Chemistry of Bis(diphenylphosphino)methane

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1 Introduction

Tertiary phosphine ligands have played a major role in modern co-ordination chemistry.[1] These ligands are easy to synthesize, and the electronic and steric properties of the ligands can be varied in a systematic way by varying the substituents on phosphorus[2] and by varying the backbone length (see below). The ligands bind strongly to many transition metals in low oxidation states, and are commonly used to stabilize organometallic and hydride derivatives of the elements, either in isolated compounds or as intermediates in homogeneous catalysis.

In forming chelate complexes, the optimum ring size for a metal having natural bond angles at 90° to one another is five and it has long been known that bis(diphenylphosphino)ethane, dppe, is an excellent chelate ligand. Bis(diphenylphosphino)methane, dppm, can chelate but the four-membered ring so formed is strained, and the ligand has a greater tendency to act either as a monodentate ligand or as a bridging bidentate ligand. The chelating tendency also decreases as the chain length increases, so that for the ligands $Ph_2P(CH_2)_nPPh_2$ the tendency to chelation is greatest for $n = 2$. A particularly good example is seen in the complexes $[RhCl(CO)\{Ph_2P(CH_2)_nPPh_2\}]$, which are dimers, (1), when $n = 1$, 3, or 4 but a monomer, (2), when $n = 2$.[3]

It is the ability of dppm to form bridged binuclear complexes such as (1)* that has led to the recent interest in this and related ligands. Because metal–phosphorus bonds are often very strong, the bridging diphosphine ligand can lock together two metal atoms in close proximity and hence promote organometallic reactions involving two metal centres. Such reactions are often invoked in heterogeneous catalysis or in homogeneous catalysis using binuclear or cluster complex catalysts, and many useful models for these reactions can be developed using these locked-in binuclear phosphine-bridged complexes. The role of the phosphine is then to prevent dissociation of dimer to monomer, to promote bridging by other groups, and to promote binuclear reactions involving formation and cleavage of metal–metal bonds. This area of endeavour will form a major part of this review. There

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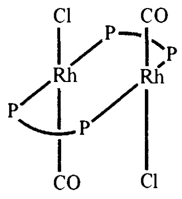
* In structural formulae, dppm and related ligands will generally be drawn without the phenyl substituents, *e.g.* $p \wedge p$ = dppm.

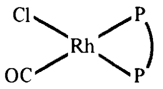
[1] C. A. McAuliffe and W. Levason, 'Phosphine, Arsine and Stibine Complexes of the Transition Elements', Elsevier, Amsterdam, 1979.

[2] C. A. Tolman, *Chem. Rev.*, 1977, 77, 313.

[3] A. R. Sanger, *J. Chem. Soc., Chem. Commun.*, 1975, 893.



(1)



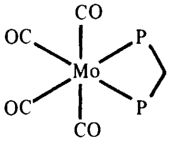
(2)

have already been a number of excellent reviews including work on dppm complexes, but none cover the range of chemistry described here.[4-8]

2 Some Related Ligands

For the sake of simplicity, this account will describe dppm complexes only, but there are many other ligands having similar properties and a brief account of a few of them is included here.

One simple change is to replace phosphorus by other Group 5 elements, arsenic and antimony. The ligands $Ph_2AsCH_2AsPh_2$ and $Ph_2SbCH_2SbPh_2$ have been studied in some depth.[9,10] For these ligands, the longer metal–ligand bonds lead to greater ring strain in chelate complexes, and there is an even stronger tendency for them to act as monodentate or bridging ligands. Thus, for example, dppm reacts with $[Mo(CO)_4(diene)]$, diene = cyclo-octa-1,5-diene or norbornadiene, to give monomeric (3) whereas bis(diphenylstibino)methane gives dimeric (4).[11,12]



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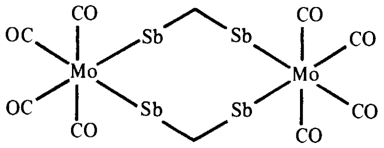

(4)

Another simple modification involves changing the substituents R in

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[4] A. L. Balch, in 'Homogeneous Catalysis with Metal Phosphine Complexes', ed. L. Pignolet, Plenum, New York, in press.

[5] M. P. Brown, J. R. Fisher, S. J. Franklin, R. J. Puddephatt, and M. A. Thomson, in 'Catalytic Aspects of Metal Phosphine Complexes', ed. E. C. Alyea and D. W. Meek, ACS Advances in Chemistry Series, 1982, **196**, 231.

[6] A. L. Balch, in ref. 5, p. 243.

[7] A. L. Balch, in 'Reactivity of Metal-Metal Bonds', ed. M. H. Chisholm, ACS Symposium Series, 1981, **155**, 167.

[8] R. J. Puddephatt, in ref. 7, p. 187.

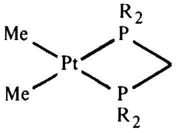
[9] R. Colton, *Aust. J. Chem.*, 1976, **29**, 1833.

[10] R. Okawara and Y. Matsumura, *Adv. Organomet. Chem.*, 1976, **14**, 187.

[11] K. K. Cheung, T. F. Lai, and K. S. Mok, *J. Chem. Soc. (A)*, 1971, 1644.

[12] T. Fukumoto, Y. Matsumura, and R. Okawara, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 711.

$R_2PCH_2PR_2$. This can easily be accomplished using the precursor $Cl_2PCH_2PCl_2$, and a number of derivatives (*e.g.* R = Me or Pr^i) have already been prepared and studied.[13,14] As well as the ability to modify electronic properties of the ligands, it is likely that steric effects will have a major influence on the bridging *vs.* chelating behaviour of these ligands. As a general rule, bulky substituents favour small-ring formation and it is therefore expected that more chelate complexes will be formed when R = Bu^t, and less when R = Me, compared to the case when R = Ph.[15] There is little evidence yet to substantiate this prediction, but it seems that for complexes $[PtMe_2(R_2PCH_2PR_2)]$ the monomeric form (5) is the more stable for R = Ph and the dimeric form (6) for R = Me.[16]



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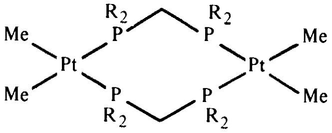


(6)

Steric effects also influence reactivity to a major extent. For example, (6), R = Me, is reactive in oxidative addition with reagents like MeI or I_2 but, when R = Ph, MeI fails to react and I_2 cleaves a methylplatinum bond.[16] Molecular models demonstrate that, in the dppm derivative, access of these reagents to the metal centre is blocked by the phenyl substituents in (6), R = Ph.

Substitution at the methylene group appears to have less effect, and the ligands dppm, $Ph_2PCHMePPh_2$, and $Ph_2PCMe_2PPh_2$ appear to behave in very similar ways, for example in gold complexes.[17]

Other ligands showing similar properties are those containing POP, PSP, or PN(R)P groupings. Of the POP ligands, $(EtO)_2POP(OEt)_2$,[18-20] $(CF_3)_2POP(CF_3)_2$,[21-23] and $(HO)_2POP(OH)_2$[24] are perhaps the most significant and they do not act as chelate ligands. This is apparently because the open POP angle of 120—150° does not allow the ligand conformation needed for chelation. When the substituents are small it is possible for four such

[13] Z. S. Novikova, A. A. Prishcenko, and I. F. Lutsenko, *J. Gen. Chem. USSR*, 1977, **47**, 707.

[14] H. H. Karsch, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 311.

[15] B. L. Shaw, *J. Organomet. Chem.*, 1980, **200**, 307.

[16] R. J. Puddephatt, M. A. Thomson, Lj. Manojlović-Muir, K. W. Muir, A. A. Frew, and M. P. Brown, *J. Chem. Soc., Chem. Commun.*, 1981, 805; S. M. Ling and R. J. Puddephatt, *Inorg. Chim. Acta Lett.*, in press.

[17] H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 728.

[18] R. J. Haines, A. Pidcock, and M. Safari, *J. Chem. Soc., Dalton Trans.*, 1977, 830.

[19] F. A. Cotton, R. J. Haines, B. E. Hanson, and J. C. Sekutowski, *Inorg. Chem.*, 1978, **17**, 2010.

[20] A. L. du Preez, I. L. Marais, R. J. Haines, A. Pidcock, and M. Safari, *J. Chem. Soc., Dalton Trans.*, 1981, 1918.

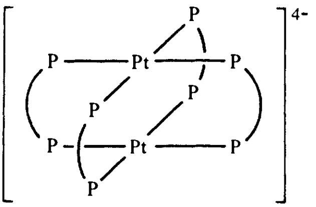
[21] A. B. Burg and R. A. Sinclair, *J. Am. Chem. Soc.*, 1966, **88**, 5354.

[22] R. A. Sinclair and A. B. Burg, *Inorg. Chem.*, 1968, **7**, 2160.

[23] H. Einspahr and J. Donohue, *Inorg. Chem.*, 1974, **13**, 1839.

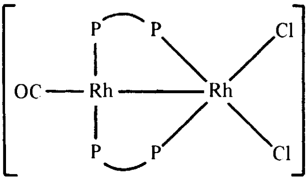
[24] M. A. F. D. R. Pinto, P. J. Sadler, S. Neilde, M. R. Sanderson, A. Subbiah, and R. Kuroda, *J. Chem. Soc., Chem. Commun.*, 1980, 13.

ligands to bridge between two metal atoms, as in the fluorescent platinum(II) derivative $[Pt_2\{\mu\text{-}(HO)(O)POP(O)(OH)\}_4]^{4-}$ of structure (7).[1]



(7)

The ligands $F_2PN(R)PF_2$, R = Me or Ph, have been studied extensively,[25] and can act as chelate, monodentate, or bridging ligands. Again the small substituents allow three or four bridging ligands as illustrated by the derivative of the unknown $[Mo_2(CO)_{11}]$, $[Mo_2(CO)_2(\mu\text{-}CO)(\mu\text{-}F_2PNPhPF_2)_3]$,[26] and the multiply bonded molybdenum derivative $[Mo_2Cl_2(\mu\text{-}F_2PNMePF_2)_4]$.[27] The ligand $(PhO)_2PNEtP(OPh)_2$ is unusual in forming a bridging complex with *trans* stereochemistry at one metal but *cis* stereochemistry at the other, in $[Rh_2Cl_2(CO)\{\mu\text{-}(PhO)_2PNEtP(OPh)_2\}_2]$ of structure (8),[28] as well as many other bridged complexes.[29]



(8)

The above discussion illustrates how the ligands X_2PYPX_2 can be modified considerably in both electronic and steric properties by systematically changing the substituents X and Y. The following discussion of dppm complexes, although substantial in itself, forms only a small part of this general field of phosphine bridged binuclear complexes.

Finally, we note that an even greater number of unsymmetrical ligands can be envisaged, though this field is in its infancy. One good example is 2-diphenyl-

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[25] R. B. King, *Acc. Chem. Res.*, 1980, **13**, 243.

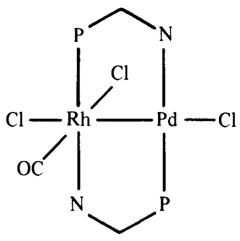
[26] M. G. Newton, R. B. King, T. W. Lee, L. Norskov-Lauritzen, and V. Kumar, *J. Chem. Soc., Chem. Commun.*, 1982, 201.

[27] F. A. Cotton, W. H. Ilsley, and W. Kaim, *J. Am. Chem. Soc.*, 1980, **102**, 1918.

[28] R. J. Haines, E. Meintjies, and M. Laing, *Inorg. Chim. Acta*, 1979, **36**, L403.

[29] G. de Leeuw, J. S. Field, R. J. Haines, B. McCulloch, E. Meintjes, C. Monberg, K. G. Moodley, G. M. Oliver, C. N. Sampson, and N. D. Steen, *J. Organomet. Chem.*, 1982, **228**, C66.

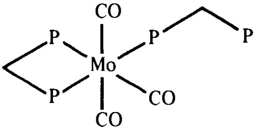
phosphinopyridine, which is particularly useful for bridging between unlike metal atoms, as in complex (9).[30]



(9)

3 Complexes with Monodentate dppm

Complexes with monodentate dppm are formed with metal halides, metal carbonyls, and several organometallic derivatives. Metal halide or pseudohalide derivatives include *trans*-$[Ni(NCS)_2(\eta^1\text{-dppm})_2]$ and the less stable $[NiCl_2(\eta^1\text{-dppm})_2]$, and the cations $[MOCl_2(\eta^1\text{-dppm})_2]^+$, M = Mo or W.[31–33] Metal carbonyl derivatives include $[Cr(CO)_5(\eta^1\text{-dppm})]$[34] and $[Fe(CO)_4(\eta^1\text{-dppm})]$,[35] as well as more complex examples containing both monodentate and bidentate dppm such as *mer* and *fac* isomers of $[Mo(CO)_3(\eta^2\text{-dppm})(\eta^1\text{-dppm})]$,[36] (10) and (11), identified by the characteristic ^{31}P n.m.r. spectra.



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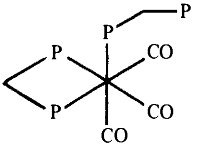


(11)

The complexes with monodentate dppm,[37,38] $[Ru(TPP)(\eta^1\text{-dppm})_2]$ (TPP = $[\text{tetraphenylporphyrin}]^{2-}$) and *trans*-$[Pd(Bu^tNC)_2(\eta^1\text{-dppm})_2]^{2+}$, (12), and with chelating and monodentate dppm,[39] $[MoCl_2(CO)_2(\eta^2\text{-dppm})(\eta^1\text{-dppm})]$, or bridging and monodentate dppm,[40] $[Pt_2H(\mu\text{-dppm})_2(\eta^1\text{-dppm})]^+$,

[30] J. P. Farr, M. M. Olmstead, and A. L. Balch, *J. Am. Chem. Soc.*, 1980, **102**, 6654.

[31] C. Ercolani, J. V. Quagliano, and L. M. Vallarino, *Inorg. Chim. Acta*, 1973, **7**, 413.

[32] K. K. Chow and C. A. McAuliffe, *Inorg. Chim. Acta*, 1974, **10**, 195.

[33] W. Levason, C. A. McAuliffe, and F. P. McCullough, *Inorg. Chem.*, 1977, **16**, 2911.

[34] J. A. Connor, J. P. Day, E. M. Jones, and G. K. McEwen, *J. Chem. Soc., Dalton Trans.*, 1973, 347.

[35] P. A. Wegner, L. E. Evans, and J. Haddock, *Inorg. Chem.*, 1975, **14**, 192.

[36] E. E. Isaacs and W. A. G. Graham, *Inorg. Chem.*, 1975, **14**, 2560.

[37] R. G. Ball, G. Domazetis, D. Dolphin, B. R. James, and J. Trotter, *Inorg. Chem.*, 1981, **20**, 1556.

[38] M. M. Olmstead, C. L. Lee, and A. L. Balch, *Inorg. Chem.*, 1982, **21**, 2712.

[39] M. G. B. Drew, A. P. Wolters, and I. B. Thomkins, *J. Chem. Soc., Dalton Trans.*, 1977, 974.

[40] Lj. Manojlović-Muir and K. W. Muir, *J. Organomet. Chem.*, 1981, **219**, 129.

(13), have been characterized crystallographically and two structures are shown in Figure 1.

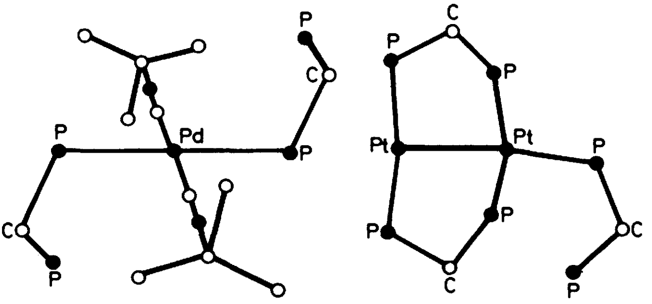
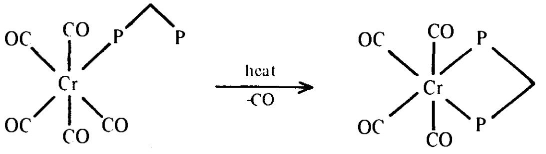


Figure 1 *Structures of trans*-$[Pd(Bu^tNC)_2(\eta^1\text{-dppm})_2]^{2+}$ *and* $[Pt_2H(\mu\text{-dppm})_2(\eta^1\text{-dppm})]^+$

Complexes (12), (13), and *trans*-$[Pt(C{\equiv}CPh)_2(\eta^1\text{-dppm})_2]$, (14), are fluxional on the n.m.r. time scale at ambient temperature,[41,42] probably as the result of an intramolecular displacement of co-ordinated phosphorus by free phosphorus in the η^1-dppm ligands. In complex (13) the μ-dppm ligands are not involved in the fluxional process, and the exchange rate is, as expected, greater for the palladium(II) derivative, (12), than for the platinum(II) derivatives (13) and (14).[38,41,42] The structures (12) and (13) (Figure 1) show how the free phosphorus atom of the η^1-dppm ligands may be expected to displace the co-ordinated phosphorus by intramolecular co-ordination.

The free phosphorus atom in η^1-dppm complexes may be oxidized to the phosphine oxide,[42] quaternized by reaction with MeI or Me_3O^+, or may be used as a ligand to the same or a different metal atom. Two examples to illustrate the latter reactions are given in equations 1 and 2.[34,43]



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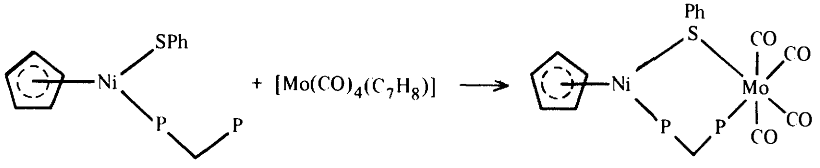

(2)

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[41] M. P. Brown, J. R. Fisher, R. H. Hill, R. J. Puddephatt, and K. R. Seddon, *Inorg. Chem.*, 1981, **20**, 3516.

[42] P. G. Pringle and B. L. Shaw, *J. Chem Soc., Chem. Commun.*, 1982, 581.

[43] F. Sato, T. Uemura, and M. Sato, *J. Organomet. Chem.*, 1973, **56**, C27.

The interconversion between monodentate and chelating dppm is also illustrated by the reaction.[31,32]

$$[NiCl_2(\eta^2\text{-dppm})] + dppm \rightleftharpoons [NiCl_2(\eta^1\text{-dppm})_2]$$

There is some evidence that steric effects may limit the ability of dppm to bridge in some cases. Thus, $[Fe(CO)_2(\eta^1\text{-}Ph_2P(CH_2)_nPPh_2)(\eta\text{-}C_5H_5)]^+$ is a good ligand for cobalt(II) through the free phosphine when $n = 2$ or 3, but not for $n = 1$.[44]

4 Complexes with Chelate dppm

When dppm acts as a chelate ligand the MP_2C skeleton is essentially planar, as seen for example in *trans*-$[RhHCl(dppm)_2]^+$, (15), whose structure is given in Figure 2.[45] The strain in these chelate complexes is seen by the low PMP angles of 67—74° and the PCP angles of about 95°, compared to normal bond angles of 90° and 109° respectively. Even greater strain would be expected for metal ions preferring tetrahedral or trigonal co-ordination geometries, and no such complexes have been characterized unambiguously, although there is some evidence for monomeric pseudotetrahedral $[CoCl_2(dppm)]$ in solution.[46] In $[Fe(CO)_3(dppm)]$ the chelating dppm spans an axial and an equatorial site, with a natural bond angle of 90°, rather than two equatorial sites.[47]

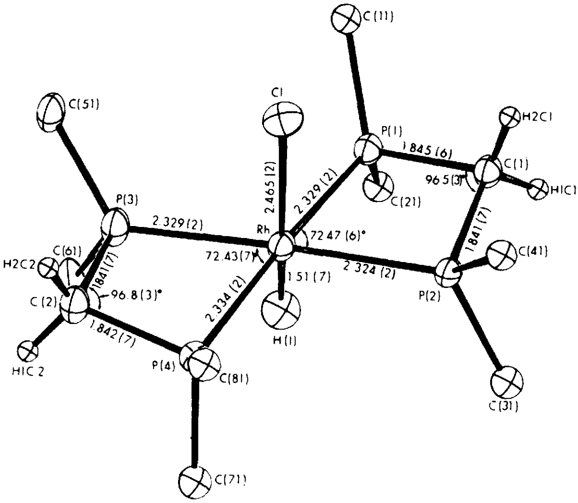

Figure 2 *The structure of trans*-$[RhHCl(dppm)_2]^+$

There are a great number of complexes with chelating dppm, some of which have already been mentioned, and no attempt at comprehensive coverage will be

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[44] M. L. Brown, J. L. Cramer, J. A. Ferguson, T. J. Meyer, and N. Winterton, *J. Am. Chem. Soc.*, 1972, **94**, 8707.

[45] M. Cowie and S. K. Dwight, *Inorg. Chem.*, 1979, **18**, 1209.

[46] K. K. Chow and C. A. McAuliffe, *Inorg. Chim. Acta*, 1975, **14**, 121.

[47] F. A. Cotton, K. I. Hardcastle, and G. A. Rusholme, *J. Coord. Chem.*, 1973, **2**, 217.

made. The series of Group 6 carbonyl derivatives is noteworthy in its completeness; for example, *cis*-[Mo(CO)$_4$(dppm)], *cis*-[Mo(CO)$_2$(dppm)$_2$] and [Mo(dppm)$_3$] are all known.[11,48–50] Several platinum complexes [PtX$_2$(dppm)]; X = Cl, Br, I, Me, Ph, 4-tolyl, as well as [Pt(dppm)$_2$]$^{2+}$, and the unsymmetrical complexes [PtClR(dppm)], R = Me, 4-tolyl, are also known.[51–56] The latter complexes isomerize in solution to the ionic binuclear derivatives [Pt$_2$R$_2$(μ-Cl)(μ-dppm)$_2$]Cl.[53,56] It is not clear what factors influence the relative stabilities of the monomeric and dimeric isomers, but it may be relevant that complexes [PtClRL$_2$] have a strong preference for the *trans* stereochemistry, which is possible for the dimer but not for monomeric [PtClR(dppm)].

Steric effects also are likely to promote chelation. For example with dppm: Rh ratio of 2:1 in (15) and in [Rh(dppm)$_2$]$^+$, dppm acts as a chelate whereas with dppm: Rh ratio of 1:1 bridging dppm is observed (see later).[57] It is likely that the Rh$_2$(μ-dppm)$_4$ skeleton would be very congested and hence is not formed, whereas the Rh$_2$(μ-dppm)$_2$ skeleton is not too crowded.

5 Complexes with Bridging dppm

A. Compounds without Metal–Metal Bonds or other Bridging Groups.—In this class there are compounds with one, two, or three μ-dppm ligands. A good example of a complex with one μ-dppm ligand is [(CO)$_4$FePPh$_2$CH$_2$PPh$_2$Fe(CO)$_4$], (16). On photolysis a carbonyl group is lost and a metal–metal bonded complex [Fe$_2$(CO)$_6$(μ-CO)(μ-dppm)], (17), is formed. It is likely that this reaction is facilitated by the proximity of the two metal centres in (16).[35,58] Another interesting case is the ruthenium(II) derivative [{RuCl(bipy)$_2$}$_2$(μ-dppm)]$^{2+}$, which can be oxidized to the Ru$^{\text{II}}$,Ru$^{\text{III}}$ and then the Ru$^{\text{III}}$,Ru$^{\text{III}}$ analogue without disruption of the μ-dppm ligand.[59]

Complexes with two *trans* μ-dppm ligands are most common in rhodium(I) chemistry and have been thoroughly investigated.[60–67] A typical structure of

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[48] A. M. Bond, R. Colton, and J. J. Jackowski, *Inorg. Chem.*, 1975, **14**, 274.

[49] M. Hidai, K. Tominari, and Y. Uchida, *J. Am. Chem. Soc.*, 1972, **94**, 110.

[50] M. W. Anker, J. Chatt, G. J. Leigh, and A. G. Wedd, *J. Chem. Soc., Dalton Trans.*, 1975, 2639.

[51] M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1977, 951.

[52] T. G. Appleton, M. A. Bennett, and I. B. Tomkins, *J. Chem. Soc., Dalton Trans.*, 1976, 439.

[53] S. J. Cooper, M. P. Brown, and R. J. Puddephatt, *Inorg. Chem.*, 1981, **20**, 1374.

[54] P. S. Braterman, R. J. Cross, Lj. Manojlović-Muir, K. W. Muir, and G. B. Young, *J. Organomet. Chem.*, 1975, **84**, C40.

[55] R. J. Puddephatt and M. A. Thomson, *J. Organomet. Chem.*, 1982, **238**, 231.

[56] G. K. Anderson, H. C. Clark, and J. A. Davies, *J. Organomet. Chem.*, 1981, **210**, 135.

[57] B. R. James and D. Mahajan, *Can. J. Chem.*, 1979, **57**, 180.

[58] F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, 1974, **96**, 4422.

[59] B. P. Sullivan and T. J. Meyer, *Inorg. Chem.*, 1980, **19**, 752.

[60] J. T. Mague, *Inorg. Chem.*, 1969, **8**, 1975.

[61] M. Cowie and S. K. Dwight, *Inorg. Chem.*, 1980, **19**, 2500.

[62] J. T. Mague and J. P. Mitchener, *Inorg. Chem.*, 1969, **8**, 119.

[63] A. L. Balch, *J. Am. Chem. Soc.*, 1976, **98**, 8049.

[64] A. L. Balch and B. Tulyathan, *Inorg. Chem.*, 1977, **16**, 2840.

[65] A. L. Balch, J. W. Labadie, and G. Delker, *Inorg. Chem.*, 1979, **18**, 1224.

[66] J. T. Mague and S. H. DeVries, *Inorg. Chem.*, 1980, **19**, 3743.

[67] A. R. Sanger, *J. Chem. Soc., Dalton Trans.*, 1981, 228, and references therein.

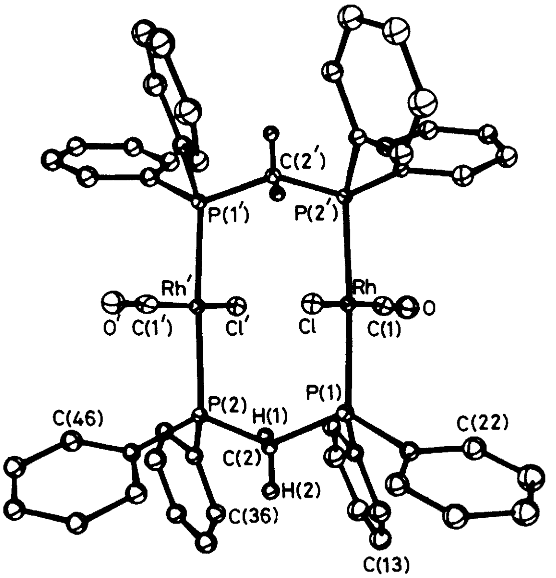
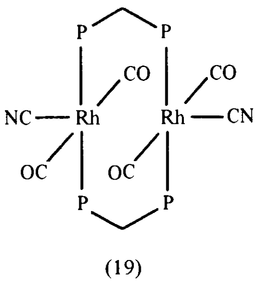


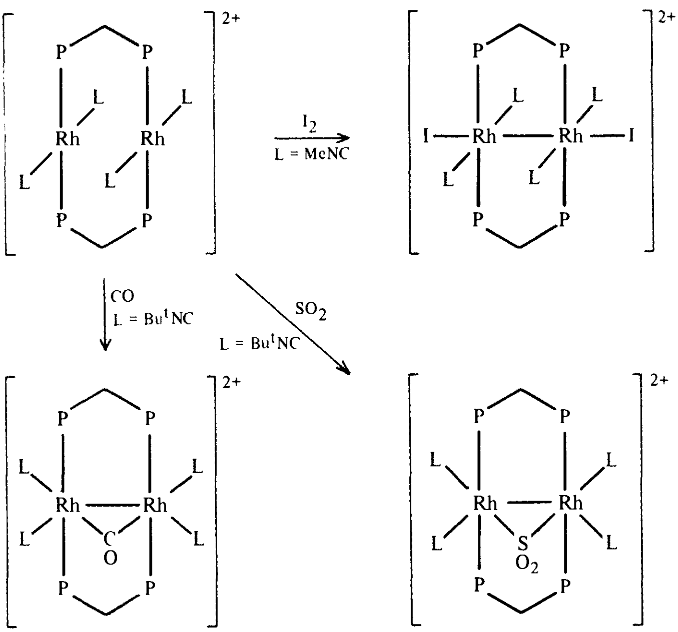
Figure 3 *The structure of the face-to-face dimer* $[Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2]$

$[Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2]$, (18), is shown in Figure 3. Similar complexes with chloro and carbonyl ligands replaced by ligands such as isocyanides, giving for example $[Rh_2(MeNC)_4(\mu\text{-dppm})_2]^{2+}$, are readily prepared.[63,66] These compounds are usually described as face-to-face complexes for obvious reasons (Figure 3), and there is evidence of weak metal–metal interactions, although no formal metal–metal bond is present.[63–65] The complexes will undergo binuclear oxidative addition reactions and will add the unsaturated molecules CO and SO_2 between the metal centres, in each case producing rhodium–rhodium bonded complexes (Scheme 1).[63–66]

A further development is the synthesis of face-to-face complexes with square pyramidal rhodium(I) centres as in complex (19).[67]

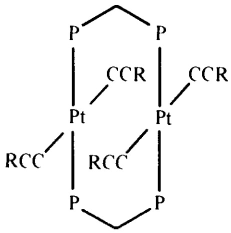


(19)



Scheme 1

The face-to-face dimers are much more elusive with other metals, and the first platinum(II) complexes of formula $[Pt_2(C{\equiv}CR)_4(\mu\text{-dppm})_2]$, R = Me, CF_3, Ph, or 4-tolyl, (20), were prepared only recently.[42,55]



(20)

Complexes $[M_2Cl_4(\mu\text{-dppm})_2]$, M = Pd or Pt, may be generated but they rapidly rearrange to the monomeric forms $[MCl_2(dppm)]$.[68,69] The complex $[Pt_2Cl_2Me_2(\mu\text{-dppm})_2]$[53] rearranges rapidly to the ionic form $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2]Cl$. Other face-to-face compounds have been proposed as reaction

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[68] C. T. Hunt and A. L. Balch, *Inorg. Chem.*, 1981, **20**, 2267.

[69] R. J. Puddephatt, unpublished work.

intermediates but have not been directly characterized.[70-72] The factors affecting the relative stabilities of these isomers are not understood.

Complexes with two *cis* bridging dppm ligands are much less common, and are limited to the dimethylplatinum(II) derivative (6)[16] and the π-allylrhodium(I) complex $[Rh_2(\eta^3\text{-}CH_2CMeCH_2)_2(\mu\text{-dppm})_2]$.[73] The former complex has a twist saddle conformation (Figure 4), and undergoes two fluxional processes involving a twisting motion and a saddle inversion process.[16]

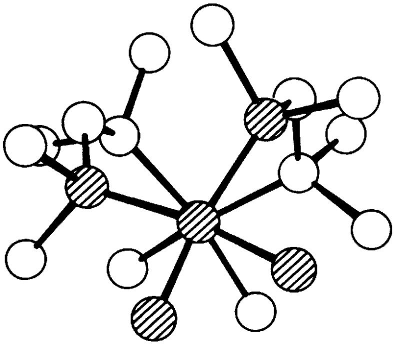
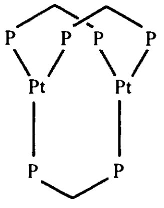


Figure 4 *The structure of* $[Pt_2Me_4(\mu\text{-dppm})_2]$, *showing a view along the* Pt—Pt *axis*

The only compounds with three μ-dppm ligands are $[M_2(\mu\text{-dppm})_3]$, M = Pd or Pt.[74,75] There is evidence from electronic spectroscopy of weak metal–metal interaction and the platinum derivative has been shown to have the 'manxane' structure (21), each platinum having trigonal planar stereochemistry.



(21)

These compounds have a very rich chemistry as shown by the reactions of Scheme 2.[4,68,71,75,76]

It can be seen that oxidative addition can give either oxidation of each metal

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[70] C. L. Lee, C. T. Hunt, and A. L. Balch, *Organometallics*, 1982, **1**, 824.

[71] A. L. Balch, C. T. Hunt, C. L. Lee, M. M. Olmstead, and J. P. Farr, *J. Am. Chem. Soc.*, 1981, **103**, 3764.

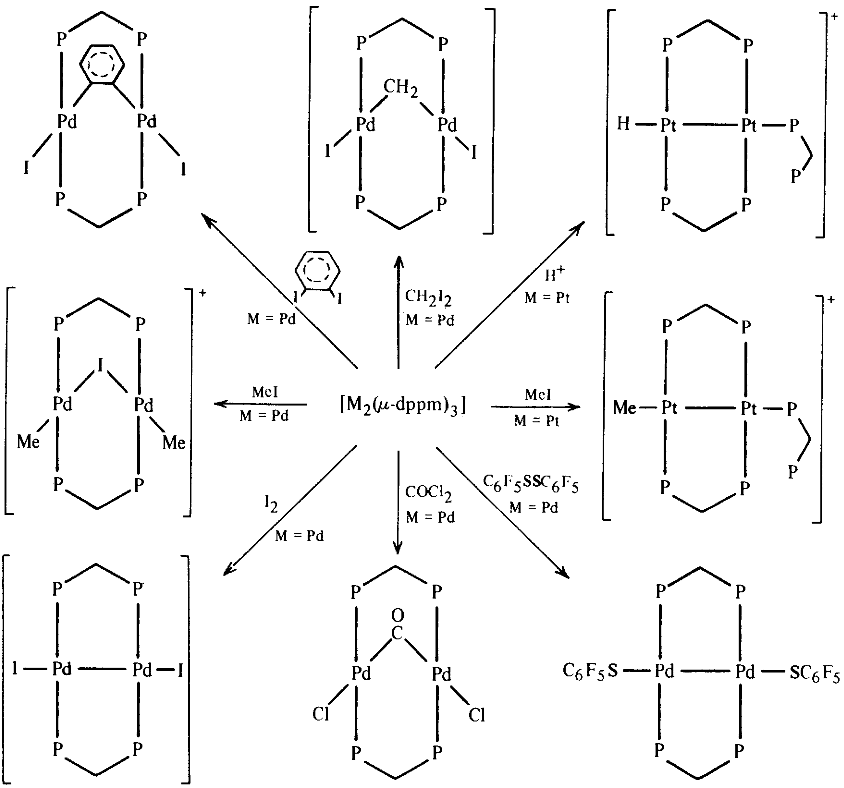
[72] R. H. Hill and R. J. Puddephatt, *Inorg. Chim. Acta*, 1981, **54**, L277.

[73] M. D. Fryzuk, *Inorg. Chim. Acta*, 1981, **54**, L265.

[74] E. W. Stern and P. K. Maples, *J. Catal.*, 1972, **27**, 120.

[75] M. C. Grossel, M. P. Brown, C. D. Nelson, A. Yavari, E. Kallas, R. P. Moulding, and K. R. Seddon, *J. Organomet. Chem.*, 1982, **232**, C13; Lj. Manojlović-Muir, personal communication.

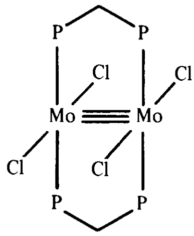
[76] K. A. Azam, R. J. Puddephatt, M. P. Brown, and A. Yavari, *J. Organomet. Chem.*, 1982, **234**, C31.



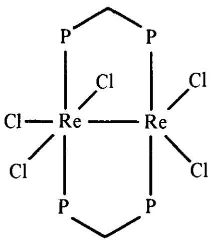
Scheme 2

by one unit with formation of a metal–metal bond or oxidation of each metal by two units, with partial (M = Pt) or complete (M = Pd) dissociation of one dppm ligand.

B. Compounds with Metal–Metal Bonds but no other Bridging Groups.—There are a number of compounds with multiple metal–metal bonds in this class, derived from the quadruply bonded $[Mo_2Cl_8]^{4-}$ and $[Re_2Cl_8]^{2-}$. The structures of the quadruply bonded $[Mo_2Cl_4(\mu\text{-dppm})_2]$, (22), and the paramagnetic



(22)



(23)

$[Re_2Cl_5(\mu\text{-dppm})_2]$, (23), have been determined crystallographically, and the complexes $[Re_2Cl_6(\mu\text{-dppm})_2]$ and $[Re_2Cl_4(\mu\text{-dppm})_2]$ are also known,[77–80] but few reactions of the products have been studied.

The best studied compounds of this kind are the singly metal–metal bonded derivatives $[MM^1X_2(\mu\text{-dppm})_2]$, $M,M^1 = Pd,Pt$, of which the mixed Pd–Pt derivative was prepared very recently.[81–86] A typical structure of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ is given in Figure 5.[84] These complexes display high

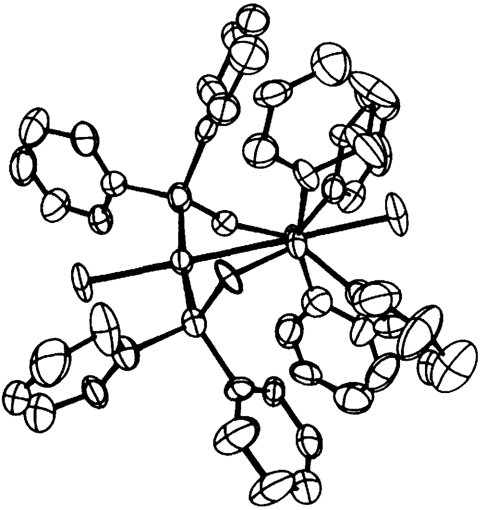


Figure 5 *The structure of* $[Pt_2Cl_2(\mu\text{-dppm})_2]$

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[77] S. A. Best, T. J. Smith, and R. A. Walton, *Inorg. Chem.*, 1978, **17**, 99.

[78] E. H. Abbott, K. S. Bose, F. A. Cotton, W. T. Hall, and J. C. Sekutowski, *Inorg. Chem.*, 1978, **17**, 3240.

[79] J. R. Ebner, D. R. Tyler, and R. A. Walton, *Inorg. Chem.*, 1976, **15**, 833.

[80] F. A. Cotton, L. W. Shive, and B. R. Stults, *Inorg. Chem.*, 1976, **15**, 2239.

[81] R. G. Holloway, B. R. Penfold, R. Colton, and M. J. McCormick, *J. Chem. Soc., Chem. Commun.*, 1976, 485.

[82] M. P. Brown, R. J. Puddephatt, and M. Rashidi, *Inorg. Chim. Acta*, 1976, **19**, L33.

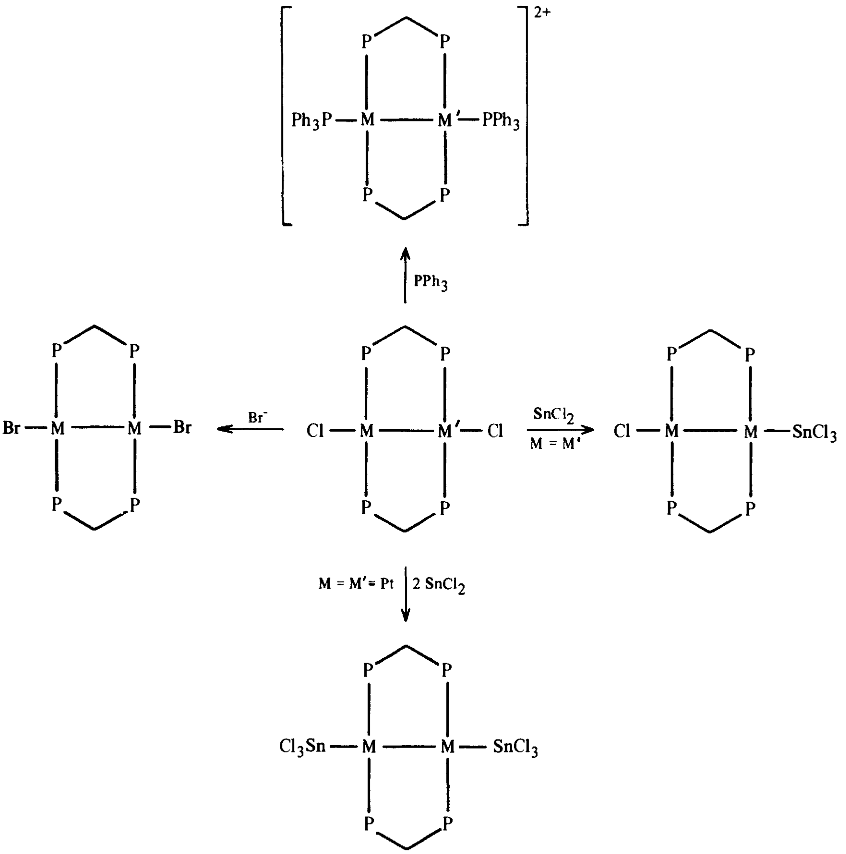
[83] M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1977, 951.

[84] Lj. Manojlović-Muir, K. W. Muir, and T. Solomun, *Actacrystallogr.*, 1979, **B35**, 1237.

[85] R. Colton, M. J. McCormick, and C. D. Pannan, *Aust. J. Chem.*, 1978, **31**, 1425.

[86] P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 81.

reactivity either by displacement of terminal chloride ligands by anionic or neutral ligands or insertion of $SnCl_2$ into the metal–chloride bonds (Scheme 3).[83,86–89]



Scheme 3

However, the addition of small molecules to the metal–metal bond is of greatest interest. Some examples of these reactions are shown in Scheme 4.[85,86,90–100] In most of these reactions the metal–metal bond is acting as a

[87] M. M. Olmstead, L. S. Benner, H. Hope, and A. L. Balch, *Inorg. Chim. Acta*, 1979, **32**, 193.

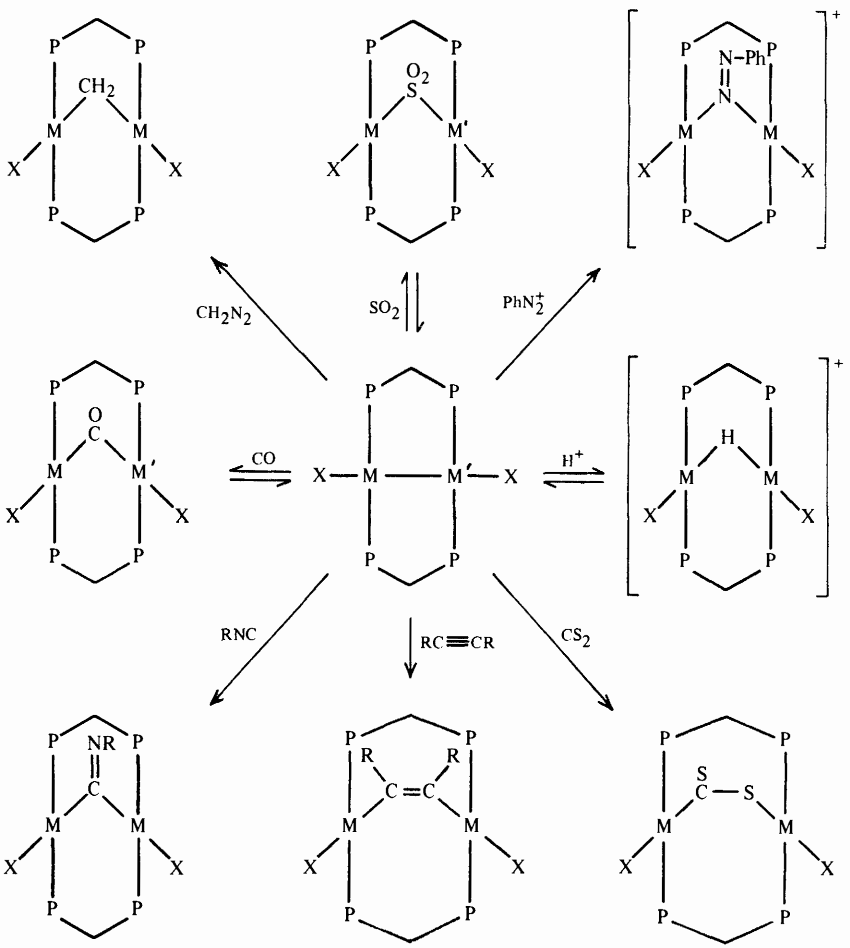
[88] M. P. Brown, S. J. Franklin, R. J. Puddephatt, M. A. Thomson, and K. R. Seddon, *J. Organomet. Chem.*, 1979, **178**, 281.

[89] M. C. Grossel, R. P. Moulding, and K. R. Seddon, *Inorg. Chim. Acta Lett.*, 1982, **64**, L275.

[90] M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1978, 1540.

[91] M. P. Brown, A. N. Keith, Lj. Manojlović-Muir, K. W. Muir, R. J. Puddephatt, and K. R. Seddon, *Inorg. Chim. Acta*, 1979, **34**, L223.

[92] M. P. Brown, J. R. Fisher, R. J. Puddephatt, and K. R. Seddon, *Inorg. Chem.*, 1979, **18**, 2808.



Scheme 4

nucleophile, as is most easily seen in the reactions with cationic reagents[95,99] H^+ and PhN_2^+. It can be seen that single atom bridges (*e.g.* CH_2, CO, SO_2, or S)[85,86,90-95] or double atom bridges (CS_2 or RC≡CR)[86,96-98,100] are

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[93] M. M. Olmstead, H. Hope, L. S. Benner, and A. L. Balch, *J. Am. Chem. Soc.*, 1977, **99**, 5502.
[94] L. S. Benner, M. M. Olmstead, H. Hope, and A. L. Balch, *J. Organomet. Chem.*, 1978, **153**, C31.
[95] A. D. Rattray and D. Sutton, *Inorg. Chim. Acta*, 1978, **27**, L85.
[96] A. L. Balch, C. L. Lee, C. H. Lindsay, and M. M. Olmstead, *J. Organomet. Chem.*, 1979, **177**, C22.
[97] C. L. Lee, C. T. Hunt, and A. L. Balch, *Inorg. Chem.*, 1981, **20**, 2498.
[98] R. J. Puddephatt and M. A. Thomson, *Inorg. Chem.*, 1982, **21**, 725.
[99] M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1978, 516.
[100] T. S. Cameron, P. A. Gardner, and K. R. Grundy, *J. Organomet. Chem.*, 1981, **212**, C19.

possible. The alkynes must have electronegative substituents (R = CF_3 or CO_2Me) in order to undergo reaction. Several of the reactions are reversible (CO, SO_2, and H^+ addition),[86,93,99] and when M = Pd, M^1 = Pt, the reversible addition of CO is catalysed by SO_2.[86]

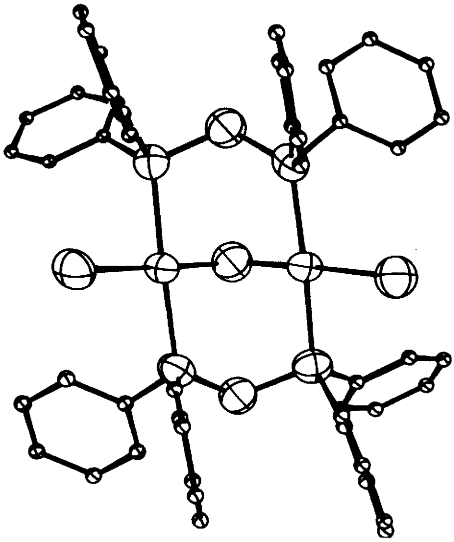
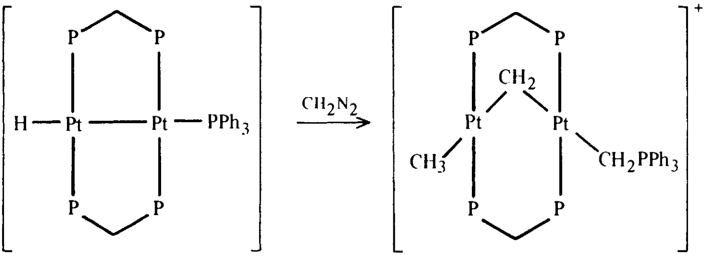


Figure 6 *The structure of* $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$

Of particular interest in these reactions is the formation of unique bonding types. For example, these constitute almost unique examples of CO and CH_2 bridging between two metal atoms in which there is no metal–metal bond. The absence of such metal–metal bonding has been established in several cases by *X*-ray structure determinations,[85,91,93,96,101] and an example is shown in Figure 6, $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$.[101] The Pt–Pt distance of 3.16 Å and the ∠(PtCPt) of 102° provide strong evidence that there is no Pt–Pt bond.

In some cases, insertion may occur into both metal–metal and metal–ligand bonds, and an example is given in equation 3.[102]



(3)

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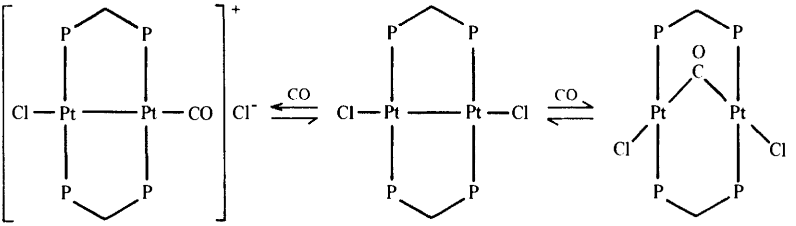
[101] Lj. Manojlović-Muir, personal communication.

[102] K. A. Azam, A. A. Frew, B. R. Lloyd, Lj. Manojlović-Muir, K. W. Muir, and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1982, 614.

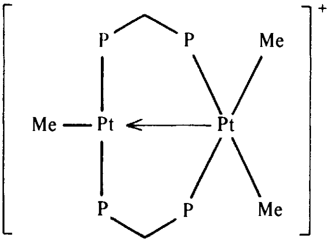
In other cases a ligand may add to a metal–metal bond or displace a terminal ligand (equation 4).[90,91,103]



(4)

Finally, further insertion reactions can lead to catalytic trimerization of alkynes using $[Pd_2Cl_2(\mu\text{-dppm})_2]$.[97]

The bridging dppm ligands are able to stabilize a donor–acceptor metal–metal bond in one case. The complex cation $[Pt_2Me_3(\mu\text{-dppm})_2]^+$ has structure (24),



(24)

with the electron-rich $PtMe_2$ centre donating electrons from the filled $5d_z{}^2$ orbital to the monomethylplatinum centre.[104] This complex is also unusual in having *cis* stereochemistry at one metal centre but *trans* stereochemistry at the other.

From the above account it should be apparent that the μ-dppm ligands can promote new chemistry by holding two metal atoms in close proximity so that they can be bridged by other more weakly bonded groups even when there is no (or only very weak) metal–metal bonding.

C. Compounds with other Bridging Groups.—There is no clearcut distinction between this section and the last, which contained many examples of compounds with bridging groups (*e.g.* Scheme 4), but the emphasis here is different. Many of these complexes have been termed 'A-frame' complexes, and examples have been prepared according to equation 5.[105–108]

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[103] Lj. Manojlović-Muir, K. W. Muir, and T. Solomun, *J. Organomet. Chem.*, 1979, **179**, 479.

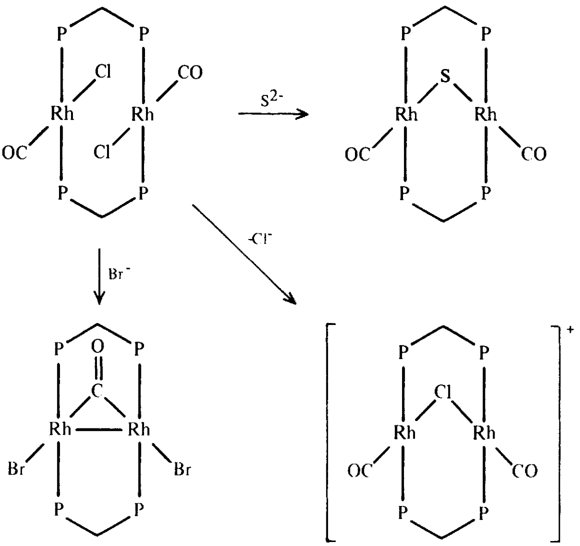
[104] M. P. Brown, S. J. Cooper, A. A. Frew, Lj. Manojlović-Muir, K. W. Kuir, R. J. Puddephatt, K. R. Seddon, and M. A. Thomson, *Inorg. Chem.*, 1981, **20**, 1500.

[105] C. P. Kubiak and R. Eisenberg, *J. Am. Chem. Soc.*, 1977, **99**, 6129.

[106] M. Cowie and S. K. Dwight, *Inorg. Chem.*, 1979, **18**, 2700.

[107] C. P. Kubiak and R. Eisenberg, *Inorg. Chem.*, 1980, **19**, 2726.

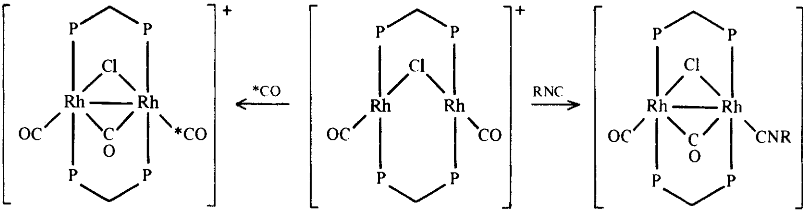
[108] M. Cowie and S. K. Dwight, *Inorg. Chem.*, 1980, **19**, 2508.



(5)

As can be seen from equation 5 and Scheme 4, the A-frame complexes may or may not have a metal–metal bond as well as a bridging ligand. The presence or absence of a metal–metal bond is predictable in terms of the normal electron-counting procedures, and a detailed molecular orbital treatment has been published which describes the bonding in a particularly lucid manner.[109]

Of especial interest is the reversible addition of small molecules to the vacant site between the two metal centres, as illustrated in Schemes 5—7.[66,67,105–118] As can be seen, the addition or loss of these small molecules occurs with making or breaking a metal–metal bond, in a similar way as shown in Scheme 4, and many further examples have been studied. In several cases, however, the incoming ligand does not attack the 'pocket' site between the metal atoms directly. Instead, attack occurs at a terminal site and a terminal carbonyl group moves to the bridging position, as illustrated in equation 6.[115]



(6)

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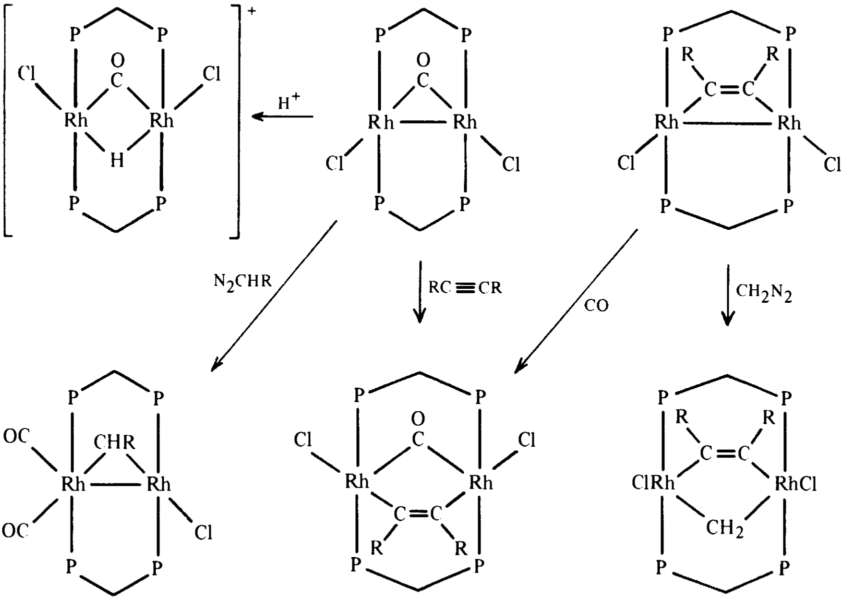
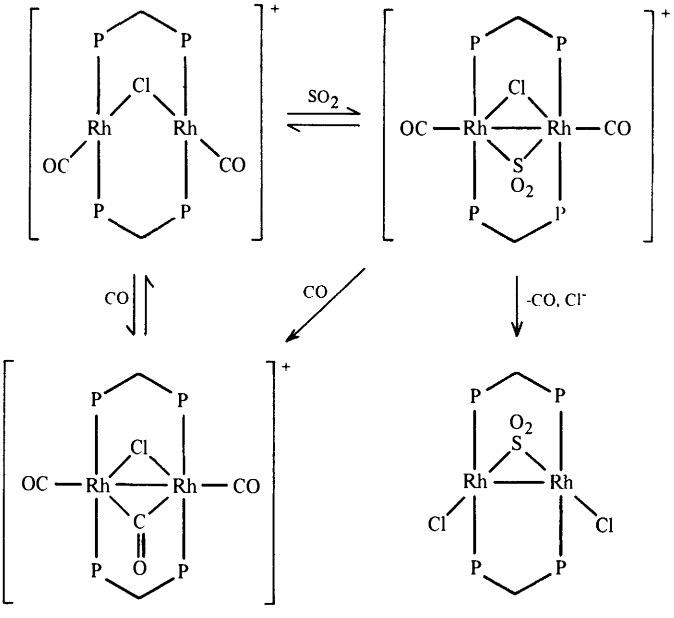
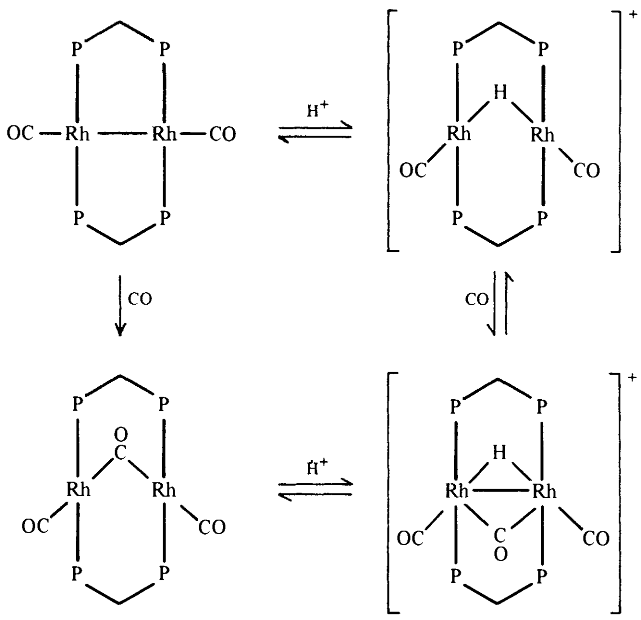
[109] D. M. Hoffman and R. Hoffmann, *Inorg. Chem.*, 1981, **20**, 3543.
[110] C. P. Kubiak and R. Eisenberg, *J. Am. Chem. Soc.*, 1980, **102**, 3637.
[111] M. Cowie and S. K. Dwight, *Inorg. Chem.*, 1980, **19**, 209.
[112] M. Cowie, *Inorg. Chem.*, 1979, **18**, 286.
[113] M. M. Olmstead, C. H. Lindsay, L. S. Benner, and A. L. Balch, *J. Organomet. Chem.*, 1979, **179**, 289.
[114] M. Cowie, J. T. Mague, and A. R. Sanger, *J. Am. Chem. Soc.*, 1978, **100**, 3628.
[115] J. T. Mague and A. R. Sanger, *Inorg. Chem.*, 1979, **18**, 2060.



Scheme 5



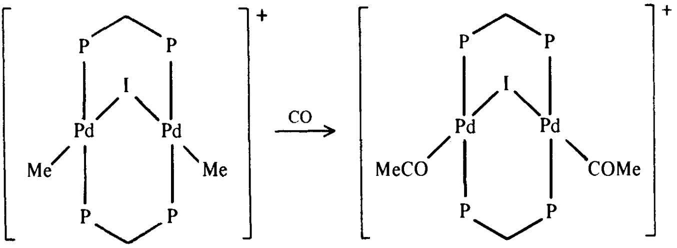
Scheme 6



Scheme 7

This topic has been illustrated with examples from rhodium chemistry, but an extensive, related chemistry of iridium is also known.[66,114,115,119] In this case hydrogen reacts with $[Ir_2(\mu\text{-}S)(CO)_2(\mu\text{-dppm})_2]$ or with $[Ir_2(\mu\text{-}Cl)(CO)_2(\mu\text{-dppm})_2]^+$ to give hydridoiridium(II) complexes.[119,120] This binuclear activation of small molecules has potential application in catalysis.[119]

The A-frame complexes of palladium and platinum do not add small molecules in the 'pocket' position, but insertion reactions can occur in some cases (equation 7).[70]

 (7)

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[116] M. Cowie and T. G. Southern, *Inorg. Chem.*, 1982, **21**, 246.

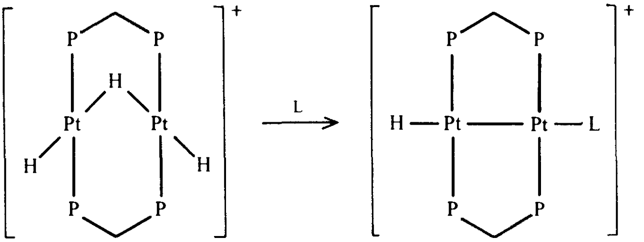
[117] M. Cowie and R. S. Dickson, *Inorg. Chem.*, 1981, **20**, 2682.

[118] M. Cowie and S. K. Dwight, *J. Organomet. Chem.*, 1981, **214**, 233.

[119] C. P. Kubiak, C. Woodcock, and R. Eisenberg, *Inorg. Chem.*, 1980, **19**, 2733.

[120] M. Cowie, personal communication.

The complex $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ undergoes reductive elimination of hydrogen on treatment with ligands such as phosphines or carbon monoxide by an associative mechanism, but by a dissociative mechanism on photolysis (equation 8). The photolysis occurs with high quantum yield; hydrogen loss is intramolecular, and reaction occurs from a singlet excited state. The reaction is noteworthy because almost all other binuclear and polynuclear hydrides are inert to photolysis.[41,72,91,121,122]

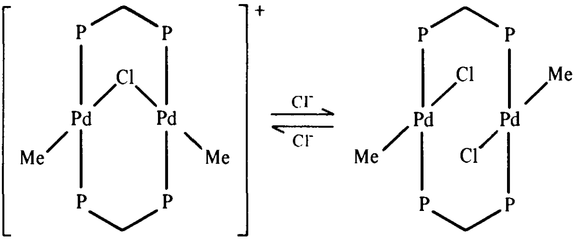


(8)

This type of binuclear reductive elimination can be reversed in some cases,[91,121,123] and a similar reductive elimination of H_2 from $[Pt_2MeH(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ or of CH_4 from $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ can also be achieved.[76,124] The reductive elimination of hydrogen is thought to be involved as an initial step in reactions of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ with alkynes and with methanethiol and diphenylphosphine (Scheme 8).[92,98]

The A-frame complexes are fluxional in some cases, with apparent rapid inversion of the A-frame structure. This reaction may occur by direct inversion[125] as in $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ or it may occur by more complex mechanisms as shown in equations 9 and 10.

In the former case, the reversible formation of the face-to-face complex



(9)

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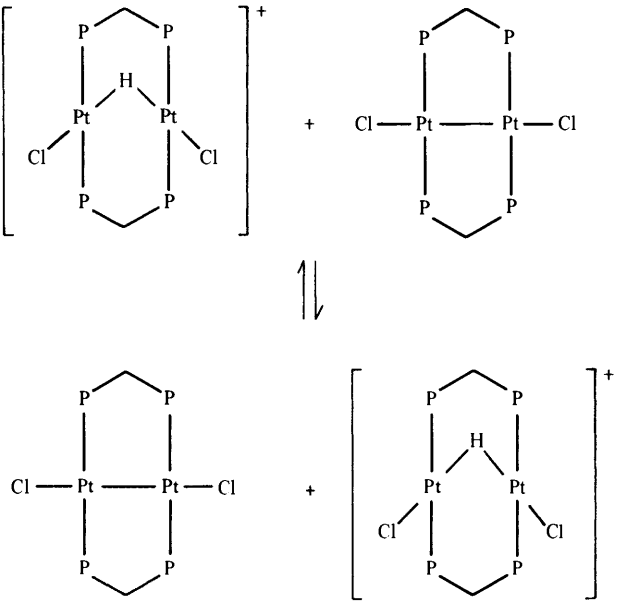
[121] H. C. Foley, R. H. Morris, T. S. Targos, and G. L. Geoffroy, *J. Am. Chem. Soc.*, 1981, **103**, 7337.

[122] R. H. Hill, P. de Mayo, and R. J. Puddephatt, *Inorg. Chem.*, 1982, **21**, 3642.

[123] J. R. Fisher, A. J. Mills, S. Sumner, M. P. Brown, M. A. Thomson, R. J. Puddephatt, A. A. Frew, Lj. Manojlović-Muir, and K. W. Muir, *Organometallics*, 1982, **1**, 1421.

[124] M. P. Brown, S. J. Cooper, A. A. Frew, Lj. Manojlović-Muir, K. W. Muir, R. J. Puddephatt, and M. A. Thomson, *J. Chem. Soc., Dalton Trans.*, 1982, 299.

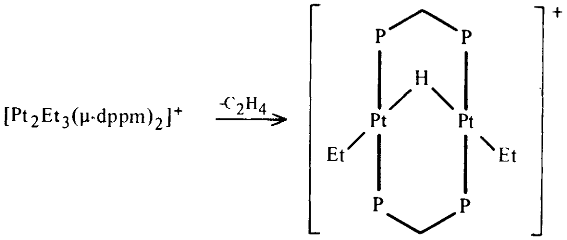
[125] R. J. Puddephatt, K. A. Azam, R. H. Hill, M. P. Brown, C. D. Nelson, R. P. Moulding, K. R. Seddon, and M. C. Grossel, *J. Am. Chem. Soc.*, in press.



(10)

leads to apparent inversion[70,71] whereas, in the latter case, intermolecular transfer of H^+ to a catalytic amount of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ leads to the same result.[125]

There is an interesting intramolecular binuclear β-elimination reaction leading to an A-frame ethyl(μ-hydrido)platinum complex, but the reverse insertion of alkenes into the $Pt_2(\mu\text{-H})$ linkage is not observed (equation 11).[126]



(11)

In most A-frame complexes the methylene groups of the dppm ligands are displaced from the M_2P_4 plane towards the apex bridging group (Figure 7). This conformation allows the phenyl substituents of dppm to bend away from the bridging group and so minimizes steric effects. The overall conformation of the 8-membered ring is then an extended boat. However, in $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$, the conformation is an extended chair (Figure 7) perhaps because steric effects are less with the small μ-hydrido ligand.

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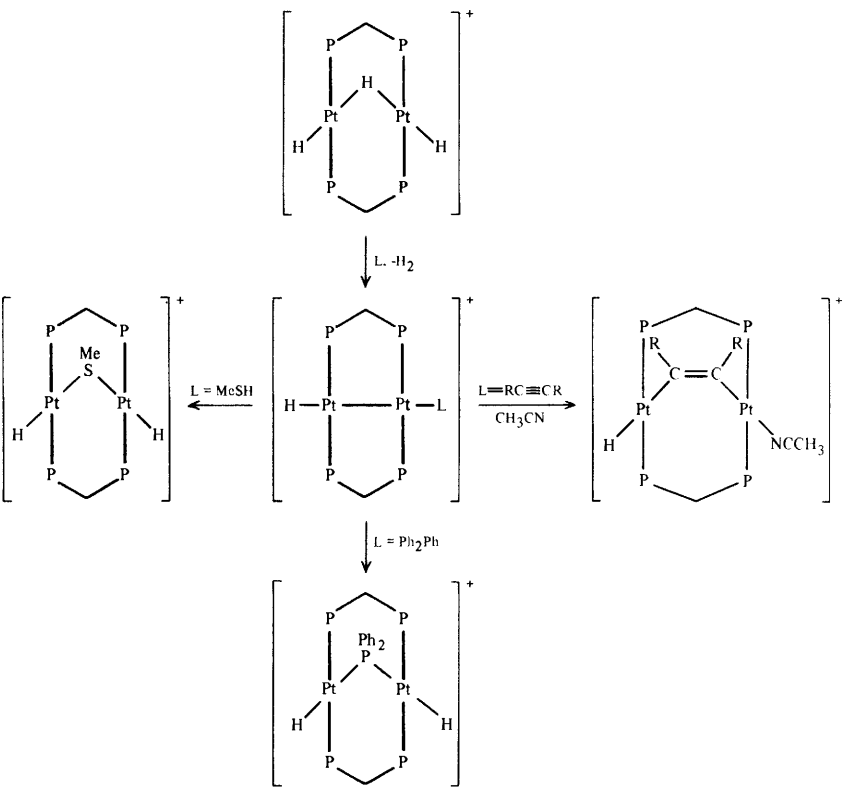
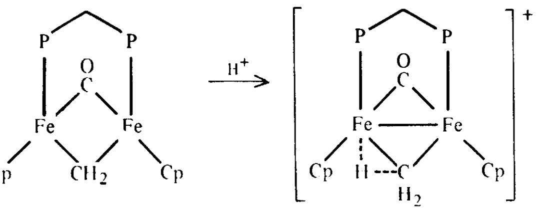
[126] K. A. Azam, M. P. Brown, S. J. Cooper, and R. J. Puddephatt, *Organometallics*, 1982, **1**, 1183.



Scheme 8

The reactions of dppm with metal carbonyls have been particularly significant for the manganese and iron group elements. Thus $[Fe_2(CO)_9]$, with three μ-CO groups, reacts with dppm to give, amongst other products, $[Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-dppm})]$ and then $[Fe_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2]$, each having only one μ-CO group.[29,35,58] Interesting derivatives of $[Fe_2(CO)_4(Cp)_2]$ are also known, and the reaction of equation 12 giving a complex with an unsymmetrical bridging methyl group is of particular significance.[127]



(12)

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[127] G. M. Dawkins, M. Green, A. G. Orpen, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1982, 41.

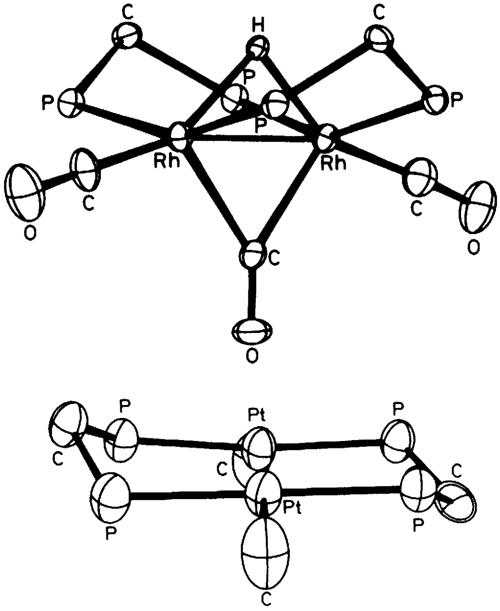
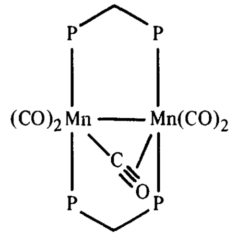
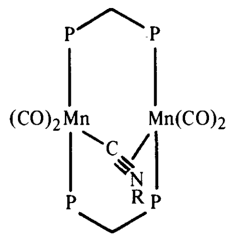


Figure 7 *The conformations of dppm ligands in* $[Rh_2(\mu\text{-}H)(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]^+$ *and in* $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$

Another very unusual bridging group is found in the derivative $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)_2]$, (25). In this complex the μ-CO group acts as a



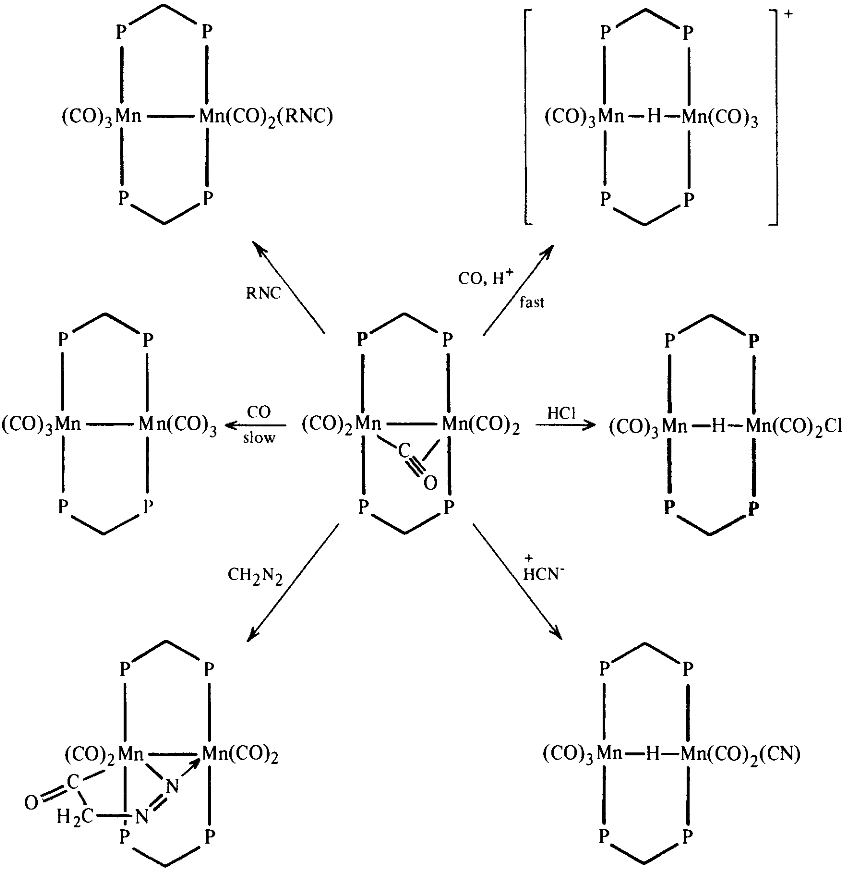
(25)



(26)

4-electron ligand, the unusual feature being the donation of two electrons from a C≡O π-bond.[128-130] A similar complex, (26), R = 4-tolyl, with a 4-electron bridging isocyanide ligand is also known.[131]

[128] C. J. Commons and B. F. Hoskins, *Aust. J. Chem.*, 1975, **28**, 1663.
[129] R. Colton and C. J. Commons, *Aust. J. Chem.*, 1975, **28**, 1673.
[130] K. G. Caulton and P. Adair, *J. Organomet. Chem.*, 1976, **114**, C11.
[131] A. L. Balch and L. S. Benner, *J. Organomet. Chem.*, 1977, **135**, 339.



Scheme 9

Complex (25) has an interesting chemistry as shown in Scheme 9. It can be seen that ligand addition occurs slowly to convert the 4-electron carbonyl group into a normal terminal carbonyl group,[130–132] and that these reactions are greatly accelerated by protonation of the Mn—Mn bond.[133] The Mn—H—Mn linkage is formulated as being linear, and this would be unique if correct. Addition of diazomethane gives an unusual dimetallacycle by coupling with one of the carbonyl ligands.[134]

Another interesting complex is $[Re_2(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]$ having a Re=Re double bond. Again this complex shows high reactivity with small molecules, giving

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[132] L. S. Benner, M. M. Olmstead, and A. L. Balch, *J. Organomet. Chem.*, 1978, **159**, 289.

[133] H. C. Aspinall and A. J. Deeming, *J. Chem. Soc., Chem. Commun.*, 1981, 724.

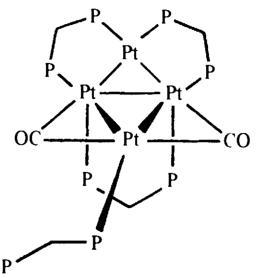
[134] G. Ferguson, W. J. Laws, M. Parvez, and R. J. Puddephatt, *Organometallics*, 1983, **2**, 276.

an adduct $[Re_2H(\mu\text{-}H)(CO)_6\{P(OMe)_3\}(\mu\text{-dppm})]$ with trimethylphosphite and insertion products $[Re_2(\mu\text{-}H)(\mu\text{-}RN{=}CH)(CO)_6(\mu\text{-dppm})]$ and $[Re_2(\mu\text{-}H)(\mu\text{-}MeCH{=}N)(CO)_6(\mu\text{-dppm})]$ with alkyl isocyanides and with methyl cyanide respectively. A further rich chemistry of this complex can be predicted.[135]

6 Cluster Complexes with dppm

The use of dppm to stabilize dimers is better known, but stabilization of cluster complexes is also known. For example, heating $[Rh_6(CO)_{16}]$ with dppm gives $[Rh_6(\mu_3\text{-}CO)_4(CO)_6(\mu\text{-dppm})_3]$, which contains an octahedron of rhodium atoms with dppm bridges between adjacent rhodium centres.[136] Similarly, $[Ru_3(CO)_{12}]$ gives $[Ru_3(CO)_{10}(\mu\text{-dppm})]$.[137]

An example of a cluster being formed from a dimer is seen in the reaction of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ with $CO\text{-}H_2O\text{-}O_2$ to give the tetranuclear $[Pt_4(\mu\text{-}CO)_2(\mu\text{-dppm})_3(Ph_2PCH_2POPh_2)]$. This has a butterfly structure (27) with one partially oxidized dppm ligand.[138]



(27)

This area should be capable of very significant future development.

7 Complexes with Deprotonated dppm

It has been known for several years that dppm can be deprotonated by strong bases to give the anion $[(Ph_2P)_2CH]^-$ and that this anion is itself a good ligand.[139,140] Many complexes of this ligand are oligomeric and sparingly soluble, but more tractable derivatives have been prepared recently (equation 13; M = Ni, Pd, or Pt).[141]

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[135] M. J. Mays, D. W. Prest, and P. R. Raithby, *J. Chem. Commun.*, 1980, 171.

[136] A. Ceriotti, G. Ciani, L. Garlaschelli, U. Sartorelli, and A. Sironi, *J. Organomet. Chem.*, 1982, **229**, C9.

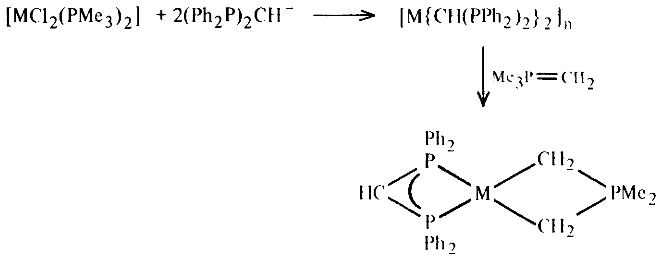
[137] F. A. Cotton and B. E. Hanson, *Inorg. Chem.*, 1977, **16**, 3369.

[138] A. A. Frew, R. H. Hill, Lj. Manojlović-Muir, K. W. Muir, and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1982, 198.

[139] K. Issleib and H. P. Abicht, *J. Prakt. Chem.*, 1970, **312**, 456.

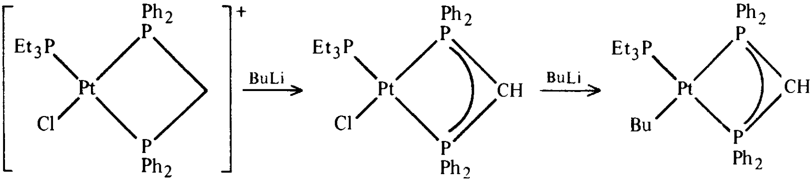
[140] K. Issleib, H. P. Abicht, and H. Winkelmann, *Z. Anorg. Allg. Chem.*, 1972, **388**, 89.

[141] J. M. Bassett, J. R. Mandl, and H. Schmidbaur, *Chem. Ber.*, 1980, **113**, 1145.



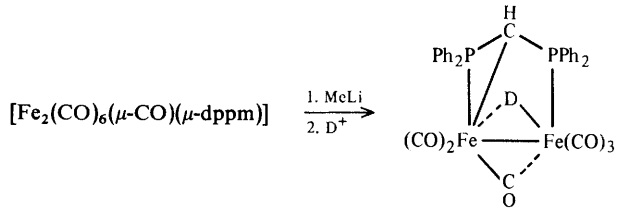
(13)

Co-ordinated dppm can also be deprotonated in some cases and this can be a particularly useful synthetic procedure (equation 14).[142]



(14)

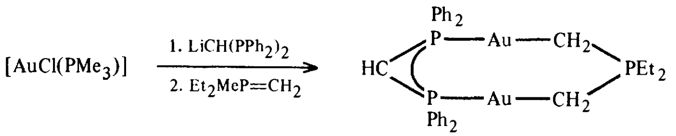
Bridging dppm as well as chelating dppm can be deprotonated in these reactions as illustrated in equation 15. Here the carbon atom as well as the phosphorus atoms co-ordinates in the product.[143]



(15)

A significant chemistry derived from the carbanion can be developed (Scheme 10).[144,145]

A number of derivatives of the elements copper and gold are known. These may be prepared by planned syntheses such as shown in equation (16).[146]



(16)

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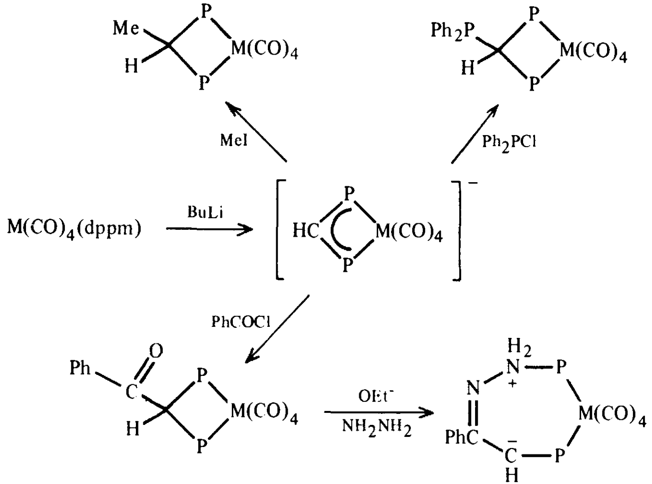
[142] J. Browning, G. W. Bushnell, and K. R. Dixon, *J. Organomet. Chem.*, 1980, **198**, C11.

[143] G. M. Dawkins, M. Green, J. C. Jeffery, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1980, 1120.

[144] S. Al-Jibori and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 286.

[145] S. Al-Jibori, W. S. McDonald, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 287.

[146] H. Schmidbaur and J. R. Mandl, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 640.

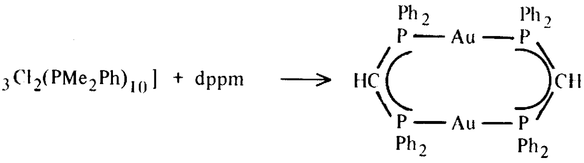


Scheme 10

However, in other cases the deprotonation of dppm has occurred in a more serendipitous way, as illustrated in equations 17—19.[147-149]

$$\text{atomic Au} + \text{dppm} \rightarrow [\text{Au}_5(\mu\text{-dppm})_3(\mu_3\text{-}\eta^3\text{-Ph}_2\text{PCHPPh}_2)]^+ \quad (17)$$

$$\text{PhCu} + \text{dppm} \rightarrow [\text{Cu}_3(\mu_2\text{-Ph}_2\text{PCHPPh}_2)(\mu_3\text{-Ph}_2\text{PCHPPh}_2)_2] \quad (18)$$



(19)

Again there is obviously great potential for expansion of this area of chemistry, based on the very recent planned syntheses described above.

8 Catalysis with dppm Complexes

The exceptional ability of complexes with the $M_2(\mu\text{-dppm})_2$ skeleton to activate small molecules by co-ordination in the bridging position has led to several attempts to develop useful catalysis by these compounds. The complexes $[Rh_2(CO)_2(\mu\text{-dppm})_2]$ and $[Pd_2Cl_2(\mu\text{-dppm})_2]$ will each add alkynes in the bridging position, and they act as catalysts for hydrogenation of acetylene to ethylene and for cyclotrimerization of alkynes respectively.[97,110] Similarly

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[147] J. W. A. van der Velden, J. J. Bour, F. A. Vollenbroek, P. T. Beurskens, and J. M. M. Smits, *J. Chem. Soc., Chem. Commun.*, 1979, 1162.

[148] A. Camus, N. Marsich, G. Nardin, and L. Randaccio, *J. Organomet. Chem.*, 1973, **60**, C39.

[149] C. E. Briant, K. P. Hall, and D. M. P. Mingos, *J. Organomet. Chem.*, 1982, **229**, C5.

$[Rh_2(\mu\text{-}S)(CO)_2(\mu\text{-dppm})_2]$, $[Ir_2(\mu\text{-}S)(CO)_2(\mu\text{-dppm})_2]$, and $[Ir_2H_2(\mu\text{-}S)(CO)_2(\mu\text{-dppm})_2]$ are catalysts for hydrogenation of acetylene and ethylene.[119] There is a correlation between hydrogenation activity and the ability of rhodium A-frame complexes to bind small molecules in the 'pocket' position,[150] but no complexes can be said to have exceptionally high activity.

The complex cations $[Rh_2(\mu\text{-}H)(CO)_3(dppm)_2]^+$ and $[Pt_2H_2(\mu\text{-}H)(dppm)_2]^+$ are catalysts for the water-gas shift reaction under mild conditions.[138,151] In each case it is considered probable that binuclear activation is involved but the detailed mechanisms are not certain. The rhodium catalyst will also act as a hydroformylation catalyst using $CO\text{-}H_2O$ as the source of hydrogen *via* the concurrent catalysis of the water-gas shift reaction.[151] The complex cation $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ is also a shortlived catalyst for reduction of CO to CH_4 using sodium borohydride as reducing agent. Again the mechanism is unknown.

These studies represent only the first preliminary survey of catalytic activity of dppm complexes, and it is too early to tell if the demonstrated ability of dppm bridged complexes to stabilize unusual bonding modes of small molecules like carbon monoxide or alkynes will form the basis for useful catalysis.

Acknowledgments. It is a pleasure to acknowledge the help of researchers in this area, A. L. Balch, M. P. Brown, M. Cowie, Lj. Manojlović-Muir, R. Hoffmann, J. T. Mague, A. R. Sanger, and K. R. Seddon, who kindly sent reprints and preprints of their recent work and, in several cases, communicated unpublished results, and B. L. Shaw who suggested that this article be written.

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[150] A. R. Sanger, personal communication.

[151] C. P. Kubiak, C. Woodcock, and R. Eisenberg, *Inorg. Chem.*, 1982, **21**, 2119.