Pt(\mu\text{-dppm})_2(\mu\text{-dppm})_2(\mu\text{-C}{\equiv}CR)IrCl$ oxidatively adds H_2 to yield the dihydride $(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2(\mu\text{-H})IrH(Cl)$ and reacts with CO to give $(RC{\equiv}C)Pt(\mu\text{-dppm})_2(\mu\text{-C}{\equiv}CR)Ir(CO)Cl$ [250].

The same reactions are possible if, instead of acetylide complexes, cyano derivatives, namely $M(CN)_2(\eta^1\text{-dppm})_2$ (M = Pd, Pt), are used [251,252] (see Fig. 11). The complexes are prepared from $[M(\eta^2\text{-dppm})_2]Cl_2$ and NaCN. Starting with MCl_2dppm leads to the "face-to-face" dinuclear derivatives, $M_2(CN)_4(\mu\text{-dppm})_2$. Addition of $AgNO_3$ followed by NaI, $AuClPPh_3$, $HgCl_2$, $Rh_2Cl_2(CO)_4$, $IrCl(CO)_2(NH_2C_6H_4Me)$ or *trans*-$IrCl(CO)(PPh_3)_2$, produced the bimetallic derivatives $(NC)_2M(\mu\text{-dppm})_2M'X_n$(M' = Ag, X_n = I; M' = Hg, X_n = Cl_2), $[NC_2M(\mu\text{-dppm})_2Au]Cl$ and $(NC)_2M(\mu\text{-dppm})_2M'(CO)Cl$ (M' = Rh, Ir). Reaction of $Pd(CN)_2(dppm)$ with $Mo(CO)_3(C_7H_8)$ led to $(NC)_2Pd(\mu\text{-dppm})_2Mo(CO)_3$ [252].

Acetylide complexes of palladium were found to behave similarly to those of platinum and thus the reaction of $[Pd(\eta^2\text{-dppm})_2](Cl)_2$ with $Hg(C{\equiv}CR)_2$ affords the bimetallic derivative $Pd(C{\equiv}CR)_2(\mu\text{-dppm})_2HgCl_2$ which, upon treatment with Na_2S, produces $Pd(C{\equiv}CR)_2(\eta^1\text{-dppm})_2$ [253]. Further reaction with derivatives of Ag, Rh, Ir, Mo or W affords respectively $Pd(C{\equiv}CR)_2(\mu\text{-dppm})_2AgX$ (X = Cl, I), $[Pd(C{\equiv}CPh)(\mu\text{-C}{\equiv}CPh)(\mu\text{-}$

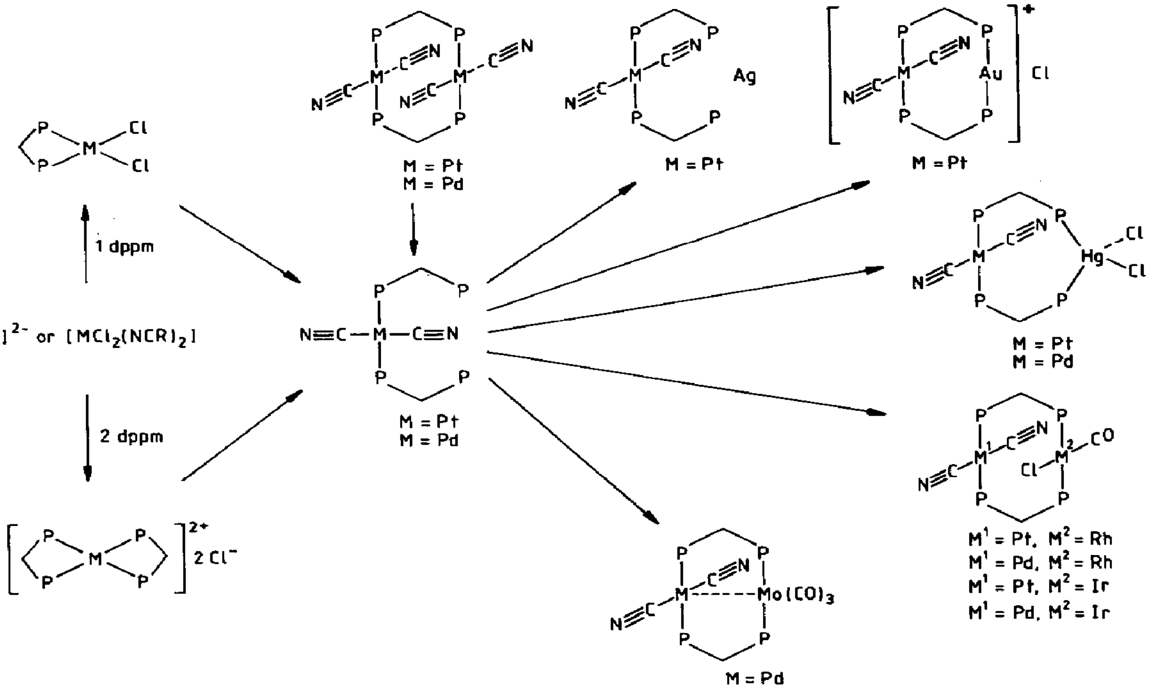


Fig. 11. Some reactions of the cyano derivatives $M(CN)_2(\eta^1\text{-dppm})_2$.

$\text{dppm})_2M(CO)]Cl$ (M = Rh, Ir), and $Pd(C{\equiv}CPh)(\mu\text{-}C{\equiv}CPh)(\mu\text{-dppm})_2M(CO)_3$ (M = Mo, W) [253].

The use of dialkyl, diaryl, or metallacyclic complexes has also been investigated as possible precursors for bimetallic compounds, but this time the dppm ligands were found to be all *cis* or *cis* on one center and *trans* on the other [254,256].

The metallacycle $Pt[CH_2\text{–}(CH_2)_2\text{–}CH_2](\eta^2\text{-dppm})$ is readily prepared from $PtCl_2(\eta^2\text{-dppm})$ and $Li(CH_2)_4Li$ and can be converted into $Pt(CH_2)_4(\eta^1\text{-dppm})_2$ upon addition of dppm. Further treatment with $[AgI(PPh_3)]_4$, $AgPF_6$, $AuCl(PPh_3)$, $MCl(CH_3)(COD)$, produces the bimetallic complexes $(CH_2)_4Pt(\mu\text{-dppm})_2AgI$, $[(CH_2)_4Pt(\mu\text{-dppm})_2M]X$ (M = Ag, X = PF_6; M = Au, X = Cl), $[(CH_2)_4Pt(\mu\text{-dppm})_2MCH_3]Cl$ (M = Pt, Pd) [255].

If $Pt(C_{10}H_7)_2(\eta^1\text{-dppm})_2$ is used as starting material, a platinum–rhodium complex, $(C_{10}H_7)_2Pt(\mu\text{-dppm})_2RhCl(CO)$, can be obtained upon reaction with $Rh_2Cl_2(CO)_4$. The analogous $Pt(C_6H_4Me\text{-}o)(\eta^1\text{-dppm})_2$ leads to a similar platinum–rhodium derivative or reacts with $PtMe_2(COD)$ to give the asymmetrical $(C_6H_4Me\text{-}o)_2Pt(\mu\text{-dppm})_2PtMe_2$. A number of bimetallic complexes were also obtained from $PtMe_2(\eta^1\text{-dppm})$ in the presence of dppm. This led to PtAg and PtAu complexes as well as, in the presence of MClMe(COD) (M = Pd, Pt), to the formation of $[\mathrm{Me_2Pt}(\mu\text{-dppm})_2\mathrm{MMe}]^+$ [256].

In addition to cyano and acetylide complexes, isonitrile-containing derivatives seemed valuable precursors to heterobimetallic complexes. Thus, reaction of *cis*-$\mathrm{PtCl_2}$(dppm) with ^{t}BuNC produces $[\mathrm{Pt_2}(\mu\text{-dppm})_2({}^t\mathrm{BuNC})_4]^{4+}$ whereas $[\mathrm{M(CNR)_2}(\eta^1\text{-dppm})_2]^{2+}$ was prepared from $[\mathrm{M}(\eta^2\text{-dppm})_2]\mathrm{Cl_2}$ (M = Pd, Pt) and RNC (R = Me, ^{t}Bu) [258]. Subsequent addition of $\mathrm{AgPF_6}$, $\mathrm{HgCl_2}$ or $\mathrm{Rh_2Cl_2(CO)_4}$ led to bis-dppm bridged heterobimetallic derivatives but which were not isolated pure, whereas when using $[\mathrm{MClL}]_n$ (M = Ag, L = RCN, $n = 1$; M = Ag, L = $\mathrm{PPh_3}$, $n = 4$; M = Au, L = $\mathrm{PPh_3}$, $n = 1$), the new bimetallic complexes $[\mathrm{(RNC)ClPt(dppm)_2MCl]Cl}$ (M = Ag, Au) could be obtained. The silver derivative can further be used for a transmetallation reaction and in the presence of $\mathrm{Rh_2Cl_2(CO)_4}$, $[\mathrm{(RNC)ClPt}(\mu\text{-dppm})_2\mathrm{RhClCO}][\mathrm{RhCl_2(CO)_2}]$ was obtained [258].

Isonitrile complexes of rhodium and iridium were also used for the preparation of bimetallic complexes and, thus, the known $\mathrm{M_2(CN{}^tBu)_4}(\mu\text{-dppm})_2\mathrm{Cl_2}$ (M = Rh or Ir) were treated with excess dppm in order to prepare complexes similar to those of Pt, but the system is labile at 20 °C whereas at −60 °C $[\mathrm{M(CN{}^tBu)_2}(\eta^1\text{-dppm})_3]\mathrm{Cl}$ was formed. A number of bimetallic complexes of the type $[\mathrm{L(RNC)M(dppm)_2M'Cl}_n]\mathrm{X}_{2-n}$ (L = RNC, CO; M = Rh, Ir, M′ = Ag, Au; X = Cl, $\mathrm{PF_6}$; $n = 0, 1$) could thus be prepared [304].

An iron derivative containing a monodentate dppm group, namely $\mathrm{Fe(CO)_4}$(dppm) has also been employed for the preparation of the bimetallic species. $\mathrm{(CO)_3Fe}(\mu\text{-dppm})\mathrm{RhCl(CO)}$ and $\mathrm{(CO)_3Fe}(\mu\text{-CO})(\mu\text{-dppm})\mathrm{PtBr_2}$, both containing a single dppm bridge [259] were thus prepared.

Another method largely employed for the preparation of bimetallic species in the use of complexes containing chelating dppm groups and ring opening reactions. This was first used by Shaw and co-workers [260] in the complex $[\mathrm{Ir(dppm)_2CO]Cl}$. Reactions with CuC≡CPh, AuC≡CPh, AgOAc/PhC≡CH afford $\mathrm{(PhC{\equiv}C)(CO)Ir}(\mu\text{-dppm})_2\mathrm{CuCl}$, $[\mathrm{(PhC{\equiv}C)(CO)Ir}(\mu\text{-dppm})_2\mathrm{Au}]\mathrm{Cl}$ and $[\mathrm{CPhC{\equiv}C)(CO)Ir}(\mu\text{-dppm})_2\mathrm{AgCl}$, respectively. Interestingly, the reaction of the iridium silver complex with $\mathrm{NaBPh_4}$ followed by exposure to $\mathrm{H_2}$ produces $[\mathrm{(PhC{\equiv}C)(CO)HIr}(\mu\text{-H})\mathrm{(dppm)_2Ag}]\mathrm{BPh_4}$ [260].

Ring opening of chelating ligands was also achieved starting with $\mathrm{OsCl_2(dppm)_2}$ which in the presence of $\mathrm{Rh_2X_2(CO)_4}$ (X = Cl, Br) afforded $\mathrm{Cl_2Os}(\mu\text{-dppm})_2(\mu\text{-CO})_2\mathrm{RhX}$ [261].

The use of compounds containing both a chelating and bridging dppm group is also possible as demonstrated by the reactions of $\mathrm{M(CO)_3}(\eta^1\text{-dppm})(\eta^2\text{-dppm})$ with Rh [262], Ir [262], Cu [263], Ag [263] or Au [263] derivatives. This afforded complexes of the type $\mathrm{(CO)_3M}(\mu\text{-}$

$\mathrm{dppm)_2M'X(CO)}$ of dppm or $\mathrm{[(CO)_3M(\mu\text{-}dppm)_2M'(CO)_2]PF_6}$ ($\mathrm{M' = Cr}$, Mo, W; $\mathrm{M' = Rh}$, Ir) which could also be obtained by ring opening reactions of $\mathrm{[M'(CO)(dppm)_2]Cl}$.

Similarly, in the presence of dppm $\mathrm{XMn(CO)_5}$ gives $\mathrm{MnX(CO)_2(\eta^1\text{-}dppm)(\eta^2\text{-}dppm)}$ which reacts with $\mathrm{Pt(PPh_3)_4}$ under CO to yield $\mathrm{(CO)_3Mn(\mu\text{-}dppm)_2PtX}$ (X = Br, Cl) containing an Mn–Pt bond; the complexes can be protonated reversibly into $\mathrm{[(CO)_3Mn(\mu\text{-}dppm)_2PtHX]Br}$. The reaction of $\mathrm{MnX(CO)_2(dppm)_2}$ with $\mathrm{PtHX'(PPh_3)_2}$ (X = Cl, Br; X' = Cl, Br) leads to the neutral $\mathrm{[X(CO)_2Mn(\mu\text{-}dppm)_2PtHX']}$ [264].

$\mathrm{(CO)_3Mn(\mu\text{-}dppm)_2PtCl}$ reacts with $\mathrm{LiC{\equiv}CPh}$ or $\mathrm{PhC{\equiv}CH\text{-}NEt_3}$ to yield $\mathrm{(CO_2)Mn(\mu\text{-}dppm)_2(\mu\text{-}CO)PtC{\equiv}CPh}$. Protonation affords $\mathrm{[(CO)_3Mn(\mu\text{-}H)(\mu\text{-}dppm)_2Pt(C{\equiv}CPh)]BF_4}$ whereas reduction with $\mathrm{NaBH_4}$ or $\mathrm{N_2H_4 \cdot H_2O}$ leads to the hydride $\mathrm{[(CO)_2Mn(\mu\text{-}dppm)_2(\mu\text{-}CO)PtH]}$ which can be reversibly protonated to $\mathrm{[(CO)_3Mn(\mu\text{-}H)(\mu\text{-}dppm)_2PtH]BF_4}$. Treatment of $\mathrm{(CO)_3Mn(\mu\text{-}dppm)_2PtBr}$ with $\mathrm{TlPF_6/CO}$ leads to the cationic $\mathrm{[(CO)_3Mn(\mu\text{-}dppm)_2Pt(CO)]BF_4}$ which is protonated to the dication $\mathrm{[(CO)_3Mn(\mu\text{-}H)(\mu\text{-}dppm)_2PtCO]BF_4}$, $\mathrm{PF_6}$ and reacts with NaOMe to afford $\mathrm{(CO)_2Mn(\mu\text{-}dppm)_2(\mu\text{-}CO)PtCO_2Me}$. Cationic isocyanide Mn–Pt complexes were similarly prepared [265].

The last method extensively used by Shaw and co-workers for the preparation of bimetallic species is transmetallation which allowed the preparation in high yield of compounds which were not otherwise accessible or had been obtained only in low yield [260,266,267]. For example, $\mathrm{(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2W(CO)_3}$ can be prepared readily from $\mathrm{(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2AgCl}$ and $\mathrm{W(CO)_3(NCMe)_3}$ [266,268].

The analogous platinum–molybdenum compound has been prepared using $\mathrm{Mo(CO)_3(C_7H_8)}$ whereas using $\mathrm{Cr(CO)_4(nbd)}$, a Pt–Cr complex was formed but not isolated. These complexes are fluxional, corresponding to rapid terminal bridging $\mathrm{C{\equiv}CR}$ interchange with inversion of the $\mathrm{Pt(\mu\text{-}dppm)_2M}$ boat-shaped eight-membered ring. Finally, protonation of the Pt–W complex leads to $\mathrm{[(RC{\equiv}C)Pt(\mu C{=}CHR)(\mu\text{-}dppm)_2W(CO)_3]^+}$ [268]. Starting with $\mathrm{(RC{\equiv}C)_2Pt(\mu\text{-}dppm)_2MX_\mathit{n}}$ leads for example, after reaction with $\mathrm{Rh_2Cl_2\ (CO)_4}$, to $\mathrm{[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2RhCO]^+}$ ($\mathrm{MX\mathit{n} = HgCl_2}$) or with $\mathrm{Ir_2Cl_2(C_8H_{14})_4}$ to $\mathrm{(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2IrCl}$ ($\mathrm{MX_\mathit{n} = AgI}$) [267].

In a quite different but very interesting reaction, Shaw and co-workers could also prepare heterobimetallic derivatives containing bridging dppe ligands, $\mathrm{(CO)_4M(\mu\text{-}dppe)_2M'(CO)_4}$ (M,M' = Cr, Mo, W) from the reaction of $\mathrm{M(CO)_4PPh_2H}$ with $\mathrm{M'(CO)_4[PPh_2(CH{=}CH_2)]_2}$ in the presence of potassium t-butoxide [302].

Another method has been used by Braunstein et al. [269] for preparing dppm bridged polymetallic derivatives, i.e. reaction of a carbonyl metallate anion with chloro complexes containing the dppm ligand. For example, reaction of $[PdCldppm]_2$ with $NaMn(CO)_5$ yields as the minor product $ClPd(\mu\text{-dppm})_2Mn(CO)_3$ as well as the structurally characterized cluster $Pd_2Mn_2(CO)_9(dppm)_2$. The same compounds are obtained if the reaction mixture $Pd(PhCN)_2 + 2NaMn(CO)_5$ is treated with dppm [269].

The same dinuclear (Mn–Pd) complex and its bromo analogue were also prepared at the same time by another method, i.e. reaction of $MnX(CO)_5$ with $Pd_2(dppm)_3$ or $Pd(dba)_2$ in the presence of dppm [270,271]. Metathetical reaction of the bromo complex with NaX affords various derivatives of similar structure, $XPd(\mu\text{-dppm})_2Mn(CO)_3$ (X = Cl, Br, I, N_3, NCO, SCN, $SnCl_3$) whereas protonation leads to unstable hydrido complexes [271].

Similar reactions were also performed in order to prepare ruthenium–manganese compounds and thus the reaction of $RuCl_2(dppm)_2$ with $NaMn(CO)_5$ leads to the preparation of $Cl(CO)Ru(\mu\text{-CO})_2(\mu\text{-dppm})_2Mn(CO)_2$ through the ionic intermediate $[RuCl(THF)(dppm)_2][Mn(CO)_5]$ [272,273]. Previously, Braunstein et al. [162,274] have developed this method considerably to prepare mixed–metal clusters containing three or four different metals. For example, reaction of the dinuclear $PdPtCl_2(dppm)_2$ with $Co(CO)_4^-$ or $Mn(CO)_5^-$ affords $PdPtM(CO)_n(dppm)_2$ (M = Co, $n = 7$; M = Mn, $n = 9$). Further reaction of the cobalt-containing cluster successively with iodide and $[Fe(CO)_3(NO)]^-$ or $[Mn(CO)_5]^-$ produces $PdPtFeCo(CO)_6(NO)(dppm)_2$ and $PdPtMnCo(CO)_8(dppm)_2$ [162b]. Similarly, the reaction of the dinuclear $Pd_2Cl_2(dppm)_2$ with $Co(CO)_4^-$, $Mo(CO)_3Cp^-$ and $W(CO)_3Cp^-$ yields the novel heterometallic cluster, $Pd_2Co_2(CO)_7(dppm)_2$ and $Pd_2MClCp(CO)_2(dppm)_2$ (M = Mo, W) [162a]. With $Na_2Fe(CO)_4$, the similar reaction leads to $FePd_2(dppm)_2(CO)_4$ or $FePdPt(dppm)_2(CO)_4$ [274]. Coordination of dppm to preexisting heterometallic derivatives in order to stabilize them has also been used. Thus, reaction of dppm with $Pt[M(CO)_2(\eta^5\text{-}C_5H_4R)]_2(PhCN)_2$ affords $[(\eta^5\text{-}C_5H_4R)M(CO)_2(\mu\text{-dppm})Pt(dppm)]^+$ (M = Mo, R = H, Me; M = W, R = H), a complex containing both a chelating and a bridging dppm ligand. Its reaction with $NaBH_4$ produces $(\eta^5\text{-}C_5H_4R)M(CO)_2(\mu\text{-dppm})PtH(\eta^1\text{-dppm})$ [275].

Stone and co-workers [276,277] have also employed this method. For example addition of dppm to $PtW[\mu\text{-C(OMe)R}](CO)_5(COD)$ (R = C_6H_4Me-4) affords $PtW[\mu\text{-C(OMe)R}](\mu\text{-dppm})(CO)_5$ which has been structurally characterized. Reactions with HBF_4 and BBr_3 afford $[PtW(\mu\text{-CR})(\mu\text{-dppm})_2(CO)_5]BF_4$ and $PtWBr(\mu\text{-CR})(\mu\text{-dppm})_2(CO)_5$, respectively. Further reaction of the cationic species with nucleophilic agents leads to $PtW(\mu\text{-CRR}')(\mu\text{-dppm})(CO)_5$ (R′ = Me, H, C≡Ct-Bu or SC_6H_4Me-4) [276]. In contrast, treatment of $PtW[\mu\text{-C(OMe)Me}](CO)_5(COD)$ with dppm affords $PtW[\mu\text{-C(OMe)Me}](CO)_5(dppm)$ in which the dppm ligand is chelating. This compound isomerizes slowly in toluene to the bridging dppm complex and chromatography over basic alumina affords $PtW(\mu\text{-}C{=}CH_2)(dppm)(CO)_5$. Protonation of $PtW(\mu\text{-}C(OMe)Me)(\mu\text{-}dppm)(CO)_5$ affords $[PtW(\mu\text{-}CMe)(\mu\text{-}dppm)(CO)_5]BF_4$ which reacts in turn with strong bases to give the vinylidene complex $PtW(\mu\text{-}C{=}CH_2)(\mu\text{-}dppm)(CO)_5$ [277].

Reaction of $[N(PPh_3)_2][ReM(\mu\text{-}CH(C_6H_4Me\text{-}4)(CO)_9]$ with $R_2PCH_2PR_2$ (R = Me, Ph) affords $[N(PPh_3)_2][ReM(\mu\text{-}CH(C_6H_4Me\text{-}4)(\mu\text{-}R_2PCH_2PR_2)(CO)_7]$ (M = W, R = Ph; M = Cr, Mo or W, R = Me). Interestingly, protonation of this complex leads to $ReW(\mu\text{-}CH_2C_6H_4Me\text{-}4)(\mu\text{-}R_2PCH_2PR_2)(CO)_7$ which contains an asymmetrical bridging *p*-tolyl methyl group coordinated to the rhenium by a σ-bond and to the tungsten by a two-electron three-center $C{-}H \rightarrow W$ bond. Further reaction with $P(OMe)_3$ affords $ReW(\mu\text{-}OCCH_2C_6H_4Me\text{-}4)(\mu\text{-}dppm)(CO)_6P(OMe)_3$ [278].

The complex $FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(dppm)(HB(pz)_3)$ ($HB(pz)_3$ = tris-(pyrazol-1-yl)-borate) was prepared from dppm and $FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(HB(pz)_3)$; it loses CO to give $FeW(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(\mu\text{-}dppm)(CO)_2(HB(pz)_3)$. Alkylation with SO_3CF_3Me affords $FeW(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}COMe)(\mu\text{-}dppm)(CO)_2(HB(pz)_3)][SO_3CF_3]$ [279].

Dixneuf and co-workers [280] who have studied in detail the chemistry of phosphido-bridged ruthenium–cobalt derivatives, have attempted the substitution of CO groups of $(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ with dppm. According to the reaction conditions (THF, 40 °C, 12 h or THF reflux 10 h), two different isomeric products are obtained which contain respectively a chelating or a bridging dppm ligand, $(CO)_2(dppm)Ru(\mu\text{-}PPh_2)Co(CO)_3$ and $(CO)_3Ru(\mu\text{-}dppm)(\mu\text{-}PPh_2)Co(CO)_2$ [280].

As part of a study of reactivity of complexes containing dimetallated olefins, Mague [281] has prepared $IrRhCl_2(CO)(\mu\text{-}CO)(\mu\text{-}RC{=}CR)(dppm)_2$ ($R = CO_2Me$, CF_3). The complex loses CO at reflux under N_2 to give $IrRhCl_2(CO)(\mu\text{-}RC{=}CR)(dppm)_2$ whereas reaction with $AgClO_4$ under CO yields $IrRh(CO)_2Cl(\mu\text{-}CO)(\mu\text{-}RC{=}CR)(dppm)_2$ ($R = CO_2Me$). This compound can be reversibly decarbonylated to give $IrRhCl(CO)_2(\mu\text{-}RC{=}CR)(dppm)_2$ [281].

Finally, a ruthenium–gold hydride cluster, $[Au_2Ru(\mu\text{-}H)_2(dppm)_2(PPh_3)_2][NO_3]_2$, has been prepared from $RuH_2(dppm)_2$ and $AuPPh_3NO_3$. The two dppm ligands remain chelating on ruthenium [282].

In our laboratory, we have looked for a general method of preparation of ruthenium containing heterobimetallic hydride derivatives. The first starting complex used was $Ru(COD)(\eta^1\text{-}dppm)(\eta^2\text{-}dppm)$, ($COD = C_8H_{12}$) [71]. However with $[RhCl(CO)_2]_2$ at room temperature, redistribution occurs to give $Ru(CO)(COD)dppm$ and $[RhCl(CO)dppm]_2$. Nevertheless, a mixed-metal species $RuRhCl(CO)_3(dppm)_2$ is obtained at 80 °C through a complicated mechanism [283,284]. The same complex is obtained with a better yield under CO. The complex reacts with H_2 or $NaBH_4$ in THF to give

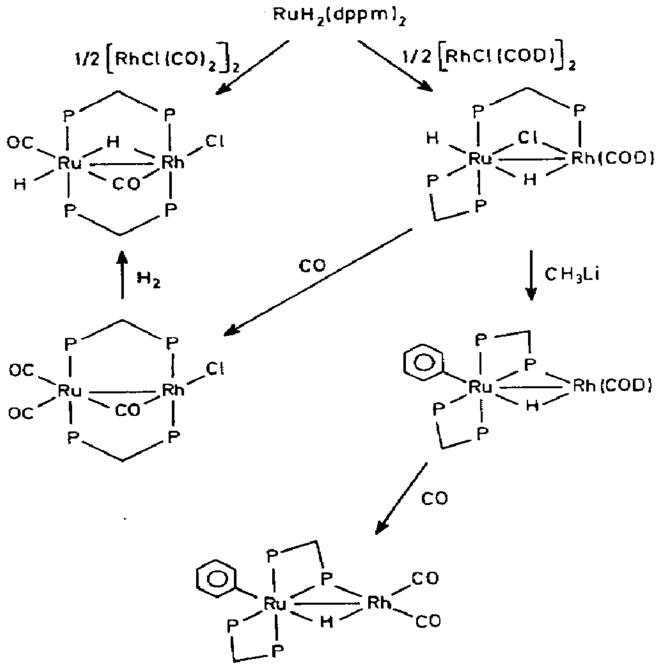


Fig. 12. Preparation of a series of Ru–Rh dppm complexes.

$RuRhH_2Cl(CO)_2(dppm)_2$ containing one bridging and one terminal hydride group. The same dihydride was obtained from $RuH_2(dppm)_2$ and $[RhCl(CO)_2]_2$ through a pathway which probably involved Lewis acid–Lewis base association followed by ring opening of the dppm ligand [283,284] (see Fig. 12).

Since this method seemed easy, other reactions were undertaken with $[RhCl(COD)]_2$, $[RhCl(COT)_2]_2$ (COT = C_8H_{14}) and $[IrCl(COD)]_2$. In all cases, complexes containing both a chelating and a bridging dppm ligand were obtained, (dppm)HRu(μ-H)(μ-Cl)(μ-dppm)RhClCOD [284,285], (dppm)HRu(μ-H)(μ-Cl)(μ-dppm)$Rh(COT)_2$ [286], (dppm)HRu(μ-H)(μ-dppm)(μ-Cl)Ir(COD) [284,285]. The three reactions are quantitative but the RuRh(COT) and RuIrCOD derivatives are unstable and after redistribution $RuHCl(dppm)_2$ can be isolated.

However, $RuRhH_2Cl(COD)(dppm)_2$ is obtained pure in 95% yield and has shown a remarkable reactivity. Reaction with H_2 leads to decomposition whereas with CO, $RuRhCl(CO)_3(dppm)_2$ is obtained after ring opening of the chelating dppm ligands. With $P(OMe)_3$ the bimetallic structure is broken into $RuHCl(dppm)_2P(OMe)_3$ and $RhH(P(OMe)_3)_4$. As the chloride group is probably responsible for the redistribution reactions which led specifically to decomposition under H_2, reduction reactions were attempted in order to prepare bimetallic hydrido complexes.

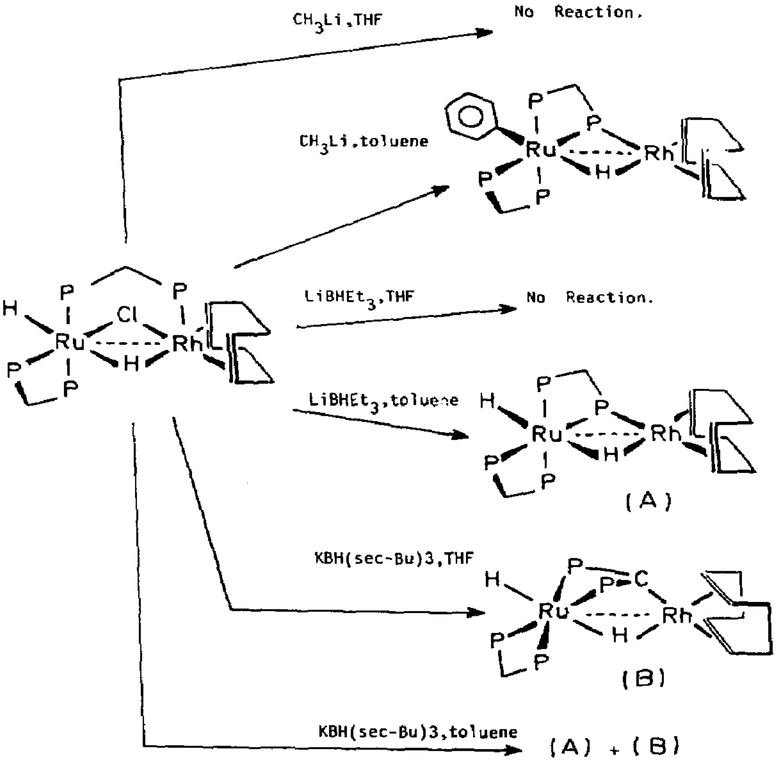


Fig. 13. Selective formation of bis (diphenylphosphino)methanido or phosphido-bridged ruthenium–rhodium complexes as a function of solvent and reagent basicity.

Interestingly, with MeLi in toluene, after reductive elimination of methane from an unstable hydrido methyl derivative, there is rupture of a P–C bond of dppm in order to ensure an 18-electron configuration on ruthenium. The complex RuRhHPh(dppm)(μ-PhPCH$_2$PPh$_2$)(COD) is obtained. It contains a phosphido bridge together with a *trans* hydrido phenyl configuration on ruthenium [284,285].

A similar reaction occurs in toluene between RuRhH$_2$Cl(COD)(dppm)$_2$ and a solution of LiBHEt$_3$ which leads to an analogous phosphido-bridged derivative but this time containing a *trans* dihydride configuration on ruthenium [287], RuRhH$_2$(PhPCH$_2$PPh$_2$)(dppm)(COD). However, this reaction does not proceed in THF, probably because the solvent prevents initial attack of the anion on rhodium. (See Fig. 13.) If KBH(sec-Bu)$_3$ is used in THF, a selective reaction occurs which leads eventually to the dihydrido complex RuRhH$_2$(Ph$_2$PCHPPh$_2$)(dppm)(COD) containing a bisdiphenylmethanido bridge between ruthenium and rhodium [287]. However in toluene a mixture of both RuRhH$_2$(Ph$_2$PCHPPh$_2$)(dppm)(COD) and RuRhH$_2$(PhPCH$_2$PPh$_2$)(dppm)(COD) is obtained. This indicates that most

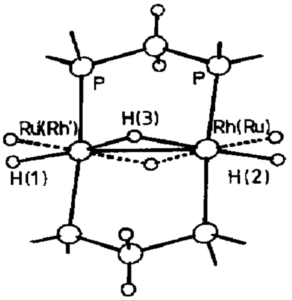


Fig. 14. Perspective view of the Rh–Ru(dppm)$_2$ core of a very unsaturated complex showing the crystallographic disorder.

probably two mechanisms operate, one involving abstraction of a dppm proton while the other attacks the anion on rhodium. RuRhH$_2$Cl(COD)(dppm)$_2$ was also reacted with NaBH$_4$ in THF or toluene in order to prepare bimetallic polyhydro complexes and thus, by this method, we could prepare RuRhH$_3$(dppm)$_2$, a very unsaturated heterobimetallic trihydride (Fig. 14). The complex adopts an A-frame geometry and remarkably the three hydrides are rigid at the NMR time scale between room temperature and 183 K. The crystal structure shows a ruthenium–rhodium distance (2.7894(4) Å) significantly shorter than that of other hydrido-bridged ruthenium–rhodium and could account for a double metal–metal bond [288].

RuRhH$_2$Cl(COD)(dppm)$_2$ can also react with acids, whether Brönsted or Lewis. Thus, the reaction with HBF$_4\cdot$Et$_2$O produces [(dppm)$_2$Ru(μ-H)(μ-Cl)Rh(COD)]BF$_4$, a complex containing two chelating dppm ligands on ruthenium and an asymmetrical bridging hydride [289]. Its reaction with CO leads to [(CO)$_2$Ru(μ-dppm)$_2$(μ-H)(μ-Cl)RhCO]BF$_4$ after ring opening of the dppm ligands. This reaction sequence represents an unusual example of dppm motion in a dinuclear complex.

In the presence of an excess of [RhCl(COD)]$_2$ at 80 ° C, RuRh$_2$H$_2$Cl(PhPCH$_2$PPh$_2$)(COD)$_2$(dppm)$_2$ is obtained whereas with CuCl, the trimetallic complex RuRhCuH$_2$Cl$_2$(COD)(dppm)$_2$ is formed. However, during this reaction, there is not as expected the rupture of a Ru–P bond but rather rupture of the Rh–P one and this η^1-dppm ligand can then coordinate to CuCl. The trimetallic complex is not very stable and is slowly converted in solution into (dppm)$_2$Ru(μ-H)$_2$CuCl, a typical adduct of the Lewis base RuH$_2$(dppm)$_2$ with the Lewis acid CuCl. This Ru–Cu complex is more easily prepared from RuH$_2$(dppm)$_2$ and CuCl [289].

The same reactions are possible with [Cu(CH$_3$CN)$_4$]BF$_4$ and in that case, they lead to [(dppm)$_2$Ru(μ-H)$_2$Cu(CH$_3$CN)]BF$_4$ [290]. The complex undergoes a ring opening reaction under CO to yield [(CO)$_2$Ru(μ-dppm)$_2$(μ-H)$_2$Cu(CH$_3$CN)]BF$_4$, but reacts with CO$_2$ or C$_2$H$_4$ to give as the only

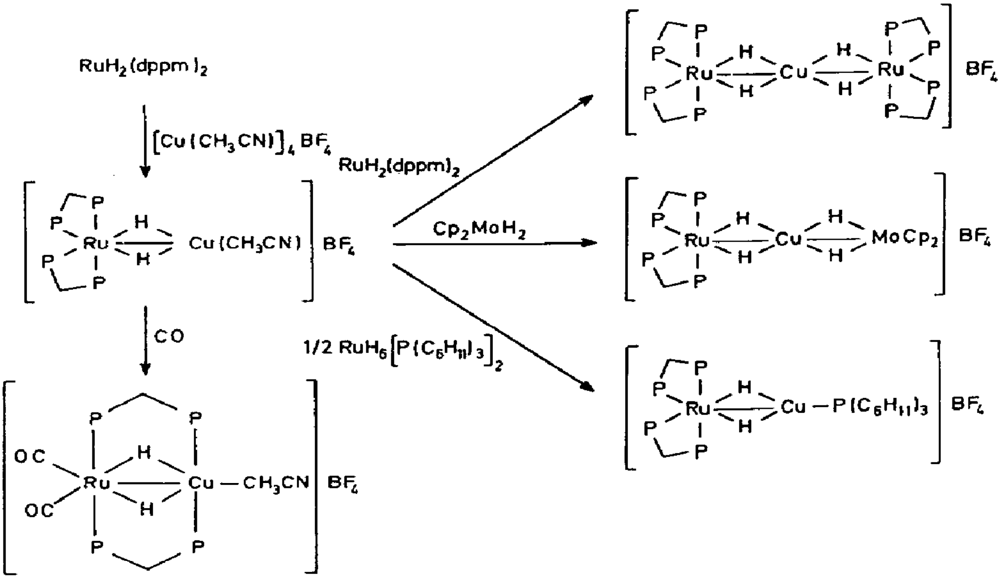


Fig. 15. Preparation and reactivity of hydrido Ru–Cu complexes.

characterized product the trinuclear $[\{(dppm)_2Ru(\mu\text{-}H)_2\}_2Cu]BF_4$ in moderate yield. This complex is more easily prepared from $RuH_2(dppm)_2$ and $[Cu(CH_3CN)_4]BF_4$ [290] in a 2 : 1 ratio. Heterotrimetallic complexes can also be prepared in this way either through the reaction of $[(dppm)_2Ru(\mu\text{-}H)_2Cu(CH_3CN)]BF_4$ with $CpMoH_2$ or directly from successive addition of $[Cu(CH_3CN)_4]BF_4$ and Cp_2MoH_2 to $RuH_2(dppm)_2$. In each case, $[(dppm)_2Ru(\mu\text{-}H)_2Cu(\mu\text{-}H)_2MoCp_2]BF_4$ is obtained in quantitative yield. However, a similar reaction with $RuH_6(PCy_3)_2$ leads to the quantitative transfer of phosphine to copper to give $[(dppm)_2Ru(\mu\text{-}H)CuPCy_3]BF_4$.

$RuH_2(dppm)_2$ is also a remarkable precursor for association with early transition metals. Thus, it reacts with $Mo(CO)_6$ at 80 °C to give $MoRu(CO)_6(dppm)_2$ [291]. The crystal structure of the complex shows the presence of a semi bridging CO group of a long metal–metal distance (3.058(1) Å). It is to be noticed that the analogous complex $CrFe(CO)_6(dmpm)_2$ has been recently prepared by Wilkinson and coworkers [54]. The complex also shows a long metal–metal distance (3.111(6) Å) but the authors still postulate a dative Fe → Cr interaction [54]. The molybdenum–ruthenium complex shows quite a rich reactivity. Thus, its IR spectrum is different whether measured in solution, or after recrystallization from toluene or THF. After recrystallization from toluene, the bond at 1685 cm^{-1} is indicative of the "atypical" semi-bridging CO group whereas the yellow complex obtained from THF shows a bond at 1715 cm^{-1} indicative of a "ketonic" CO group. Both complexes in solution show the same NMR

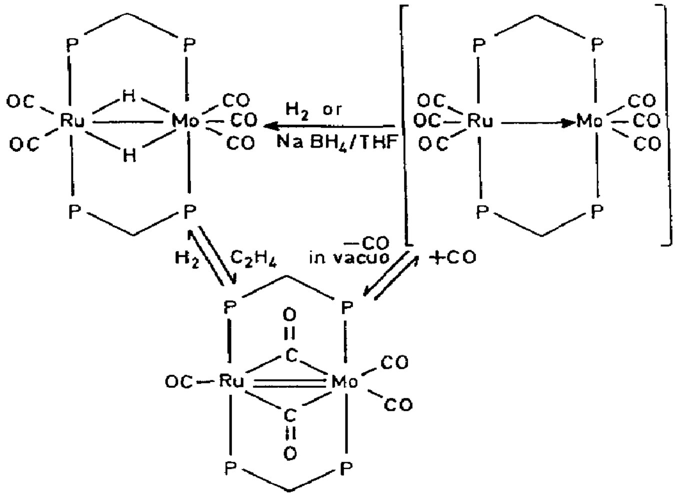


Fig. 16. Dppm bridged Mo–Ru complexes exhibiting a facile heterobimetallic activation of H_2.

spectra and the same IR spectrum which does not show any bond lower than 1800 cm^{-1} because in solution the complex could adopt a configuration where all the CO groups are terminal and a dative Ru → Mo bond is present as for $CrFe(CO)_6(dmpm)_2$ (see Fig. 16).

$MoRu(CO)_6(dppm)_2$ loses CO reversibly in vacuo to give $MoRu(CO)_3(\mu\text{-}CO)_2(\mu\text{-dppm})_2$, and air-sensitive complex containing two bridging carbonyl groups. Both Mo–Ru complexes react with H_2 to give $MoRu(\mu\text{-}H)_2(CO)_5(dppm)_2$. The two H atoms are indiscernible by NMR at any temperature, and H_2 can be eliminated in vacuo when heating or when passing ethylene through the solution but T_1 measurements are not in favour of its formulation as a real molecular hydrogen complex [292]. The complex also reacts with CF_3CO_2H to give the toluene-soluble complex $MoRu(\mu\text{-}H)(\mu\text{-}OCOCF_3)(CO)_5(dppm)_2$ [292].

D. HETEROBIMETALLIC COMPLEXES CONTAINING OTHER RELATED LIGANDS

Related ligands have also been used for the preparation of heterobimetallic complexes. Without trying to be exhaustive, we can quote a few examples of such complexes and of their reactivity. These ligands can be symmetrical with the two phosphine units linked by groups other than the methylene one of dppm (O, NR...) or unsymmetrical in which a PPh_2 moiety is replaced by derivatives of N or other elements.

Balch and co-workers [293,294] have used the 2-diphenylphosphinopyridine ligand (PPh_2Py) to prepare heterobimetallic derivatives prior to the use of dppm. Examples of such complexes involve RhPd and RhPt associations such as $Cl_2(CO)Rh(\mu\text{-}PPh_2Py)_2PtCl_x$ ($x = 1$, 3) [293] or $ClPt(\mu\text{-}CO)(\mu\text{-}PPh_2Py)_2MCl(CO)_2$ (M = Mo, W) [294] shown to contain a semi-bridging carbonyl group. Interestingly, whereas in the case of two platinum metals the bonding of PPh_2Py is symmetrical, i.e. each metal atom accommodates one phosphorus and one nitrogen, in the case of the Pt–M (M = Mo, W) derivatives, the two phosphorus atoms lie on platinum while the two nitrogen atoms are coordinated by molybdenum or tungsten.

In our group, the ligand diethyl(diphenylphosphino methyl)amine (ddpa $= (C_6H_5)_2PCH_2N(C_2H_5)_2$) has been used [295] to form the complex RhCl(CO)$(ddpa)_2$. This reacts easily, thanks to its uncoordinated amine termination with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ and $PdCl_2(COD)$ to form homo- and heterodinuclear species formulated from NMR and IR data as, respectively, $Rh_2(\mu\text{-}Cl)Cl(CO)(\mu\text{-}ddpa)$ and $PdRh(\mu\text{-}Cl)Cl_2(CO)(\mu\text{-}ddpa)_2$. In both compounds, the ddpa ligands are thought to retain a head-to-head arrangement in contrast with the head-to-tail disposition observed with PPh_2Py [296].

Balch et al. [297] have also studied the ligand $Ph_2PCH_2AsPh_2$(dapm) and they could show that the first product of the reaction of $Pt(dapm)_2Cl_2$ with $Rh_2Cl_2(CO)_4$ is $Cl(CO)Rh(\mu\text{-}dapm)_2PtCl_2$ which contain two *trans* diphenylarsino groups on rhodium and two *cis* diphenylphosphino groups on platinum. The complex isomerizes in chloroform into $Cl_2(CO)Rh(\mu\text{-}dapm)_2PtCl$ which then contains a Rh–Pt bond (Rh–Pt = 2.692(1) Å).

The properties of some bisdiphenylarsinomethane (dpam) complexes have been compared with those of similar dppm complexes. It was thus possible to prepare *cis*-$[Me_2Pt(\mu\text{-}dpam)]_2$, *cis*-$Me_2Pt(\eta^1\text{-}dpam)_2$, *trans*-$Cl_2Pt(\eta^1\text{-}dpam)_2$ and *trans*-$[Cl\text{-}Pt(\mu\text{-}dpam)]_2$ as well as the heterobimetallic derivative $Cl_2Pt(\mu\text{-}dpam)_2HgCl_2$ [298]. This will probably lead to a new class of heterobimetallic complexes of an unsymmetrical ligand.

Finally, other ligands containing a single atom between two diphenylphosphino groups have also recently been used. We can quote for example Ph_2POPPh_2 or $Ph_2PNHPPh_2$ used to prepare bimetallic Mo–Cr and Mo–Fe derivatives, respectively, as well as the trinuclear $Cl_2Pd[(\mu\text{-}PPh_2OPPh_2)Mo(CO)_5]_2$ [300] and some mono- and dinuclear palladium and platinum derivatives, as well as the bimetallic derivatives $[(C_6F_5)_2M(\mu\text{-}Ph_2PNHPPh_2)_2Ag]ClO_4$ [301].

E. CONCLUSION

This review shows that dppm can coordinate to virtually all metals of the periodic table and that a large number of heterobimetallic complexes are now known.

Recently, a number of research groups have developed methods of rational synthesis of complexes containing two identical, or two or more different metal atoms so that it is now possible to design a desired product containing a specific combination of metals. This is probably favorable ground for further development of the reactivity studies.

From another historical point of view, dppm is probably the best example of chemists' attempts to conceive an inert linkage between two metal atoms and in this context, has offered the prototype for almost twenty years of reactivity studies "on two metal centers". However, the dppm metal core of the bridged complexes, long regarded as being inert, now shows numerous and interesting examples of a specific role in reactivity.

Thus, most complexes are not rigid but fluxional and the dppm ligand can undergo ring opening or ring formation reactions. It even acts as a trifunctional ligand since the methylene protons can be activated. The phosphorus–carbon bonds also offer various examples of intra- or intermolecular dissociative behaviour. These new considerations are clearly derived from the increasing number of reactivity studies and research of catalytic applications and lead to a new metal assisted organic chemistry of the ligand.

A third interesting point is the tendency for researchers to synthesize and study the reactivity of less stable species, particularly hydrides and polyhydrido derivatives in connection with research of catalytic application. In this specific field also, recent discoveries such as the desulfurization of H_2S are encouraging for the future use of such complexes.

Finally the chemistry of dppm complexes is now extending rapidly, as quoted in the text, to other similar ligands of the type $R_2PCH_2PR_2$ and also to new types of dissymmetric bifunctional ligands.

REFERENCES

1 (a) E.L. Muetterties, Bull. Soc. Chim. Belg., 84 (1975) 959.
  (b) R. Poilblanc, J. Organomet. Chem., 94 (1975) 241.
  (c) R. Poilblanc, Nouv. J. Chim., 2 (1978) 145.
  (d) E.L. Muetterties and J. Stein, Chem. Rev., 79 (1979) 479.
  (e) J.P. Collman, R.K. Rothrock, R.G. Finke and E.J. Rose Munch, Inorg. Chem., 21 (1982) 146.
2 R.J. Puddephatt, Chem. Soc. Rev., (1983) 99.
3 D.J. Brauer, S. Hietkamp and O. Stelzer, J. Organomet. Chem., 299 (1986) 137.
4 F.A. Cotton, S.A. Duraj and W.J. Roth, Inorg. Chem., 23 (1984) 4113.
5 F.A. Cotton and W.J. Roth, Inorg. Chem., 22 (1983) 3654.
6 F.A. Cotton, S.A. Duraj, L.R. Falvello and W.J. Roth, Inorg. Chem., 24 (1985) 4389.
7 A.R. Chakravarty, F.A. Cotton, M.P. Diebold, D.B. Lewis and W.J. Roth, J. Am. Chem. Soc., 108 (1986) 971.
8 R.B. King and K.S. Raghuveer, Inorg. Chem., 23 (1984) 2483.

9 G.R. Clark and P.W. Clark, J. Organomet. Chem., 255 (1983) 205.
10 M.Y. Darensbourg, R. El Mehdawi, T.J. Delord, F.R. Fronczek and S.F. Watkins, J. Am. Chem. Soc., 106 (1984) 2583.
11 E.H. Abbott, K.S. Bose, F.A. Cotton, W.T. Hall and J.C. Sekutowski, Inorg. Chem., 17 (1978) 3240.
12 F.L. Campbell III, F.A. Cotton and G.L. Powell, Inorg. Chem., 23 (1984) 4222.
13 E. Carmona, A. Galindo, L. Sanchez, A.J. Nielson and G. Wilkinson, Polyhedron, 3 (1984) 347.
14 A. Blagg, S.W. Carr, G.R. Cooper, I.D. Dobson, J.B. Gill, D.C. Goodall, B.L. Shaw, N. Taylor and T. Boodington, J. Chem. Soc., Dalton Trans., (1985) 1213.
15 H. Dadkham, J.R. Dilworth, K. Fairman, C.T. Kan, R.L. Richards and D.L. Hughes, J. Chem. Soc., Dalton Trans., (1985) 1523.
16 S. Al-Jibori and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1982) 286; Inorg. Chim. Acta, 74 (1983) 235.
17 G.R. Cooper, D.M. McEwan and B.L. Shaw, Inorg. Chim. Acta, 76 (1983) L165.
18 G.R. Cooper, F. Hassan, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Chem. Commun., (1985) 614.
19 S. Al-Jibori, M. Hall, A.T. Hutton and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1984) 863.
20 S. Al-Jibori and B.L. Shaw, J. Organomet. Chem., 272 (1984) 213.
21 G.A. Carriedo, V. Riera and J. Santamaria, J. Organomet. Chem., 234 (1982) 175 and references cited therein.
22 G.A. Carriedo, M.C. Crespo, V. Riera, M.G. Sanchez, M.L. Valin, D. Moreiras and X. Solans, J. Organomet. Chem., 302 (1986) 47.
23 C.J. Commons and B.F. Hoskins, Aust. J. Chem., 28 (1975) 1663.
24 R. Colton and C.J. Commons, Aust. J. Chem., 28 (1975) 1673.
25 J.A. Marsella and K.G. Caulton, Organometallics, 1 (1982) 274.
26 T.W. Turney, Inorg. Chim. Acta, 64 (1982) L141.
27 G. Ferguson, W.J. Laws, M. Parvez and R.J. Puddephatt, Organometallics, 2 (1983) 276.
28 H.,C. Aspinall and A.J. Deeming, J. Chem. Soc., Dalton Trans., (1985) 743.
29 A.J. Deeming and S. Donovan-Mtunzi, Organometallics, 4 (1985) 693.
30 H.C. Aspinall, A.J. Deeming and S. Donovan-Mtunzi, J. Chem. Soc., Dalton Trans., (1983) 2669.
31 A.J. Deeming and S. Donovan-Mtunzi, J. Chem. Soc., Dalton Trans., (1985) 1609.
32 H.C. Aspinall and A.J. Deeming, J. Chem. Soc., Chem. Commun. (1983) 838.
33 T.E. Wolff and L.P. Klemann, Organometallics, 1 (1982) 1667.
34 F.R. Lemke and C.P. Kubiak, J. Chem. Soc., Chem. Commun., (1985) 1729.
35 K.W. Lee, W.T. Pennington, A.W. Cordes and T.L. Brown, Organometallics, 3 (1984) 404.
36 K.W. Lee and T.L. Brown, Organometallics, 4 (1985) 1030.
37 K.W. Lee, W.T. Pennington, A.W. Cordes and T.L. Brown, J. Am. Chem. Soc., 107 (1985) 631.
38 K.W. Lee and T.L. Brown, Organometallics, 4 (1985) 1025.
39 M.J. Mays, D.W. Prest, P.R. Raithby and A.G. Orpen, J. Chem. Soc., Dalton Trans., (1982) 737.
40 D.W. Prest, M.J. Mays, G. Orpen and P.R. Raithby, J. Chem. Soc., Dalton Trans., (1982) 2021.
41 T. Sowa, T. Kawamura, T. Yamabe and T. Yonezawa. J. Am. Chem. Soc., 107 (1985) 6471.

42 T.J. Barder, F.A. Cotton, D. Lewis, W. Schwotzer, S.M. Tetrick and R.A. Walton, J. Am. Chem. Soc., 106 (1984) 2882.
43 K.R. Dunbar, D. Powell and R.A. Walton, J. Chem. Soc., Chem. Commun., (1985) 114.
44 K.R. Dunbar, D. Powell and R.A. Walton, Inorg. Chem., 24 (1985) 2842.
45 T.J. Barder, F.A. Cotton, K.R. Dunbar, G.L. Powell, W. Schwotzer and R.A. Walton, Inorg. Chem., 24 (1985) 2550.
46 F.A. Cotton, K.R. Dunbar, A.C. Price, W. Schwotzer and R.A. Walton, J. Am. Chem. Soc., 108 (1986) 4843.
47 L.R. Falvello, S.M. Tetrick and R.A. Walton, J. Am. Chem. Soc., 107 (1985) 3524.
48 T.J. Barder, D. Powell and R.A. Walton, J. Chem. Soc., Chem. Commun., (1985) 550.
49 T.J. Barder, F.A. Cotton, L.R. Falvello and R.A. Walton, Inorg. Chem., 24 (1985) 1258.
50 L.B. Anderson, T.J. Barder and R.A. Walton, Inorg. Chem., 24 (1985) 1421.
51 F.A. Cotton, K.R. Dunbar, L.R. Falvello and R.A. Walton, Inorg. Chem., 24 (1985) 4180.
52 D.R. Root, C.H. Blevins, D.L. Lichtenberger, A.P. Sattelberger and R.A. Walton, J. Am. Chem. Soc., 108 (1986) 953.
53 G. De Leeuw, J.S. Field, R.J. Haines, B. Mc Culloch, E. Meintjes, F. Monberg, G.M. Olivier, P. Ramdial, C.N. Sampson, B. Sigwarth, N.D. Steen and K.G. Moodley, J. Organomet. Chem., 275 (1984) 95.
54 W.K. Wong, K.W. Chiu, G. Wilkinson, M. Motevalli and M.B. Hursthouse, Polyhedron, 4 (1985) 1231.
55 W.K. Wong, K.W. Chiu, G. Wilkinson, A.J. Howes, M. Motevalli and M.B. Hursthouse, Polyhedron, 4 (1985) 603.
56 G.M. Dawkins, M. Green, J.C. Jeffery, C. Sambale and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1983) 499.
57 N.M. Domerty, G. Hogarth, S.A.R. Knox, K.A. Macpherson, F. Melchior and A.G. Orpen, J. Chem. Soc., Chem. Commun., (1986) 540.
58 G.M. Dawkins, M. Green, A.G. Orpen and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1982) 41.
59 M.E. Wright, G.J. Long, D.E. Tharp and G.O. Nelson, Organometallics, 5 (1986) 779.
60 M.E. Wright, T.M. Mezza, G.O. Nelson, N.R. Armstrong, V.W. Day and M.R. Thompson, Organometallics, 2 (1983) 1711.
61 M. Lehmann and G. Wilkinson, J. Chem. Soc., Dalton. Trans., (1981) 191.
62 A.R. Chakravarty, F.A. Cotton and L.R. Falvello, Inorg. Chem., 25 (1986) 214.
63 B.P. Sullivan and T.J. Meyer, Inorg. Chem., 19 (1980) 752.
64 D.L. Davies, B.P. Gracey, V. Guerchais, S.A.R. Knox and A.G. Orpen, J. Chem. Soc., Chem. Commun., (1984) 841.
65 N.G. Connelly, N.J. Forrow, B.P. Gracey, S.A.R. Knox and A.G. Orpen, J. Chem. Soc., Chem. Commun., (1985) 14.
66 J.A. Clucas, M.H. Harding, B.S. Nicholls and A.K. Smith, J. Chem. Soc., Dalton. Trans., (1985) 1835.
67 See for example: G. Lavigne, N. Lugan and J.J. Bonnet, Organometallics, 1 (1982) 1040; N. Lugan, J.J. Bonnet and J.A. Ibers, J. Am. Chem. Soc., 107 (1985) 4484; C. Bergounhou, J.J. Bonnet, P. Fompeyrine, G. Lavigne, N. Lugan and F. Mansilla, Organometallics, 5 (1986) 60 and references cited therein.
68 A. Colombie, G. Lavigne and J.J. Bonnet, J. Chem. Soc., Dalton Trans., (1986) 899.
69 J.S. Holmgren, J.R. Shapley, J.R. Shapley, S.R. Wilson and W.T. Pennington, J. Am. Chem. Soc., 108 (1986) 508.
70 J. Chatt and R.T. Hayter, J. Chem. Soc., (1961) 896.

71 B. Chaudret, G. Commenge and R. Poilblanc, J. Chem. Soc., Dalton. Trans., (1984) 1635.
72 N.M. Taquikhan and R. Mohiuddin, Polyhedron, 2 (1983) 1247.
73 A.R. Chakravarty, F.A. Cotton and W. Schwotzer, Inorg. Chim. Acta, 84 (1984) 179.
74 B.P. Sullivan and T.J. Meyer, Inorg. Chem., 21 (1982) 1037.
75 N.M. Taquikhan, M.C. Bajaj, Md. R. H. Siddiqui, B. Taquikhan, M.S. Reddy and K.V. Reddy, J. Chem. Soc., Dalton Trans., (1985) 2603.
76 G. Smith, D.J. Cole-Hamilton, A.C. Gregory and N.G. Gooden, Polyhedron, 1 (1982) 97.
77 G. Smith, D.J. Cole-Hamilton, M. Thornton-Pett and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1983) 2501.
78 G. Smith and D.J. Cole-Hamilton, J. Chem. Soc., Dalton Trans., (1984) 1203.
79 G. Smith, L.H. Sutcliffe and D.J. Cole-Hamilton, J. Chem. Soc., Dalton Trans., (1984) 1209.
80 G. Smith, D.J. Cole-Hamilton, M. Thornton-Pett and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1985) 387.
81 R. Obeso Rosete, D.J. Cole-Hamilton and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1984) 2067.
82 D.C. Liles, M.E. Oosthuizen, A. Shaver, E. Singleton and M.B. Wiege, Organometallics, 5 (1986) 591.
83 E.B. Boyar, P.A. Harding, S.D. Robinson and C.P. Brock, J. Chem. Soc., Dalton Trans., (1986) 1771.
84 E.J. Probitts, D.R. Saunders, M.H. Stone and R.J. Mawby, J. Chem. Soc., Dalton Trans., (1986) 1167.
85 W.K. Wong, K.W. Chiu, G. Wilkinson, A.J. Howes, M. Motevalli and M.B. Hursthouse, Polyhedron, 4 (1985) 603.
86 A.R. Chakravarty, F.A. Cotton and W. Schwotzer, Inorg. Chem., 23 (1984) 99.
87 B.E. Hanson, P.E. Fanwick and J.S. Mancini, Inorg. Chem., 21 (1982) 3811.
88 B.E. Hanson and J.S. Mancini, Organometallics, 2 (1983) 126.
89 E.C. Lisic and B.E. Hanson, Inorg. Chem., 6 (1986) 813.
90 W.J. Laws and R.J. Puddephatt, J. Chem. Soc., Chem. Commun., (1983) 1020.
91 C. Carriedo, P. Gomez-Sal, P. Royo, S. Martinez-Carrera and S. Garcia-Blanco, J. Organomet. Chem., 301 (1986) 79.
92 D.J. Elliot, D.G. Olah, A.N. Hughe, S.I. Khan and S. Maciaszek, Inorg. Chim. Acta, 96 (1985) L29.
93 H.H. Karsch, B. Milewski-Mahrla, J.O. Besenhard, P. Hoffmann, P. Stauffert and T.A. Albright, Inorg. Chem., 25 (1986) 3811.
94 J.T. Mague and J.P. Mitchener, Inorg. Chem., 8 (1969) 119.
95 M. Cowie and S.K. Dwight, Inorg. Chem., 19 (1980) 2500.
96 M.I.S. Kenney, J.W. Kenney III and G.A. Crosby, Organometallics, 5 (1986) 231.
97 L. Gelmini, D.W. Stephan and S.J. Loeb, Inorg. Chim. Acta, 98 (1985) L3; Organometallics, 5 (1986) 231.
98 M. Cowie and T.G. Southern, Inorg. Chem., 21 (1982) 246.
99 I.R. Mc Keer and M. Cowie, Inorg. Chim. Acta, 65 (1982) L107.
100 M. Cowie, R.S. Dickson and B.W. Hames, Organometallics, 3 (1984) 1879.
101 B.R. Sutherland and M. Cowie, Inorg. Chem., 23 (1984) 1290.
102 J.A.E. Gibson and M. Cowie, Organometallics, 3 (1984) 722.
103 J.A.E. Gibson and M. Cowie, Organometallics, 3 (1984) 984.
104 A.R. Sanger, Inorg. Chim. Acta, 99 (1985) 95.

105 J.T. Mague and S.H. Devries, Inorg. Chem., 21 (1982) 1632.
106 J.T. Mague, Inorg. Chem., 22 (1983) 45.
107 J.T. Mague, Inorg. Chem., 22 (1983) 1158.
108 S.P. Deraniyagala and K.R. Grundy, Organometallics, 4 (1985) 424.
109 M. Cowie and S.J. Loeb, Organometallics, 4 (1985) 852.
110 S.P. Deraniyagala and K.R. Grundy, Inorg. Chem., 24 (1985) 50.
111 S.P. Deraniyagala and K.R. Grundy, Inorg. Chim. Acta, 84 (1984) 205.
112 S.P. Deraniyagala and K.R. Grundy, Inorg. Chim. Acta, 101 (1985) 103.
113 S.P. Deraniyagala and K.R. Grundy, J. Chem. Soc., Dalton. Trans., (1985) 1577.
114 C.P. Kubiak and R. Eisenberg, J. Am. Chem. Soc., 102 (1980) 3637.
115 C.P. Kubiak, C. Woodcock and R. Eisenberg, Inorg. Chem., 21 (1982) 2119.
116 C. Woodcock and R. Eisenberg, Organometallics, 1 (1982) 886.
117 C. Woodcock and R. Eisenberg, Inorg. Chem., 23 (1984) 4207.
118 C. Woodcock and R. Eisenberg, Inorg. Chem., 24 (1985) 1285.
119 D.H. Berry and R. Eisenberg, J. Am. Chem. Soc., 107 (1985) 7181.
120 S.I. Hommeltoft, D.H. Berry and R. Eisenberg, J. Am. Chem. Soc., 108 (1986) 5345.
121 C. Woodcock and R. Eisenberg, Organometallics, 4 (1985) 4.
122 J.A. Ladd, M.M. Olmstead and A.L. Balch, Inorg. Chem., 23 (1984) 2318.
123 For recent leading references see for example: A.L. Balch, R.R. Guimerans and J. Linehan, Inorg. Chem., 24 (1985) 290; A.L. Balch, L.A. Fossett, R.R. Guimerans and M.M. Olmstead, Organometallics, 4 (1985) 781; A.L. Balch, L.A. Fossett, J. Linehan and M.M. Olmstead, Organometallics, 5 (1986) 691.
124 A.L. Balch, L.A. Fossett, M.M. Olmstead, D.E. Oram and P.E. Reedy, Jr., J. Am. Chem. Soc., 107 (1985) 5272.
125 A.L. Balch, J.C. Linehan and M.M. Olmstead, Inorg. Chem., 24 (1985) 3975.
126 D.R. Womack, P.D. Enlow and C. Woods, Inorg. Chem., 22 (1983) 2653.
127 P.D. Enlow and C. Woods, Inorg. Chem., 24 (1985) 1273.
128 L.A. Oro, D. Carmona, P.L. Perez, M. Esteban, A. Tiripicchio and M. Tiripicchio-Camellini, J. Chem. Soc., Dalton Trans., (1985) 973.
129 F.J. Lahoz, A. Tiripicchio, M. Tiripicchio-Camellini, L. Oro and M.T. Pinillos, J. Chem. Soc., Dalton Trans., (1985) 1487.
130 L.A. Oro, D. Carmona and J. Reyes, J. Organomet. Chem., 302 (1986) 417.
131 F. Faraone, G. Bruno, S. Lo Schiavo, G. Tresoldi and G. Bombieri, J. Chem. Soc., Dalton Trans., (1983) 433.
132 F. Faraone, G. Bruno, S.Lo. Schiavo and G. Bombieri, J. Chem. Soc., Dalton. Trans., (1984) 533.
133 F. Faraone, S. Lo Schiavo, G. Bruno and G. Bombieri, J. Chem. Soc., Chem. Commun., (1984) 6.
134 G. Bruno, S. Lo Schiavo, P. Priraino and F. Faraone, Organometallics, 4 (1985) 1098.
135 S. Lo Schiavo, G. Bruno, F. Nicolo, P. Piraino and F. Faraone, Organometallics, 4 (1985) 2091.
136 S. Lo Schiavo, G. Bruno, P. Piraino and F. Faraone, Organometallics, 5 (1986) 1400.
137 B.E. Mann, N.J. Meanwell, C.M. Spencer, B.F. Taylor and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1985) 1555.
138 K.W. Chiu, H.S. Rzepa, R.N. Sheppard, G. Wilkinson and W.K. Wong, J. Chem. Soc., Chem. Commun., (1982) 482; Polyhedron, 1 (1982) 809.
139 P.E. Kreter and D.W. Meek, Inorg. Chem., 22 (1983) 319.
140 See for example, J.S. Field, R.J. Haines, E. Meintjes, B. Sigwarth and P.H. Van Rooyen, J. Organomet. Chem., 268 (1984) C43; J. Ellermann, G. Szucsanyi, K. Geibel and E. Wilhelm, J. Organomet. Chem., 263 (1984) 297.

141 J.T. Mague and S.H. De Vries, Inorg. Chem., 21 (1982) 1632.

142 J.T. Mague, C.L. Klein, R.J. Majeste and E.D. Stevens, Organometallics, 3 (1984) 1860.

143 B.R. Sutherland and M. Cowie, Inorg. Chem., 23 (1984) 2324.

144 B.R. Sutherland and M. Cowie, Organometallics, 3 (1984) 1869.

145 B.R. Sutherland and M. Cowie, Organometallics, 4 (1985) 1637.

146 M. Cowie, G. Vasapollo, B.R. Sutherland and J.P. Ennett, Inorg. Chem., 25 (1986) 2648.

147 B.R. Sutherland and M. Cowie, Organometallics, 4 (1985) 1801.

148 B.R. Sutherland and M. Cowie, Can. J. Chem., 64 (1986) 464.

149 D.L. De Laet, D.R. Powell and C.P. Kubiak, Organometallics, 4 (1985) 954.

150 D.L. De Laet, P.E. Fanwick and C.P. Kubiak, Organometallics, 5 (1986) 1807.

151 G.G. Stanley, J.A. Osborn and P.H. Bird, Abstr. 190th Am. Chem. Soc. Nat. Meeting, Chicago, IL, Sept. 1985, Abstr. INOR 365.

152 K.R. Pörschke, Y-H Tsay and C. Krüger, Inorg. Che., 25 (1986) 2097.

153 C.T. Hunt and A.L. Balch, Inorg. Chem., 21 (1982) 1641 and references cited therein.

154 M.M. Olmstead, H. Hope, L.S. Benner and A.L. Balch, J. Am. Chem. Soc., 99 (1977) 5502.

155 C-L Lee, B.R. James, D.A. Nelson and R.T. Hallen, Organometallics, 3 (1984) 1360.

156 C.T. Hunt and A.L. Balch, Inorg. Chem., 21 (1982) 1641.

157 C.T. Hunt and A.L. Balch, Inorg. Chem., 21 (1982) 1242.

158 M.M. Olmstead, C-L Lee and A.L. Balch, Inorg. Chem., 21 (1982) 2712.

159 C.L. Lee, C.T. Hunt and A.L. Balch, Organometallics, 1 (1982) 824.

160 C.L. Lee, G. Besenyei, B.R. James, D.A. Nelson and M.A. Lilga, J. Chem. Soc., Chem. Commun., (1985) 1174.

161 G. Nemra, P. Lemoine, P. Braunstein, C. Dimeric de Bellefon and M. Riess, J. Organomet. Chem., 304 (1986) 245.

162 (a) P. Braunstein, J.M. Jud, Y. Dusausoy and J. Fisher, Organometallics, 2 (1983) 180. (b) P. Braunstein, C. de Meric de Bellefon and M. Riess, J. Organomet. Chem., 262 (1984) C14.

163 J.V. Caspar, J. Am. Chem. Soc., 107 (1985) 6718.

164 B. Kellerberger, S.J. Young and J.K. Stille, J. Am. Chem. Soc., 107 (1985) 6105.

165 M.L. Kullberg and C.P. Kubiak, Organometallics, 3 (1984) 632.

166 M.L. Kullberg, F.R. Lemke, D.R. Powell and C.P. Kubiak, Inorg. Chem., 24 (1985) 3589.

167 M.L. Kullberg and C.P. Kubiak, Inorg. Chem., 25 (1986) 26.

168 L. Manojlovic-Muir, K.W. Muir, B.R. Lloyd and R.J. Puddephatt, J. Chem. Soc., Chem. Commun., (1983) 1336.

169 L. Manojlovic-Muir, K.W. Muir, B.R. Lloyd and R.J. Puddephatt, J. Chem. Soc., Chem. Commun., (1985) 536.

170 B.R. Lloyd and R.J. Puddephatt, Inorg. Chim. Acta, 90 (1984) L77.

171 A.W. Hanson, A.J. Mac Alees and A. Taylor, J. Chem. Soc., Perkin Trans. 1, (1985) 441.

172 M.A. Khan and A.J. Mac Alees, Inorg. Chim. Acta, 104 (1985) 109.

173 A.B. Goel and S. Goel, Inorg. Chim. Acta, 98 (1985) 67.

174 S. Al-Jibori and B.L. Shaw, Inorg. Chim. Acta, 65 (1982) L123.

175 M.P. Brown, R.J. Puddephatt, M. Rashidi and K.R. Seddon, J. Chem. Soc., Dalton. Trans., (1977) 951.

176 M.P. Brown, R.J. Puddephatt, M. Rashidi and K.R. Seddon, J. Chem. Soc., Dalton. Trans., (1978) 516.

177 R.J. Puddephatt, in M.H. Chisholm (Ed.), Reactivity of Metal–Metal Bonds, ACS Symp. Ser. No. 155, American Chemical Society, Washington DC, 1981.

178 A.A. Few, L. Manojlovic-Muir and K.W. Muir, J. Chem. Soc., Chem. Commun., (1980) 624.

179 M.P. Brown, S.J. Cooper, A.A. Frew, L. Manojlovic-Muir, K.W. Muir, R.J. Puddephatt and M.A. Thompson, J. Chem. Soc., Dalton. Trans., (1982) 299.

180 H.C. Foley, R.H. Morris, T.S. Targos and G.L. Geoffrey, J. Am. Chem. Soc., 103 (1981) 7337.

181 R.H. Hill, P. De Mayo and R.J. Puddephatt, Inorg. Chem., 21 (1982) 3642.

182 J.R. Fisher, A.J. Mills, S. Summer, M.P. Brown, M.A. Thompson, R.J. Puddephatt, A.A. Frew, L. Manojlovic-Muir and K.W. Muir, Organometallics, 1 (1982) 1421.

183 A.J. McLennan and R.J. Puddephatt, Organometallics, 5 (1986) 811.

184 K.A. Azam, R.H. Hill and R.J. Puddephatt, Can. J. Chem., 62 (1984) 2029.

185 R.J. Puddephatt, K.A. Azam, R.H. Hill, M.P. Brown, C.D. Nelson, R.P. Moulding, K.R. Seddon and M.C. Grossel, J. Am. Chem. Soc., 105 (1983) 5642.

186 (a) A.A. Frew, R.H. Hill, L. Manojlovic-Muir, K.W. Muir and R.S. Puddephatt, J.Chem. Soc., Chem. Commun., (1982) 198.
(b) J.R. Fisher, A.J. Mills, S. Summer, M.P. Brown, M.A. Thompson, R.S. Puddephatt, A.A. Frew, L. Manojlovic-Muir and K.W. Muir, Organometallics, 1 (1982) 1421.

187 R.J. Puddephatt and M.A. Thomson, Inorg. Chem., 21 (1982) 725.

188 K.A. Azam and R.J. Puddephatt, Organometallics, 2 (1983) 1396.

189 A.J. Mc Lennan and R.J. Puddephatt, Organometallics, 4 (1985) 485.

190 K.A. Azam, M.P. Brown, S.J. Cooper and R.J. Puddephatt, Organometallics, 1 (1982) 1183.

191 A.J. Mc Lennan and R.J. Puddephatt, J. Chem. Soc., Chem. Commun., (1986) 422.

192 K.A. Azam, A.A. Frew, B.R. Lloyd, L. Manojlovic-Muir, K.W. Muir and R.J. Puddephatt, Organometallics, 4 (1985) 1400.

193 S. Muralidharan and J.H. Espenson, Inorg. Chem., 22 (1983) 2787.

194 S. Muralidharan, J.H. Espenson and S.A. Ross, Inorg. Chem., 25 (1986) 2557.

195 R.J. Blau and J.H. Espenson, J. Am. Chem. Soc., 108 (1986) 1962.

196 R.J. Blau, J.H. Espenson, S. Kim and R.A. Jacobson, Inorg. Chem., 25 (1986) 757.

197 S. Muralidharan and J.H. Espenson, J. Am. Chem. Soc., 106 (1984) 8104.

198 K.R. Grundy and K.N. Robertson, Organometallics, 2 (1983) 1736.

199 M.C. Grossel, M.P. Brown, C.D. Nelson, A. Yavari, E. Kallas, R.P. Moulding and K.R. Seddon, J. Organomet. Chem., 232 (1982) C13.

200 L. Manojlovic-Muir, K.W. Muir, M.C. Grossel, M.P. Brown, C.D. Nelson, A. Yavari, E. Kallas, R.P. Moulding and K.R. Seddon, J. Chem. Soc., Dalton Trans., (1986) 1955.

201 L. Manojlovic-Muir and K.W. Muir, J. Chem. Soc., Chem. Commun., (1982) 1155.

202 S.I. Al-Resayes, P.B. Hitchcock and J.F. Nixon, J. Organomet. Chem., 267 (1984) C13.

203 K.A. Azam, M.P. Brown, R.H. Hill, R.J. Puddephatt and A. Yavari, Organometallics, 3 (1984) 697.

204 M.P. Brown, A. Yavari, R.H. Hill and R.J. Puddephatt, J. Chem. Soc., Dalton Trans., (1985) 2421.

205 S.S.M. Ling, I.R. Jobe, A.J. Mc Lennan, L. Manojlovic-Muir, K.W. Muir and R.J. Puddephatt, J. Chem. Soc., Chem. Commun., (1985) 566.

206 L. Manojlovic-Muir, I.R. Jobe, S.S.M. Ling, A.J. Mc Lennan and R.J. Puddephatt, J. Chem. Soc., Chem. Commun., (1985) 1725.

207 K.A. Azam, G. Ferguson, S.S.M. Ling, M. Parvez, R.J. Puddephatt and D. Srokowski, Inorg. Chem., 24 (1985) 2799.

208 L. Manojlovic-Muir, K.W. Muir, A.A. Frew, S.S.M. Ling, M.A. Thomson and R.J. Puddephatt, Organometallics, 3 (1984) 1637.

209 S.S.M. Ling, I.R. Jobe, L. Manojlovic-Muir, K.W. Muir and R.J. Puddephatt, Organometallics, 4 (1985) 1198.
210 S.S.M. Ling, N.C. Payne and R.J. Puddephatt, Organometallics, 4 (1985) 1546.
211 L. Manojlovic-Muir, S.S.M. Ling and R.J. Puddephatt, J. Chem. Soc., Dalton Trans., (1986) 151.
212 M.C. Grossel, R.P. Moulding and K.R. Seddon, Inorg. Chim. Acta Lett., 64 (1982) L275.
213 G. Ferguson, B.R. Lloyd and R.J. Puddephatt, Organometallics, 5 (1986) 344.
214 M.P. Brown A. Yavari, L. Manojlovic-Muir, K.W. Muir, R.P. Moulding and K.R. Seddon, J. Organomet. Chem., 236 (1982) C33.
215 M.P. Brown, A. Yavari, L. Manojlovic-Muir and K.W. Muir, J. Organomet. Chem., 256 (1983) C19.
216 A.T. Hutton, B. Shabanzadeh and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1982) 1345.
217 A.T. Hutton, B. Shabanzadeh, B.L. Shaw, J. Chem. Soc., Chem. Commun., (1983) 1053.
218 F.S.M. Hassan, D.M. Mac Ewan, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1985) 1501.
219 R. Uson, J. Fornies, P. Espinet and C. Fortuno, J. Chem. Soc., Dalton Trans., (1986) 1849.
220 Y. Yamamoto, K. Takahashi and H. Yamazaki, J. Am. Chem. Soc., 108 (1986) 2458.
221 A. Camus, N. Marsich and G. Pellizer, J. Organomet. Chem., 259 (1983) 367.
222 A.M. Manotti-Lanfredi, F. Ugozzoli, A. Camus and N. Marsich, Inorg. Chim. Acta, 99 (1985) 111.
223 A.M. Manotti-Lanfredi, A. Tiripicchio, A. Camus and N. Marsich, J. Chem. Soc., Chem. Commun., (1983) 1126.
224 D.M. Ho and R. Bau, Inorg. Chem., 22 (1983) 4073.
225 M. Lusser and P. Peringer, Polyhedron, 4 (1985) 1997.
226 M. Schmidbaur, A. Wohlleben, U. Schubert, A. Frank and G. Huttner, Chem. Ber., 110 (1977) 2751.
227 C.E. Briant, K.P. Hall and D.M.P. Mingos, J. Organomet. Chem., 229 (1982) C5.
228 R. Uson, A. Laguna, M. Laguna, E. Fernandez, M.D. Villacampa, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1983) 1679.
229 R. Uson, A. Laguna, M. Laguna, B.R. Manzano, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1984) 839.
230 R. Uson, A. Laguna, M. Laguna, B.R. Manzano, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1985) 2417.
231 R. Uson, A. Laguna, M. Laguna, M.C. Gimeno, P.G. Jones, C. Fittschen and G.M. Sheldrick, J. Chem. Soc., Chem. Commun., (1986) 509.
232 S. Al-Baker, W.E. Hill and C.A. McAuliffe, J. Chem. Soc., Dalton Trans., (1985) 2655.
233 H. Schmidbaur, Th. Pollock, R. Herr, F.E. Wagner, R. Bau, J. Riede and G. Müller, Organometallics, 5 (1986) 566.
234 P. Peringer and M. Lusser, Inorg. Chem., 24 (1985) 109.
235 M. Lusser and P. Peringer, Chem. Ber., 118 (1985) 2140.
236 N.W. Alcock, M.M. Colquhoun, G. Haran, J.F. Sawyer and M.G.H. Wallbridge, J. Chem. Soc., Dalton Trans., (1982) 2243.
237 H. Schmidbaur, S. Lauteschläger and G. Müller, J. Organomet. Chem., 281 (1985) 25.
238 H. Schmidbaur, S. Lauteschläger and G. Müller, J. Organomet. Chem., 281 (1985) 33.
239 H.H. Karsch, A. Appelt and G. Müller, Angew. Chem., Int. Ed. Engl., 25 (1986) 823.
240 P.G. Pringle and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1982) 81.
241 P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1983) 889.

242 P.G. Pringle and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1982) 581.
243 C.R. Langrick, D.M. McEwan, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1983) 2487.
244 D.M. McEwan, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Chem. Commun., (182) 1240.
245 D.M. McEwan, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1982) 859.
246 C.R. Langrick, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1985) 1015.
247 G.R. Cooper, A.T. Hutton, C.R. Langrick, D.M. McEwan, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1984) 855.
248 W.S. Mc Donald, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1982) 861.
249 A.T. Hutton, C.R. Langrick, D.M. Mc Ewan, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1985) 2121.
250 D.M. McEwan, D.P. Markham, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1986) 1809.
251 P.G. Pringle and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1982) 956.
252 F.S.M. Hassan, D.P. Markham, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1985) 279.
253 C.R. Langrick, P,.G. Pringle and B.L. Shaw, Inorg. Chim. Acta, 76 (1983) L263.
254 P.G. Pringle and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1982) 1313.
255 P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1984) 849.
256 A.T. Hutton, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1985) 1677.
258 C.R. Langrick, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1984) 1233.
259 G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Chem. Commun., (1986) 13.
260 A.T. Hutton, P.G. Pringle and B.L. Shaw, Organometallics, 2 (1983) 1889.
261 J.A. Iggo, D.P. Markham, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Chem. Commun., (1985) 432.
262 A. Blagg, G.R. Cooper, P.G. Pringle, R. Robson and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1984) 933.
263 A. Blagg, A.T. Hutton, B.L. Shaw and M. Thornton-Pett, Inorg. Chim. Acta, 100 (1985) L33.
264 S.W. Carr, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Dalton Trans., (1985) 2131.
265 S.W. Carr and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1986) 1815.
266 A. Blagg, A.T. Hutton, P.G. Pringle and B.L. Shaw, Inorg. Chim. Acta, 76 (1983) L265.
267 G.R. Cooper, A.T. Hutton, D.M. McEwan, P.G. Pringle and B.L. Shaw, Inorg. Chim. Acta, 76 (1983) L267.
268 A. Blagg, A.T. Hutton, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1984) 1815.
269 P. Braunstein, J.M. Jud and J. Fischer, J. Chem. Soc., Chem. Commun., (1983) 5.
270 B.F. Hoskins, R.J. Steen and T.W. Turney, Inorg. Chim. Acta, 77 (1983) L69.
271 B.F. Hoskins, R.J. Steen and T.W. Turney, J. Chem. Soc., Dalton Trans., (1984) 1831.
272 S. Sabo, B. Chaudret and D. Gervais, J. Organomet. Chem., 258 (1983) C19.
273 S. Sabo, B. Chaudret and D. Gervais, J. Organomet. Chem., 292 (1985) 411.
274 P. Braunstein, J. Kervennal and J.L. Richert, Angew. Chem., Int. Ed. Engl., 24 (1985) 768.
275 P. Braunstein, C. de Meric de Bellefon, M. Lanfranchi and A. Tiripicchio, Organometallics, 3 (1984) 1772.

276 K.A. Mead, I. Moore, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1983) 2083.
277 M.R. Awang, J.C. Jeffery and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1983) 2091.
278 J.C. Jeffery, A.G. Orpen, F.G.A. Stone and M.J. Went, J. Chem. Soc., Dalton Trans., (1986) 173.
279 M. Green, J.A.K. Howard, A.P. James, A.N. de M. Jelfs, C.M. Nunn and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1986) 1697.
280 S. Guesmi, P.H. Dixneuf, N.J. Taylor and A.J. Catty, J. Organomet. Chem., 303 (1986) C47.
281 J.T. Mague, Organometallics, 5 (1986) 918.
282 B.D. Alexander, B.J. Johnson, S.M. Johnson, A.L. Casalnuovo and L.H. Pignolet, J. Am. Chem. Soc., 108 (1986) 4409.
283 B. Chaudret, B. Delavaux and R. Poilblanc, Nouv. J. Chim., 7 (1983) 679.
284 B. Delavaux, B. Chaudret, J. Devillers, F. Dahan, G. Commenges and R. Poilblanc, J. Am. Chem. Soc., 108 (1986) 3703.
285 B. Delavaux, B. Chaudret, F. Dahan and R. Poilblanc, Organometallics, 4 (1985) 935.
286 B. Chaudret and R. Poilblanc, unpublished results.
287 H. Benlaarab, B. Chaudret, F. Dahan and R. Poilblanc, J. Organomet. Chem., 320 (1987) C51.
288 B. Delavaux, B. Chaudret, N.J. Taylor, S. Arabi and R. Poilblanc, J. Chem. Soc., Chem. Commun., (1985) 805.
289 B. Delavaux, B. Chaudret, F. Dahan and R. Poilblanc, J. Organomet. Chem., 376 (1986) 69.
290 B. Delavaux, T. Arliguie, B. Chaudret and R. Poilblanc, Nouv. J. Chim., 10 (1986) 619.
291 B. Chaudret, F. Dahan and S. Sabo, Organometallics, 4 (1985) 1490.
292 B. Chaudret, H. Benlaarab, R. Poilblanc, S. Sabo, unpublished results.
293 J.P. Farr, M.M. Olmstead, F.E. Wood and A.L. Balch, J. Am. Chem. Soc., 105 (1983) 792 and references cited therein.
294 J.P. Farr, M.M. Olmstead, N.M. Rutherford, F.E. Wood and A.L. Balch, Organometallics, 2 (1983) 1758.
295 R. Turpin, P. Dagnac and R. Poilblanc, J. Organomet. Chem., 319 (1987) 247.
296 A.L. Balch, R.R. Guimerans, J. Linehan and F.E. Wood, Inorg. Chem., 24 (1985) 2021.
297 A.L. Balch, R.R. Guimerans, J. Linehan, M.M. Olmstead and D.E. Oram, Organometallics, 4 (1985) 1445.
298 G.B. Jacobsen and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1985) 692.
299 E.H. Wong, F.C. Bradley, L. Prasad and E.H.J. Gabe, J. Organomet. Chem., 263 (1984) 167.
300 R. Uson, J. Fornies, R. Navarro and J.I. Cebollada, J. Organomet. Chem., 304 (1986) 381.
301 R.H. Hill and R.J. Puddephatt, J. Am. Chem. Soc., 105 (1983) 5797.
302 A.T. Hutton, B. Shabanzadeh and B.L. Shaw, J. Chem. Soc. Chem. Commun., (1984) 549.
303 C.R. Langrick and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1985) 511.
304 J.A. Iggo and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1985) 1009.