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4,4′-OCTAFLUOROBIPHENYLGOLD(I) COMPLEXES

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Summary

ClAu(tht) and LiRRLi (RR = 4,4′-C_6F_4–C_6F_4; tht = tetrahydrothiophen) react to give (HRR)Au(tht) and (tht)AuRRAu(tht), which with neutral or anionic ligands, undergo two types of reactions: (a) replacement of the tht and formation of the complexes (HRR)AuL, LAuRRAuL (L = PPh_3, $SbPh_3$ or phen), $[(HRR)AuCl]^-$ or $[ClAuRRAuCl]^-$; (b) migration of the organic groups, leading to complexes of the types $[AuL_4][Au(RRH)_2]$ (L = $SbPh_3$, L_2 = pdma), $[Au(pdma)_2]_2[Au_4(RR)_3(pdma)_2]$ or $[N(PPh_3)_2][Au(RR)]$.

Introduction

Several binuclear organogold(I) complexes, containing, the moiety Au(μ-L–L)Au, where the bridging ligand L–L is a C,C-donor, such as dialkylphosphonium-bismethylide [1–3], an alkenyl group [4–5] or 1,1′-ferrocenyl [6,7] are known, although no similar complex with an aryl group as bridging ligand has so far been reported. Our attempts to link two Au centres via a bridging 1,4-C_6F_4 group proved unsuccessful and gave only mononuclear compounds.

In the present paper we describe the preparation of binuclear gold(I) complexes containing 4,4′-octafluorobiphenyl (R–R in the following). In some cases the R–R groups undergo rearrangements (similar to those observed for C_6F_5 groups between two Au centres [8,9] or between gold(I) and silver(I) centres [10]) which give rise to the formation of tetranuclear gold(I) complexes. The synthesis and reactivity of complexes of the types: (HRR)AuL, LAuRRAuL (L = PPh_3, $SbPh_3$, 1,10-phenanthroline (phen)), $[AuL_4][Au(RRH)_2]$ (L = $SbPh_3$, 2 L = *o*-phenylenebis(dimethylarsine) (pdma)), $[Au(pdma)_2]_2[Au_4(R–R)_3(pdma)_2]$, $[N(PPh_3)_2]$-[(HRR)AuCl] and $[N(PPh_3)_2][ClAuRRAuCl]$ are reported.

Results and discussion

Addition of solid ClAu(tht) (tht = tetrahydrothiophen) to a suspension of LiRRLi, followed by exposure to atmospheric moisture leads to a solution which

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TABLE 1

ANALYTICAL DATA FOR COMPLEXES I–XVIII

Complex	Yield (%)	M.p. (°C)	Analyses (Found (calcd.)(%))				Λ_M (ohm^{-1} cm^2 mol^{-1})	Mol.wt. Found (calcd.)
			C	H	N	Au		
(HRR)Au(tht)	24	142(d)	32.75	1.7		33.3	1	621
(I)			(33.0)	(1.55)		(33.85)		(582)
(tht)AuRRAu(tht)	63	135(d)	27.8	2.0		46.4	2	826
(II)			(27.75)	(1.85)		(45.5)		(866)
(HRR)AuPPh$_3$	87	166	47.25	2.3		26.9	3	796
(III)			(47.65)	(2.15)		(26.05)		(756)
(HRR)Au(phen)	59	195(d)	42.35	1.55	4.05	28.85	1	684
(IV)			(42.75)	(1.35)	(4.15)	(29.2)		(674)
[(HRR)Au)$_2$(dppm)]	77	192(d)	42.5	2.0		28.75	1	1373
(V)			(42.9)	(1.75)		(28.7)		(1373)
[Au(SbPh$_3$)$_4$][Au(RRH)$_2$]	75	199(d)	48.15	2.65		16.9	60	
(VI)			(48.05)	(2.6)		(16.4)		
[Au(pdma)$_2$][Au(RRH)$_2$]	71	201	33.95	2.3		26.0	77	
(VII)			(33.85)	(2.2)		(25.25)		
[N(PPh$_3$)$_2$][(HRR)AuCl]	56	192(d)	53.1	2.9	1.5	19.1	99	
(VIII)			(54.0)	(2.95)	(1.3)	(18.45)		

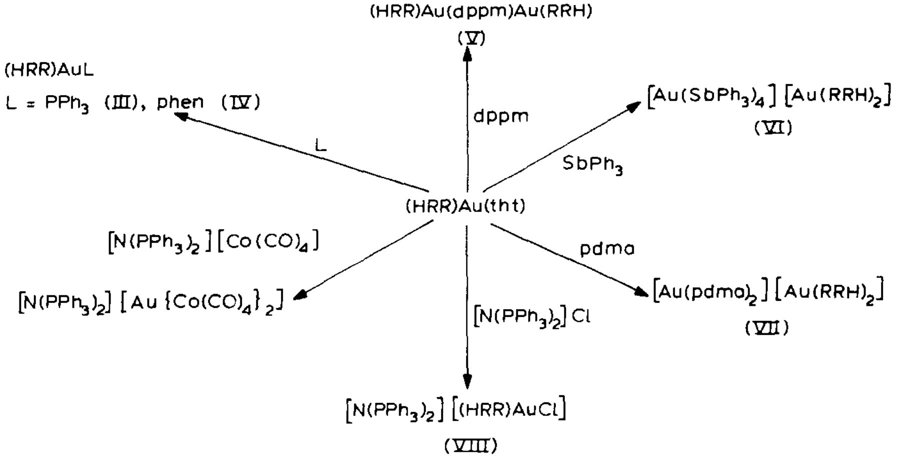
$Ph_3PAuRRAuPPh_3$	77	283(d)	47.7	2.45		31.9	8	1155
(IX)			(47.45)	(2.5)		(32.45)		(1215)
$Ph_3SbAuRRAuSbPh_3$	82	160(d)	41.0	2.45		(28.9		
(X)			(41.3)	(2.15)		(28.2)		
(phen)AuRRAu(phen)	62	225(d)	41.7	1.65	5.0	36.75		
(XI)			(41.15)	(1.55)	(5.35)	(37.5)		
$[Au_2(RR)(dppm)]_n$	70	300	41.35	2.3		35.9		
(XII)			(41.35)	(2.05)		(36.65)		
$[Au(pdma)_2]_2[Au_4(RR)_3(pdma)_2]$	85	210(d)	30.4	2.65		31.1	238	
(XIII)			(30.45)	(2.55)		(31.2)		
$[N(PPh_3)_2]_2[ClAuRRAuCl]$	80	192(d)	54.25	3.3	1.75	22.05	220	
(XIV)			(54.9)	(3.3)	(1.5)	(21.45)		
$[N(PPh_3)_2][Au(RR)]$	50	300	56.05	3.15	1.35	18.9		
(XV)			(55.9)	(2.95)	(1.35)	(19.1)		
$[NBu_4]_2[Au_4(RR)_3(pdma)_2]$	52	198(d)	38.5	3.65	1.2	28.6	218	
(XVI)			(38.65)	(3.4)	(1.0)	(28.85)		
$[Au(pdma)_2[ClO_4$	37	205(d)	27.5	3.7		23.3	110	
(XVII)			(27.65)	(3.7)		(22.65)		
$[N(PPh_3)_2]_2[C_6F_5AuRRC_6F_5]$	65	> 300	55.5	3.0	1.5	19.55	255	
(XVIII)			(54.85)	(2.9)	(1.35)	(18.75)		

contains a mixture of (HRR)Au(tht) (I) and (tht)AuRRAu(tht) (II) (eq. 1)

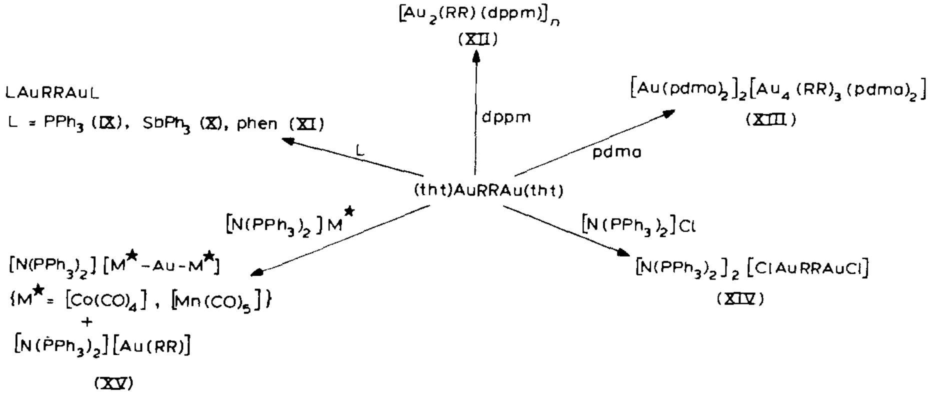
$$\begin{aligned} 2\,\mathrm{LiRRLi} + 3\,\mathrm{ClAu(tht)} + \mathrm{H_2O} \rightarrow \underset{\text{(I)}}{\mathrm{(HRR)Au(tht)}} + \underset{\text{(II)}}{\mathrm{(tht)AuRRAu(tht)}} + \\ 3\,\mathrm{LiCl} + \mathrm{LiOH} \qquad (1) \end{aligned}$$

Owing to their different solubilities in ether-hexane, the two complexes can be readily separated (see Experimental). The white air- and moisture-stable solids are non-conducting and monomeric in solution (Table 1).

The reactivity of I and II with neutral and anionic ligands has been studied; the results are listed in Schemes 1 and 2.



SCHEME 1



SCHEME 2

Complex I shows a behaviour which is similar to that reported for $C_6F_5Au(tht)$ [9]. Thus, with L = PPh_3, 1,10-phenanthroline (phen), or bis(diphenylphosphino)methane (dppm), displacement of tht takes place, leading to the neutral complexes (III–V) (Scheme 1). In the last case the binuclear complex V is obtained, even if an excess of dppm is used.

With L = $SbPh_3$ or *o*-phenylenebis(dimethylarsine) (pdma) the substitution of the tht along with the migration of the HRR groups gives rise to the formation of the ionic complexes VI or VII whose cation is tetra-coordinated [9,11]. Nevertheless their conductivity in acetone (see Table 1) is lower than that of $[AuL_4][Au(C_6F_5)_2]$ [9] and also lower than the expected for a 1 : 1 electrolyte, probably owing to the equilibrium represented in eq. 2

$$2\,(HRR)AuL_n \rightleftharpoons [AuL_{2n}]^+ + [Au(RRH)_2]^- \qquad (2)$$

L = $SbPh_3$ ($n = 2$) or pdma ($n = 1$)

With anionic ligands the same two types of behaviour are again observed; thus, with Cl^- substitution, formation of the dichloro-organoaurate VIII takes place, whereas with $[Co(CO)_4]^-$ the complex $[N(PPh_3)_2][Au\{Co(CO)_4\}_2]$ [12] can be isolated along with oils which could not be crystallized but which, in accordance with their IR spectra, are supposed to contain $[N(PPh_3)_2][Au(RRH)_2]$, resulting from the rearrangement of the organic groups between the gold(I) centres.

The reaction of complex II (see Scheme 2) with L = PPh_3 or phen affords neutral complexes of the general formula LAuRRAuL (IX,XI), with L = $SbPh_3$ the same result is obtained even if an excess (1/4) of the stibine is used, in contrast to the reaction observed for complex I. With L = dppm a white solid of the general formula $Au_2(RR)(dppm)$ is formed, which being insoluble in organic solvents is likely to be a polymer whose AuRRAu moeities are bridged by the diphosphine groups.

Addition of L = pdma to dichloromethane solutions of II gives a white precipitate of the general formula $Au_2(RR)(pdma)_2$ (XIII), for which the ionic structure $[Au(pdma)_2]_2[(pdma)AuRRAuRRAuRRAu(pdma)]$ can be proposed in accordance with the following observations:

(a) Though only slightly soluble, its solutions in acetone are conducting. Conductance measurements at different concentrations give a value for B in the Onsager equation [13] ($\Lambda_e = \Lambda_0 - B\sqrt{c}$) of 920, pointing to a 1 : 2 electrolyte [14].

(b) Its ^{19}F NMR spectrum ($CDCl_3$) shows two multiplets at δ −118.6 and −140.1 ppm, corresponding to the *ortho* and *meta* fluorine atoms.

(c) Addition of $[NBu_4][Au(C_6F_5)_2]$ to a dichloromethane suspension of XIII gives the white insoluble compound $[NBu_4]_2[(pdma)AuRRAuRRAuRRAu(pdma)]$ (XVI), whilst the previously reported compound $[Au(pdma)_2][Au(C_6F_5)_2]$ [9] can be isolated from the solution (eq. 3):

$$[Au(pdma)_2]_2[Au_4(RR)_3(pdma)_2] + 2\,[NBu_4][Au(C_6F_5)_2] \rightarrow$$

$$\underset{\text{(XVI)}}{[NBu_4]_2[Au_4(RR)_3(pdma)_2]} + 2\,[Au(pdma)_2][Au(C_6F_5)_2] \qquad (3)$$

Acetone solutions of complex XVI also conduct (value for B in the Onsager equation 850 (1 : 2 electrolyte)). Its ^{19}F NMR spectrum ($CDCl_3$) shows two multiplets at δ −115.6 and −141.6 ppm. Furthermore, the presence of two types of gold atoms is also confirmed by ^{197}Au Mössbauer spectroscopy, though the signals are of different intensity. There is a strong doublet with parameters (*IS* 5.65(5), *QS* 10.80(10) mm s^{-1}, line width 2.12 mm s^{-1}) similar to $[NBu_4][AuR_2]$ (R = C_6F_5, $C_6F_3H_2$) [15] which must belong to the central gold atoms. The As-bound atoms also give a doublet, but the low-velocity peak is buried under the more intense peak,

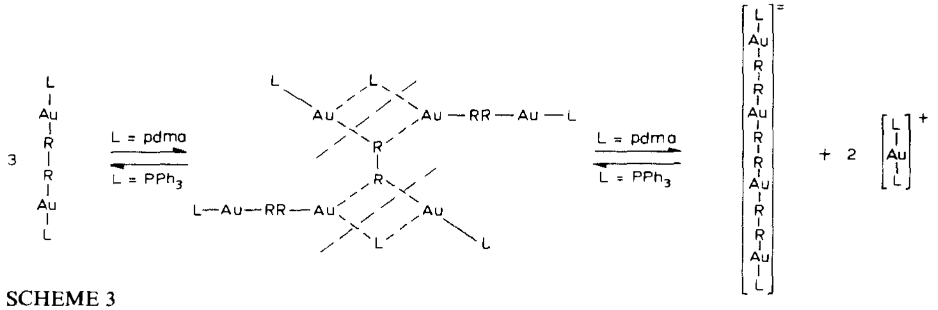
and is difficult to locate accurately. It was therefore not possible to elucidate whether these gold atoms are bi- or tri-coordinated, i.e. whether in this case the pdma acts as a monodentate or as a chelating ligand.
(d) The reaction of XIII with $[NBu_4]ClO_4$ occurs similarly to that represented in eq. 3, under formation of XVI and $[Au(pdma)_2]ClO_4$ (XVII), (eq. 4)

$$[Au(pdma)_2]_2[Au_4(RR)_3(pdma)_2] + 2\,[NBu_4]ClO_4 \rightarrow [NBu_4]_2[Au_4(RR)_3(pdma)_2] + 2\,\underset{(XVII)}{[Au(pdma)_2]ClO_4} \qquad (4)$$

XVII is a white solid, which is conducting in acetone solution (1 : 1 electrolyte) (see Table 1).

The rearrangement observed in the reaction with L = pdma (Scheme 2) is thought to take place via a mechanism, similar to a previously proposed one [8], involving the formation of an intermediate whose RR groups are capable of bridging two gold centres [16], as may be seen from Scheme 3.

Addition of a stoichiometric amount of PPh_3 to complex XIII leads to the neutral complex IX, i.e. depending upon the character of the ligand the rearrangement of the organic groups can be reversed (Scheme 3).



SCHEME 3

Complex II reacts with $[N(PPh_3)_2]Cl$ to give the chloro derivative XIV (Scheme 2), a white solid, which is conducting in acetone solution (1 : 2 electrolyte). In its IR spectrum the vibration due to ν(Au–Cl) is observed at 335 cm^{-1}. It reacts with AgC_6F_5 according to eq. (5)

$$[N(PPh_3)_2]_2[ClAuRRAuCl] + 2\,AgC_6F_5 \rightarrow 2\,AgCl + \underset{(XVIII)}{[N(PPh_3)_2]_2[C_6F_5AuRRAuC_6F_5]} \qquad (5)$$

Complex XVIII is a white solid, which is conducting in acetone solution (1 : 2 electrolyte).

The reaction of II with $[N(PPh_3)_2]M^\star$ ($M^\star = [Co(CO)_4]^-$ or $[Mn(CO)_5]^-$) leads to the trimetallic complexes $[N(PPh_3)_2][M^\star\text{–Au–}M^\star]$ [12] and to a white solid, whose elemental analyses coincide with those expected for the formula $[N(PPh_3)_2][Au(RR)]$. Since it is only very slightly soluble in organic solvents it was not possible to determine its conductivity and thus elucidate its molecularity.

Experimental

IR spectra were recorded with a Perkin–Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 5×10^{-4} *M* acetone solutions with a Philips PW 9509 conductimeter. Molecular weights were determined in ca. 10^{-3} *M* $CHCl_3$ solution using the isopiestic method on a Hitachi-Perkin–Elmer 115 apparatus. ^{19}F NMR spectra were recorded on a Varian FT 80A spectrometer with $CFCl_3$ as external standard. Analyses (C, H) were carried out with a Perkin–Elmer 240 microanalyzer. Au was determined by ashing the samples with an aqueous solution of hydrazine.

The yields, melting points, C, H, N and Au analyses, conductivities, and molecular weights of the novel complexes are listed in Table 1.

Preparation of the complexes

(HRR)Au(tht) (I) and (tht)AuRRAu(tht) (II)

To a solution of 4,4′-BrC_6F_4–C_6F_4Br (1.140 g, 2.5 mmol) in 140 ml of diethyl ether at −78°C and under nitrogen, Li(n-Bu) (5 mmol) was added dropwise. After 45 min stirring, AuCl(tht) [17] (1.683 g, 5.25 mmol) was added and stirred for 30 min while the temperature was maintained at −78°C. The mixture was slowly (3 h) allowed to warm to room temperature, and then filtered (in the presence of air) through a layer (1 cm) of anhydrous magnesium sulphate. The filtrate was concentrated to ca. 8 ml, and 40 ml of hexane were added to separate the white solid of complex II. Concentration of the ether-hexane filtrate to ca. half the volume led to the precipitation of I, which was filtered off and recrystallized from dichloromethane-hexane.

(HRR)AuL (L = PPh_3 (III) or phen (IV)) and (HRR)Au(dppm)Au(RRH) (V)

To a solution of I (0.116 g, 0.2 mmol) in 30 ml of ether or dichloromethane was added the appropriate ligand (L = PPh_3 (0.053 g, 0.2 mmol), phen (0.040 g, 0.2 mmol) or dppm (0.038 g, 0.1 mmol)) and the mixture was stirred at room temperature for 30 min. Evaporation to ca. 5 ml and addition of hexane led to the precipitation of the complexes III and IV. IV is very slightly soluble in ether and was precipitated upon addition of phenanthroline.

$[AuL_4][Au(RRH)_2]$ (L = $SbPh_3$ (VI) or L_2 = pdma (VII))

To a solution of I (0.116 g, 0.2 mmol) in 25 ml of ether was added L (L = $SbPh_3$ (0.142 g, 0.4 mmol) or pdma (0.08 ml, 0.4 mmol)). Complexes VI or VII precipitated spontaneously as white solids. After 15 min stirring, they were filtered off and recrystallized from dichloromethane-hexane.

$[N(PPh_3)_2][(HRR)AuCl]$ (VIII)

To a solution of I (0.116 g, 0.2 mmol) in 20 ml of ethanol was added $[N(PPh_3)_2]Cl$ (0.115 g, 0.2 mmol) and the mixture was stirred at room temperature for 1 h. The white precipitate VIII was filtered off and recrystallized from dichloromethane-hexane.

LAuRRAuL (L = PPh_3 (IX), $SbPh_3$ (X) or phen (XI)) and $[Au_2(RR)(dppm)]_n$ (XII))

To a dichloromethane (20 ml) solution or ether (50 ml) suspension of II (0.174 g, 0.2 mmol) was added the appropriate ligand (L = PPh_3 (0.106 g, 0.4 mmol), $SbPh_3$

(0.142 g, 0.4 mmol), phen (0.080 g, 0.4 mmol) or dppm (0.076 g, 0.2 mmol)) and the mixture was stirred at room temperature for 10 h. Complexes X, XI and XII, insoluble in ether, were filtered off. For IX, the dichloromethane solution was evaporated to ca. 5 ml and hexane was added to precipitate the complex.

$[Au(pdma)_2]_2[Au_4(RR)_3(pdma)_2]$ (XIII)

To a solution of pdma (0.044 ml, 0.2 mmol) in 10 ml of dichloromethane under nitrogen was added II (0.087 g, 0.1 mmol). XIII, precipitated as a white solid, was filtered off after 15 min stirring (at room temperature). More of XIII was obtained after the addition of ether.

$[N(PPh_3)_2]_2[ClAuRRAuCl]$ (XIV)

To a suspension of II (0.13 g, 0.15 mmol) in 20 ml of ethanol was added $[N(PPh_3)_2]Cl$ (0.172 g, 0.3 mmol) and the mixture was stirred at room temperature for 16 h. The white precipitated XIV was filtered off and washed with (5 × 3 ml) of ethanol.

$[N(PPh_3)_2][Au(RR)]$ (XV)

Dry nitrogen was bubbled through a solution of II (0.174 g, 0.2 mmol) in 50 ml of dichloromethane and $[N(PPh_3)][Co(CO)_4]$ [18] (0.284 g, 0.4 mmol) or $[N(PPh_3)_2][Mn(CO)_5]$ [19] (0.293 g, 0.4 mmol) was added. Under nitrogen, and at room temperature, the mixture was stirred for 10 min. Concentration to ca. 5 ml and addition of 30 ml of ether led to the separation of the white XV. The ether filtrate contained $[N(PPh_3)_2][Au\{Co(CO)_4\}_2]$ or, $[N(PPh_3)_2][Au\{Mn(CO)_5\}_2]$ [12].

$[NBu_4]_2[Au_4(RR)_3(pdma)_2]$ (XVI)

To a suspension of XIII (0.309 g, 0.082 mmol) in 15 ml of dichloromethane was added $[NBu_4][Au(C_6F_5)_2]$ [17] (0.126 g, 0.164 mmol) and the mixture was stirred at room temperature for 6 h. The white precipitate XVI was filtered off. The filtrate was evaporated to ca. 5 ml and 15 ml of ether was added to precipitate $[Au(pdma)_2][Au(C_6F_5)_2]$ [9].

$[Au(pdma)_2]ClO_4$ (XVII)

To a suspension of XIII (0.50 g, 0.13 mmol) in 15 ml of dichloromethane was added $[NBu_4]ClO_4$ (0.089 g, 0.26 mmol) and the mixture was stirred at room temperature for 6 h. The precipitated complex XVI was filtered off. The filtrate was concentrated to ca. 5 ml and 20 ml of ether was added to separate out the white complex XVII.

$[N(PPh_3)_2]_2[C_6F_5AuRRAuC_6F_5]$ (XVIII)

To a solution of AgC_6F_5 [20] (0.3 mmol) in 25 ml of ether was added XIV (0.275 g, 0.16 mmol) and the mixture was stirred at room temperature for 15 min. The precipitated AgCl and XVIII were filtered off and washed with 3 × 5 ml of ether. Dichloromethane (30 ml) was added to separate the insoluble AgCl. The filtrate was concentrated to ca. 5 ml and XVIII was precipitated upon addition of ether.

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References

1 H. Schmidbaur and R. Franke, Inorg. Chim. Acta, 13 (1975) 85.
2 H. Schmidbaur, J.R. Mandl, W. Richter, V. Bejenke, A. Franck and G. Huttner, Chem. Ber., 110 (1977) 1576.
3 H. Schmidbaur, Pure Appl. Chem., 50 (1979) 19.
4 C.M. Mitchell and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1972) 102.
5 A. Johnson and R.J. Puddephatt, J. Chem. Soc., Dalton Trans., (1978) 980.
6 E.G. Perevalova, D.A. Lemenovskii, O.B. Afanasova, V.P. Dyadchenko, K.I. Grandberg and A.N. Nesmeyanov, Izv. Akad. Nauk. SSSR, Ser. Khim., (1972) 2594.
7 H. Schmidbaur, Organogold Compound, in Gmelin Handbuch der Anorganischen Chemie, Springer-Verlag, Berlin, 1980, p. 269.
8 R. Usón, A. Laguna and P. Brun, J. Organomet. Chem., 182 (1979) 449.
9 R. Usón, A. Laguna, J. Vicente, J. García, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1981) 655.
10 R. Usón, A. Laguna, M. Laguna, B.R. Manzano, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., in press.
11 P.G. Jones, Z. Naturforsch, 37b (1982) 937.
12 R. Usón, A. Laguna, M. Laguna, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1981) 366.
13 R.D. Feltham and R.G. Hayter, J. Chem. Soc., (1964) 4587.
14 R. Usón, J. Gimeno, J. Forniés and F. Martínez, Inorg. Chim. Acta, 50 (1981) 173.
15 K. Moss, R.V. Parish, A. Laguna, M. Laguna and R. Usón, J. Chem. Soc., Dalton Trans., (1983) 2071.
16 R. Usón, A. Laguna and P. Brun, J. Organomet. Chem., 197 (1980) 369.
17 R. Usón, A. Laguna and J. Vicente, J. Chem. Soc., Chem. Commun., (1976) 353; J. Organomet. Chem., 131 (1977) 471.
18 J.K. Ruff and W.J. Schlientz, Inorg. Synth., 15 (1974) 84.
19 D.N. Duffy and B.K. Nicholson, J. Organomet. Chem., 164 (1979) 227.
20 R. Usón, A. Laguna and J.A. Abad, J. Organomet. Chem., 246 (1983) 341.