Organogold Chemistry: I Structure and Synthesis

R V Parish

Department of Chemistry, UMIST, Manchester, M60 1QD, UK

Organogold chemistry is enjoying a resurgence of interest as useful applications, largely physical or medicinal, are being found. There is also a wide range of novel molecules, some with curious structures. This article reviews the structures and syntheses of recently discovered gold compounds. A later article will describe their reactions and applications.

Organogold derivatives have been known for almost 100 years. Many fascinating compounds and reactions have been discovered but, until recently, they have found little practical application. However, the last ten to fifteen years have seen the development of new materials with potential applications in non-linear optics, conjugated linear polymers (potential molecular wires), liquid crystals, chemical vapour deposition and anti-tumour agents (see Box 1). On the other hand, in marked contrast to the neighbouring noble metals, compounds of gold have been very little used in homogeneous catalysis (but see reference 1). This review attempts to update previous treatments (see, for

example, reference 2), and deals with the preparation, structures, properties and applications of some of the more interesting organogold systems; the examples given are drawn principally from those reported during the last ten years (a more comprehensive treatment is found in reference 3). The intention is to exemplify rather than to be comprehensive, and no mention at all is made of cluster compounds. Complexes in which carbonyl, cyano, or isonitrile ligands provide the only Au-C bonds are also ignored. For convenience, the review is divided into two parts: this part deals with the wide variety of organic ligands now available and the structure and synthesis of the gold compounds derived from them; the second part treats the reactions and applications of these compounds.

Box 1 Potential applications for gold compounds

COMPOUNDS AND STRUCTURES

Organic derivatives of gold are known for both of the common oxidation states, +1 and +3, and there is an increasing number of gold(II) derivatives. The normal and predominant coordination numbers of gold are two for gold(I) and four for gold(III); as is common in this part of the Periodic Table, this gives stable configurations with 14 and 16 electrons respectively.

Homoleptic compounds AuR or AuR_3 are therefore electron deficient and are unstable and highly reactive. This is true even though they achieve the 'normal' coordination number through polymerization *via* bridging alkyl or aryl groups and three-centre two-electron bonds (see below). The principal examples of

Gold(I)			Gold(III)		
AuR(L)	AuR_2^-	AuRX_2L	$\text{AuR}_2(\text{X})\text{L}$	AuR_3L	AuR_4^-
AuR(X)^-		AuRX_3^-	AuR_2X_2^-	AuR_3X^-	

Box 2 The possible stoichiometries (*L* = neutral ligand; *X* = anionic ligand; *R* = organic group)

stable compounds of empirical formula AuR are those in which the *R*-groups carry a functionality which allows polymerization by coordination to neighbouring gold atoms (*eg* $[\text{AuC}\equiv\text{CR}]_n$). Compounds formulated originally as ' AuR_3 ' or ' $\text{AuR}_3(\text{OEt}_2)$ ' are probably $\text{Li}[\text{AuR}_3\text{Br}]$ (*eg* *R* = CH_3 , C_6F_5) (4).

Provided additional ligands are present to make up the coordination number, compounds of all possible stoichiometries are known, with one or two *R*-groups bonded to gold(I) and from one to four to gold(III) (Box 2). The structures of these compounds are as expected, linear and square planar; where appropriate, geometrical isomers can usually be obtained. In effect, the *R*-groups are carbanions acting as conventional, mononegative, two-electron ligands. Being amongst the softest ligands known*, they transfer much electron density to the gold atom; this is demonstrated, for instance, by Mössbauer spectroscopic data (5, 6), and they exert a high *trans*-influence. Compounds in which two *R*-groups are mutually *trans* are therefore generally of lower stability, and other soft ligands usually adopt positions *cis* to the *R*-group. For the same reason, $[\text{AuR}_2]^-$ and $[\text{AuR}_4]^-$ are highly reactive. In all cases, derivatives of the harder perfluoro-organic groups $-\text{CF}_3$ and $-\text{C}_6\text{F}_5$ show considerably greater stability.

Box 3 Gold compounds with less conventional ligand systems

* The 'hardness' and 'softness' of metal ions and ligands correlates with their polarizability: metal ions which are small and highly charged, and ligands which are small and electronegative, are 'hard'. Large polarizable metal ions or ligand donor atoms are 'soft'. The *trans*-influence is the influence that a ligand has on the strength of the metal-ligand bond *trans* to itself and increases with the softness of the influencing ligand. The sequence of increasing softness of some common ligands is: $\text{Cl}^- < \text{Br}^- < \text{RS}^- < \text{R}_3\text{P} < \text{ylide} < \text{Ar}^- < \text{R}^-$.

V

VI

VII

VIII

σ -Bonded organic ligands can be of all common types: alkyl, aryl, vinylic, acetylenic. The aryl derivatives in particular lend themselves to the formation of chelates when suitable substituents are present; naturally, the stereochemistry required means that these are limited to gold(III); examples are shown as I–IV (7–10).

Considerable attention has also been given to the synthesis of derivatives containing less conventional ketonyl, diketonyl, carbene, or ylide ligands; examples are given in Box 3 (typical references: 11–19). The distinction between the different types is not always obvious, and more than one can occur in the same molecule. A carbene may be considered, formally at least, as a neutral divalent carbon ligand, $:CY_2$, where Y is often an alkoxy or amido group. The most common ylide ligands are effectively deprotonated phosphonium cations, *eg* $:CH_2PPh_3$ (derived from the methyltriphenylphosphonium cation, $CH_3Ph_3P^+$), therefore also neutral. The dimethyldiphenylphosphonium cation can undergo two deprotonation stages to give $:CH_2PPh_2CH_2^-$, which can act simultaneously as a conventional σ -bonded ligand and as a ylide; however, the negative charge is delocalized, and this ligand forms symmetrical bridges: two such ligands bind to two gold atoms forming an eight-membered ring system (V, VI). The dpmm ligand, $Ph_2PCH_2PPh_2$, forms a similar cyclic bis-gold(I) complex which can be deprotonated to give VII. Although ylidic, this complex does not

Box 5 Examples of carbon-centred and hypervalent gold compounds

contain gold-carbon bonds. It can, however, use the residual electron density on the bridging carbon atom to bind extra gold atoms (VIII); to distinguish complexes of this type from conventional σ -bonded organogold compounds, they are often called methanide complexes. Despite the unconventionality of some of these organic ligands, and the curiosity and complexity of some of the structures (Box 4, references 20–23), the stereochemistry at gold is highly normal.

The cyclic digold(I) ylide complexes are readily oxidized to give gold(III) complexes with conventional square planar $AuCl_2X_2$ coordination but retaining the ring structure, VI, IX (24). With a single molar equivalent of halogen, gold(II) derivatives (*eg* X) are obtained (25–26). Although the gold atoms now formally have a d^9 configuration, the complexes are all diamagnetic; the coordination is square planar and includes a short bond to the second gold atom. This

Box 4 Some 'exotic' ylidic and methanidic structures

Figure 1 MO schemes

behaviour is, of course, analogous to the long-established mercury(I) compounds.

IX

X

In recent years a series of compounds has been discovered in which carbon atoms are σ -bonded to one to six $\text{Au}^{\text{I}}\text{L}$ units, where L is a tertiary phosphine (Box 5 – references 27–31). In those involving four-coordinate carbon, the structures are basically tetrahedral but the Au-C-Au angles are often smaller than the tetrahedral angle rather than larger as might have been expected on steric grounds. Even more curiously, the coordination number of the carbon atom increases readily above four, to five and even six; $\text{C}(\text{AuL})_4$ can be obtained only when L is a bulky ligand, such as $\text{P}(\text{C}_6\text{H}_{11})_3$. It should also be mentioned that analogous ‘hypervalent’ compounds are known with central atoms other than carbon (*eg* boron, oxygen, nitrogen, phosphorus, arsenic).

Satisfactory molecular orbital schemes may be constructed, in which the available valence electrons just fill the bonding molecular orbitals (Figure 1). The driving force for the formation of these remarkable compounds is the tendency for gold atoms to attract each other and for weak $\text{Au}\cdots\text{Au}$ bonding interactions to stabilize the compounds. Such interactions appear in a wide range of compounds (32, 33), and are estimated to have a strength comparable to hydrogen-bonds, *ca* 30 kJ mol^{-1} . This effect has been named ‘aurophilicity’ (31), and is thought to be due to relativistic effects arising from the high nuclear charge (33 and references therein). Under its influence, electrons are accelerated to velocities comparable to that of light and they

Figure 2 The molecular structure of $[\text{AuC}\equiv\text{CBu}^t]_n$ (Reprinted with permission from reference 37).

experience an increase of mass. This affects their energies and, for the valence shell, allows much more orbital mixing than would otherwise be expected. These effects operate for all heavy atoms, but just happen to have a maximum at gold.

Other electron-deficient gold(I) compounds are best exemplified by $\text{Au}_2\text{Zn}_2\text{Ph}_6$, for which structure **XI** has been proposed (34). This type of bridging has been confirmed in the ferrocene derivative **XII**, $(\text{C}_5\text{H}_5)\text{Fe}[\text{C}_5\text{H}_4(\text{AuPPh}_3)_2]^+$ (35). The well-established (36) gold(I) alkynyl, $[\text{Au}(\text{C}\equiv\text{CBu}^t)]_n$, was for a long

XI

XII

time assumed to have a tetrameric square structure ($n = 4$), which would allow the triple bond to occupy the second coordination site at an adjacent gold atom, and thus remove the electron deficiency. This material has recently been crystallized and found (37) to have a much more fascinating, complicated structure involving all possible bonding situations: one gold atom has two σ -bonded alkynyl groups, one is π -bonded to two triple bonds, and a third has one σ - and one π - bond. Two of each of these units are bound together in a ring in which the gold atoms form a flat regular hexagon, and two rings are interlaced (see Figure 2). A similar mix of σ - and π -bonded groups may occur in the gold(I) derivative of a propargyl-substituted calixarene, **XIII**, (38) and is also seen in **XIV** and **XV** (39, 40). Apart from the polymeric alkynyl derivatives, there is little evidence for π -bonded complexes. The highly unstable (explosive) cyclopentadienyl $[\text{Au}(\text{C}_5\text{H}_5)]_n$ could polymerize either via three-centre bonds or by π -bonding analogous to that of the alkynyls, but nothing is known of its structure. In the substituted monomeric derivatives, such as $\text{Ph}_3\text{PAu}(\text{C}_5\text{H}_5)$, the cyclopentadienyl group is expected to be bound as a σ -bonded monohapto ligand (η^1 , two-electron donor). However, these molecules are fluxional on the NMR timescale and all carbon atoms are equivalent; as in other cases, the 1,2-shift may involve transient π -bonded intermediates (41).

SYNTHESIS

The most versatile and most often used method for the preparation of organogold compounds is the transmetallation reaction (2). Organolithium or Grignard reagents readily replace halide bound to gold. For gold(I), it is necessary to start with a complexed halide, AuX(L) (Equation 1), and to avoid an excess of the organometallic reagent unless it is intended to obtain

the di-organoaurate(I) ion (Equation 2). Satisfactory Grignard reagents can be made from fluoro-aryls, but trifluoromethyl derivatives are best formed from $\text{Cd}(\text{CF}_3)_2$ (42). With gold(III) halides, the diorgano derivative AuR_2X is the usual first product when starting from Au_2X_6 or $\text{H[AuX}_4]$. Again further reaction occurs readily with lithium reagents, to give $[\text{AuR}_3\text{X}]^-$ or $[\text{AuR}_4]^-$; this is also a convenient way of making mixed organic-ligand derivatives, which do not appear to undergo disproportionation. Mono-organo-gold(III) derivatives are usually obtained from organomercury reagents, and this is most commonly done with potential chelate ligands such as azobenzene or dimethylaminobenzylamine, *eg* to obtain **I** or **IV** (7, 43, 44).

In the normal solvents (acetone or acetonitrile), the reactions represented by Equations 3 and 4 ($\text{Q} = \text{Na}$ or Me_4N ; $\text{tht} = \text{tetrahydrothiophene}$) are generally more efficient, but they appear to be finely balanced equilibria; it is sometimes necessary to add Me_4NCl to encourage the precipitation of $(\text{Me}_4\text{N})_2[\text{Hg}_2\text{Cl}_6]$ (43). For some ligands (*eg* as in **XVI**, **XVII**) even this is not effective, but reaction will proceed if a more polar solvent is chosen, such as DMSO (10). It has been postulated that these reactions proceed via a bridged intermediate, **XVIII**, and that the solvent may inhibit the coordination of the N-donor group to the mercury atom and allow it to bind to the gold (10). This is

XVI

XVII

XVIII

XIX

XX

XXI

consistent with the failure of the lithium derivatives of these and similar ligands to react with $[\text{AuCl}_4]^-$ (43); presumably the organolithium is chelated, again discouraging the formation of the Au-N bond.

Solvent effects are also important in direct auration reactions of aromatic systems by gold(III) halides. The first arylgold derivative, $[\text{AuPhCl}_2]_2$, reported in 1931, was obtained by direct reaction between benzene and Au_2Cl_6 (45). Alkyl benzenes would also react but not benzenes with potentially coordinating substituents; for instance, azobenzene gave XIX. More recently it

was found that some of these adducts will undergo an *ortho*-metallation reaction, such as the transformation of XX into XXI (46). This is effected by refluxing the adduct in aqueous acetonitrile (3:1), and similar reactions have been used recently to prepare a range of C,N-bonded gold(III) chelates containing six-membered rings such as XXII, including one in which an alkyl carbon atom has been metallated (XXIII) (47). Although it has not been commented on, the role of the solvent must be critical here, in allowing the escape or, more probably, the solvation of the liberated HCl.

A versatile method involving exchange of organic groups has been developed. Reaction of $[\text{AuCl}_2]^-$ with thallium(I) acetylacetonate produces $[\text{Au}(\text{acac})_2]^-$ (XXIV). This complex reacts with organic molecules having a moderately acidic hydrogen (HR) to liberate acetylacetonate and form the corresponding $[\text{AuR}_2]^-$ (48). For instance, the ethynyl complex $[\text{Au}(\text{C}\equiv\text{CH})_2]^-$ is readily made this way (49); as the $[\text{N}(\text{PPh}_3)_2]^+$ salt, this anion is much more stable than previously reported (50). Simple gold(I) alkynyls are still made by the traditional method (36) which was effectively the reaction of $[\text{AuBr}_2]^-$ with $\text{HC}\equiv\text{CR}$ in the presence of sodium acetate. Similar proton-elimination reactions are used to prepare the substituted derivatives $\text{LAuC}\equiv\text{CR}$ from LAuCl (see, for example, references 51–55); alternatively, $[\text{AuC}\equiv\text{CR}]_n$ is treated with the ligand (56).

XXV

XXVI

The unusual compound III is prepared by bromination of a gold(I) derivative of styryldiphenylphosphine (XXV). Oxidation occurs rapidly at the gold atom to give XXVI which

XXII

XXIII

XXIV

undergoes slow rearrangement to **III** (9, 57). Analogous reactions occur with the corresponding allyl-substituted phosphine (9).

Carbene complexes can be obtained by transmetalation, involving metal carbonyl derivatives (Equation 5) (14) or by nucleophilic attack on an isonitrile (Equation 6) (13). Ylides are usually obtained by deprotonation of a methyl phosphonium salt, using butyl lithium or sodium hydride. They are strong ligands and readily replace halides, or other weakly bound ligands from gold(I) complexes (Equations 7, 8) (22, 48). In some cases a ligand already bound may act

as the deprotonating agent (Equations 9–11) (18, 48). A range of methanide complexes can be obtained by making use of the basicity of an ylide carbon atom (Equations 12–15) (18, 58).

Finally, many of the hypervalent compounds are made by an ingenious reaction in which a dimethoxyboryl compound undergoes displacement of the B(OMe)_2 group by an AuL^+ group and simultaneously becomes transformed into a BF_4^- anion by the addition of CsF (in THF solution) (Equations 16, 17) (25, 26).

CONCLUSIONS

This survey shows that, despite the enormous variety of types of organogold compound now known, some apparently rather exotic, their coordination numbers and stereochemistries obey simple rules: gold(I) is two-coordinate and linear, and gold(III) is four coordinate and square planar. While other structures are known (a few three- and four- coordinate gold(I) complexes, a very small number of five coordinate gold(III) complexes) they do not appear in organogold chemistry except perhaps as reaction intermediates.

An increasing number of applications for gold compounds can be envisaged, and many of these are based on the organogolds; these will be discussed in a second article. These applications depend on the ways in which organogold compounds react, and these reactions will also be surveyed.

ABOUT THE AUTHOR

Dick Parish is Reader in Chemistry at UMIST and has a long-standing interest in the chemistry of gold, particularly of compounds with actual or potential medicinal interest, and in the application of Mössbauer spectroscopy to coordination chemistry, including that of gold.

REFERENCES

- 1 S. Komiya, T. Sone, Y. Usui, M. Hirano and A. Fukuoka, *Gold Bull.*, 1996, **29**, 131
- 2 R.J. Puddephatt in *Comprehensive Organometallic Chemistry*, (ed. G. Wilkinson, F.G.A. Stone, and E.W. Abel), Pergamon, Oxford, 1982; Gmelin's *Handbuch der Anorganischen Chemie: Goldorganische Verbindungen*, (ed. H. Schmidbaur), Springer Verlag, Berlin, 1980
- 3 A. Grohmann, H. Schmidbaur, *Comprehensive*

- Organometallic Chemistry II*, (ed. J. Wardell, E.W. Abel, F.G.A. Stone and G. Wilkinson), Pergamon, Oxford, 1995
- 4 R. Usón, A. Laguna and P. Brun, *J. Organomet. Chem.*, 1979, **182**, 449; R. Usón, A. Laguna and J. Vicente, *J. Organomet. Chem.*, 1979, **131**, 471
 - 5 R.V. Parish, *Gold Bull.*, 1982, **15**, 51; 'Mössbauer Spectroscopy Applied to Inorganic Chemistry', Ed. J.G. Long, Plenum Press, New York, Vol 1, 1984, p. 589
 - 6 F. Bonati, A. Burin, B.R. Pietroni, E. Torregiani, S. Calogero and F.E. Wagner, *J. Organomet. Chem.*, 1991, **408**, 125; G. Banditelli, F. Bonati, S. Calogero, G. Valle, F.E. Wagner and R. Wordel, *Organometallics*, 1986, **5**, 1346
 - 7 J. Vicente, M.T. Chichote and M.D. Bermúdez, *Inorg. Chim. Acta*, 1982, **63**, 35
 - 8 R.V. Parish and J.P. Wright, unpublished observations
 - 9 M.A. Bennett, K. Hoskins, W.R. Kneen, R.S. Nyholm, R. Mason, P.B. Hitchcock, and G.B. Robertson and A.D.C. Towl, *J. Am. Chem. Soc.*, 1971, **93**, 4592; M.A. Bennett, *J. Organomet. Chem.*, 1986, **300**, 7
 - 10 P.A. Bonnardel, R.V. Parish and R.G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1996, 3185
 - 11 D. Gibson, B.F.G. Johnson and J. Lewis, *J. Chem. Soc.*, 1970, 367
 - 12 J. Vicente, M.D. Bermúdez, M.P. Carillo and P.G. Jones, *J. Chem. Soc., Dalton Trans.*, 1992, 1975
 - 13 W.P. Fehlhammer and W. Finck, *J. Organomet. Chem.*, 1991, **414**, 261
 - 14 E.O. Fischer and M. Böck, *J. Organomet. Chem.*, 1988, **287**, 279; E.O. Fischer, M. Böck and R. Aumann, *Chem. Ber.* 1983, **116**, 3618
 - 15 R. Usón, A. Laguna, M. Laguna, M.C. Gimeno, A. de Pablo, P.G. Jones, K. Mayer-Bäse, and C.F. Erdbrügger, *J. Organomet. Chem.*, 1987, **336**, 461
 - 16 H. Schmidbaur, J.R. Mandl, A. Wohlleben-Hammer and A. Fügner, *Z. Naturforsch.*, 1978, **33B**, 1325
 - 17 H. Schmidbaur and R. Franke, *Angew. Chem., Int. Ed Engl.*, 1973, **12**, 416
 - 18 R. Usón, A. Laguna, M. Laguna and M.C. Gimeno, *J. Chem. Soc., Dalton Trans.*, 1989, 1883
 - 19 R. Usón, A. Laguna, M. Laguna, A. Usón and M.C. Gimeno, *J. Chem., Soc., Dalton Trans.*, 1988, 710
 - 20 E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna, and J.M. Lopez de Luzuriaga, *Angew. Chem., Int. Ed Engl.*, 1994, **33**, 87
 - 21 J. Vicente, M.T. Chichote, M.C. Lagunas and P.G. Jones, *J. Chem. Soc., Dalton Trans.*, 1991, 2579
 - 22 J. Vicente and M.Y. Chichote, I. Saura-Llamas, *J. Chem. Soc., Dalton Trans.*, 1990, 1941
 - 23 E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna, J.M. López-de-Luzuriaga and M.A. Rodriguez, *Chem. Ber.*, 1995, **128**, 121
 - 24 H.H. Murray, L.C. Porter, J.P. Fackler and R.G. Raptis, *J. Chem. Soc., Dalton Trans.*, 1996, 2669; R.G. Raptis, J.P. Fackler, J.D. Basil and D.D. Dudis, *Inorg. Chem.*, 1991, **30**, 3072
 - 25 J.D. Basil, H.H. Murray, J.P. Fackler, J. Tocher, A.M. Mazany, T.J. Delord, B.T. Bancroft, H. Knachel, D.S. Dudis and D.O. Marler, *J. Am. Chem. Soc.*, 1985, **107**, 6908; H.H. Murray, J.P. Fackler and B. Trczinska-Bancroft, *Organometallics*, 1985, **4**, 1633
 - 26 H. Schmidbaur and R. Franke, *Inorg. Chim. Acta*, 1975, **13**, 85
 - 27 S. Bommers, H. Beruda, N. Dufour, M. Paul, A. Schier and H. Schmidbaur, *Chem. Ber.*, 1995, **128**, 137
 - 28 O. Steigelman and H. Schmidbaur, *Z. Naturforsch.*, 1993, **47b**, 1721
 - 29 O. Steigelman, P. Bissinger and H. Schmidbaur, *Z. Naturforsch.*, 1992, **48b**, 72
 - 30 F. Scherbaum, A. Grohmann, G. Müller and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 463
 - 31 F. Scherbaum, A. Grohmann, B. Huber, C. Krüger and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1544
 - 32 P.G. Jones, *Gold Bull.*, 1981, **14**, 102, 159; 1983, **16**, 114; 1986, **19**, 46
 - 33 H. Schmidbaur, *Gold Bull.*, 1990, **23**, 11
 - 34 P.W.J. de Graaf, J. Boersma and G.J.M. van der Kerk, *J. Organomet. Chem.*, 1977, **127**, 391
 - 35 A.N. Nesmeyanov, E.G. Perevalova, K.I. Grandberg and D.A. Lemonvskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 1124
 - 36 G.E. Coates and C. Parkin, *J. Chem. Soc.*, 1962, 3220
 - 37 D.M.P. Mingos, J. Yau, S. Menzer and D.J. Williams, *Angew. Chem., Int. Ed Engl.*, 1995, **34**, 1894
 - 38 W. Xu, J.J. Vittal and R.J. Puddephatt, *Can. J. Chem.*, 1996, **74**, 766
 - 39 H. Lang, K. Köhler and L.Z. Solnai, *J. Chem. Soc., Chem. Commun.*, 1996, 2043

-
- 40 J.R. Berenguer, J. Forniés, E. Lalinde, F. Martinez, E. Urriolabeitia and A.J. Welch, *J. Chem. Soc., Dalton Trans.*, 1994, 1291
- 41 C.H. Campbell and M.L.H. Green, *J. Chem. Soc.*, 1971, 3283
- 42 H.K. Nair and J.A. Morrison, *J. Organomet. Chem.*, 1989, **376**, 149
- 43 J. Vicente, M.T. Chichote and M.D. Bermúdez, *J. Organomet. Chem.*, 1984, **268**, 191
- 44 R.V. Parish, B.P. Howe, J.P. Wright, J. Mack, R.G. Pritchard, R.G. Buckley, A.M. Elsome and S.P. Fricker, *Inorg. Chem.*, 1996, **35**, 1659
- 45 M.S. Kharasch and H.S. Isbell, *J. Am. Chem. Soc.*, 1931, **53**, 2701, 3503
- 46 E.C. Constable and T.A. Leese, *J. Organomet. Chem.*, 1989, **363**, 419
- 47 M.A. Cinellu, A. Zucca, S. Stoccoro, G. Minghetti, M. Manassero and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1995, 2865; *ibid.*, 1996, 4217
- 48 J. Vicente, M.T. Chichote, I. Saura-Llamas and M.C. Lagunas, *J. Chem. Soc., Chem. Commun.*, 1992, 915
- 49 J. Vicente, M.T. Chichote and M-D. Abrisqueta, *J. Chem. Soc., Dalton Trans.*, 1995, 497
- 50 R. Nast and U. Kirner, *Z. Anorg. Allg. Chem.*, 1964, **330**, 311
- 51 T.E. Müller, D.M.P. Mingos and D.J. Williams, *J. Chem. Soc., Chem. Comm.*, 1984, 1787
- 52 R.J. Cross, *J. Chem. Soc., Dalton Trans.*, 1986, 411
- 53 D. Li, X. Hong, C.M. Che, W.C. Lo and S.M. Peng, *J. Chem. Soc., Dalton Trans.*, 1993, 2929
- 54 M.J. Irwin, G. Jia, N.C. Payne and R.J. Puddephatt, *Organometallics*, 1996, **15**, 51
- 55 G. Jia, N.C. Payne, J.J. Vittal and R.J. Puddephatt, *Organometallics*, 1993, **12**, 4771
- 56 H. Xiao, K-K. Cheung and C.M. Che, *J. Chem. Soc., Dalton Trans.*, 1996, 3699
- 57 R.V. Parish and H. Sailes, unpublished observations
- 58 E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna and J.M. López de Luzuriaga, *J. Chem. Soc., Dalton Trans.*, 1992, 3365