Coordination Chemistry Reviews, 67 (1985) 311—323
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

6. GOLD

W.E. SMITH

CONTENTS

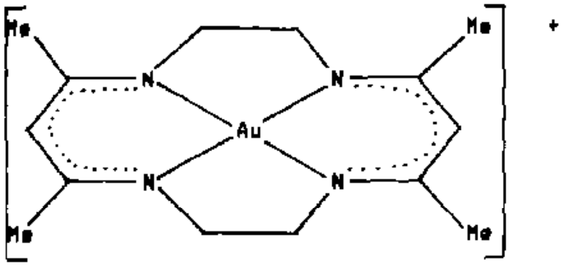
INTRODUCTION

This year, there has been a further erosion of the difference between the traditional inorganic complex chemistry and the organometallic chemistry of gold. This arises both because there has been a continued interest in gold clusters with a very marked increase in interest in clusters containing other metals as well as gold, and because the increasing use of X-ray structural analysis has revealed that many gold complexes with sulphur and phosphorus ligands have an architecture to rival that found in the organometallic field. The result of this work, and the continued use of simple organometallic reagents such as dimethyl gold compounds, makes it necessary to continue last year's practice of including in the review such organometallic chemistry as relates directly to the properties of the gold moiety.

6.1 GOLD(III)

Among the complexes of gold(III) with nitrogen ligands which are reported this year, the gold macrocycle (*1*) is an interesting addition to the very few known examples of gold complexes of this type [1]. It was made from $[Au(en)_2]Cl_3$ and the β-diketone and the structure is planar (whereas the structure of equivalent first-row complexes is saddle-shaped). This indicates a different bonding pattern for gold(III), and emphasises the tendency of

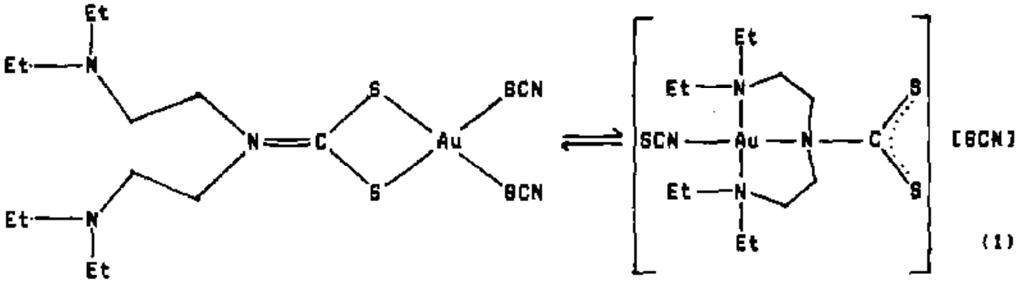
0010-8545/85/$4.55



(*1*)

gold(III) to planar coordination.

A novel example of the range of gold bonding types possible is the double linkage isomerism that occurs in complexes of the ligand tetraalkyldiethylamino dithiocarbamate. With sulphur coordination to the gold, the remaining positions are taken up by thiocyanate ligands coordinated through the sulphur, whereas with nitrogen coordination to the gold the thiocyanate is also coordinated through the nitrogen [2]. This is illustrated in equation (1).



(1)

Three studies report complexes made with sulphur compounds. $[Bu_4N][Au(S_2C_6H_3Me)_2]$ contains square planar gold coordinated to the four thiolato groups, with the aromatic rings tipped to one side [3]. One aspect of the chemistry of gold-sulphur complexes which is little studied, but may occur quite frequently, is the reaction of the coordinated ligand. SO_2 coordination to the sulphur or aromatic groups of $[Au(S_2C_6H_3Me)_2]^-$ is postulated on the basis of NMR evidence [3]. A range of maleonitrile dithiolate, $[mnt]^{2-}$, complexes containing gold(III) or gold(I) have been isolated, with planar four-coordinate or linear structures, respectively.[4]. The complex $[Au(mnt)L]^+$ (L = bipy or phen) is a good example of a mixed chelate complex of gold(III). [TTF][$AuCl_4$]$_2$ and [TTF][$AuCl_2$] (TTF = tetrafulralene; the sites contain the monopositive and dipositive cations, respectively) have been prepared and the oxidation potential of the gold(III) has been shown to be strongly dependent on solvent, with ethanenitrile producing a greater potential than ethanol [5].

Other compounds reported this year include complexes of di-2-pyridyl-ketone (dpk) which have the formula [$AuCl_2$(dpk.H_2O)]Cl and [Au(dpk.H_2O)$_2$][ClO_4]$_3$. The X-ray structure of the former shows a planar gold atom coordinated to two nitrogen atoms and two chloride ions [6]. Complexes with 3-methyl-1H-pyrazole and 3,5-dimethyl-1H-pyrazole of formula $AuCl_3L$ and HL[$AuCl_4$] [7], and a complex of *N*-ethoxycarbonyl-pyrrole-2-thiocarboxamide (eth) of formula Au(eth)$_2$Cl [8] have been characterised, and the oxidative addition of $(SCN)_2$ or molecular iodine to Au(PMe_3)(CN) produces the complexes [Au(PMe_3)(CN)$(SCN)_2$] and [Au(PMe_3)(CN)I_2], respectively [9]. Inorganic compounds reported this year include the gold molybdate complex [NH_4]$_3$Au(MoO_4)$_3$.$3H_2O$ from chloroauric acid and [NH_4]$_6$[Mo_7O_{24}] [10]. When the gold complex is heated, a second complex [NH_4]Au(MoO_4)$_2$ is formed. The structure of hydrated potassium tetrachloroaurate(III) shows, as expected, square-planar gold atoms, but the potassium ions and water molecules combine to form infinite chains along the *c* axis and are important elements in determining the crystal structure [11].

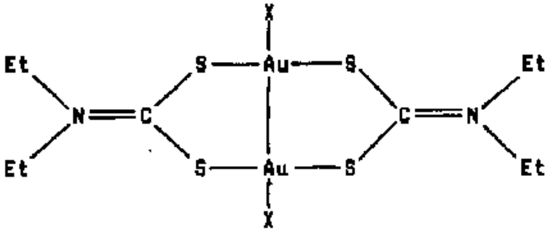
Raman spectra have been reported for both square-planar tetraamminegold(III) nitrate and its deuterate [12], and for the phosphorus pentachloride-gold trichloride system [13]. In the latter case, the compound $AuCl_3.PCl_5$ was isolated and shown to be [PCl_4][$AuCl_4$], and the strength of the $[AuCl_4]^-$ unit was illustrated when it was detected intact in the molten phase. Gold(III) can be used to promote the hydrolysis of various sulphur-containing compounds, and it has been shown this year that, rather unusually, the slow step in this reaction is a slow metal transfer reaction analogous to slow proton transfer reactions [14].

The use of gold(I) complexes in the treatment of rheumatoid arthritis was reviewed last year as a consequence of the impact of a new orally active gold(I) compound. Gold(III) compounds are not used since they are toxic, and this year the reasons for this toxicity have been investigated *in vitro*. It was found that the tetrabromoaurate(III) ions cause oxidative cleavage of disulphide bonds in insulin and other proteins and peptides [15]. The reactions which occur include that shown in equation (2).

$$3RSSR + 10[AuBr_4]^- + 18H_2O \longrightarrow 6[RSO_3]^- + 10Au + 40Br^- + 36H^+ \qquad (2)$$

6.2 GOLD(II)

As usual, there are few reports of gold(II) compounds this year. One set of compounds of diethyldithiocarbonate, of formula (*2*), have been isolated at 77 K [16]. They are green and revert to mixed-valence compounds of the type $[Au(Et_2NCS_2)_2][AuX_2]$ on warming. If the ethyl groups are replaced by butyl groups, the stability of the compounds is increased. The $[Au_2(Et_2NCS_2)_2]$ precursor contains an eight-membered ring with linear S-Au-S bonds in it, and in this it contrasts with silver where the $[Ag_6(Et_2NCS_2)_6]$ unit has a central silver-sulphur cluster. This cluster is more stable to oxidation, although different complexes are isolated at 77 K and room temperature.



(2; X = Br, I, SCN or SeCN)

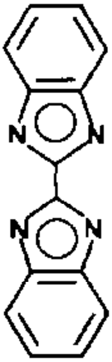
6.3 GOLD(I)

Although gold(I) complexes are usually linear, higher coordination numbers are becoming increasingly common and at least as far as phosphines are concerned three- and four-coordinate gold compounds can no longer be considered as unusual. One paper [17] lists sixteen three-coordinate and eight four-coordinate gold(I) complexes known from previous work, and then reports several novel examples to add to this list. The predominant ligands are phosphines, but bipy, $[SCN]^-$, $[CN]^-$, $[SnCl_3]^-$, phen and phosphites are present in conjunction with them. The methods of analysis for higher coordination include X-ray structure determination, ^{31}P NMR and Mössbauer spectroscopy. In Mössbauer spectroscopy, the standard point charge (isomer shift) approach works well for both two and three coordination and can be used effectively in compounds containing more than one gold site. For example, the Mössbauer spectrum of the novel compound $[Au(AsPh_3)_3][NO_3]$ is a doublet with the lower energy peak three times the size of the higher one. This is interpreted as indicating a 1:1 mixture of two-coordinate gold giving a standard doublet of equal intensities and a single peak typical of tetrahedral coordination due to an $[Au(AsPh_3)_4][ClO_4]$ species. Further, the Mössbauer spectrum of Myocrisin and Solganol, the gold drugs with thiomalate and thioglucose ligands, indicates linear gold coordination in these polymeric species but it also indicates the presence of more than one gold site [18]. The gold in the new orally active drug auranofin, which is *P* and *S* coordinated, is also linear as indicated last year by EXAFS and this year by Mössbauer spectroscopy. The crystal structure is now available [19] and confirms these assignments.

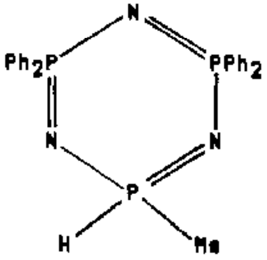
Returning to the theme of three and four coordination, it was stated last year that the postulate of tetrahedral coordination in gold(I) phosphorus compounds was not justified, at least at room temperature and in the solid state. However, $[Au(PPh_2Me)_4][PF_6]$ has a regular tetrahedron of phosphorus atoms round the gold and seems a good example of just this type of coordination [20]. $[(Ph_3P)Au][BPh_4]$ on the other hand contains trigonally coordinate gold [21] and $[\{(Ph_3P)Au\}_3S][PF_6]$ [22] has the sulphur coordinated to three gold atoms.

Other examples of higher coordination in gold(I) chemistry break away from the dependence on phosphorus ligands. A complex of 1,2-phenylene dimethylarsine (L) of formula $[L_2Au][Au(C_6F_5)_2]$ [23] and an antimony containing complex $[Au(SbPh_3)_4][Au(C_6F_5)_2]$ have been prepared. In both cases, the gold is tetrahedrally coordinated. An example of a thiolate producing higher coordination than two is tetrathiosquaric acid [24].

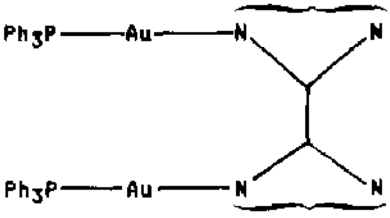
Among other ligands used this year are good examples of a complex 'soft' nitrogen ligand (*3*) [25] and of a N/P ring system (*4*) [26]. With (*3*), the coordination to gold is linear and all nitrogens can be involved in complexing, with other ligands used to complete structures such as (*5*). With ligand (*4*), gold is always coordinated through the phosphorus and the molecules are fluxional with rapid proton transfer to a ring nitrogen. Gold(I) derivatives of pyrazoles exhibit linear gold coordination to a nitrogen of the ring. The ligand can form an anion bridge between two gold ions [27].



(3)



(4)



(5)

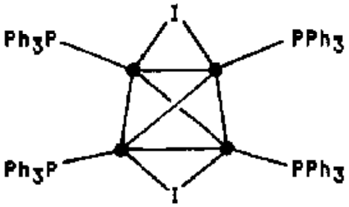
Another bridging ligand is 1,2-bis(diphenylphosphino)ethene, which binds two AuCl moieties [28]. Finally, returning to more established bonding patterns, a range of complexes of the type $[Au(SR)_2]^-$ have been prepared and the Au-S vibrations assigned [29]. A study of the solubility of gold sulphide in aqueous sulphide solution indicated the presence of a range of complexes including $Au(HS)(H_2S)$, $[Au_2(HS)_2S]^{2-}$ and $[Au(HS)(OH)]^-$ [30], and the stability of gold thiosulphate complexes in the presence of copper and silver thiosulphate was investigated [31].

Thus, the coordination chemistry of gold is becoming better documented with a wider range of soft ligands such as arsines, stibines, selenides, 'soft' nitrogen ligands and more complex phosphorus ligands widening the available choice. The increasing number of examples of higher coordination is a notable feature of this extension of the chemistry and this, allied to the complex nature of many compounds and the ease with which they can rearrange, made the need for more precise spectroscopic techniques to complement the increasing use of X-ray analysis all the more urgent.

6.4 CLUSTER COMPOUNDS

Gold cluster compounds are still a very active area of research, with some new directions becoming evident this year. It was suggested last year that an $\{Au_{13}\}$ moiety which has a centred icosahedral structure might turn out to be a common type of gold cluster, and a new example $[Au_{13}(PMe_2Ph)_{10}Cl_2][PF_6]$ has been synthesised [32]. The preparation involves addition of $[Ti(C_7H_8)_2]$ to a toluene solution of $AuCl(PR_3)$, instead of the more conventional routes, and the yield is high. The cluster $[Au_8(PPh_3)_7][NO_3]_2$ was made by treating $[Au_8L_8][NO_3]_2$ ($L = PPh_3$) with a phosphine scavenger and it, like $[Au_9L_8]^{3+}$ clusters, is based on a centred icosahedron with vacant sites [33].

The largest cluster so far reported is, on the basis of analysis and molecular weight measurements, $[Au_{15}(PPh_3)_{12}Cl_6]$ and, on the basis of Mössbauer measurements, it contains four types of gold but again the nucleus is an $\{Au_{13}\}$ cluster [34]. On the other hand, there have been a number of reports on systems containing a much simpler tetranuclear gold cluster. For example, reaction of $[Au_9(PPh_3)_8][NO_3]_3$ with KI in propanone gives a tetranuclear arrangement with a terminal phosphine on each gold and two bridging iodines (*6*) [35]. Iodine coordination in this manner is unusual. Another interesting set of compounds are gold oxonium salts, $[\{(Ph_3P)Au\}_3O]X$ (X = BF_4, CF_3CO_2 or MO_4), which contain a pyramidal $\{Au_3O\}$ unit, with the oxygen lying above the $\{Au_3\}$ plane [36].



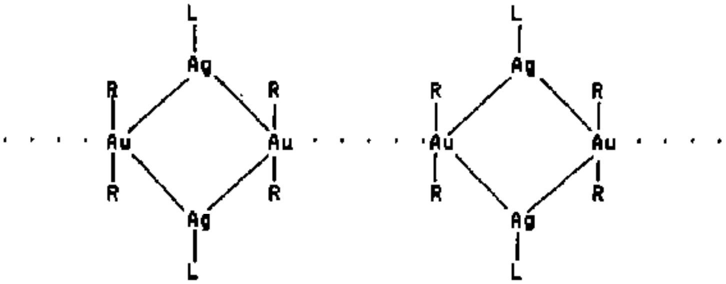
(6)

An example from a different area of chemistry is the structure reported for the intermetallic phase $Rb_4Au_7Sn_2$ which contains two gold tetrahedra linked at one corner [37].

There are quite a number of mixed-metal gold clusters this year, indicating a considerable expansion of interest in this field. One with a tetrahedral arrangement is prepared by adding $Li[Co(CO)_4]$ in thf to $[Au_8(PPh_3)_7]^{2+}$ to give $[Au_6(PPh_3)_4\{Co(CO)_4\}_2]$ [38]. This is the first heteronuclear gold-cobalt cluster, and it consists of two gold tetrahedra with a common edge and $Co(CO)_4$ units bonded to the apical gold atoms. $[\{Au(PPh_3)\}_3V(CO)_5]$ is based on a structural unit of one vanadium and three gold atoms arranged in a tetrahedron and it is the first example of a gold-vanadium cluster [39].

The theme of mixed-metal bonding involving gold has been developed further. The first inorganic, as opposed to organometallic, gold-platinum compound $[(PPh_3)_2ClPtAu(PPh_3)]$ was prepared [40]. Gold compounds containing the entity $[(C_6F_5)_3Au\text{-}M(CO)_nL]$ (L = cp or CO; M = Mn, Co, Mo or W) have been prepared and also contain gold-metal bonds [41]. The crystal structure of $[N(PPh_3)_2][Au\{Co(CO)_4\}_2]$ revealed a linear Co-Au-Co arrangement [42] and that of $[Os_6Au(CO)_{20}H_2]^-$ has a square planar arrangement about the gold with bonds to two $\{Os_3(CO)_{10}H\}$ units *via* the osmium, and two short Au-O distances [43].

Reaction of $[Bu_4N][Au(C_6F_5)_2]$ and $Ag[ClO_4]$ produces a gold/silver chain polymer, (*7*) [44]. The metal clusters $NaAu_3Si$ and $NaAu_3Ge$ contain a triangle of gold atoms with the other metals coordinated in the apical positions [45] on either side of the plane, and an analogous structure (with a triangle of cobalt atoms and an iron and gold atom in the apical positions) is shown by $[FeCo_3(CO)_{12}Au(PPh_3)]$ [46].

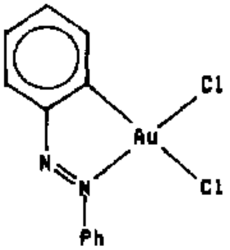


(*7*; R = Ph, L = tetrahydrothiophen)

Clearly much more can be done in this area, and taken together with the increasingly prevalent inorganic and organometallic "clusters" or complex molecules, it would seem that a fruitful area of chemistry could develop: already one set of gold-lithium cluster compounds has been patented as hydrogenation catalysts [47].

6.5 ORGANOMETALLIC COMPOUNDS

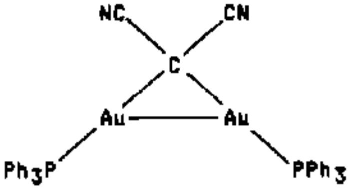
Two years ago, a novel gold(III) compound with a monodentate azo group coordinated to an $AuCl_3$ moiety was reported and last year a complex with a gold(III) phenyl bond, $[\{Au(C_6H_5)Cl_2\}_2]$, formed by the action of $[AuCl_4]^-$ in benzene was described [48]. This year, a complex (*8*), with both a metal azo



(*8*)

and metal carbon bond, made by the reaction of [$AuCl_3$(tht)] (tht = tetrahydrothiophen), has been described and the structure deduced on the basis of spectroscopic evidence [49].

A number of compounds with both P-Au and C-Au bonds have been reported. Direct reaction of [{(Ph_3P)Au}$_3$O][BF_4]$^-$ with cyclopentadiene, cyanoacetic ester or malonitrile produced a series of complexes, including {(Ph_3P)Au}$_2$C(CN)$_2$, for which structure (*9*) was determined [50], and six [51], eight [52] and twelve [51] membered rings containing gold, carbon and phosphorus (and in some cases lithium and boron) have also been described. The six and twelve membered rings were prepared from a cyclic lithium compound with Me_2AuCl, and the eight membered ring from (Ph_2P)$_2$CRLi and Cl(R_3P)Au.



(9)

The complexes $Me_3AuCH_2S(O)Me_2$ and $Me_3AuCH_2PPh_3$ are tetra-coordinated σ-bonded alkyls; NMR, XPES and UVPES data indicate that the ylide linkage reduces the charge on the metal and as a result the complexes are surprisingly stable [53]. Among the other studies which lie on the borderline between organometallic chemistry and inorganic chemistry, are the use of [(Ph_4C_4)AuCl(tht)] or [{(Ph_4C_4)AuCl}$_2$] as reagents to form other auracyclopentadiene complexes, such as [(Ph_4C_4)Au(acac)] [54], the synthesis of new binuclear and mononuclear alkyl complexes [55] and new gold-carbene complexes made by carbene transfer from a tungsten compound [56].

6.6 PHYSICAL METHODS

Gold can be trapped in a variety of oxidation states in halide lattices and this year the UV-VIS spectrum of both Au^+ [57] and Au^- [58] doped KCl have been reported. The Au^+ ion has its most intense bands at 280 and 190 nm, with weaker features at about 330 nm, whereas the main bands in the Au^- system are at 310 nm and below 220 nm. Further, Au(0) can be doped in a silver halide crystal which, on oxidation in a chlorine atmosphere, produces the new gold(III) compound $AgAuCl_4$ [59]. There is band in this system at about 345 nm which is typical of other [$AuCl_4$]$^-$ containing species.

In addition to the techniques already discussed, a wide range of physical methods have been employed in gold studies. Mass spectrometry has been used to identify the polymeric nature of AuF_4, $[O_2][AuF_6]$ and AuF_3, which contain Au–Au bonds [60], and XPES measurements confirm that the complex $Au(dmso)Cl_2$ contains both gold(I) and gold(III) [61]. The assignment of gold–oxygen Raman active vibrations has been made for a wide range of compounds [62] and NQR spectra for gold halides have been reported [63]. SCF-X_α-SW calculations of the species $M(CO)_n$ (n = 1–3) found in matrix isolation experiments for copper, silver and gold indicate that metal-ligand bonding is predominantly σ, and the complexes are less stable than similar complexes of Group VIII metals because of the reduced π-bonding [64]. Both the stability of gold(III)-sulphur compounds [65] and the nature of gold Mössbauer hyperfine structure [66] have been investigated theoretically. In the former case, the stability is related to the relative position of the metal *d* orbitals and non-bonding sulphur orbitals, and in the latter the role of 5*d*, 6*s* and 6*p* metal orbitals were examined. In both cases a substantial relativistic correction was required.

The vibrational spectroscopy of gold(I) thiocyanate complexes has proved ideal to examine the effect of the second ligand in linear $[(R_3P)Au(SCN)]$ complexes. The complexes are linear and neutral so that no steric or outer ion control is to be expected, and with a range of phosphine ligands all are Au–S bonded in the solid state: the ratio of AuSCN to AuNCS bonding was studied. The results confirm the idea that the site *trans* to a *trans*-directing ligand becomes 'harder' in complexes of class B metals; SeCN, on the other hand, is always bonded through the selenium and being 'softer' competes with the phosphorus making the Au–P bond weaker than with SCN. The use of Au–Cl vibrations from RAuX materials of this type is difficult since crystal packing effects are as large as ligand shifts, but the Au–P band is of value [67].

A number of electrochemical experiments designed with quite different objectives in mind have appeared. In studies of gold plating and dissolution, the build-up of $[Au(CN)_4]^-$ (which changes plating thickness with age) in gold cyanide baths, and chemical and electrochemical solutions, was suggested [68]. The dissolution of gold at the anode proceeds by the adsorption of the cyanide and the initial formation of AuCN from adsorbed $[Au(CN)_2]^-$ is the slow step [69]. The importance of electrode-substrate interactions is emphasised in a number of studies. The oxidation of allyl alcohol on a gold electrode is affected by the adsorption step, possibly due to an interaction between antibonding electrons of the alcohol and *d* electrons of the gold [70]. The photo-currents set up in an irradiated gold electrode are probably initiated by the oxidation of water [71]. An absorbed layer of 4,4'-bipyridine modifies a gold electrode so that it can be used in electrochemical experiments with proteins such as cytochrome c. The 4,4'-bipyridine lies between a form flat on the electrode surface and a perpendicular one which, it is suggested, is required for efficient electron transfer to the protein [72,73].

6.7 MISCELLANEOUS

Among other reports of interest this year were a study of the kinetic changes caused by the mutual influence of ligands in gold(III) complexes [74] and a study of $[Au(CN)_2]^-$ ions absorbed in gold colloids [75]. Gold colloids have also been used to estimate trace amounts of mercury in gold-bearing rock using a mercury influenced reduction process [76]. The effect of ligand structure on the extraction of gold by various organic sulphides [77] and extraction procedures using diantipyrylthiourea [78] or chloro-*S*-dodecylisothiourea have also been reported [79].

6.8 CONCLUSIONS

Quite a number of potentially interesting developments in gold chemistry were suggested this year, but the biggest area or growth seems to be in the use of gold in complex but regular structures, both in inorganic chemistry and in organometallic chemistry. Much has been said about the bonding of gold in such complexes over the years, but with so many orbitals closely spaced and large relativistic effects being reported, the only obvious conclusions are qualitative ones. In particular, the 'soft' nature of gold makes it more akin to the 'soft' ligands with which it coordinates than is the case in many other metal systems, with the consequence that the parallel growth of inorganic and organometallic chemistry is not surprising. With the advent of more efficient X-ray structural determinations, the likelihood is that this area will continue to attract attention for some time to come, but from a chemist's point of view, the deficiency in the techniques available for studies of gold chemistry must now be for the solution and amorphous states where improvements noted this year will require to continue if an effective approach is to be achieved.

REFERENCES

1 J.H. Kim and G.W. Everett, Jr., *Inorg. Chem.*, 20 (1981) 853.
2 D.C. Calabro and J.L. Burmeister, *Inorg. Chim. Acta*, 53 (1981) L47.
3 M.A. Mazid, M.I. Razi and P.J. Sadler, *Inorg. Chem.*, 20 (1981) 2872.
4 R. Uson and J. Vincente, *Inorg. Chim. Acta*, 52 (1981) 29.
5 A.R. Siedle, G.A. Candela, T.F. Finnegan, R.P. van Duyne, T. Cape, G.F. Kokozka, P.C. Woyciejes and J.A. Hashmall, *Inorg. Chem.*, 20 (1981) 2635.

6 G. Annibale, L. Canovese, L. Cattalini, G. Natile, M. Biagini-Cingi, A. Mannotti-Lanfredi and A. Tiripiccho, *J. Chem. Soc. Dalton*, (1981) 2280.

7 V.A. Belonosov, N.J. Ushakova and Ya.V. Salyn, *Zh. Neorg. Khim.*, 26 (1981) 963.

8 T. Singh and U. Agarwala, *Indian J. Chem.*, 19A (1980) 991.

9 J.B. Melpolder and J.L. Burmeister, *Synth. React. Inorg. Met.-Org. Chem.*, 11 (1981) 167.

10 B.N. Ivanov-Emin and S. Olguni-Quinones, *Koord. Khim.*, 7 (1981) 890.

11 F. Theobald and H. Omrani, *Acta Cryst., Sect. B*, 36 (1980) 2923.

12 M. Manfait and A.J.P. Alix, *Inorg. Chim. Acta*, 50 (1981) 147.

13 W. Brockner and B. Demircan, *Z. Naturforsch., Teil A*, 35 (1980) 1379.

14 G. Patel and R.S. Satchell, *Inorg. Chim. Acta*, 54 (1981) L97.

15 P.L. Witkiewicz and C.F. Shaw (III), *J. Chem. Soc. Chem. Commun.*, (1981) 1111.

16 B.L. Calabro, B.A.A. Harrison, G.T. Palmer, M.K. Moguel, R.L. Rebbert and J.L. Burmeister, *Inorg. Chem.*, 20 (1981) 4311.

17 R.V. Parish, O. Parry and C.A. McAuliffe, *J. Chem. Soc. Dalton*, (1981) 2098.

18 K. Brown, R.V. Parish and C.A. McAuliffe, *J. Am. Chem. Soc.*, 103 (1981) 4943.

19 D.T. Hill and B.M. Sutton, *Cryst. Struct. Commun.*, 9 (1980) 679.

20 R.C. Elder, E.H. Zeiher, M. Onady and R.R. Whittle, *J. Chem. Soc. Chem. Commun.*, (1981) 900.

21 P.G. Jones, *Acta Cryst., Sect. B*, 36 (1980) 3105.

22 P.G. Jones, G.M. Sheldrick and E. Hadicke, *Acta Cryst., Sect. B*, 36 (1980) 2777.

23 R. Uson, A. Laguna, J. Vincente, J. Garcia, P.G. Jones and G.M. Sheldrick, *J. Chem. Soc. Dalton*, (1981) 655.

24 P.G. Jones, G.M. Sheldrick, A. Fuerner, P. Goetzfried and W. Beck, *Chem. Ber.*, 114 (1981) 1413.

25 R. Uson, J. Gimeno, J. Fornies, F. Marinez and C. Fernandes, *Inorg. Chim. Acta*, 54 (1981) L95.

26 K.C. Dash, A. Schmidpeter and H. Schmidbaur, *Z. Naturforsch., Teil B*, 35 (1980) 1286.

27 G. Banditelli, A.L. Bandini, G. Minghetti and F. Bonati, *Canad. J. Chem.*, 59 (1981) 1241.

28 P.G. Jones, *Acta Cryst., Sect. B*, 36 (1980) 2775.

29 G.A. Bowmaker and B.C. Dobson, *J. Chem. Soc. Dalton*, (1981) 267.

30 V.I. Belevantsev and B.I. Peshchevitskii, *Izv. Sib. Otd. Akad. Nauk. SSSR*, 1 (1981) 81; [*Chem. Abstr.*, 94 (1981) 198448].

31 A.E. Agadzhanvan and K.A. Ter-Arakelyan, *Arm. Khim. Zh.*, 34 (1981) 112; [*Chem. Abstr.*, 94 (1981) 146098].

32 C.E. Briant, B.R.C. Theobald, J.W. White, L.K. Bell, D.M.P. Mingos and A.J. Welch, *J. Chem. Soc. Chem. Commun.*, (1981) 201.

33 J.A. van der Velden, J.J. Baur, W.P. Bosman and J.H. Noordik, *J. Chem. Soc. Chem. Commun.*, (1981) 1218.

34 G. Schmid, R. Pfeil, R. Boese, F. Banderman, S. Meyer, G.H.M. Calis and J.W.A. van der Velden, *Chem. Ber.*, 114 (1981) 3634.

35 F. Demartin, M. Manassero, L. Naldini, R. Ruggeri and M. Sansoni, *J. Chem. Soc. Chem. Commun.*, (1981) 222.

36 A.N. Nesmeyanov, E.G. Perevalova, Y.T. Struchkov, M.Y. Antipin, K.I. Grandberg and V.P. Dvadchenko, *J. Organomet. Chem.*, 201 (1980) 343.

37 H.D. Sinnen and H.U. Schuster, *Z. Naturforsch., Teil B*, 36 (1981) 833.

38 J.W.A. van der Velden, J.J. Bour, B.F. Otterloo, W.P. Bosman and J.H. Noordik, *J. Chem. Soc. Chem. Commun.*, (1981) 583.

39 J.E. Ellis, *J. Am. Chem. Soc.*, 103 (1981) 6106.

40 O. Rossell and J. Sales, *Inorg. Chim. Acta*, 53 (1981) L1.

42 R. Uson, A. Laguna, M. Laguna, P.G. Jones and G.M. Sheldrick, *J. Chem. Soc. Dalton*, (1981) 366.

43 B.F.G. Johnson, D.A. Ranner, J. Lewis and P.R. Raithby, *J. Organomet. Chem.*, 21 (1981) C33.

44 R. Uson, A. Laguna, M. Laguna, P.G. Jones and G.M. Sheldrick, *J. Chem. Soc. Chem. Commun.*, (1981) 1097.

45 W. Doering and H.U. Schuster, *Z. Naturforsch.*, *Teil B*, 35 (1980) 1482.

46 J.W. Lauker and K. Wald, *J. Am. Chem. Soc.*, 103 (1981) 7648.

47 J.G. Noltes, J.T.B.H. Jastrzebski and G. van Koten, U.S. Patent, 4,243,604.

48 R. Uson, J. Vincente, J.A. Cirac and M.T. Chicote, *J. Organomet. Chem.*, 198 (1980) 105.

49 J. Vincente and M.T. Chicote, *Inorg. Chim. Acta*, 54 (1981) L259.

50 E.I. Smyslova, E.G. Perevalova, V.P. Dyadchenko, K.I. Grandberg, Y.L. Slovokhotov and Y.T. Struchov, *J. Organomet. Chem.*, 215 (1981) 269.

51 H. Schmidbaur, G. Meller, K.C. Dash and B. Milewski-Mahria, *Chem. Ber.*, 114 (1981) 441.

52 H. Schmidbaur, J.R. Mandl, J.M. Bassett, G. Blaschke and B. Zimmer-Gasser, *Chem. Ber.*, 114 (1981) 433.

53 J. Stein, J.P. Fackler, C. Paparizos and H.W. Chen, *J. Am. Chem. Soc.*, 103 (1981) 2192.

54 R. Uson, J. Vincente and M.T. Chicote, *J. Organomet. Chem.*, 209 (1981) 271.

55 R. Nast, P. Schneller and A. Hengefeld, *J. Organomet. Chem.*, 214 (1981) 273.

56 R. Aumann and E.O. Fischer, *Chem. Ber.*, 114 (1981) 1853.

57 G.M. Ribeiro and B.J.O. Franco, *J. Phys. C.*, 13 (1980) L809.

58 D. Lemoyne, *J. Phys. C.*, 13 (1980) 6189.

59 C.R. Hall and M.J.A. Smith, *J. Phys. Chem. Solids*, 42 (1981) 421.

60 I.S. Gotkis and A.V. Gusarov, *Izv. Vyssh. Uchebm. Zaved Khim.*, 24 (1981) 250; [*Chem. Abstr.*, 94 (1981) 166698].

61 B.A. Schoenfelner and R.A. Potts, *J. Inorg. Nucl. Chem.*, 43 (1981) 1051.

62 D.W. Freeman and F.G. Baglin, *Inorg. Nucl. Chem. Lett.*, 17 (1981) 161.

63 Z.A. Fokina, S.I. Kuznetsov and E.A. Bryukhova, *Koord. Khim.*, 6 (1980) 1463.

64 D.F. McIntosh, G.A. Ozin and R.P. Messmer, *Inorg. Chem.*, 20 (1981) 3640.

65 J.A. Tossell and D.J. Vaughan, *Inorg. Chem.*, 20 (1981) 3333.

66 D. Guenzburger and D.E. Ellis, *Phys. Rev. B*, 22 (1980) 4203.

67 J.B. Melpolder and J.L. Burmeister, *Inorg. Chim. Acta*, 49 (1981) 115.

68 Y. Okinaka and G. Wolowodiuk, *J. Electrochim. Soc.*, 128 (1981) 288.

69 C.P. Thurgood, D.W. Kirk and F.R. Foulkes, *J. Electrochem. Soc.*, 128 (1981) 1680.

70 R. Celdran and J.J. Gonzalez-Velasco, *Electrochim. Acta*, 26 (1981) 525.

71 T. Wantanabe and H. Gerischer, *J. Electroanal. Chem. Interfacial Electrochem.*, 122 (1981) 73.

72 W.J. Albery, M.J. Eddowes, H.A.O. Hill and A.R. Hillman, *J. Am. Chem. Soc.*, 103 (1981) 3904.

73 K. Uosaki and H.A.O. Hill, *J. Electroanal. Chem. Interfacial Electrochem.*, 122 (1981) 321.

74 B.I. Peshchevitskii and I.G. Shamovskaya, *Koord. Khim.*, 6 (1980) 1657.

75 K.U. von Raben, R.K. Chang and B.L. Laube, *Chem. Phys. Lett.*, 79 (1981) 465.

76 S. Chen, *Fen. Hsi. Hua. Hsuch.*, 9 (1981) 160.

77 Y.I. Murinov, R.A. Khisamutdinov and Y.E. Nikitin, *Zh. Neorg. Khim.*, 25 (1980) 2784.

78 V.O. Kordyukevich, N.P. Rudenko and V.I. Kuznetsov, *Zh. Neorg. Khim.*, 25 (1980) 2764.

79 C. Chang, H. Huang and P. Chao, *K'Ohsueh T'Tung Pao*, 26 (1981) 538; [*Chem. Abstr.*, 95 (1981) 50304].