X-Ray Structural Investigations of Gold Compounds

A COMPILATION OF REFERENCE DATA. SUPPLEMENT II.

Peter G. Jones

Inorganic Chemistry Institute, University of Göttingen, Federal Republic of Germany

This article continues the series previously published in Gold Bulletin (1981, 14, 102-118 and 159-166; 1983, 16, 114-124) and covers the period 1983-mid 1985.

Our knowledge of the structural chemistry of gold has continued to expand rapidly. The presentation of the new data is similar to that in Supplement I. Moreover, the references, figures and tables are numbered to follow on from Supplement I and the same section headings have been used, except in Section I, which has been extended to cover simple inorganic complexes.

The author's thanks are again due to the following for the help in compiling the supplement: Drs. O. Kennard and S. Bellard, Cambridge Crystallographic Data Centre; Professor G. Bergerhoff, Inorganic Structure Database, Bonn.

Addenda to Supplement I

The following structures are complete or supplementary publications of those previously reported as preliminary or private communications, or are accurate redeterminations of older structures:

The minerals sylvanite AuAgTe_4 (168, 251), krennerite $\text{Au}_{1-x}\text{Ag}_x\text{Te}_2$ with $x \approx 0.2$ and calaverite AuTe_2 (168, 253); the clusters $[\text{Au}_9(\text{PPh}_3)_8]^+$ (187, 254), $[\text{Au}_4\text{I}_2(\text{dppm})_3]$ (195, 255), $[\text{Au}_7(\text{PPh}_3)_7]^+$ (190, 256-8); the bimetallic complex polymer $[\text{AuAg}(\text{C}_6\text{F}_5)_2(\text{SC}_4\text{H}_8)]$ (214, 259); the distorted four-coordinate $[(\text{Ph}_3\text{P})_3\text{Au}(\text{SCN})]$ (238, 260); the mixed cluster $[\text{CoRu}_3(\text{CO})_{13}(\text{AuPPh}_3)]$ (203b, 261), the dithioacetate complex $[(\text{CH}_3\text{CS}_2\text{Au})_4]$ (44a, 262); the hydride complex $[\text{Ph}_3\text{PAu}(\mu\text{-H})\text{Cr}(\text{CO})_5]$ (200, 263); and the mixed clusters $[\text{Ru}_4(\text{CO})_{12}(\mu\text{-H})(\text{AuPPh}_3)_3]$ (209, 264), $[\text{Ru}_3(\text{CO})_{10}(\mu_3\text{-COMe})(\text{AuPPh}_3)]$ (207, 264a), $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})_2(\mu_3\text{-COMe})(\text{AuPPh}_3)]$ (209, 264a) and $[\text{Ru}_3(\mu_3\text{-COMe})(\text{CO})_9(\text{AuPPh}_3)_3]$ (209, 264a).

The three mineral structures showed considerable differences from the earlier studies (atom displacements of up to 50 pm), with disorder of Te in calaverite being associated with variable oxidation number (and thus coordination geometry) of one gold site.

One correction of Supplement I is necessary; although of limited accuracy, the structure determination of $[\text{Au}_9(\text{PPh}_3)_8]^+$ located Au, P and C atoms, not just Au and P as previously stated (187, 254).

I. Simple Inorganic Compounds and Complexes

The $[\text{Au}(\text{OH})_4]^-$ ion has been structurally characterised for the first time as its strontium salt (265); the ion possesses crystallographic symmetry 4, but is very close to the ideal $4/mmm$ with Au-O 198.0 pm.

The compound $[\text{Au}(\text{OTeF}_5)_3]_2$ forms $\text{X}_2\text{AuX}_2\text{AuX}_2$ units ($\text{X} = \text{OTeF}_5$) analogous to Au_2Cl_6 ; the two AuO_4 planes are related by a dihedral angle of 36° . The Au-O bond lengths of 178, 182 pm

(terminal) and 223, 229 pm (bridging) show an atypically large difference; cf. 212, 217 pm respectively in $\text{Au}_2\text{O}_6^{6-}$ (123).

The structure determination was complicated by the presence of a superstructure; the gold atom sites appear to be partially occupied (266).

Considerable interest has attached to the preparation of polyanions involving the chalcogens, in particular sulphur and tellurium; see Fig. 45. $[\text{AuS}_9]^-$ (267) is a cyclic anion with a linear S-Au-S moiety; the unusual length of the polysulphide chain is probably determined by the need to attain normal bond angles at Au and S. $[\text{Au}_{12}\text{S}_8]^{4-}$ (268), which possesses a crystallographic inversion centre, is a cube with sulphur atoms at the vertices and gold atoms at the midpoint of each edge. $[\text{Au}_2\text{S}_8]^{2-}$ (crystallographic symmetry 2) (268a) is a twisted ten-membered ring with a short Au...Au contact (312 pm) and an associated distortion from linearity at gold; S-Au-S 166.4° (see section IV).

Reactions of potassium/gold/tellurium alloys lead to novel polyanions (269); $[\text{KAu}_9\text{Te}_7]^{4-}$ is a somewhat distorted fragment of a cube " $[\text{Au}_{12}\text{Te}_8]^{4-}$ " (analogous to the gold/sulphur polyanion above), missing one vertex and the associated edges. The Au-Te bond lengths are 257 pm, with short Au...Au contacts of 303.9-322.1 pm that are associated with the deviations from ideal geometry. As mentioned in earlier articles in this series, the Au_3E unit ($\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$) with short Au...Au contacts is a common, and thus presumably a stabilizing, structural feature. The anions $[\text{K}_2\text{Au}_4\text{Te}_4(\text{en})_4]^{2-}$ ($\text{en} = \text{ethylenediamine}$) and $[\text{K}_2\text{Au}_4\text{Te}_4(\text{dmf})_2(\text{CH}_3\text{OH})_2]^{2-}$ ($\text{dmf} = \text{dimethylformamide}$) both consist of alternating stacks of $[\text{Au}_4\text{Te}_4]^{4-}$ rings (rhombic distortion from the ideal square, again associated with Au...Au contacts) and $[\text{K}_2\text{en}_4]^{2+}$ or $[\text{K}_2(\text{dmf})_2(\text{CH}_3\text{OH})_2]^{2+}$ units. In all three KAuTe anions there are short K...Au contacts (346.3-387.3 pm).

Several $[\text{Au}(\text{CN})_2]^-$ salts were studied in an attempt to correlate their structures with their spectroscopic properties. $\text{Tl}[\text{Au}(\text{CN})_2]$ and $\text{Cs}[\text{Au}(\text{CN})_2]$ (270) are isostructural, with three independent anions. The structure of the thallium salt was investigated by neutron diffraction; because of pseudosymmetry, all Au-C and $\text{C} \equiv \text{N}$ distances were constrained to be equal. Some Au...Au distances between anions are short (303.7, 306.8 pm). The mixed salt $\text{Cs}_2\text{Na}[\text{Au}(\text{CN})_2]_3$ shows no such short contacts ($\text{Au...Au} > 344$ pm) (271).

The azide complex $[\text{Ph}_4\text{As}]^+[\text{Au}(\text{N}_3)_4]^-$ (272) crystallises in the same space group as many other salts of similar constitution (e.g. the chloride analogue). The Au-N distance is 202.8 pm. The anion possesses crystallographic symmetry 4.

II. Gold Cluster Compounds

These compounds, although their chemistry is not the growth area it once was, still excite considerable interest.

$[\text{Au}_6(\text{Ph}_3\text{P})_6]^{2+}$ (273) exhibits the predicted metal core geometry (an edge-shared bitetrahedron); this is in contrast to the octahedral $[\text{Au}_6\{\text{P}(p\text{-C}_6\text{H}_4\text{Me})_3\}_6]^{2+}$ (18).

The first example of skeletal isomerism of a metal cluster is provided by $[\text{Au}_5\{\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3\}_5](\text{NO}_3)_3$ (274). Two

modifications were obtained from the same recrystallisation; the green, tetragonal modification is closely related to the PF_6^- salt of $[\text{Au}_5\{\text{P}(p\text{-C}_6\text{H}_4\text{Me})_3\}_5]^{3+}$ (21, 186a) and is thus a fragment of a centred icosahedron, whereas the brown, orthorhombic modification is virtually identical to its BF_4^- salt (188), being a centred crown. This is a striking example of the small difference in energy between alternative geometries.

The first example of an Au_{10} cluster is $[Au_{10}Cl_3(PCy_2Ph)_6]^+$ (275), which exhibits a central gold atom surrounded by three $AuCl$ groups and three pairs of AuP groups (approximate symmetry D_{3h}). This compound can thus be described as toroidal rather than spherical (i.e. it is not an icosahedral fragment).

It appears that all high nuclearity gold clusters can be classified as toroidal or spherical, and the electronic structures can be rationalised on this basis. For diagrams of the foregoing structures the reader is referred to the review in *Gold Bulletin* by Mingos (276).

The electronic equivalence (isolobality) of $AuPR_3$ fragments to bridging hydrides in metal clusters has led to the attempt to replace one or more bridging hydrides of $B_{10}H_{14}$ by $AuPR_3$; one of the products thus obtained was $[(B_{10}H_{12})_2Au_6(PEt_3)_4]$ (Fig. 46), which contains a radially compressed Au_6 octahedron in which two gold atoms are each incorporated in $B_{10}Au$ polyhedra (277). It is noteworthy that the central moiety, if formally regarded as Au_6^{4+} , is more easily compatible with octahedral geometry than Au_6^{2+} , in which two electrons occupy non-bonding orbitals (278).

III. Compounds with Gold-Transition Metal Bonds

This section accounts for almost half the gold X-ray structures published from 1983-85. The discovery that the $AuPR_3$ fragment is isolobal to H has led to the synthesis of large number of transition metal clusters incorporating gold as a peripheral $AuPR_3$ or $(AuPR_3)_n$ fragment. A recent review by Braunstein and Rose in *Gold Bulletin* (279) has presented a summary of mixed cluster structures; Table XI(a) gives, for completeness, references to structures in Ref. 279 that have not been presented previously in this series. Table XI(b) presents structures *not* included in Ref. 279 (generally because they are too recent or did not match the criteria for inclusion in that reference). (See p50-51 for Table XI).

The largest mixed cluster deserves special mention; $[Au_{13}Ag_{12}(Ph_3P)_{12}Cl_6]$ (cation, charge unknown) (312) consists, in idealised form, of three interpenetrating icosahedra; the "layers" consist of $Ag/Au_5/Au/Ag_5/Au/Ag_5/Au/Au_5/Ag$ (corresponding to the fivefold symmetry of a ideal icosahedron). Unfortunately, the usual problems attendant upon structure determinations of gold clusters (183a) prevented great accuracy, but the Au-Ag bond lengths lie in the range 254-326 pm, Au-Au 257-304 pm (typical e.s.d.'s 1-2 pm).

The last part of this section deals with non-cluster compounds involving gold-transition metal bonds. The chain polymer $[Au(C_6F_5)_2Ag(L)]_n$ ($L = C_6H_6$) is closely related to the previously reported analogue ($L = SC_4H_8$) (259, 214; Fig. 39), but with somewhat different bond lengths (Au-Au 301.3, Au-Ag 270.2, 279.2 pm). The alkylidyne-bridged $[AuW_2(\mu-CR)_2(CO)_4(\eta-C_5H_5)_2]^+$ ($R = p-MeC_6H_4$) (313, 314) possesses crystallographic symmetry 2, with Au-W 275.2 pm, W-Au-W 162.8°, Au-C 211.9 pm. In $[Mn_2(\mu-PPh_2)(CO)_8(AuPMe_2Ph)]$ (315) the gold itself functions as a bridge between the manganese atoms, with Au-Mn 269.6, 268.1 pm; the complex is a hydride analogue. The Cr-Au-Cr unit has been observed for the first time in $[Au\{Cr(CO)_3(\eta-C_5H_5)\}_2]^-$ (316); the Au-Cr bond lengths are 264.1, 263.5 pm with Cr-Au-Cr 162.2°, and the CO ligands bend back sharply towards gold (Au-Cr-CO 62-68°), as has been observed in similar complexes (29, 197). ($AuPPh_3$) functions as a simple ligand in $[Ir(dppe)_2(AuPPh_3)]^{2+}$ (317), with Ir-Au 262.5 pm, Ir-Au-P 168.7°; in $[Re(C_5H_5)(CO)(p-N_2C_6H_4OMe)(AuPPh_3)]$ (318), with Au-Re 261.5 pm, Re-Au-P 175.3°; and in $[Ph_3PAuCo(CO)_5(PPh_3)]$ (318a), with Au-CO 245.0 pm, Co-Au-P 176.8°.

The addition of AuI across an $Os=C$ double bond leads to $[Os(CH_2AuI)Cl(NO)(PPh_3)_2]$ (319). The Au-Os interaction is described as fairly weak, with Au-C 225, Au-Os 283.8, Au-I 280.0 pm, Os-Au-I 156.6°, although Au-Os in clusters can be as long as 296 pm (303). Finally in this Section, the bridging ligand $L = 2$ -[bis(diphenylphosphino)methyl]pyridine has been used to facilitate the formation of an Au-Rh bond of 285.4 (average of two independent molecules) pm in $[RhAuL_2]^{2+}$ (320). The gold is also coordinated by two phosphorus atoms to give a T-shaped geometry; cf. Ref. 86.

IV. Gold(I) Complexes with Short Au...Au Contacts

Qualitative molecular orbital studies (321) have provided an explanation for the prevalence of this structural feature in the typical 8-membered ring form, represented by $[\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{Au}]_2$ (322) with Au...Au 304.0 pm.

Similar intramolecular interactions presumably contribute to the stability of the $[(\text{R}_3\text{PAu})_3\text{X}]^+$ cations ($\text{X} = \text{O}, \text{S}, \text{Se}$), e.g. $[(\text{Cy}_2\text{PhAu})_3\text{O}]^+$ (275); a similar unit is present in $[(\text{Ph}_3\text{PAu})_4\text{N}]^+$ (323), with Au...Au 301.2-316.0 pm for three gold atoms and > 332.1 pm for contacts involving the fourth atom. The angles Au-N-Au mirror this distortion of the ideal tetrahedral structure, lying in the range 94.3 - 120.7° .

The striking homoleptic arylgold complex $[\text{Au}(\text{mes})]_5$ (mes = mesityl) (324), a molecule in the form of a five-pointed star (Fig. 47), shows large deviations from the expected linear coordination at Au(I) (C-Au-C 148.3 - 152.9°) associated with Au...Au 269.2-271.0 pm; these very short contacts must represent substantial bonding interactions.

Short intermolecular contacts occur in the (under old nomenclature) ethylenethiourea derivatives chloro (N-propyl-1,3-imidazolidine-2-thione)gold(I) (325; Au...Au 316.5 pm) and its N-ethyl analogue (325a; 331.0 pm) and, in more complicated form, in the ionic compounds $(\text{py}_2\text{Au})^+(\text{AuBr}_2^-)$ (326) and $(\text{tht}_2\text{Au})^+(\text{AuI}_2^-)$ (tht = tetrahydrothiophene; 327). $(\text{py}_2\text{Au})^+(\text{AuBr}_2^-)$ exists in two forms; the triclinic form contains Au_4 zigzag chains $\text{AuBr}_2\text{-Au}(\text{py})_2\text{-Au}(\text{py})_2\text{-AuBr}_2$ with Au...Au 324.6, 349.6, 324.6 pm, whereas the monoclinic form contains infinite $\text{-AuBr}_2\text{-Au}(\text{py})_2\text{-chains}$ with Au...Au 330.2, 356.3 pm.

These distances are perhaps rather long compared with the usual range of Au...Au contacts; in the endless zigzag $\text{-AuI}_2\text{-Au}(\text{tht})_2\text{-chains}$ of $(\text{tht}_2\text{Au})^+(\text{AuI}_2^-)$, however, much shorter contacts are observed (296.7, 298.0 pm).

The molecular complexes $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SAuX}$ ($\text{X} = \text{Cl}, \text{Br}$; 327a) are isostructural, with an almost linear ...Au...Au... chain close to a crystallographic 4_1 axis; Au...A 329 pm ($\text{X} = \text{Br}$), 330 pm ($\text{X} = \text{Cl}$).

A complicated Au...Au chain with linking chlorines is present in the mixed valence compound $[\text{Au}^{\text{III}}(\text{terpy})\text{Cl}]_2[\text{Au}^{\text{I}}\text{Cl}_2]_3[\text{Au}^{\text{III}}\text{Cl}_4]$ (328) with Au^{III} (cation)... Au^{I} 330 pm, Au^{I} ... Au^{I} 309 pm. The mixed-valence $[\text{ClAu}^{\text{I}}(\text{dppm})\text{Au}^{\text{I}}(\text{dppm})\text{Au}^{\text{I}}\text{Cl}]^+[\text{Au}^{\text{III}}\text{Cl}(\text{C}_6\text{F}_5)_3]^-$ (329) shows Au...Au 306.7, 316.4 pm in the cation (but no such contacts involving Au^{III}); all the linearly coordinated Au^{I} atoms are arranged approximately parallel to each other.

Two structures contain a $\text{C}(\text{AuPPh}_3)_2$ unit, the short Au...Au contact of which seems to correspond to a stabilizing factor.

The cyclopentadiene derivative $\text{C}_5\text{H}_4(\text{AuPPh}_3)_2$ shows Au...Au 274.7 pm; the structure is, however, of low accuracy (330).

The structure of the ylid complex $[(\text{AuPPh}_3)_2(\mu\text{-C}(\text{PPh}_3)\text{CO}_2\text{Et})]^+$ (Fig. 48a), with Au...Au 289.2 pm, is consistent with some degree of three-centre (Au_2C) bonding (331).

Fig. 47 The homoleptic arylgold(I) complex $[\text{Au}(\text{mesityl})]_5$. A crystallographic mirror plane passes through Au(3) and the C(1) mesityl group. H atoms omitted. After (324)

Fig. 48 Some organogold(I) derivatives. (a) The ylid complex $[\text{Au}(\text{PPh}_3)_2(\mu\text{-C}(\text{PPh}_3)\text{CO}_2\text{Et})]^+$, with a three-centre Au_2C system. H atoms omitted. After (331). (continued)

Table XI(a)
Mixed Metal Clusters (as reviewed by Braunstein & Rosé)

Compound	Ref.	Comments
$[\text{Fe}_3(\mu_3\text{-HC=NBu}^t)(\text{CO})_9(\text{AuPPh}_3)]$	280	a
$[\text{Ru}_3(\mu\text{-Cl})(\text{CO})_{10}(\text{AuPPh}_3)]$	281	b, c
$[\text{Pt}_3(\mu\text{-CO})_3(\text{PCy}_3)_3(\text{AuPCy}_3)_3]$	282	
$[\text{FeCoRu}(\mu_3\text{-PMe})(\text{CO})_9(\text{AuPPh}_3)]$	283	d
$[\text{NiOs}_3(\mu\text{-H})_2(\eta\text{-C}_5\text{H}_5)(\text{CO})_9(\text{AuPPh}_3)]$	284	b
$[\text{Ru}_5\text{C}(\text{CO})_{15}\text{Cl}(\text{AuPPh}_3)]$	285	
$[\text{Ru}_5\text{C}(\text{CO})_{15}(\mu\text{-Br})(\text{AuPPh}_3)]$	285	
$[\text{Ru}_5\text{C}(\text{CO})_{15}(\text{NO})(\text{AuPPh}_3)]$	286	
$[\text{Os}_{10}\text{C}(\text{CO})_{24}(\text{AuPPh}_3)]^-$	287	a
$[\text{Fe}(\text{CO})_4(\text{AuPPh}_3)_2]$	288	e, f
$[\text{Os}(\text{CO})_4(\text{AuPPh}_3)_2]$	289	e
$[\text{Pt}(\text{PEt}_3)_2\text{Cl}(\text{AuPPh}_3)_2]^+$	290	e
$[\text{Pt}_2(\text{CN-xyllyl})_4(\text{PPh}_3)_2(\text{AuPPh}_3)_2]^{2+}$	291	e
$[\text{Fe}_3(\mu_3\text{-S})(\text{CO})_9(\text{AuPPh}_3)_2]$	292	e
$[\text{Ru}_2\text{Co}_2(\text{CO})_{12}(\text{AuPPh}_3)_2]$	292	e
$[\text{Ru}_3(\mu_3\text{-S})(\text{CO})_8(\text{PPh}_3)(\text{AuPPh}_3)_2]$	293	e
$[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-COMe})(\text{CO})_9(\text{AuPPh}_3)_2]$	293	e
$[\text{Ru}_3\text{CoH}(\text{CO})_{12}(\text{AuPPh}_3)_2]$	261	e
$[\text{Os}_5\text{C}(\text{CO})_{14}(\text{AuPPh}_3)_2]$	294	g
$[\text{Ru}_6\text{C}(\text{CO})_{16}(\text{AuPPh}_2\text{Me})_2]$	295	h
$[\text{Ru}_5\text{WC}(\text{CO})_{17}(\text{AuPEt}_3)_2]$	295	e
$[\text{Os}_6(\text{CO})_{22}(\text{AuPPh}_3)_2]$	296	
$[\text{Ir}(\text{NO})_3(\text{PPh}_3)_2(\text{AuPPh}_3)_3]$	297	e
$[\text{Fe}(\text{CO})_4(\text{Au}_2\text{dppm})_2]$	298	e
$[\text{Fe}(\text{CO})_4(\text{Au}_2\text{dppe})_2]$	298	e

Table XI (Continued : key to symbols)

- a Geometry markedly different from hydride analogue (for Au_n fragments that allow Au-Au bonding this must be so)
- b Geometry as for hydride analogue (other groups may be changed, e.g. CO is regarded as equivalent to PPh_3 ; PPh_3 to PEt_3 ; etc)
- c Au bridges two Ru atoms, not three as stated in Abstract
- d Limited data presented also for $[\text{FeCoRu}(\mu_3\text{-S})(\text{CO})_9(\text{AuPPh}_3)]$ (disordered)
- e Contains one or more Au-Au bonds (lengths from 259.0 - 317.6 pm)
- f Au-Au 302.8 pm, not 297.7 as quoted in Ref (279)
- g Structure markedly different from Fe analogue (205)
- h The PEt_3 analogue is reported as probably isostructural
- i No Au-P bond
- j Crystallographic symmetry 2
- k Hydride structural analogue of cluster with different metal of same group
- l Markedly different geometry from hydride analogue with different metal of same group

Table XI(b)
Further Mixed-Metal Clusters

Compound	Ref.	Geometry	Bond lengths (pm)		Comments
			Au-M	Au-Au	
[Ir ₃ H ₆ (dppf) ₃ Au(NO ₃)]	297	Tetrahedron	269.6-271.8		b, i
[IrH(NO ₃)(PPh ₃) ₂ (AuPPh ₃) ₂] ⁺	299	Triangle	267.3, 269.7	272.8	b?, e
[Fe ₄ (COMe)(CO) ₁₂ (AuPEt ₃)]	300	Fe ₄ butterfly, Au bridges hinge	266.6, 267.5		b?
[Os ₃ (CO) ₁₀ (AuPEt ₃) ₂]	301	Os ₃ triangle, both Au bridge same edge	276.0, 276.2		b, j
[Os ₃ (PPh ₃)(HNC ₅ H ₄ N)(CO) ₈ (AuPPh ₃)]	302	Os ₃ triangle, Au bridges edge	273.8, 278.8		b
[Os ₄ (CO) ₁₃ (AuPEt ₃) ₂]	303	Os ₄ tetrahedron, Au bridge two adjacent edges	273.9-286.3	312.8	
[Os ₄ (CO) ₁₂ (AuPMePh ₂) ₂]	303	Os ₄ butterfly, each Au bridges wingtips and one hinge atom	278.4-283.1		
[Os ₃ (μ-CH-CHPh)(CO) ₁₀ (AuPPh ₃)]	304	Au bridges edge of Os ₃ triangle	273.8, 279.5		b
[Os ₃ (μ-CH-CHC ₆ F ₅)(CO) ₁₀ (AuPPh ₃)]	304	ditto	276.6, 277.7		b
[Ru ₃ (μ-H)(μ ₃ -PPh)(CO) ₉ (AuPMe ₂ Ph)]	305	Au bridges edge of Ru ₃ triangle	274.9, 276.3		b
[Ru ₅ C(Ph ₃ P)(μ-I)(CO) ₁₃ (AuPPh ₃)]	306	Ru ₄ butterfly, 5th Ru bridges wingtips, Au bridges hinge	266.1, 283.7		b
[Ru ₅ C(μ-MeCO)(CO) ₁₄ (AuPPh ₃)]	307	ditto	272.1, 276.4		k
[Ru ₅ C(η ⁵ -C ₅ H ₅)(CO) ₁₃ (AuPPh ₃)]	307	ditto	275.0, 278.0		
[Ru ₄ C(CO) ₁₂ (AuPMe ₂ Ph) ₂]	308	Ru ₄ butterfly, Au1 bridges wingtips, Au2 bridges hinge	Au1 286 (av.) Au2 280 (av.) Au1-C 210.4		
[Ru ₄ C(CO) ₁₂ I(AuPEt ₃)]	308	as above, but I replaces Au2. Very long hinge	292 (av.) Au-C 207.8		
[Ru ₄ C(H)(CO) ₁₂ (AuPPh ₃)]	308	as above, but H replaces Au2. Long hinge	295 (av.) Au-C 206.6		k
[Ru ₃ (μ ₃ -C≡CHBu ^t)(CO) ₉ (AuPPh ₃) ₂]	309	Trigonal bipyramid: one Au axial, one equatorial	axial 282.6 278.1 equatorial 282.9, 280.0	303.3	e
[Ru ₃ (μ ₃ -C ₁₂ H ₁₅)(CO) ₈ (AuPPh ₃) ₃]	310	Ru ₃ Au ₂ trigonal bipyramid, third Au caps RuAu ₂ face	273.7-293.4	284.0-291.1	e
[Ru ₃ H(μ ₃ -S)(CO) ₉ (AuPPh ₃)]	311	Butterfly (Au wingtip)	275.9, 273.6		b
[Ru ₃ (μ ₃ -SBu ^t)(CO) ₉ (AuPPh ₃)]	311	ditto	277.3, 276.6		
[Ru ₃ (μ ₃ -S)(CO) ₉ (AuPPh ₃) ₂]	311	Trigonal bipyramid; one Au axial, one equatorial	Axial 282.1, 278.3 Equatorial 286.7, 285.9	296.7	e

V. Other Linear Gold(I) Complexes

Compounds of the form R_3PAuX ($R = Ph$ unless otherwise stated) are well-represented. Gold has little affinity for oxygen ligands, but the compounds $X = \text{acetate}$ (332) and $X = \text{benzoate}$ (333; benzene solvate) are well-defined; the Au-P bonds are short (220.7, 221.3 pm respectively), corresponding to the weak Au-O interactions.

The organometallic derivatives $X = CCl_2(CN)$ (334) and the 1-anion of dicyclopropyl ketone (335), (Fig. 48b) extend the work of the Moscow group (see also Ref. 330, previous section).

The former exhibits disorder of the $CCl_2(CN)$ group about the threefold axis containing P-Au-C; the latter is a precisely determined structure, with Au-C 206.5 pm.

The acetylide ($X = C \equiv C.C_6F_5$) (336) shows the short Au-C bond (199.3 pm) expected for an sp -hybridised carbon atom.

The "carbenate" ($X = C(OMe)=N(p-C_6H_4CH_3)$) (337) has three crystallographically independent molecules, with Au-C 201.2, 204.4, 205.6 pm. Two cyclopentadienide derivatives ($L = C_5H_5$, $R = Pr^i$), (Fig. 48c), (338); ($L = C_5(CO_2Me)_5$), (339) both contain anions bonded to gold mainly through only one carbon (Au-C 212.4, 219.9 pm respectively), although the two neighbouring carbons are both relatively close to the metal atom (278.1, 268.8; 270.5, 281.3 pm respectively).

This unusual bonding mode is already known in the compound $X = C_5Ph_4H$ (224, 226).

Attempts to increase the coordination number of gold in the compounds of Ref. 339 lead to $[(Ph_3P)_2Au]^+ [C_5(CO_2Me)_5]^-$, with Au-P 229.7, 230.0 ppm.

For compounds with aromatic nitrogen anions ($R = Cy$, $L = 2\text{-isopropyl-imidazolate}$, 340; $L = \text{adeninate}$, 341) the Au-N distances are 201.9, 203.8 pm respectively; the donor atom of the adeninate is established as N9. A related cation $[Ph_3PAu(3,5\text{-dimethylpyrazole})]^+$ (342) has also been investigated, but with moderate precision; the donor nitrogen appears to be the one bearing no hydrogen atom.

The diphosphine-bridged complexes $[ClAuPPh_2(CH_2)_3PPh_2AuCl]$ (343) and *trans*- $[(C_6F_5Au(dppm))_2Pd(C_6F_5)_2]$ (344) show no unusual features. A further bimetallic species with a bridging ligand is $[(C_5Me_5)Rh(\mu\text{-indolyl})AuPPh_3]^+$ (345) in which the indolyl ligand is σ -bonded through nitrogen to Au (204 pm) but η^6 -bonded to Rh.

Amongst compounds with sulphur ligands, the dithiolate derivative $[Ph_4As]^+[Au(SPh)_2]^-$ is the first such to be crystallographically studied (346); Au-S 226.2, 227.1 pm.

A related S-Au-S system is seen in the ethylenethiourea derivative (bis(N-propyl-1,3-imidazolidine-2-thione)gold(I) chloride, with Au-S 228.3, 229.1 pm; cf. 227.8, 227.9 pm in the unsubstituted complex (75), which is, however, distorted by hydrogen bonding.

The nine-membered (Au_3N_6) ring in $\text{tris}[\mu\text{-}3,5\text{-bis(trifluoromethyl)pyrazolato-N,N'}]\text{trigold(I)}$ (348) contains three N-Au-N units (Fig. 49). Unlike a similar ring system with C-Au-N bonding (50) there are no Au...Au contacts $< 3.34 \text{ \AA}$. The short Au-N bonds (av. 193 pm) are taken as evidence for a π -interaction between the metal atoms and the pyrazolato rings; however, the structure refinement was rather unsatisfactory because of crystal decomposition effects.

Fig. 48 Some organogold(I) derivatives. (continued) (b) An auroated cyclopropyl ketone. H atoms omitted. After (335). (c) The gold(I) cyclopentadienide complex $[Pr_3PAu(C_5H_5)]$. Au-C(1) is the main gold- C_5H_5 interaction, but Au-C(2) and Au-C(5) are also relatively short (278.1, 268.8 pm respectively). H atoms omitted. After (338)

Amongst organogold(I) derivatives (see also previous section), a bis-carbene complex cation $[(p\text{-CH}_3\text{C}_6\text{H}_4\text{NH})_2\text{C}]_2\text{Au}^+$ showed no evidence for an Au-C bond order higher than 1; Au-C 202, 202 pm (349).

A further carbene complex, $[\text{NCAuCOCH}_2\text{CH(Ph)NH}]$, was obtained by the reaction of coordinated cyanide with the epoxide styrol oxide (350); Au-CN 200, Au-C(carbene) 202 pm.

A striking organometallic mixed-metal unit is provided by $[\text{Au}_2\text{Li}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_4]$ (351), (Fig. 50); the gold atoms are coordinated by two aryl groups (mean Au-C 206 pm) and the lithium atoms each by two nitrogen donors, but there are short Li-C(ipso) contacts (mean 246 pm) and even short Li-Au contacts (mean 288 pm). The mean C-Au-C angle is 166° , which suggests some perturbation by weak interactions with Li.

VI. Gold(I) complexes with higher coordination number

Two salts of the $[\text{Au}(\text{dppe})_2]^+$ cation have been studied (Cl^- , 352; SbF_6^- , 353); these show a flattened tetrahedral coordination with Au-P 238.4-241.2 and 238.9-241.6 pm respectively.

The three-coordinate $\text{MoS}_4(\text{AuPEt}_3)_2$ (354) is closely related to

$\text{WS}_4(\text{AuPh}_2\text{MeP})_2$ (88) and the authors suggest a direct Mo-Au interaction (Au...Mo 281.5 pm).

R_3PAu units are capable of bridging B-B edges of boranes; this is seen in $[\text{Ph}_3\text{PAu}(\text{B}_5\text{H}_8)]$ (355) with Au-B 226.9, 228.1 pm; $[\text{Ph}_3\text{PAu}(\text{B}_{10}\text{H}_8\text{C}_2\text{Ni})(\text{C}_5\text{H}_5)]$ (356) with Au-B 230.8 and 225.6 pm; and $[\text{Cy}_3\text{PAu}(\text{B}_{10}\text{H}_{13})]$ (277; no bond lengths given). These are further examples of the Au/H analogy described above.

VII. Square Planar Gold(III) Complexes

Four salts of the AuCl_4^- ion were reported, with the cations bis(alpha-picoline N-oxide)hydronium (357; Au-Cl 225.6-227.7 pm), bis(3-methylpyridine N-oxide)hydronium (358; Au-Cl 227.5, 228.6 pm), bis(2-nonylpyridine N-oxide)hydronium, with applications for solvent extraction of AuCl_4^- (359; eight independent Au-Cl from 225.6-230.6 pm), and alaninium (360, mean Au-Cl 229.2 pm).

The simple halide complexes $\text{Et}_3\text{PAuBr}_3$ (361; Au-Br 246.8 pm *trans*, 240.7 and 241.6 pm *cis* to P) and *trans*- $[\text{Au}(\text{NH}_3)_2\text{Br}_2]^+ \text{Br}^-$ (362; *2/m* symmetry, Au-N 204.0, Au-Br 242.8 pm) show no unusual features.

Fig. 49 Tris[μ -3,5-bis(trifluoromethyl)pyrazolato-N,N']trigold(I), a gold(I) pyrazolate with an Au_3N_6 ring. H and F atoms omitted. After (348)

Fig. 50 The remarkable gold(I)-lithium complex $[\text{Au}_2\text{Li}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_4]$. Short contacts to lithium are indicated by open bonds (av. Li-C 246, Li-Au 288 pm). H atoms omitted. After (351)

The sole report of an Au(III) complex with only oxygen ligands is the acetate $\text{Au}_2\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_8 \cdot 2\text{H}_2\text{O}$ (363), (Fig. 51); the symmetry of the formula unit is 2, but close to D_{4d} , with Au-O 197.4-199.2 pm.

Surprisingly few sulphur derivatives have been reported. In $[(\text{PhCS}_2)\text{Au}(\text{S}_2\text{C}=\text{CPh}_2)]$ (262) the Au-S bond lengths to the doubly charged anion (229.6 pm) are appreciably shorter than those to the singly charged anion (236.9 pm).

The thiolate complex $[(\text{CH}_3)_2\text{AuSEt}]_2$ (364) is a dimer with bridging sulphur ligands; the central Au_2S_2 rhombus shows a hinge angle of 141.3° about the S...S axis, with Au-S 241.0-242.5 pm.

The range of $\text{Au}^{\text{III}}\text{-N}$ complexes has been much wider. LAuCl_3 structures have been reported for L = 7-methyl-4-azafluorene (365; Au-N 209, 211 pm in two independent molecules, but low precision) and L = prazepam, a benzo-diazepine drug (366; Au-N 203.0 pm).

Studies of the tridentate "terpy" ligand included the structure of $[\text{Au}(\text{terpy})\text{Cl}]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (328), with Au-N *trans* to Cl 194 pm; *cis* 203 pm.

The first characterisation of a gold amide was provided by the X-ray structure of $[(\text{CH}_3)_2\text{AuNMe}_2]_2$ (367), (Fig. 52a); the central Au_2N_2 ring is exactly planar, with Au-C 205.4, 205.8, and Au-N 214.0 pm.

Fig. 51 The gold(III) acetate complex $[\text{Au}_2\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_8]$, with crystallographic twofold symmetry. H atoms and water of crystallization omitted. After (363)

Fig. 52 Novel Au(III) complexes with nitrogen ligands: (a) The first characterized gold-amide derivative, $[(\text{CH}_3)_2\text{AuNMe}_2]_2$. The dimeric structure is reminiscent of Au_2Cl_6 and $\text{Au}_2\text{O}_6^{6-}$; it displays crystallographic inversion symmetry. H atoms omitted. After (367). (b) The dication $[\text{Au}(2\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)(\text{py})_2]^{2+}$. After (368)

A further novelty is the organometallic Au(III) dication $[\text{Au}(2\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)(\text{py})_2]^{2+}$ (368), (Fig. 52b), with Au-C 202.8, Au-NMe₂ 206.9, Au-N(py) 215.5 (*trans* to C), 201.6 (*trans* to NMe₂) pm. The same workers produced the related cationic complex (bis[2-(phenylazo) phenyl]gold(III), in $[\text{Au}(2\text{-C}_6\text{H}_4\text{NNPh})_2]^+ [\text{AuCl}_4]^-$ (369); the *cis* Au-N bond lengths are 217 pm and the *cis* Au-C 199, 200 pm. Another example of C_2N_2 coordination is seen in the dimethylgold(III)tris(pyrazolyl)borate structure $[\text{Me}_2\text{Au}\{\text{BH}(\text{C}_3\text{H}_3\text{N}_2)_3\}]$ (370), which displays closely similar bond lengths to the iso-electronic $[\text{Me}_2\text{Au}\{\text{CH}(\text{pz})_3\}]^+$ (250).

Oxidative addition to typical digold(I) 8-membered rings leads to Au(II) (Section X) and Au(III) species. The latter, here CH₂-bridged A-frames, have been structurally characterised; [CH₂{Au(CN)PPh₂(CH₂)₂}₂] (371) shows mean Au-CH₂(bridge) 203.3, 203.4 pm, Au-CH₂(ring, only two values given) 210.6, 212.2, Au-O (only 1 value given) 207.3 pm. The NO₂ group is disordered.

Another complex with four Au-C bonds is *cis*-[Au{C(NHTol)=N-N(Ph)C(NHTol)}(C₆F₅)₂] (373), (Fig. 53), a typical product of the reaction of isocyanide complexes with hydrazines. The pattern of Au-C bond lengths suggests a higher *trans* influence for imidoyl than for carbene; imidoyl C 205.3, carbene C 205.3, C₆F₅ *trans* to imidoyl 209.7, C₆F₅ *trans* to carbene 206.7 pm.

Further C₆F₅ complexes investigated were [(dppm)Au(C₆F₅)₂]⁺ and [ClAu(C₆F₅)₃]⁻ (329). The former displays *m* symmetry, with Au-C 207.1 pm; the latter has Au-C(*trans* to Cl) 203, *cis* 206, 207 pm.

VIII. Gold(III) Compounds with Higher Coordination Number

Gold(III) compounds often involve short axial contacts (ca. 300 pm) to the otherwise square planar coordinated metal. Only contacts less than 300 pm will be presented here; for longer contacts, see the individual references of section VII.

The diradical C₄Ph₄ (1,2,3,4-tetraphenyl buta-1,3-diene-1,4-diyl) forms a wide variety of Au(III) complexes; [AuCl(C₄Ph₄)(phen)]

(374) also contains the bidentate 1,10-phenanthroline ligand. The distorted pentacoordination that results is typical of Au(III) complexes where a bidentate ligand is forced to occupy the coordination sphere, in that the Au-N distances differ greatly; 218.4, 275.5 pm.

The hydrated ketone derivative [Me₂Au{C(OH)₂(2-pyridyl)₂}]NO₃ (375) shows a weak Au...O interaction of 285.0 pm, although the oxygen atom is forced by the chelate ring geometry to occupy a site near gold. See also (250).

A more regular pentacoordination is observed in the borane complex [6,9-(S₂CNEt₂)-*arachno*-6,9-Au₂B₈H₁₀] (376), with Au-S 239.8, 240.1, Au-B 221.3, 221.9, 225.5 pm (crystallographic *m* symmetry). See also (155-157).

IX. Mixed Au(I)/Au(III) Compounds

The tridentate ligand bis(diphenylphosphino)methanide, (Ph₂P)₂CH⁻, has been employed in the preparation of the mixed oxidation state complexes [(C₆F₅)₂Au^{III}(PPh₂CHPPh₂)Au^I(C₆F₅)] and [(C₆F₅)₂Au^{III}(PPh₂CHPPh₂)Au^I(Ph₂PCHPPh₂)Au^{III}(C₆F₅)₂]⁺ (377). Both complexes exhibit crystallographic *m* symmetry (through Au and methanide C).

Au(I)/Au(III) complexes may also arise as isomers of Au(II) complexes; such a case is the 8-membered ring system [Au^I{Ph₂P(S)CH₂}₂Au^{III}I₂] (322).

X. Gold(II) Complexes

All the complexes described in Table XII were prepared by oxidative addition to eight-membered ring digold(I) systems.

Fig. 53 An Au(III) complex with four carbon ligands: *cis*-[Au{C(NHTol)=N-N(Ph)C(NHTol)}(C₆F₅)₂]. After (373)

Table XII
Gold(II) Complexes
Basic formula:

X	YZ	Au-Au (pm)	Ref.
CH ₂	Cl ₂	259.7	163
CH ₂	I ₂	265.4	378
CH ₂	I, CH ₃	269.5	378
CH ₂	(CN) ₂	263.7	371
S	I ₂	260.7	322
CH ₂	I, CH ₂ Cl	268.1	379

References

- 251 F. Pertlik, *Tschermaks Min. Petr. Mitt.*, 1984, **33**, 203-212
- 252 F. Pertlik, *Tschermaks Min. Petr. Mitt.*, 1984, **33**, 253-262
- 253 F. Pertlik, *Z. Kristallogr.*, 1984, **169**, 227-236
- 254 J.W.A. van der Velden, J.J. Bour, W.P. Bosman, J.H. Noordik and P.T. Beurskens, *J.R. Neth. Chem. Soc.*, 1984, **103**, 13-16
- 255 J.W.A. van der Velden, J.J. Bour, R. Pet, W.P. Bosman and J.H. Noordik, *Inorg. Chem.*, 1983, **22**, 3112-3115
- 256 J.W.A. van der Velden, P.T. Beurskens, J.J. Bour, W.P. Bosman, J.H. Noordik, M. Kolenbrander and J.A.K.M. Buskes, *Inorg. Chem.*, 1984, **23**, 146-151
- 257 P.T. Beurskens and W.P. Bosman, *J. Cryst. Spect. Res.*, 1984, **14**, 293-297
- 258 R.E. Marsh, *Inorg. Chem.*, 1984, **23**, 3682
- 259 R. Usón, A. Laguna, M. Laguna, B.R. Manzano, P.G. Jones and G.M. Sheldrick, *J. Chem. Soc. Dalton Trans.*, 1984, 285-292.
- 260 J.A. Muir, M.M. Muir, S. Arias, P.G. Jones and G.M. Sheldrick, *Inorg. Chim. Acta*, 1984, **81**, 169-174
- 261 M.I. Bruce and B.K. Nicholson, *Organometallics*, 1984, **3**, 101-108
- 262 B. Chiari, O. Piovesana, T. Tarantelli and P.F. Zanazzi, *Inorg. Chem.*, 1985, **24**, 366-371
- 263 M. Green, A.G. Orpen, I.D. Salter and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 2497-2503
- 264 J.A.K. Howard, I.D. Slater and F.G.A. Stone, *Polyhedron*, 1984, **3**, 567-573
- 264a L.W. Bateman, M. Green, K.A. Mead, R.M. Mills, I.D. Slater, F.G.A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 2599-2608
- 265 P.G. Jones and G.M. Sheldrick, *Acta Crystallogr.*, 1984, **C40**, 1776-1777
- 266 P. Huppmann, H. Hartl and K. Seppelt, *Z. anorg. allg. Chem.*, 1985, **524**, 26-32
- 267 G. Marbach and J. Strähle, *Angew. Chem.*, 1984, **96**, 229-230
- 268 G. Marbach and J. Strähle, *Angew. Chem.*, 1984, **96**, 695-696
- 268a A. Müller, M. Römer, H. Bögge, E. Krickmeyer and K. Schmitz, *Inorg. Chim. Acta*, 1984, **85**, L39-L41
- 269 R.C. Haushalter, *Angew. Chem.*, 1985, **97**, 412-414
- 270 N. Blom, A. Ludi, H.-B. Bürgi and K. Tichý, *Acta Crystallogr.*, 1984, **C40**, 1767-1769
- 271 N. Blom, A. Ludi and H.-B. Bürgi, *Acta Crystallogr.*, 1984, **C40**, 1770-1772
- 272 W. Beck and H. Nöth, *Chem. Ber.*, 1984, **117**, 419-422
- 273 C.E. Briant, K.P. Hall and D.M.P. Mingos, *J. Organomet. Chem.*, 1983, **254**, C18-C20
- 274 C.E. Briant, K.P. Hall and D.M.P. Mingos, *J. Chem. Soc., Chem. Comm.*, 1984, 290-291
- 275 C.E. Briant, K.P. Hall, A.C. Wheeler and D.M.P. Mingos, *J. Chem. Soc., Chem. Comm.*, 1984, 248-250
- 276 D.M.P. Mingos, *Gold Bull.*, 1984, **17**, 5-12
- 277 A.J. Wynd, S.E. Robins, D.A. Welch and A.J. Welch, *J. Chem. Soc., Chem. Comm.*, 1985, 819-820
- 278 D.M.P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1976, 1163-1169
- 279 P. Braunstein and J. Rosé, *Gold Bull.*, 1985, **18**, 17-30
- 280 M.I. Bruce and B.K. Nicholson, *J. Organomet. Chem.*, 1983, **250**, 627-638
- 281 G. Lavigne, F. Papageorgiou and J.-J. Bonnet, *Inorg. Chem.*, 1984, **23**, 609-613
- 282 C.E. Briant, R.W.M. Wardle and D.M.P. Mingos, *J. Organomet. Chem.*, 1984, **267**, C49-C51
- 283 K. Fischer, M. Müller and H. Vahrenkamp, *Angew. Chem.*, 1984, **96**, 138-139
- 284 P. Braunstein, J. Rosé, A.M. Manotti-Lanfredi, A. Tiripicchio and E. Sappa, *J. Chem. Soc., Dalton Trans.*, 1984, 1843-1848
- 285 B.F.G. Johnson, J. Lewis, J.N. Nicholls, J. Puga and K.H. Whitmire, *J. Chem. Soc., Dalton Trans.*, 1983, 787-797
- 286 B.F.G. Johnson, J. Lewis, W.J.H. Nelson, J. Puga, P.R. Raithby, D. Braga, M. McPartlin and W. Clegg, *J. Organomet. Chem.*, 1983, **243**, C13-C16
- 287 B.F.G. Johnson, J. Lewis, W.J.H. Nelson, M.D. Vargas, D. Braga and M. McPartlin, *J. Organomet. Chem.*, 1983, C69-C73
- 288 J.W. Lauher and K. Wald, unpublished, quoted in Ref. (289)
- 289 B.F.G. Johnson, J. Lewis, P.R. Raithby and A. Sanders, *J. Organomet. Chem.*, 1984, **260**, C29-C32
- 290 P. Braunstein, H. Lehner, D. Matt, A. Tiripicchio and M. Tiripicchio-Camellini, *Angew. Chem.*, 1984, **96**, 307-308
- 291 C.E. Briant, D.I. Gilmour and D.M.P. Mingos, *J. Organomet. Chem.*, 1984, **267**, C52-C55
- 292 E. Roland, K. Fischer and H. Vahrenkamp, *Angew. Chem.*, 1983, **95**, 324-325
- 293 L.J. Farrugia, M.J. Freeman, M. Green, A.G. Orpen, F.G.A. Stone and I.D. Salter, *J. Organomet. Chem.*, 1983, **249**, 273-288
- 294 B.F.G. Johnson, J. Lewis, W.J.H. Nelson, J.N. Nicholls, J. Puga, P.R. Raithby, M.J. Rosales, M. Schröder and M.D. Vargas, *J. Chem. Soc., Dalton Trans.*, 1983, 2447-2457
- 295 S.R. Bunkhall, H.D. Holden, B.F.G. Johnson, J. Lewis, G.N. Pain, P.R. Raithby and M.J. Taylor, *J. Chem. Soc., Chem. Comm.*, 1984, 25-27
- 296 B.F.G. Johnson, J. Lewis, W.J.H. Nelson, P.R. Raithby and M.D. Vargas, *J. Chem. Soc., Chem. Comm.*, 1983, 608-610
- 297 A.L. Casalnuovo, L.H. Pignolet, J.W.A. van der Velden, J.J. Bour and J.J. Steggerda, *J. Am. Chem. Soc.*, 1983, **105**, 5957-5958
- 298 C.E. Briant, K.P. Hall and D.M.P. Mingos, *J. Chem. Soc., Chem. Comm.*, 1983, 843-845
- 299 A.L. Casalnuovo, T. Laska, P.V. Nilsson, J. Olofsson, L.H. Pignolet, W. Bos, J.J. Bour and J.J. Steggerda, *Inorg. Chem.*, 1985, **24**, 182-187
- 300 C.P. Horwitz, E.M. Holt and D.F. Shriver, *J. Am. Chem. Soc.*, 1985, **107**, 281-282
- 301 K. Burgess, B.F.G. Johnson, D.A. Kaner, J. Lewis, P.R. Raithby and S.N.A.B. Syed-Mustaffa, *J. Chem. Soc., Chem. Comm.*, 1983, 455-457
- 302 K. Burgess, B.F.G. Johnson, J. Lewis and P.R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1983, 1661-1665
- 303 C.M. Hay, B.F.G. Johnson, J. Lewis, R.C.S. McQueen, P.R. Raithby, R.M. Sorrell and M.J. Taylor, *Organometallics*, 1985, **4**, 202-205
- 304 M.I. Bruce, E. Horn, J.G. Matison and M.R. Snow, *J. Organomet. Chem.*, 1985, **286**, 271-287
- 305 M.J. Mays, P.R. Raithby, P.L. Taylor and K. Henrick, *J. Chem. Soc., Dalton Trans.*, 1984, 959-967
- 306 A.G. Cowie, B.F.G. Johnson, J. Lewis, J.N. Nicholls, P.R. Raithby and M.J. Rosales, *J. Chem. Soc., Dalton Trans.*, 1983, 2311-2321
- 307 A.G. Cowie, B.F.G. Johnson, J. Lewis, J.N. Nicholls, P.R. Raithby and A.G. Swanson, *J. Chem. Soc., Chem. Comm.*, 1984, 637-639
- 308 A.G. Cowie, B.F.G. Johnson, J. Lewis and P.R. Raithby, *J. Chem. Soc., Chem. Comm.*, 1984, 1710-1712
- 309 M.I. Bruce, E. Horn, O.B. Shawkataly and M.R. Snow, *J. Organomet. Chem.*, 1985, **280**, 289-298
- 310 M.I. Bruce, O.B. Shawkataly and B.K. Nicholson, *J. Organomet. Chem.*, 1984, **275**, 223-232
- 311 M.I. Bruce, O.B. Shawkataly and B.K. Nicholson, *J. Organomet. Chem.*, 1985, **286**, 427-437
- 312 B.K. Teo and K. Keating, *J. Am. Chem. Soc.*, 1984, **106**, 2224-2226
- 313 M.R. Awang, G.A. Carriedo, J.A.K. Howard, K.A. Mead, I. Moore, C.M. Nunn and F.G.A. Stone, *J. Chem. Soc., Chem. Comm.*, 1983, 964-966
- 314 G.A. Carriedo, J.A.K. Howard, K. Marsden, F.G.A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1984, 1589-1595
- 315 J.A. Iggo, M.J. Mays, P.R. Raithby and K. Henrick, *J. Chem. Soc., Dalton Trans.*, 1984, 633-641
- 316 P. Braunstein, U. Schubert and M. Burgard, *Inorg. Chem.*, 1984, **23**, 4057-4064
- 317 A.L. Casalnuovo, T. Laska, P.V. Nilsson, J. Olofsson and L.H. Pignolet, *Inorg. Chem.*, 1985, **24**, 233-235
- 318 C.F. Barrientos-Penna, F.W.B. Einstein, T. Jones and D. Sutton, *Inorg. Chem.*, 1985, **24**, 632-634
- 318a J. Bashkin, C.E. Briant, D.M.P. Mingos and R.W.M. Wardle, *Transition Met. Chem.*, 1985, **10**, 113-114
- 319 A.F. Hill, W.R. Roper, J.M. Waters and A.H. Wright, *J. Am. Chem. Soc.*, 1983, **105**, 5939-5940
- 320 R.J. McNair, P.V. Nilsson and L.H. Pignolet, *Inorg. Chem.*, 1985, **24**, 1935-1939

- 321 Y. Jiang, S. Alvarez and R. Hoffmann, *Inorg. Chem.*, 1985, **24**, 749-757
- 322 A.M. Mazany and J.P. Fackler jr., *J. Am. Chem. Soc.*, 1984, **106**, 801-802
- 323 Y.L. Slovokhotov and Y.T. Struchkov, *J. Organomet. Chem.*, 1984, **277**, 143-146
- 324 S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Comm.*, 1983, 1304-1306
- 325 M.S. Hussain and A.A. Isab, *J. Coord. Chem.*, 1985, **14**, 17-26
- 325a M.S. Hussain and A.A. Isab, *Transition Met. Chem.*, 1984, **9**, 398-401
- 326 W. Conzelmann, W. Hiller, J. Strähle and G.M. Sheldrick, *Z. anorg. allg. Chem.*, 1984, **512**, 169-176
- 327 S. Ahlstrand, B. Norén and A. Oskarsson, *Inorg. Chem.*, 1985, **24**, 1330-1333
- 327a J. Strähle, W. Hiller and W. Conzelmann, *Z. Naturforsch.*, 1984, **39b**, 538-541
- 328 L.S. Hollis and S.J. Lippard, *J. Am. Chem. Soc.*, 1983, **105**, 4293-4299
- 329 R. Usón, A. Laguna, M. Laguna, E. Fernandez, M.D. Villacampa, P.G. Jones and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1983, 1679-1685
- 330 E.G. Perevalova, K.I. Grandberg, T.V. Baukova, V.P. Dyadchenko, Y.L. Slovokhotov and Y.T. Struchkov, *Koord. Khim.*, 1982, **8**, 1337-1348
- 331 J. Vicente, M.T. Chicote, J.A. Cayuelas, J. Fernandez-Baeza, P.G. Jones, G.M. Sheldrick and P. Espinet, *J. Chem. Soc., Dalton Trans.*, 1985, 1163-1168
- 332 P.G. Jones, *Acta Crystallogr.*, 1984, **C40**, 1320-1322
- 333 P.G. Jones, *Acta Crystallogr.*, 1985, **C41**, 905-906
- 334 E.G. Perevalova, Y.T. Struchkov, V.P. Dyadchenko, E.I. Smyslova, Y.L. Slovokhotov and K.I. Grandberg, *Izv. Akad. Nauk. SSSR, Ser. Khim. (Engl.)*, 1984, 2529-2536
- 335 E.G. Perevalova, I.G. Bolesov, Y.T. Struchkov, I.F. Leschova, Y.S. Kalyuzhnaya, T.I. Voyevodskaya, Y.L. Slovokhotov and K.I. Grandberg, *J. Organomet. Chem.*, 1985, **286**, 129-143
- 336 M.I. Bruce, E. Horn, J.G. Matison and M.R. Snow, *Aust. J. Chem.*, 1984, **37**, 1163-1170
- 337 M. Lanfranchi, M.A. Pellinghelli, A. Tiripicchio and F. Bonati, *Acta Crystallogr.*, 1985, **C41**, 52-55
- 338 H. Werner, H. Otto, T. Ngo-Khac and C. Burschka, *J. Organomet. Chem.*, 1984, **262**, 123-126
- 339 M.I. Bruce, J.K. Walton, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 809-814
- 340 B. Bovio, F. Bonati, A. Burini and B.R. Pietroni, *Z. Naturforsch.*, 1984, **39b**, 1747-1754
- 341 Y. Rosopulos, U. Nagel and W. Beck, *Chem. Ber.*, 1985, **118**, 931-942
- 342 J.R. Lechat, R.H. de A. Santos, G. Banditelli and F. Bonati, *Cryst. Struct. Comm.*, 1982, **11**, 471-477
- 343 M.K. Cooper, L.E. Mitchell, K. Hentrick, M. McPartlin and A. Scott, *Inorg. Chim. Acta*, 1984, **84**, L9-L10
- 344 R. Usón, A. Laguna, J. Fornies, I. Valenzuela, P.G. Jones and G.M. Sheldrick, *J. Organomet. Chem.*, 1983, **273**, 129-139
- 345 A. Tiripicchio, M. Tiripicchio-Cammellini, R. Usón, L.A. Oro and J.A. Cabeza, *J. Organomet. Chem.*, 1983, **244**, 165-174
- 346 P.A. Bates and J.M. Waters, *Acta Cryst.*, 1985, **C41**, 862-865
- 347 M.S. Hussain and A.A. Isab, *Transition Met. Chem.*, 1985, **10**, 178-181
- 348 B. Bovio, F. Bonati and G. Banditelli, *Inorg. Chim. Acta*, 1984, **87**, 25-33
- 349 G. Banditelli, F. Bonati, S. Calogero and G. Valle, *J. Organomet. Chem.*, 1984, **275**, 153-160
- 350 W. Beck, W. Weigand, U. Nagel and M. Schaal, *Angew. Chem.*, 1984, **96**, 377-378
- 351 G. van Koten, J.T.B.H. Jastrzebski, C.H. Stam and N.C. Niemann, *J. Am. Chem. Soc.*, 1984, **106**, 1880-1881
- 352 P.A. Bates and J.M. Waters, *Inorg. Chim. Acta*, 1984, **81**, 151-156
- 353 S.J. Berners-Price, M.A. Mazid and P.J. Sadler, *J. Chem. Soc., Dalton Trans.*, 1984, 969-984
- 354 E.M. Kinsch and D.W. Stephan, *Inorg. Chim. Acta*, 1985, **96**, L87-L90
- 355 N.W. Alcock, L. Parkhill and M.G.H. Wallbridge, *Acta Crystallogr.*, 1985, **C41**, 716-718
- 356 G.K. Barker, N.R. Godfrey, M. Green, H.E. Parge, E.G.A. Stone and A.J. Welch, *J. Chem. Soc., Chem. Comm.*, 1985, 277-279
- 357 M.S. Hussain and S.A.A. Al-Hamoud, *Inorg. Chim. Acta*, 1984, **82**, 111-117
- 358 M.S. Hussain and S.A.A. Al-Hamoud, *J. Chem. Soc., Dalton Trans.*, 1985, 749-753
- 359 M.G.B. Drew, L.R. Graves and M.J. Hudson, *J. Chem. Soc., Dalton Trans.*, 1985, 771-775
- 360 E. Ambach, M.M. Singh, U. Nagel and W. Beck, *Z. Naturforsch.*, 1984, **39b**, 1129-1134
- 361 D.S. Eggleston, D.F. Chodosh, D.T. Hill and G.R. Girard, *Acta Crystallogr.*, 1984, **C40**, 1357-1359
- 362 K. Kaas and L.H. Skibsted, *Acta Chem. Scand.*, 1985, **139**, 1-14
- 363 P.G. Jones, *Acta Crystallogr.*, 1984, **C40**, 804-805
- 364 H.W. Chen, C. Paparizos and J.P. Fackler jr., *Inorg. Chim. Acta*, 1985, **96**, 137-149
- 365 L.G. Kuz'mina, Y.T. Struchkov, L.P. Grigor'eva, Z.I. Ezhkova, V.A. Belonosov, A.K. Molodkin, V.G. Pleshakov and B.E. Zaitsev, *Russ. J. Inorg. Chem.*, 1982, **27**, 695-698
- 366 G. Minghetti, M.L. Ganadu, C. Foddai, M.A. Cinellu, F. Cariati, F. Demartin and M. Manassero, *Inorg. Chim. Acta*, 1984, **86**, 93-100
- 367 H.-N. Adams, U. Grässl, W. Hiller and J. Strähle, *Z. anorg. allg. Chem.*, 1983, **504**, 7-12
- 368 J. Vicente, M.-T. Chicote, M.-D. Bermúdez, P.G. Jones and G. M. Sheldrick, *J. Chem. Res. (S)*, 1985, 72-73
- 369 J. Vicente, M.-T. Chicote, M.-D. Bermúdez, X. Soláns and M. Font-Altaba, *J. Chem. Soc., Dalton Trans.*, 1984, 557-562
- 370 A.J. Canty, N.J. Minchin, J.M. Patrick and A.H. White, *Aust. J. Chem.*, 1983, **36**, 1107-1113
- 371 H.H. Murray, A.M. Mazany and J.P. Fackler jr., *Organometallics*, 1985, **4**, 154-157
- 372 H.C. Knachel, D.S. Dudis and J.P. Fackler jr., *Organometallics*, 1984, **3**, 1312-1313
- 373 R. Usón, A. Laguna, M.D. Villacampa, P.G. Jones and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1984, 2035-2038
- 374 R. Usón, J. Vicente, M.-T. Chicote, P.G. Jones and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1983, 1131-1136
- 375 P.K. Byers, A.J. Canty, L.M. Engelhardt, J.M. Patrick and A.H. White, *J. Chem. Soc., Dalton Trans.*, 1985, 981-986
- 376 M.A. Beckett, J.E. Crook, N.N. Greenwood and J.D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1984, 1427-1431
- 377 R. Usón, A. Laguna, M. Laguna, B.R. Manzano, P.G. Jones and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1984, 839-843
- 378 J.P. Fackler jr. and J.D. Basil, *Organometallics*, 1982, **1**, 871-873
- 379 H.H. Murray, J.P. Fackler jr. and A.M. Mazany, *Organometallics*, 1984, **3**, 1310-1311