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Bis(diphenylphosphino)-methanide or -amide and its derivatives as ligands in gold chemistry: a review *

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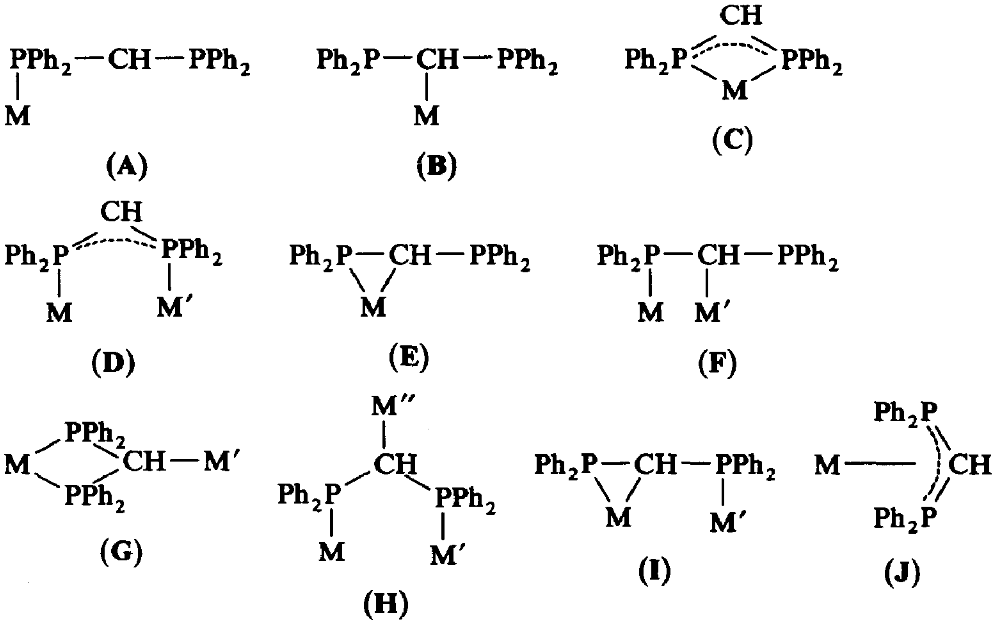
Introduction

Although the chemistry of the diphosphinomethanes, mainly of bis(diphenylphosphino)methane (dppm) [1], has been very extensively reported, the chemistry of bis(diphenylphosphino)methanide has received less attention, in spite of the considerable coordination potential of this ligand arising from the presence of one additional donor atom relative to dppm. Scheme 1 shows its possible coordination modes.

Form C [2] is the best represented in the chemistry of various metals, only a few



Scheme 1

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* Dedicated to Professor F. Gordon A. Stone on the occasion of his 65th birthday.

examples of **B** [2h,2i,3], **D** [2c,4], **E** [5] and **F** [6] have been reported, and **A** is unknown.

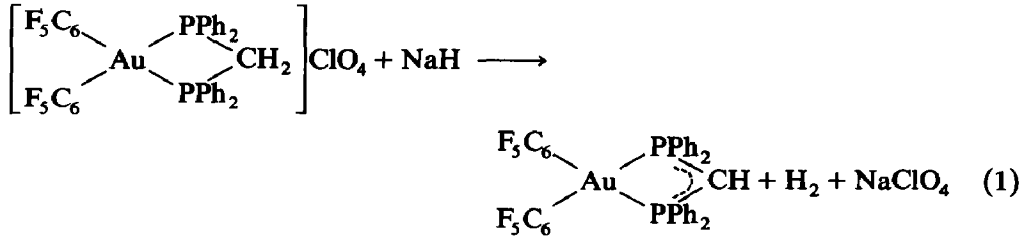
We find it of interest to seek to all of the possible coordination modes of this ligand. Additional forms **G**, **H** and **J** can be formed by coordination of different metal centers to methanide complexes of the types **C** and **D**. It is noteworthy that coordination types **G** [2e,7], **H** [8], **I** [9] or **J** [10] are little represented in the literature, and complexes containing them were more or less serendipitously.

Use of the bis(diphenylphosphino)amide ligand has been far less studied, and no tridentate complexes have been reported apart from the complexes of silver and gold considered below.

Bis(diphenylphosphino)-methanide or -amide complexes

The initial objective this work was to obtain complexes containing tridentate bis(diphenylphosphino)-methanide or -amide. These are formed by coordination to various metal centers in gold (or to a lesser extent in silver) complexes of the types **C** and **D**.

A complex containing the methanide ligand as a P,P′-chelate has been made [11] by proton abstraction with NaH from a dppm cationic complex containing the ClO_4^- ion as counterion. This method gives satisfactory results only when the starting complex contains both an acidic proton and an anion, Cl^- or ClO_4^-, able to accept the Na^+ cation, (eq. 1).



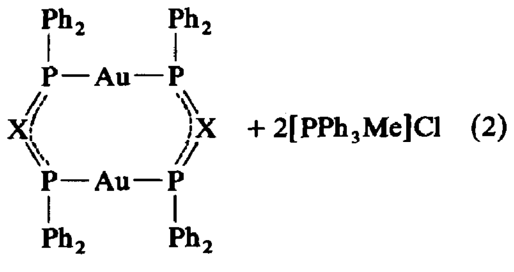
(1)

The complex *cis*-$[Au(C_6F_5)_2(Ph_2AsCHAsPh_2)]$ (**2**) [12] has been obtained similarly.

In contrast, binuclear complexes involving bis(diphenylphosphino)-methanide or -amide acting as P,P′-bridging ligands are formed in the reaction of halo(ylide)gold(I) complexes with the relevant diphosphine (eq. 2) [13,14].

This reaction can be regarded as a transylidation, which gives in this case not a new ylide complex but a methanide or amide complex.

$2[AuCl(CH_2PPh_3)] + Ph_2P{-}XH{-}PPh_2 \longrightarrow$



(X = CH (**3**), N (**4**))

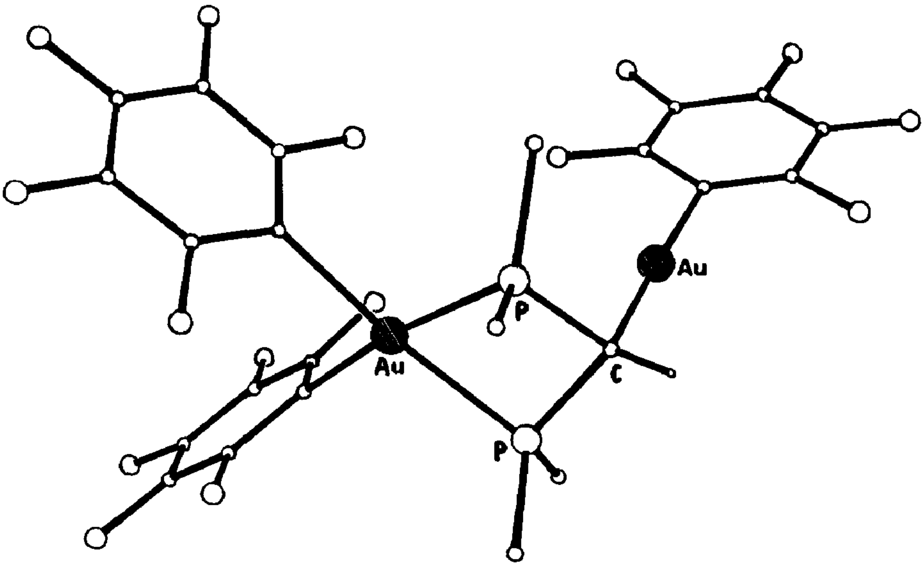


Fig. 1. X-ray structure of $[Au(C_6F_5)_2\{Ph_2PCH(AuC_6F_5)PPh_2\}]$ (6).

When using $[Ag(CH_2PPh_3)_2]ClO_4$ as starting material reaction 2 follows a similar course and the complex $[N(Ph_2PAgPPh_2)_2N]$ (5) can be isolated [14].

Reactions of complexes **1** and **3–5** (complex **2** does not give clean reactions) with various silver or gold complexes containing labile ligands such, as $AgClO_4$, $[Ag(OClO_3)(PPh_3)]$, $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene), $[Au(2,4,6\text{-}C_6F_3H_2)(tht)]$, $[AuCl(tht)]$ or $[Au(tht)_2]ClO_4$, give tri- or poly-nuclear complexes with the new metal centres bonded to C or N atoms of the starting complexes [11,13,14]. The structures of $[Au(C_6F_5)_2(Ph_2PCH(AuC_6F_5)PPh_2)]$ (6), $[Au\{Au(C_6F_5)_2(Ph_2PCHPPh_2)\}_2]$ (7), $[(C_6F_5)AuCH(Ph_2PAuPPh_2)_2CHAu(C_6F_5)]$ (8), and

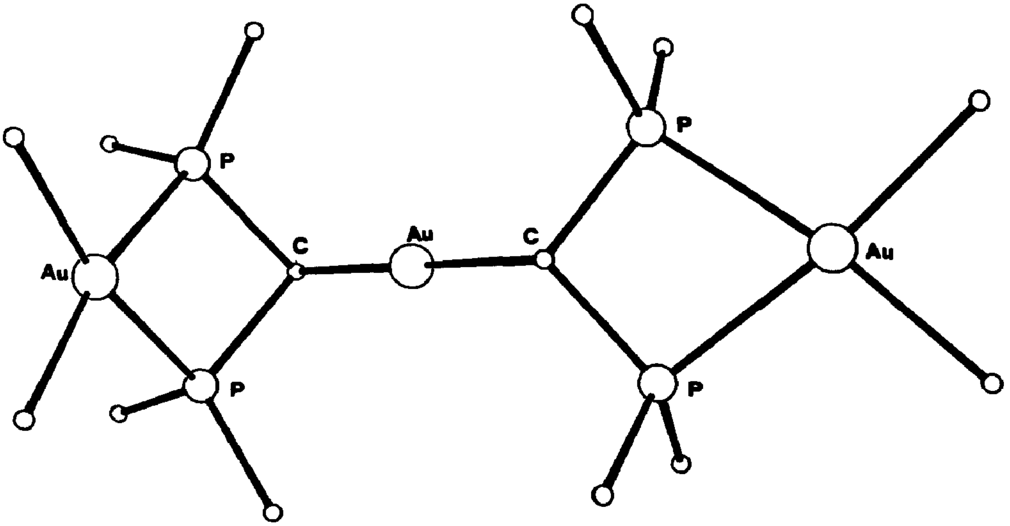


Fig. 2. X-ray structure of $[Au\{Au(C_6F_5)_2(Ph_2PCHPPh_2)\}_2]$ (7), phenyl and pentfluorophenyl rings are represented only by the *ipso* carbon atoms.

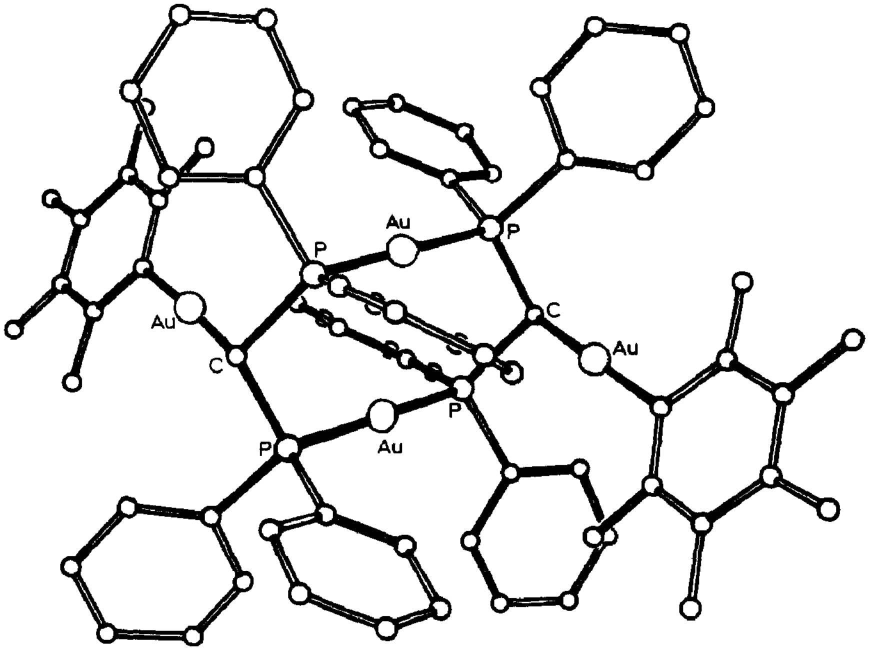


Fig. 3. X-ray structure of $[(C_6F_5)AuCH(Ph_2PAuPPh_2)_2CHAu(C_6F_5)]$ (**8**).

$[PPh_3(O_3ClO)AgN(Ph_2PAuPPh_2)_2NAg(OClO_3)PPh_3]$ (**9**) are shown in Fig. 1-4. The new metal fragments are bonded at CH or N groups, proving that at these positions there is sufficient electron density to form bonds with the appropriate metal centers. The methanide derivatives **1**–**3** show a strong band at 1200–1250 cm^{-1} in the IR spectra that can be assigned to a P–CH–P moiety. This band disappears upon coordination of C atom in the polynuclear derivatives.

It is noteworthy that the reaction of [AuCl(tht)] or $[AuCl(AsPh_3)]$ with the chelate methanide complex **1** does not, as was expected, give the derivative $[Au(C_6F_5)_2\{Ph_2PCH(AuCl)PPh_2\}]$ but involves opening of the AuPCP ring is to give the trinuclear complex $[Au(C_6F_5)_2Cl\{Ph_2PCH(AuL)PPh_2\}AuCl]$ (**10**) [15].

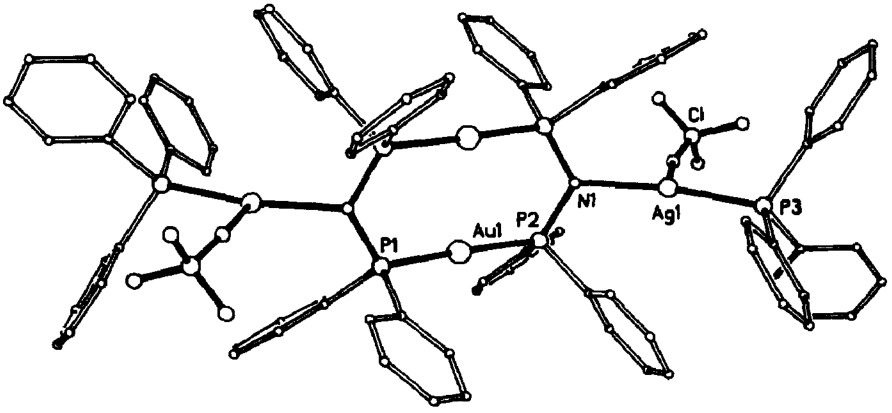


Fig. 4. X-ray structure of $[PPh_3(O_3ClO)AgN(Ph_2PAuPPh_2)_2NAg(OClO_3)PPh_3]$ (**9**).

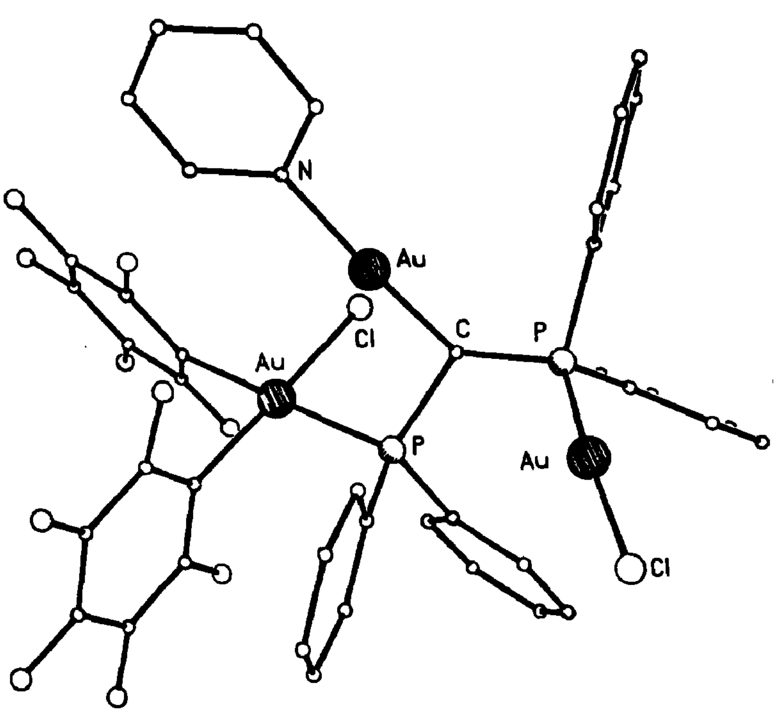


Fig. 5. X-ray structure of $[Au(C_6F_5)_2Cl\{Ph_2PCH(Aupy)PPh_2\}AuCl]$ (**10**).

Figure 5 shows the structure of the corresponding complex in which the tht ligand has been replaced by pyridine

Attempts were made to obtain double deprotonation of dppm gold derivatives, or a further deprotonation of some of the above methanide complexes, in order to provide systems which, by reaction with other metal fragments should give polynuclear complex, with these ligands acting as eight electron donor, (as can be seen in a few examples in the literature [2e,8c]), but the attempts were unsuccessful. This we decided make some changes in dppm ligand in order to increase the acidity of methylene protons.

Alkyldiphenylphosphonio(diphenylphosphino)methanide complexes

First, the introduction of one alkyl group on a P edge gave cationic ligands $[Ph_2P\text{-}CH_2\text{-}PPh_2R]^+$ ($R = CH_3$, $CH_2C_6H_5$ or $CH_2\text{-}C_6F_5$) in the acidity of the methylene protons, α,α' to P atoms is increased. From these monodentate ligands, gold precursors $[AuR_n(Ph_2PCH_2PPh_2R)]ClO_4$ with $R_n = C_6F_5$, $(C_6F_5)_3$, or $(C_6F_5)_2Cl$, can be readily obtained. Further treatment with NaH led to the corresponding methanide complexes (eq. 3) [17,18].

$$[AuR_n(Ph_2PCH_2PPh_2R)]ClO_4 + NaH \longrightarrow [AuR_nPh_2PCHPPh_2R] + H_2 + NaClO_4 \quad (3)$$

($R_n = C_6F_5$ (**11**), $(C_6F_5)_3$ (**12**), or $(C_6F_5)_2Cl$ (**13**))

Unfortunately the introduction of the phosphonium group does not lead to any significant advantage, since in all the cases studied only a single deprotonation took

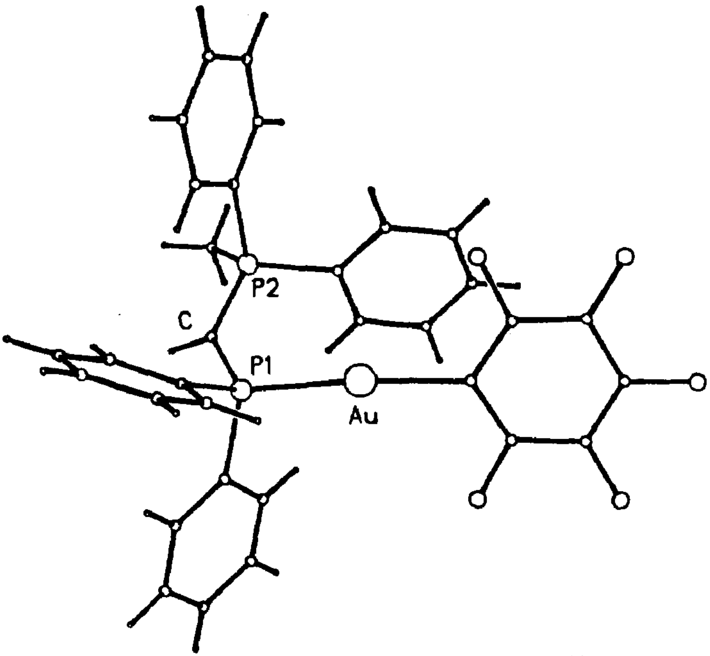


Fig. 6. X-ray structure of $[Au(C_6F_5)(PPh_2CHPPh_2Me)]$ (11).

place, including the reaction of *cis*-$[Au(C_6F_5)_2Cl(PPh_2CH_2PPh_2R)]ClO_4$ with NaH, which gave only the methanide **13** even though two leaving groups, Cl and ClO_4, are present. Moreover the methanide derivatives are much more stable than those

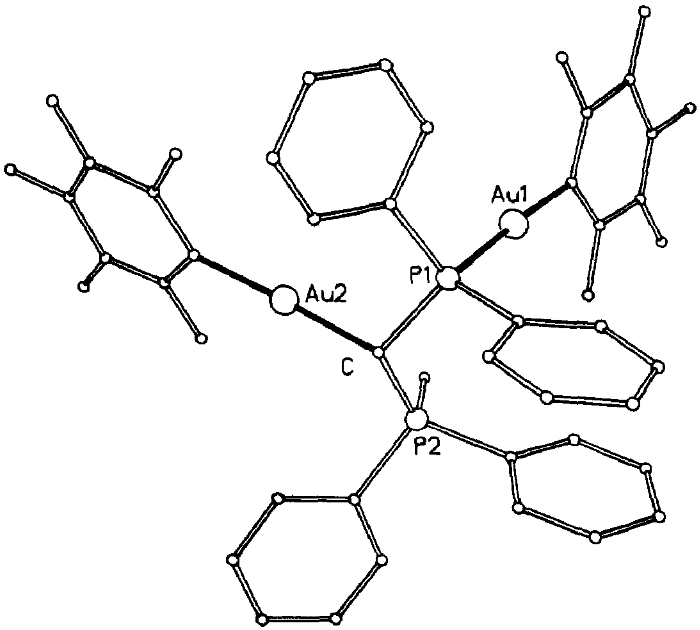


Fig. 7. X-ray structure of $[Au(C_6F_5)\{Ph_2PCH(AuC_6F_5)PPh_2Me\}]$ (14).

previously considered (1–5), and, for example, the X-ray structure of $Au(C_6F_5)(PPh_2CHPPh_2Me)$ (**11**) has been determined, and is shown in Fig. 6.

The methanide complexes **11–13** react with $[Au(C_6F_5)tht]$, $[AuCl(tht)]$, $AgClO_4$ or $[Au(tht)_2]ClO_4$ to give polynuclear complexes that are more stable towards air and moisture than the starting complexes. The derivatives **11–13** show a strong band at 1200–1250 cm^{-1} in the IR spectra that can be assigned to the P–CH–P moiety, which is not present in the polynuclear derivatives. Figure 7 shows the crystal structure of $[Au(C_6F_5)(Ph_2PCH(AuC_6F_5)PPh_2Me)]$ (**14**).

Mono and disulphides of diphosphines

Another way of increasing the acidity of methylene protons in dppm involves oxidation of one or two phosphorus centres, to give phosphine oxides or sulphides. However, phosphine oxides are not good ligands towards gold, and so we decided to use phosphine sulphides.

We first used the monosulphide of dppm, a ligand described by Sheiffer [19] but subsequently little studied [20]. We have developed a strategy, that can also be used with other metals, involving treatment of a monodentate dppm complex with sulfur (eq. 4) [21]

$$[Au(C_6F_5)_2Cl(dppm)] + \tfrac{1}{8}S_8 \longrightarrow \underset{(\mathbf{15})}{[Au(C_6F_5)_2Cl(dppmS)]} \qquad (4)$$

The resulting complex **15** reacts with NaH to give a 5-membered auracycle methanide $[Au(C_6F_5)_2(Ph_2PCHPPh_2S)]$ (**16**), which was characterized by X-ray diffraction (Fig. 8). The reaction of **15** with gold and silver compounds readily gives polynuclear complexes containing methylene carbon–metal bonds.

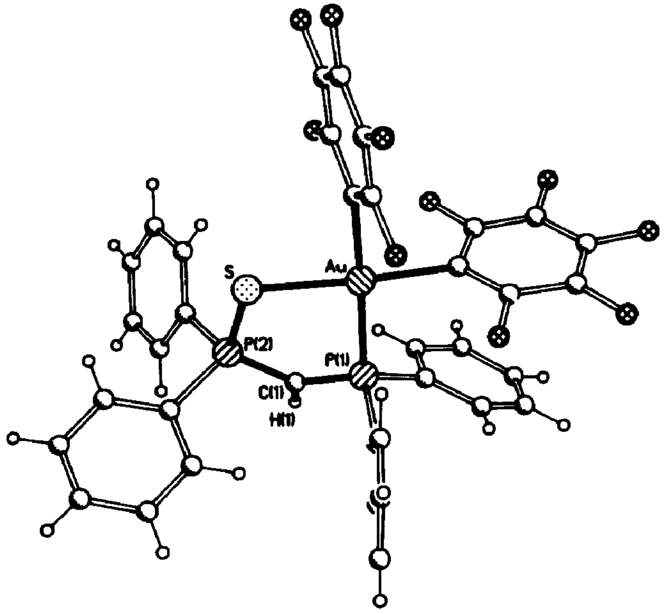


Fig. 8. X-ray structure of $[Au(C_6F_5)_2(Ph_2PCHPPh_2S)]$ (16).

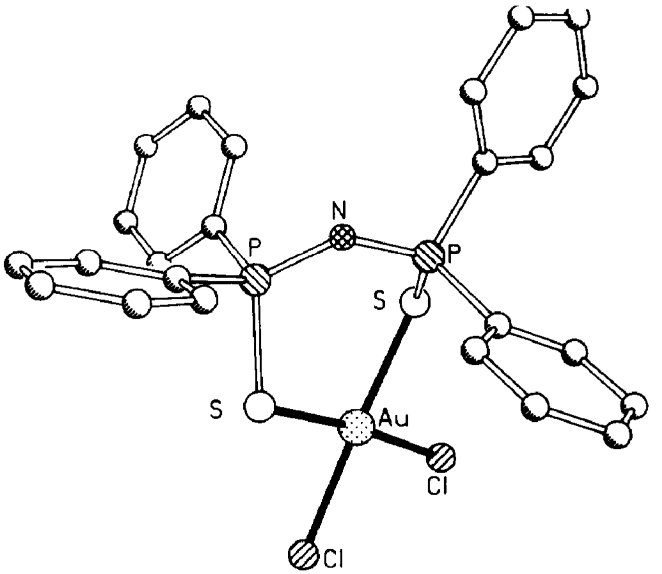


Fig. 9. X-ray structure of $[AuCl_2(SPPh_2NPPh_2S)]$ (**22**).

A different coordination chemistry can be observed by use of the disulphide $[(S)PPh_2CH_2PPh_2(S)]$(dppmS$_2$), which can be readily prepared [22]. Equations 5 and 6 illustrate the formation of a complex containing the disulphide ligand present in a chelating form and its subsequent deprotonation with NaH to give a 4-membered auracycle in which the methanide ligand acts as a S,C-chelate [23].

$$[Au(C_6F_5)_2(OEt_2)_2]ClO_4 + dppmS_2 \longrightarrow \underset{\mathbf{(17)}}{[Au(C_6F_5)_2(SPPh_2CH_2PPh_2S)]} \qquad (5)$$

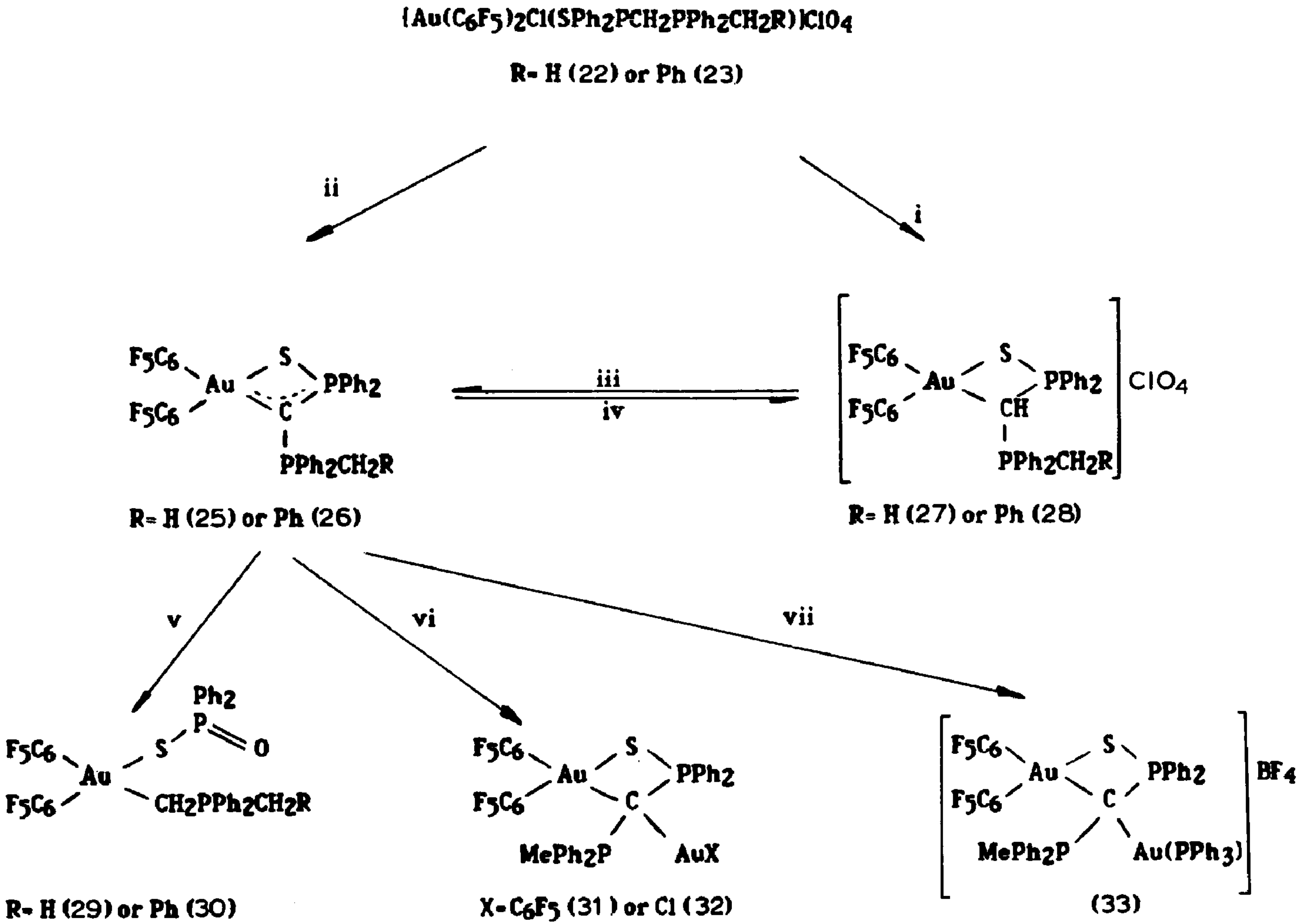
$$\mathbf{17} + NaH \longrightarrow \underset{\mathbf{(18)}}{[\overline{Au(C_6F_5)_2(SPPh_2C}HPPh_2S)]} + H_2 + NaClO_4 \qquad (6)$$

As expected, with complex **18** the IR band about 1250 cm^{-1} is absent. However, this complex has another coordination site that can be used to give polynuclear complexes such as $[\overline{Au(C_6F_5)_2(SPPh_2C}HPPh_2S)Au(C_6F_5)]$ (**19**).

The acidity of the NH proton is increased in the disulphide bis(diphenylphosphino)amine (dppaS$_2$) as in the ligand (dppmS$_2$). Thus reaction of dppaS$_2$ with AuCl(tht) or $Au(C_6F_5)$(tht) in the absence of any deprotonating agent, gives [23] the binuclear amide complex $[N(Ph_2PSAuSPPh_2)_2N]$ (**20**). Similarly the reaction of dppaS$_2$ with $[Au_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ in 2/1 ratio gives $[Au(C_6F_5)_2(SPPh_2NPPh_2S)]$ (**21**). The amide complexes **20** and **21** do not react with $Au(C_6F_5)$tht or $[Ag(OClO_3)(PPh_3)]$, probably because of a less electronic density at the N atom, but **20** reacts [24] with chlorine in 1/2 ratio to give $[AuCl_2(SPPh_2NPPh_2S)]$ (**22**), the X-ray structure of which is shown in Fig. 9.

(Diphenylphosphinothioyl)alkyldiphenylphosphoniomethanide complexes

Conversion of one phosphorus centre in dppm into a phosphonium group or a phosphine sulphide changes the properties of the methanide centre but not so as to



Scheme 2. (i) Na_2CO_3; (ii), (iii) NaH; (iv) $HClO_4$; (v) H_2O; (vi) [AuX(tht)]; (vii) $[(AuPPh_3)_3O]BF_4$.

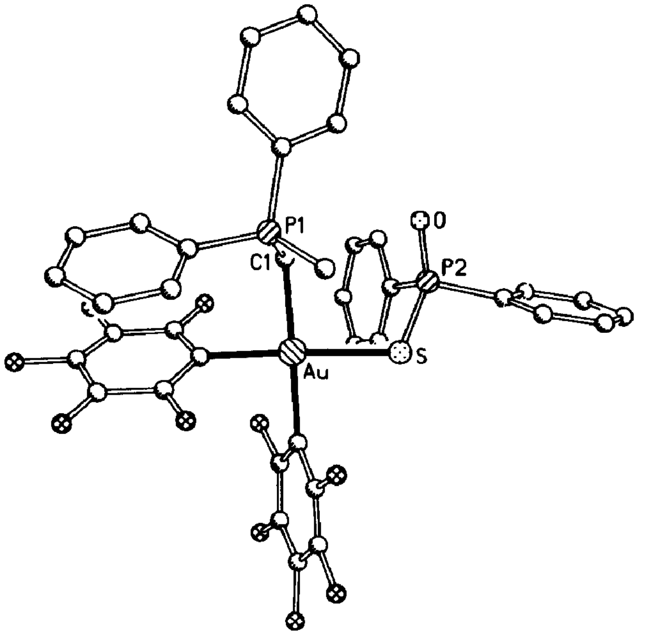
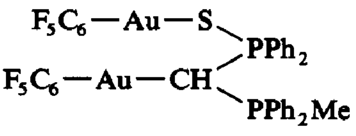


Fig. 10. X-ray structure of $[Au(C_6F_5)_2\{SP(O)Ph_2\}(CH_2PPh_2Me)]$ (**29**).

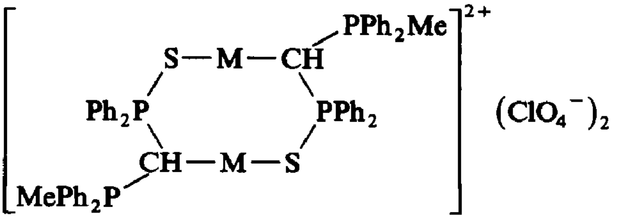
permit double deprotonation of the methylene protons. Nevertheless this objective can be achieved by a combination of both procedures; Thus the preparation of complexes containing ligands such as $[SPPh_2CH_2PPh_2R]^+$($R = CH_3$ or $CH_2C_6H_5$) enables the double deprotonation of the ligand [25] by NaH, and furthermore use of a weaker base such as Na_2CO_3 allows the selective abstraction of only one proton (see Scheme 2). Addition of $HClO_4$ to the methanide complex **25** or **26** (1/1 ratio) gives the cations **27** or **28** (Scheme 2, iv), which regenerate the neutral complexes **25** or **26** on reaction with NaH (iii)

As shown in Scheme 2, with the methanide complex the presence of an excess of electron density on the carbon atom can be used to obtain dinuclear complexes. Unfortunately no suitable crystals for X-ray diffraction studies could be obtained in the case of the methanide complexes **25** and **26** but complex **29** gave good crystals, and the Fig. 10 show its crystal structure.

Reaction of complex $[Au(C_6F_5)_3(SPPh_2CH_2PPh_2Me)]ClO_4$ with NaH gives a methanide in which only one proton has been removed, $[Au(C_6F_5)_3(SPPh_2CHPPh_2Me)]$ (**34**). It is noteworthy that the reactions of **34** with other metal fragments, such as $Au(C_6F_5)$tht, $[Au(tht)_2]ClO_4$ or $Ag(OClO_3)PPh_3$, do not give the simple dinuclear complexes with the new metal center bonded to the C methanide, but instead ligand rearrangement occurs to give $Au(C_6F_5)_3L$ (L = tht or PPh_3) and the complexes **35**–**37** [26].



(**35**)



(M = Au (**36**), Ag (**37**))

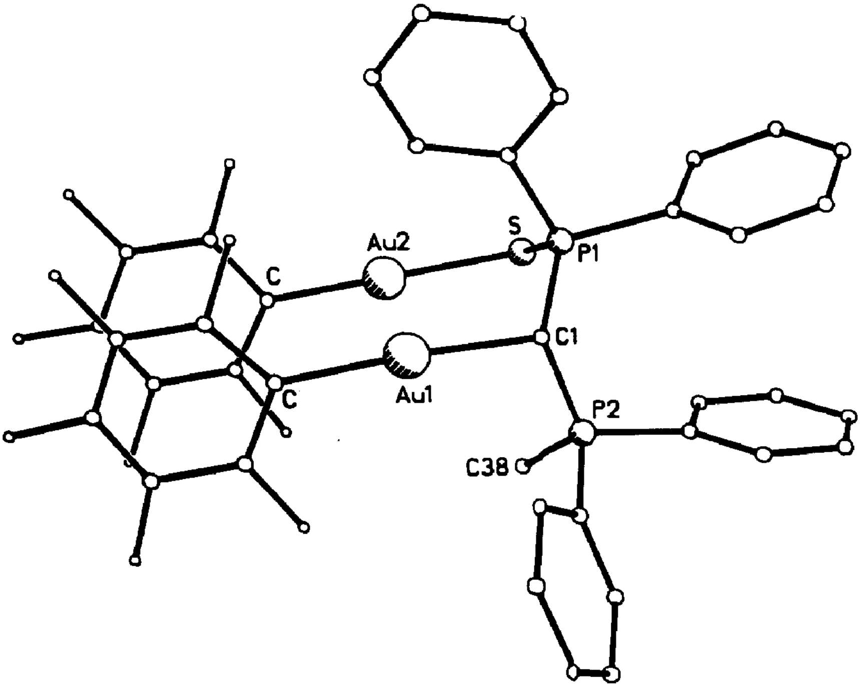


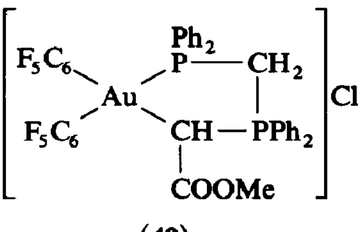
Fig. 11. X-ray structure of $[Au(C_6F_5)\{SPPh_2CH(AuC_6F_5)PPh_2Me\}]$ (35).

The observed structure of 35 (Fig. 11) is very different from that found for the analogous $[Au(C_6F_5)\{Ph_2PCH(AuC_6F_5)PPh_2Me\}]$ (14) (Fig. 7), because the two C_6F_5 rings of 35 adopt a parallel, eclipsed conformation with a corresponding short Au...Au distance of 3.224(2) Å.

Methoxycarbonylmethyl derivatives of dppm

The best results were obtained with the diphosphine with a strongly electron-withdrawing substituent such as $CH_2{-}COOMe$ or its sulphide derivative, i.e. ($[PPh_2CH_2PPh_2CH_2COOMe]^+$ or $[SPPh_2CH_2PPh_2CH_2COOMe]^+$).

Reaction of $[Au(C_6F_5)_2Cl(PPh_2CH_2PPh_2CH_2COOMe)]ClO_4$ or $[Au(C_6F_5)_2Cl(SPPh_2CH_2PPh_2CH_2COOMe)]ClO_4$ with NaH [27] gave 5- and 6-membered auracyclic methanide complexes $[Au(C_6F_5)_2(PPh_2CHPPh_2CHCOOMe)]$ (38) or $[Au(C_6F_5)_2(SPPh_2CHPPh_2CHCOOMe)]$ (39). Double deprotonation has taken place, but at different methylene protons. When other deprotonating agent such as Na_2CO_3 are used, or chlorine abstraction with $AgClO_4$, deprotonation occurs only at one methylene group, but at a different one depending on the ligand used, to give complexes 40 or 41.



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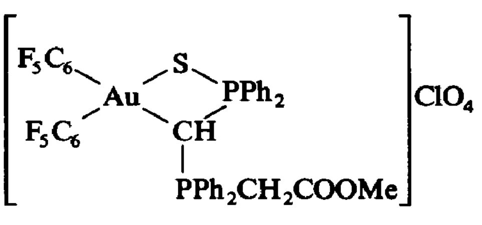

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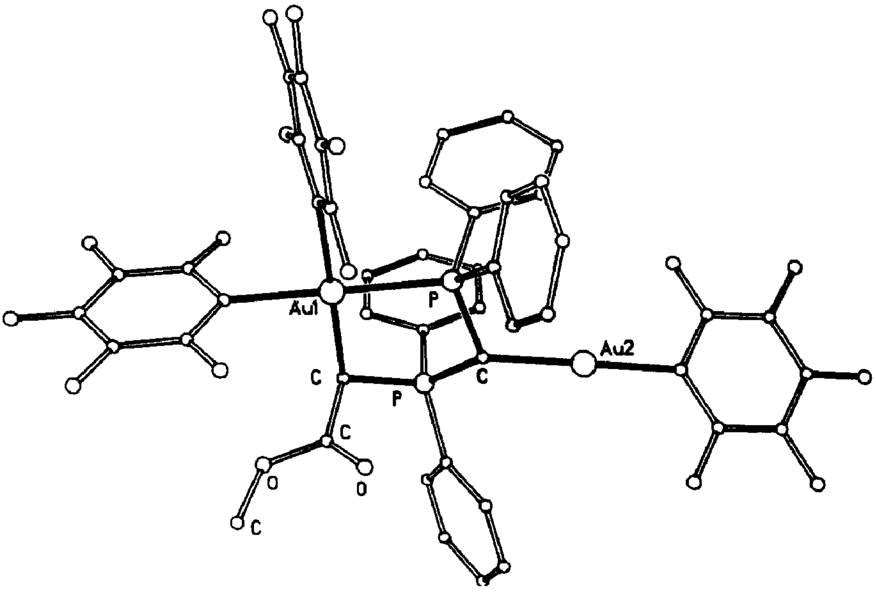
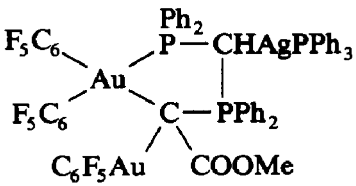


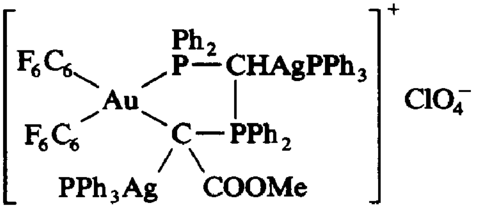
Fig. 12. X-ray structure of $[Au(C_6F_5)_2(PPh_2CH(AuC_6F_5)PPh_2CHCOOMe)]$ (**42**).

The methanide complexes **38** or **39** react with gold or silver compounds to give polynuclear derivatives with a new gold or silver centre bonded to CH group. Figure 12 shows the crystal structure of $[Au(C_6F_5)_2(PPh_2CH(AuC_6F_5)PPh_2CHCOOMe)]$ (**42**).

Of particular interest is the complex $[Au(C_6F_5)_2\{PPh_2CH(AgPPh_3)PPh_2CH\text{-}COOMe\}]ClO_4$ (**43**), because this reacts [28] with NaH in Et_2O to give a yellow solution (from which it was not possible to isolate any pure compound.) When added to a solution of $[Au(C_6F_5)(tht)]$ or $[AgOClO_3(PPh_3)]$ in 1/1 ratio gives the corresponding complexes **44** and **45**.



(**44**)



(**45**)

These latter complexes arise from triple deprotonation of a dppm derivative ligand, but, of course, at different methylene groups. So far, we have not been able to obtain suitable crystals for X-ray structure determination of these complexes, but we have good elementary analyses, and ^1H and ^{31}P NMR spectra in good accord with the proposed structures.

Acknowledgement

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References

1 R.J. Puddephatt, Chem. Soc. Rev., 12 (1983) 99.

2 (a) V.K. Issleib and H.P. Abicht, J. Prakt. Chem., 312 (1970) 456; (b) V.K. Issleib, H.P. Abicht and H. Winkelmann, Z. Anorg. Allg. Chem., 388 (1972) 89; (c) H. Schmidbaur and J.R. Mandl, Angew. Chem. Int. Ed. Engl., 16 (1977) 640; (d) J. Browning, G.W. Bushnell and K.R. Dixon, J. Organomet. Chem., 198 (1980) C11; (e) J.M. Basset, J.R. Mandl and H. Schmidbaur, Chem. Ber., 113 (1980) 1145; (f) M.P. Brown, A. Yavari, Lj. Manojlović-Muir, K.W. Muir, R.P. Moulding and K.R. Seddon, J. Organomet. Chem., 236 (1982) C33; (g) S. Al Jibori and B.L. Shaw, Inorg. Chim. Acta, 65 (1982) L123; (h) H.H. Karsch, A. Appelt and G. Hanika, J. Organomet. Chem., 312 (1986) C1; (i) H.H. Karsch, A. Appelt and G. Müller, Organometallics, 5 (1986) 1664; (j) H. Hashimoto, Y. Nakamura, and S. Okeya, Inorg. Chim. Acta, 120 (1986) L25; (k) Lj. Manojlovic-Muir and K.W. Muir, Acta Crystallogr. C. Cryst. Struct. Commun., C42 (1986) 272; (l) V. Riera and J. Ruiz, J. Organomet. Chem., 310 (1986) C36; (m) H. Hasshimoto, Y. Nakamura and S. Okeya, Inorg. Chim. Acta, 122 (1986) L9.

3 (a) A.L. Balch and D.E. Oram, Organometallics, 5 (1986) 2159; (b) M. Luser and P. Peringer, J. Organomet. Chem., 312 (1986) C61.

4 (a) H. Schmidbaur, J.R. Mandl, J.M. Bassett, G. Blaschke and B. Zimmer-Gasser, Chem. Ber., 114 (1981) 433; (b) C.E. Briant, K.P. Hall and D.M.P. Mingos, J. Organomet. Chem., 229 (1981) C5; (c) Y.F. Yu, A. Wojcicki, M. Calligaris and G. Nardin, Organometallics, 5 (1986) 47.

5 (a) H.H. Karsch, Angew. Chem. Int. Ed. Engl., 21 (1982) 921; (b) H.H. Karsch, Chem. Ber., 117 (1984) 783.

6 (a) M.P. Brown, A. Yavari, Lj. Manojlović-Muir and K.W. Muir, J. Organomet. Chem., 256 (1983) C19; (b) H. Schmidbaur, S. Lauteschläger and G. Müller, ibid., 281 (1985) 33.

7 S.I. Al-Resayes, P.B. Hitchcock and J.F. Nixon, J. Chem. Soc., Chem. Commun., (1986) 1710.

8 (a) A. Camus, N. Narsich, G. Nardin and L. Randaccio, J. Organomet. Chem., 60 (1973) C39; (b) 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; (c) M. Luser and P. Peringer, Organometallics, 3 (1984) 1916; (d) E.M. Meyer, S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, ibid., 8 (1989) 1067.

9 (a) G.M. Dawkins, M. Green, J.C. Jeffery, C. Sambale and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1980) 1120; (b) idem, J. Chem. Soc., Dalton Trans., (1983) 499; (c) J.A. Clucas, M.M. Harding, B.S. Nicholls and A.K. Smith, ibid., (1985) 1835.

10 H.H. Karsch, A. Appelt and G. Müller, Angew. Chem. Int. Ed. Engl., 25 (1986) 823.

11 R. Usón, A. Laguna, M. Laguna, B.R. Manzano, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1984) 839.

12 A. Laguna, M. Laguna, J. Fañanas, P.G. Jones and C. Fittschen, Inorg. Chim. Acta, 121 (1986) 39.

13 R. Usón, A. Laguna, M. Laguna, M.C. Gimeno, P.G. Jones, C. Fittschen and G.M. Sheldrick, J. Chem. Soc., Chem. Commun., (1986) 509.

14 R. Usón, A. Laguna, M. Laguna and M.C. Gimeno, J. Chem. Soc., Dalton Trans., (1989) 883.

15 R. Usón, A. Laguna, M. Laguna, B.R. Manzano, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1985) 2417.

16 S.O. Grim and E.D. Walton, J. Am. Chem. Soc., (1980) 871.

17 R. Usón, A. Laguna, M. Laguna, I. Lázaro, A. Morata, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1986) 669.

18 R. Usón, A. Laguna, M. Laguna, I. Lázaro and M.T. Tartón, J. Chem. Soc., Dalton Trans., (1988) 155.

19 D. Seyferth, U.S.P. 3426021/1969; Chem. Abstr., 71 (1969) 39167a; S.O. Grim and J.D. Mitchell, Synth. React. Inorg. Met-org. Chem., 4 (1974) 221.

20 S.O. Grim and J.D. Mitchell, Inorg. Chem., 16 (1977) 1762.

21 R. Usón, A. Laguna, M. Laguna, M.N. Fraile, P.G. Jones and C.F. Erdbrügger, J. Chem. Soc., Dalton Trans., (1989) 73.

22 A. Devison and D.L. Reger, Inorg. Chem., 10 (1971) 1778.

23 A. Laguna, M. Laguna, A. Rojo and M.N. Fraile, J. Organomet. Chem., 315 (1986) 269.

24 A. Laguna, M. Laguna, M.N. Fraile, E. Fernández and P.G. Jones, Inorg. Chim. Acta, 150 (1988) 233.

25 R. Usón, A. Laguna, M. Laguna, I. Lázaro, P.G. Jones and C. Fittschen, J. Chem. Soc., Dalton Trans., (1988) 2323.

26 R. Usón, A. Laguna, M. Laguna, M.N. Fraile, I. Lázaro, M.C. Gimeno, P.G. Jones, G. Reins and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1990) 333.
27 R. Usón, A. Laguna, M. Laguna, I. Lázaro and P.G. Jones, Organometallics, 6 (1987) 2326.
28 R. Usón, A. Laguna, M. Laguna and I. Lázaro, results to be published.