
Recent Advances in the Chemistry of Gold(I) Complexes with C-, N- and S-Donor Ligands Part II: Sulfur Ylide, Hydrosulfido, Sulfido, Trithiocarbonato, Dithiocarbimato and 1,1-Ethylenedithiolato Derivatives

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In these two papers we report the chemistry of gold(I) complexes with C-, N-, and S-donor ligands, as recently published by our group, and describe some previously unpublished results. In Part I, the synthesis of alkynyl, amino, imino and nitrido gold(I) complexes was reported (1). In this part, we give an account of the synthesis of gold(I) complexes with sulfur-containing ligands such as sulfur ylides, hydrosulfido, sulfido, trithiocarbonato, dithiocarbimato and 1,1-ethylenedithiolato.

INTRODUCTION

Some gold(I) complexes with S-donor ligands, such as thiomalate, thioglucose or thiopropanol, are amongst the most effective drugs for the treatment of rheumatoid arthritis (2-4). The potential of these gold(I) complexes as antitumoural, antimicrobial, antileishmaniosis and anti-HIV 1 agents has been demonstrated (4-10). However, more clinical trials and the design of new gold(I) complexes with S-donor ligands are probably necessary to realize all the possibilities in this area. This paper gives an account of the results we have recently obtained in some reactions designed to prepare new gold(I) complexes with sulfur-containing ligands. As stated previously (1), we are also interested in studying the weak Au...Au (aurophilic) interactions present in the structure of many gold(I) compounds. To observe such interactions we have prepared complexes containing several gold atoms bonded to the same donor atom or designed ligands whose geometry favours such weak bonding.

We have reported in the first part of this account (1) the use of the 'acac method' (acac = acetylacetonate) based on the general reactions (1) and (2):



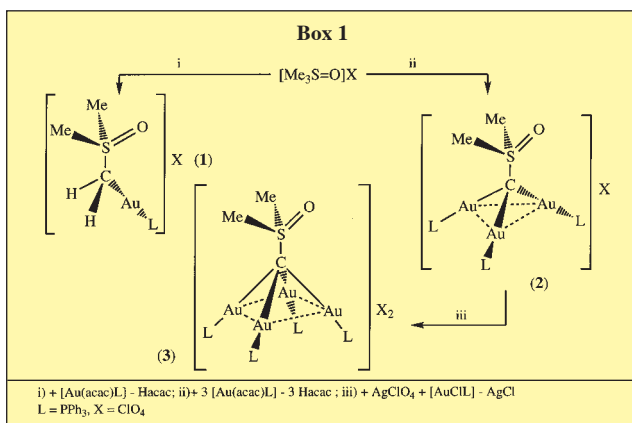
These reactions were used to prepare gold(I) complexes with ylide, thiolato, phosphide, bis(diphenylphosphino) - methanide or alkyl ligands (11-30). In the present paper we give new examples of the usefulness of this method.

GOLD(I) COMPLEXES WITH SULFUR YLIDE LIGANDS

The scarcity of gold complexes with sulfur ylide ligands (31-33) contrasts with the abundance of those with their phosphorus analogues (12, 34-41). This fact is even more surprising considering the interest in sulfur ylides and their complexes in organic or organometallic chemistry (42, 43).

The treatment of $[\text{Me}_3\text{S}=\text{O}]\text{ClO}_4$ with $[\text{Au}(\text{acac})\text{PPh}_3]$ gives, depending on the molar ratio of the reagents, mononuclear $[\text{Au}\{\text{CH}_2\text{S}-$

(=O)Me₂}(PPh₃)ClO₄ (**1**) or trinuclear [(AuPPh₃)₃-{μ₃-CS(=O)Me₂}]ClO₄ (**2**) sulfur ylide gold(I) complexes (see Box 1) (17). The 2:1 reaction, intended to produce the dinuclear complex [(AuPPh₃)₂{μ₂-CHS(=O)Me₂}]ClO₄, also gives the 1:1 (**1**) and 1:3 (**2**) products and the mixture could not be separated.



The reaction of **2** with AgClO₄ and [AuCl(PPh₃)] produced the first complex containing a hypercoordinate ylidic carbon atom [(AuPPh₃)₄{μ₄-CS(=O)Me₂}](ClO₄)₂ (**3**) the crystal structure of which shows the ylide carbon atom in a square pyramidal environment with an apical S(=O)Me₂ group and that the S-C_{ylide} bond distance [1.699(9) Å] is significantly shorter than the S-C_{methyl} distances [1.745(11), 1.756(11) Å]. **3** does not react further with [Au(OCMe₂)(PPh₃)]ClO₄ (17). The number of complexes with a clustering of AuPR₃ groups around a hypercoordinate carbon atom is limited to homoleptic species containing an interstitial carbon atom, [(AuPR₃)₅C]⁺ and [(AuPR₃)₆C]²⁺ (44-48), tetraaurio-methane and -ethanes [(AuPR₃)₄CR']⁺ (R = alkyl, aryl, R' = H, Me) (49, 50) and bis(silyl)methanium cations [(AuPPh₃)₃C(SiR₃)₂]⁺ (R₃ = Me₃, Me₂Ph).

The stepwise metallation of the same methyl group is a remarkable feature attributable to auriphilicity [see Introduction in Part I (1)] (47, 48). If this tendency were not so important one might have expected that, after the first AuPPh₃ group had replaced a hydrogen atom in a particular methyl group, further AuPPh₃ groups would replace hydrogen atoms of non-metallated methyl groups; since these methyl groups should be somewhat more acidic, in accord with the weak +I effect of the AuPPh₃ group. The same would be expected on steric grounds. In addition, in the absence of the auriphilic effect one could have expected coordination of the fourth AuPPh₃ group to the oxygen atom.

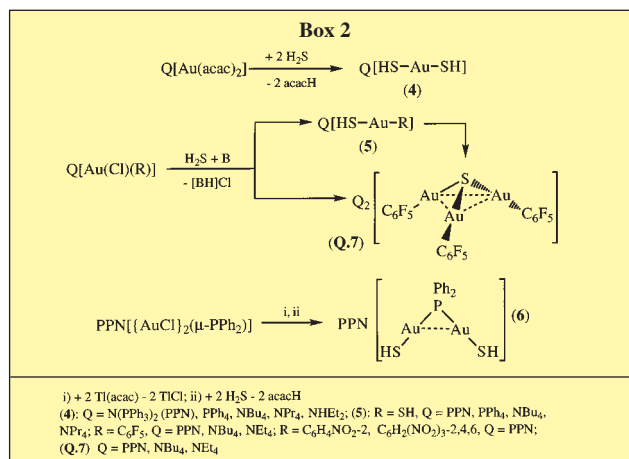
GOLD COMPLEXES WITH S-DONOR LIGANDS

Hydrosulfido and Sulfido Complexes

Interest in hydrosulfido complexes stems from the reactivity they exhibit toward organic substrates (51, 52), their proposed role as intermediates in important industrial (hydrodesulfurization) (53-55) and biological catalytic processes (56), and their use as models in theoretical studies (57).

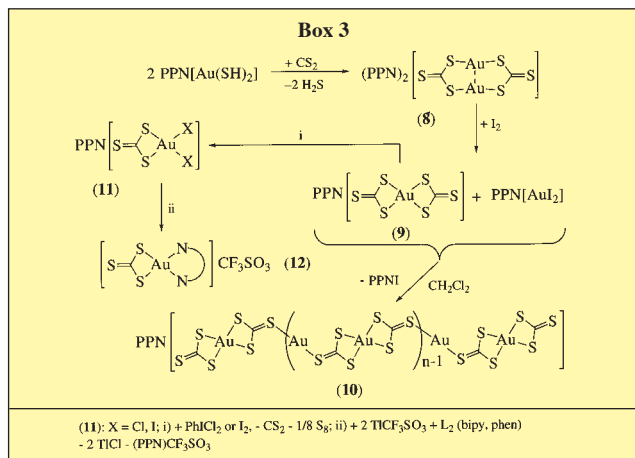
It has been suggested that considerable quantities of gold may be transported in hydrothermal ore solutions as [Au(SH)₂]⁻. Although previous solubility measurements of gold and Au₂S in aqueous sulfide or hydrogen sulfide solutions had indicated formation of this complex, it had not been isolated from these solutions (58-63). The reaction of hydrogen sulfide with acetylacetonatogold(I) complexes or with chlorogold(I) complexes in the presence of diethylamine (see Box 2) allowed us to prepare different hydrosulfidogold(I) complexes of the types [Au(SH)₂]⁻ (**4**) (14, 64), [Au(SH)(R)]⁻ (**5**) (64) [R = C₆F₅, C₆H₄NO₂-2, C₆H₂(NO₂)₃-2,4,6] and [{Au(SH)₂}(μ₂-PPh₂)]⁻ (**6**) (65). These constitute the first family of hydrosulfido complexes of gold and complex **4** is the first isolated homoleptic hydrosulfido complex of any transition metal.

The stability of these hydrosulfido complexes increases with the size of the counterions Q. Complexes with the smaller cations eliminate H₂S with accompanying formation of various sulfidogold complexes such as Q₃Q'[Au₁₂S₈] (65) (Q = Q' = NPr₄, NH₂Et₂; Q = NEt₄, Q' = NH₂Et₂) (the AsPh₄ salt had been reported previously, (66)) or Q₂{[AuC₆F₅]₃(μ₃-S)} (**Q.7**) (Q = NMe₄, NEt₄) (64). Salts of **7** with larger cations (Q = PPN, NBu₄) were prepared by reacting Me₄N.**7** with the appropriate QCl salt.



Trithiocarbonato Complexes

Trithiocarbonates are used as antiwear and antioxidant additives to extreme pressure lubricant oils and greases (67). They are also versatile intermediates for the synthesis of other thio species (68-73). Despite their synthetic and practical utility, however, few trithiocarbonato complexes have been fully characterized.

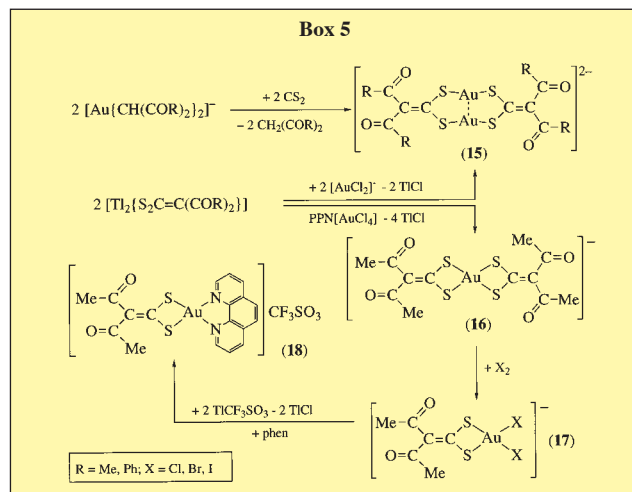
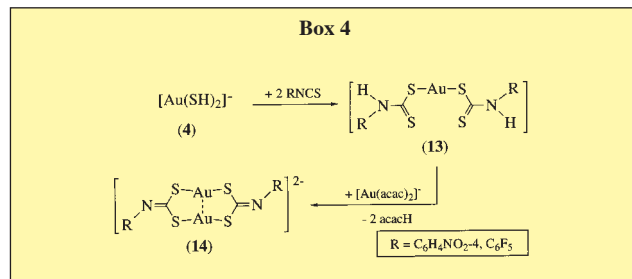


By reacting PPN[Au(SH)₂] with CS₂ we have prepared PPN[Au₂(μ₂-κ²-CS₃)₂] (**8**), the first complex containing a μ₂-κ²-bridging CS₃ ligand (see Box 3). From **8**, we have prepared the first family of trithiocarbonato gold complexes (74). The oxidation of **8** with PhICl₂ or I₂ gives a mixture of PPN[Au(CS₃)₂] (**9**) and the corresponding PPN[AuX₂] salt that can be separated. If not separated, these products react together on standing in dichloromethane to give the polymeric mixed valence complex PPN[Au^I_n{Au^{III}(CS₃)₂}_{n+1}] (**10**) (average value of n = 6) which we have characterized by its reactivity (74). The reaction of **9** with PhICl₂ or I₂ gives the gold(III) complexes PPN[AuX₂(CS₃)] (**11**) which in turn react with 2,2'-bipyridine or 1,10-phenanthroline in the presence of TlCF₃SO₃ to give the cationic complexes [Au(CS₃)(LL)]CF₃SO₃ (**12**).

Dithiocarbimato Complexes

Insertion reactions of isothiocyanates, as well as other unsaturated molecules, into the S-H bond of coordinated hydrosulfido ligands have been described previously (75). The reaction of PPN[Au(SH)₂] (**4**) with the isothiocyanates RNCS (see Box 4) gives complexes with monosubstituted dithiocarbimato ligands PPN[Au{SC(=S)NHR}₂] (**13**) (by IR, ¹H and ¹⁹F NMR) which we could not isolate in pure form (65). However, those with strong electron-withdrawing R groups (C₆H₄NO₂-4, C₆F₅) react with PPN[Au(acac)₂] to give dinuclear dithiocarbimato

complexes (PPN)₂[Au₂(μ₂-κ²-S₂C=NR)₂] (**14**) in almost quantitative yields with respect to **4**. Only two gold dithiocarbimato gold complexes Me₄N[Au(S₂C=NCN)₂] (**76**) and (PPN)₂[Au₂(μ₂-κ²-S₂C=NCN)₂] (**77**) [prepared from K₂(S₂C=NCN)] had been described previously.



Complexes with 2,2-Diacetyl- and 2,2-Dibenzoyl-1,1-ethylenedithiolato ligands

The organometallic β-diketonato complexes PPN[Au{CH(COR)₂}]₂ (R = Me, Ph) react with CS₂ to give the complexes (PPN)₂[Au₂(μ₂-κ²-S₂C=C(COR)₂)₂] (**15**) (see Box 5) (78). Insertion reactions of CS₂ into gold-element bonds are very scarce, and to date only those into the Au-C bond in [Au(η¹-C₅Me₅)(PR₃)] to give [Au(κ¹-S₂CC₅Me₅)(PR₃)_n] (R = Ph, n=2; R = Prⁱ, n=1) (79) or into an Au-Cl bond of [Au₂Cl₆] to give [AuCl₂(κ²-S₂CCl)] (**80**) have been described. We have described the insertion of CS₂ into an Au-S (or S-H) bond in PPN[Au(SH)₂] to give PPN[Au₂(μ₂-κ²-CS₃)₂] (**8**) (74) (see above). The thallium derivatives [Tl₂{S₂C=C(COR)₂] (R = Me, Ph) can be obtained by reacting the corresponding [Tl{CH(COR)₂}] complexes with CS₂. They can be used to prepare **15** or the gold(III) complex **16**. Attempts to prepare gold(II) complexes by oxidative addition of the

stoichiometric amount of halogen to **15** failed and only the gold(III) complex **16** could be isolated. This reacts further with halogen (PhICl₂, Br₂, I₂) to give mono 1,1-ethylenedithiolato complexes **17** which in turn react with 1,10-phenanthroline in the presence of TiClF₃SO₃ to give cationic complexes **18**.

CONCLUSIONS

The complexes [Au(acac)PPh₃] and [Au(acac)₂]⁻ are useful starting materials to prepare a number of types of gold(I) complexes. From the first one, we have obtained mono-, tri- and hypercoordinate tetranuclear sulfur ylide gold(I) complexes. The second complex reacts with carbon disulfide to give the 2,2-diacetyl-1,1-ethylenedithiolato complexes [Au₂{μ₂-κ²-S₂C=C(COR)₂]₂⁻ and with hydrogen sulfide to give [Au(SH)₂]⁻ which reacts with CS₂ or RNCS to give trithiocarbonato or dithiocarbimato complexes.

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ABOUT THE AUTHORS

Professors María Teresa Chicote and Jose Vicente received their PhD from Zaragoza University under the supervision of Professor Rafael Usón. They spent the year 1976 in Bristol University where they worked with Professor F Gordon A Stone. Since 1980 they have been at the University of Murcia.

Dr. María Dolores Abrisqueta and Dr. Pablo González Herrero recently received their PhD degrees from Murcia University and Rita Guerrero is now studying for her PhD. They have been working under the supervision of Professors Vicente and Chicote on the chemistry of gold(I) complexes described in this paper.

REFERENCES

- 1 J. Vicente, M.T. Chicote, M.D. Abrisqueta, P. González-Herrero and R. Guerrero, *Gold Bull.*, 1998, **31**, 83
- 2 S.J. Berners-Price and P.J. Sadler, *Coord. Chem. Rev.*, 1996, **151**, 1
- 3 S.P. Fricker, *Gold Bull.*, 1996, **29**, 53
- 4 S.L. Best and P.J. Sadler, *Gold Bull.*, 1996, **29**, 87
- 5 S.P. Fricker, *Trans. Met. Chem.*, 1996, **21**, 377
- 6 M. Viotte, B. Gautheron, M.M. Kubicki, I.E. Nifant'ev and S.P. Fricker, *Met.-Based Drugs*, 1995, **2**, 311
- 7 C.K. Mirabelli, R.K. Johnson, C.M. Sung, L. Faucette, K. Muirhead and S.T. Crooke, *Cancer Res.*, 1985, **45**, 32
- 8 S.Y.M. Chooi, P.H. Leung, K.Y. Sim, K.S. Tan and O.L. Kon, *Tetrahedron: Asymmetry*, 1994, **5**, 49
- 9 T. Okada, B.K. Patterson, S.-Q. Ye and M.E. Gurney, *Virology*, 1993, **192**, 631
- 10 T.M. Simon, D.H. Kunishima, D.H. Vibert and A. Lorber, *Cancer Res.*, 1981, **41**, 94
- 11 J. Vicente, M.T. Chicote, I. Saura-Llamas and M.C. Lagunas, *J. Chem. Soc., Chem. Commun.*, 1992, 915
- 12 J. Vicente, M.T. Chicote and M.C. Lagunas, *Inorg. Chem.*, 1993, **32**, 3748
- 13 J. Vicente, M.T. Chicote and P.G. Jones, *Inorg. Chem.*, 1993, **32**, 4960
- 14 J. Vicente, M.T. Chicote, P. González-Herrero, P.G. Jones and B. Ahrens, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1852
- 15 J. Vicente, M.T. Chicote, P. González-Herrero and P.G. Jones, *J. Chem. Soc., Dalton Trans.*, 1994, 3183
- 16 J. Vicente, M.T. Chicote, P. González-Herrero and P.G. Jones, *J. Chem. Soc., Chem. Commun.*, 1995, 745
- 17 J. Vicente, M.T. Chicote, R. Guerrero and P.G. Jones, *J. Am. Chem. Soc.*, 1996, **118**, 699
- 18 J. Vicente, M.T. Chicote and C. Rubio, *Chem. Ber.*, 1996, **129**, 327
- 19 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
- 20 E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna and J.M. Lopez de Luzuriaga, *J. Chem. Soc., Dalton Trans.*, 1992, 3365
- 21 M.C. Gimeno, A. Laguna, M. Laguna, F. Sanmartin and P.G. Jones, *Organometallics*, 1993, **12**, 3984
- 22 M.C. Gimeno, A. Laguna, M. Laguna, F. Sanmartin and P.G. Jones, *Organometallics*, 1994, **13**, 1538
- 23 J. Vicente, M.T. Chicote, J.A. Cayuelas, J. Fernández-Baeza, P.G. Jones, G.M. Sheldrick and P. Espinet, *J. Chem. Soc., Dalton Trans.*, 1985, 1163
- 24 J. Vicente, M.T. Chicote, I. Saura-Llamas, J. Turpin and J. Fernández-Baeza, *J. Organomet. Chem.*, 1987, **333**, 129
- 25 J. Vicente, M.T. Chicote, I. Saura-Llamas, P.G. Jones, K. Meyer-Bäse and C.F. Erdbrügger, *Organometallics*, 1988, **7**, 997
- 26 J. Vicente, M.T. Chicote and I. Saura-Llamas, *J. Chem. Soc., Dalton Trans.*, 1990, 1941
- 27 J. Vicente, M.T. Chicote, M.C. Lagunas and P.G. Jones, *J. Chem. Soc., Dalton Trans.*, 1991, 2579
- 28 J. Vicente, M.T. Chicote, M.C. Lagunas and P.G. Jones, *J. Chem. Soc., Chem. Commun.*, 1991, 1730
- 29 J. Vicente, M.T. Chicote and M.D. Abrisqueta, *J. Chem. Soc., Dalton Trans.*, 1995, 497
- 30 J. Vicente, M.T. Chicote, R. Guerrero and P.G. Jones, *J. Chem. Soc., Dalton Trans.*, 1995, 1251
- 31 Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1189
- 32 I.J.B. Lin, C.W. Liu, L.K. Liu and Y.S. Wen, *Organometallics*, 1992, **11**, 1447
- 33 J. Stein, J.P. Fackler Jr., C. Paparizos and H.-W. Chen, *J. Am. Chem. Soc.*, 1981, **103**, 2192
- 34 W.C. Kaska, *Coord. Chem. Rev.*, 1983, **48**, 1
- 35 A.W. Johnson, 'Ylides and Imines of Phosphorus', John Wiley and Son, New York, 1993

- 36 J.P. Fackler Jr., *Polyhedron*, 1997, **16**, 1
- 37 H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 907
- 38 J. Vicente, M.T. Chicote, M.C. Lagunas, P.G. Jones and B. Ahrens, *Inorg. Chem.*, 1997, **36**, 4938
- 39 J. Vicente, M.T. Chicote, M.C. Lagunas, P.G. Jones and E. Bembenek, *Organometallics*, 1994, **13**, 1243
- 40 D.C. Neitling, R.J. Staples and J.P. Fackler, *Inorg. Chim. Acta*, 1997, **263**, 35, and references therein
- 41 M. Bardaji, E. Cerrada, P.G. Jones, A. Laguna and M. Laguna, *J. Chem. Soc., Dalton Trans.*, 1997, 2263, and references therein
- 42 L. Weber, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 516
- 43 E.J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, 1965, **87**, 1353
- 44 F. Scherbaum, A. Grohmann, G. Müller and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 463
- 45 F. Scherbaum, A. Grohmann, B. Huber, C. Krüger and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1544
- 46 H. Schmidbaur, B. Brachthäuser and O. Steigelmann, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1488
- 47 H. Schmidbaur, *Gold Bull.*, 1990, **23**, 11
- 48 O. Steigelmann, P. Bissinger and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1399
- 49 O. Steigelmann, P. Bissinger and H. Schmidbaur, *Z. Naturforsch. B*, 1993, **48**, 72
- 50 H. Schmidbaur, F.P. Gabbai, A. Schier and J. Riede, *Organometallics*, 1995, **14**, 4969
- 51 D. Seyferth, G.B. Womack, R.S. Henderson, M. Cowie and B.W. Hames, *Organometallics*, 1986, **5**, 1568
- 52 W. Weigand, G. Bosl, C. Robl and J. Kroner, *Z. Naturforsch. B*, 1993, **48**, 627
- 53 H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 322
- 54 M. Rakowski-Dubois, *Chem. Rev.*, 1989, **89**, 1
- 55 R.J. Angelici, *Acc. Chem. Res.*, 1988, **21**, 387
- 56 D.R. English, D.N. Hendrickson, K.S. Suslick, C.W. Eigenbrot, Jr. and W.R. Scheidt, *J. Am. Chem. Soc.*, 1984, **102**, 7258
- 57 C.J. Adams, M.I. Bruce, M.J. Liddell, B.W. Skelton and A.H. White, *J. Chem. Soc., Chem. Commun.*, 1992, 1314
- 58 P.J. Renders and T.M. Seward, *Geochim. Cosmochim. Acta*, 1989, **53**, 245
- 59 D.M. Shenberger and H.L. Barnes, *Geochim. Cosmochim. Acta*, 1989, **53**, 269
- 60 K. Hayashi and H. Ohmoto, *Geochim. Cosmochim. Acta*, 1991, **55**, 2111
- 61 H. Colley, *Chem. Brit.*, 1992, **28**, 720
- 62 J.A. Tossell, *Geochim. Cosmochim. Acta*, 1996, **60**, 17
- 63 L.G. Benning and T.M. Seward, *Geochim. Cosmochim. Acta*, 1996, **60**, 1849
- 64 J. Vicente, M.T. Chicote, P. González-Herrero, C. Grünwald and P.G. Jones, *Organometallics*, 1997, **16**, 3381
- 65 J. Vicente, M.T. Chicote and P. González-Herrero, unpublished results
- 66 G. Marbach and J. Strähle, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 715
- 67 J.M. Dumdum, L.T. Mendelson and R.L. Pilling, U.S. Patent 4,908,142 (*Chem. Abs.*, 1990, **112**, 201925k)
- 68 D. Coucouvanis and J.P. Fackler Jr., *J. Am. Chem. Soc.*, 1967, **89**, 1346
- 69 I.B. Benson, J. Hunt, S.A.R. Knox and V. Oliphant, *J. Chem. Soc., Dalton Trans.*, 1978, 1240
- 70 C. Bianchini, C. Meali, A. Meli and G. Scapacci, *J. Chem. Soc., Dalton Trans.*, 1982, 799
- 71 C. Bianchini, P. Innocenti and A. Meli, *J. Chem. Soc., Dalton Trans.*, 1983, 1777
- 72 R. Usón, J. Forníés and M.A. Usón, *Syn. React. Inorg. Metal-Org. Chem.*, 1984, **14**, 355
- 73 J. Forníés, M.A. Usón, J.I. Gil and P.G. Jones, *J. Organomet. Chem.*, 1986, **311**, 243
- 74 J. Vicente, M.T. Chicote, P. González-Herrero and P.G. Jones, *Inorg. Chem.*, 1997, **36**, 5735
- 75 R.J. Angelici and R.G.W. Gingerich, *Organometallics*, 1983, **2**, 89
- 76 F.A. Cotton and J.A. McCleverty, *Inorg. Chem.*, 1967, **6**, 229
- 77 Z. Assefa, R.J. Staples and J.P. Fackler Jr., *Acta Crystallogr., Sect. C*, 1995, **51**, 2271
- 78 J. Vicente, M.T. Chicote, P. González-Herrero and P.G. Jones, *Chem. Commun.*, 1997, 2047
- 79 H. Otto and H. Werner, *Chem. Ber.*, 1987, **120**, 97
- 80 D. Jentsch, P.G. Jones, C. Thöne and E. Schwarzmann, *J. Chem. Soc., Chem. Commun.*, 1989, 1495

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