New Routes Towards Halogeno Complexes of Gold by Halide Exchange from $[Au_2Cl_6]$. Crystal and Molecular Structure of Triphenylmethylium Tetrachloroaurate(III), $[CPh_3][AuCl_4]$ †‡

Daniela Belli Dell'Amico,[a] **Fausto Calderazzo,***[a] **Antonino Morvillo,**[b] **Giancarlo Pelizzi**[c] **and Pierluigi Robino**[a]

[a] *Dipartimento di Chimica e Chimica Industriale, Sezione di Chimica Inorganica, Università di Pisa, Via del Risorgimento 35, I-56126 Pisa, Italy*

[b] *Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Via Marzolo 1, I-35131 Padova, Italy*

[c] *Istituto di Chimica Generale and Centro C.N.R. per la Strutturistica Diffratometrica, Università di Parma, Viale della Scienze, I-43100 Parma, Italy*

Anhydrous $[Au_2Br_6]$ and AuI can be obtained by halide exchange from $[Au_2Cl_6]$ with RX (X = Br or I, R = H or alkyl). The addition of $[Au_2Cl_6]$ to CPh_3Cl produces the ionic derivative $[CPh_3][AuCl_4]$ whose crystal and molecular structure has been determined by X-ray diffraction. Crystal data: space group $P2_1/c$, $a = 8.225(3)$, $b = 14.671(6)$, $c = 16.738(8)$ Å, $\beta = 97.85(2)°$ and $Z = 4$. Other organic chlorides RCl (R = Pr, $SiMe_3$ or Bu^t) react with $[Au_2Cl_6]$ with a partial reduction to the mixed-valence chloride $[Au_4Cl_8]$. Addition of $[Au_2Cl_6]$ to anhydrous iron(III) chloride produced a mass-spectrometrically active mixed iron–gold species.

Gold(III) halides $[Au_2X_6]$ (X = Cl or Br) are thermally unstable and undergo halogen elimination at high temperature.[1] On the other hand, no evidence has yet been found for the existence of gold(III) iodide,[2] and, moreover, gold(I) halides AuX (X = Cl or Br) have the tendency to disproportionate to gold metal and $[Au_2X_6]$.[2] These properties make it attractive to find alternative preparative procedures for $[Au_2X_6]$ other than that from the elements. Also the preparation of AuX (X = Cl, Br or I) by a route different from that currently in use, *i.e.* the thermal dissociation of X_2 from $[Au_2X_6]$, appears to be an interesting goal.

Since anhydrous $[Au_2Cl_6]$ is a largely available chemical,[3] we addressed ourselves to the question of whether it would be possible to derive all the halogeno complexes from $[Au_2Cl_6]$ by some unprecedented routes. A simple calculation based on the known values[4] of ΔG_f° of reagents and products shows that the exchange reaction (1) (X = Br or I) is thermodynamically

$$MCl_n + nHX \longrightarrow MX_n + nHCl \qquad (1)$$

feasible for many transition-metal chlorides and we have reported similar reactions for titanium(IV).[5] In principle the exchange reaction is favoured thermodynamically with alkyl halides too.

The present paper reports the exchange reactions for gold(III) chloride with HX and RX and a study of the products resulting from the reactions between $[Au_2Cl_6]$ and RCl. In an attempt to obtain some insight into the mechanism of the $[Au_2Cl_6]$ + RX reactions we also found that $[Au_2Cl_6]$ acts as a halogen abstractor for CPh_3Cl and we describe the crystal and molecular structure of the ionic derivative $[CPh_3][AuCl_4]$. Part of these results has been reported in a preliminary communication.[6]

Experimental

The IR spectra were measured with a Perkin-Elmer model 283 instrument equipped with a grating, each spectrum being calibrated with either a polyethylene film (between 4000 and 600 cm^{-1}), indene (between 600 and 200 cm^{-1}) or CO in the 2200–1800 cm^{-1} region: the accuracy in the latter instance is believed to be 1 cm^{-1}. Elemental (C,H) analyses were performed with a Carlo Erba model 1106 analyser. Gold analyses were carried out by calcination of the samples. Known volumes of gaseous reagents were introduced in the reaction vessels by a syringe through a rubber cap, the precision being checked by titration of some samples. The ^1H and ^{13}C NMR spectra were measured with a Varian XVR-300 instrument operating at 70.5 kG (*ca.* 7 T), using $SiMe_4$ as internal reference, mass spectra on a VG MM 16 F instrument operating at 70 eV (*ca.* 1.12×10^{-17} J) with a direct sample inlet. The X-ray powder diagrams were obtained with a Debye–Scherrer camera by using the Cu-Kα radiation (λ = 1.5418 Å) for a sample of $[Au_2Br_6]$ sealed in a glass capillary or for a sample of AuI as a thin layer protected by a plastic film in a Guinier camera.

Unless otherwise stated, all of the preparative procedures were carried under an atmosphere of prepurified dry nitrogen with pre-dried solvents. Anhydrous gold(III) chloride was prepared as reported previously.[3] Anhydrous iron(III) chloride was prepared by treatment of $FeCl_3{\cdot}6H_2O$ with $SOCl_2$.[7] The reactions were usually carried under exclusion of light (reaction vessels protected with aluminium foil).

Preparation of $[Au_2Br_6]$ *by Halogen Exchange.*—(*a*) *By reaction with* HBr. In a flask (500 cm^3) comtaining CCl_4 (100 cm^3) was introduced $[Au_2Cl_6]$ (2.24 g, 3.69 mmol), followed by evacuation and introduction of dry HBr (2.32 g, 28.7 mmol).

---

† In partial fulfilment of the thesis requirements by P. Robino, March 1989.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Reaction between $[Au_2Cl_6]$ and alkyl bromides[a]

Alkyl bromide	Excess[b]	Solvent and reaction time (h)	Product and %Au (calc.)
CH_2BrCH_2Br	High	CH_2BrCH_2Br 15	$[Au_2Br_6]$ 46.5 (45.1)
EtBr	50%	CCl_4 48	$[Au_2Br_4Cl_2]$[c] 50.3 (50.2)
	30%	CH_2Cl_2 24	$[Au_2Br_4Cl_2]$[c] 49.3 (50.2)
Pr^iBr	High	CCl_4 + Pr^iBr 72	$[Au_2Br_6]$ 46.4 (45.1)
	0	CCl_4 48	$[Au_2Br_6]$ 46.8 (45.1)
	10%	CH_2Cl_2 24	$[Au_2Br_6]$ 46.3 (45.1)
Bu^tBr	20%	CH_2Cl_2 14	AuBr (71.1) + gold 79.2

[a] Yields were always around 90%. [b] With respect to a 1:6 molar ratio of $[Au_2Cl_6]$ to RBr. [c] Formula proposed on the basis of gold content only.

The originally deep red solid turned black-violet within 0.5 h. The mixture was stirred for 24 h at room temperature; the IR spectra of the supernatant solution, measured after 2, 7 and 24 h, showed that the intensity of the HCl (2830 cm^{-1}) and HBr (2515 cm^{-1}) bands did not undergo any further substantial change after the first spectrum. The black-violet solid was then filtered off and dried *in vacuo* (2.67 g, 83% yield); it gave a correct Au analysis for $[Au_2Br_6]$ (Found: 45.3. Calc. 45.1%). The X-ray powder diagram of the product agreed with that calculated on the basis of the known crystal structure.[8] The IR spectrum in the low-wavenumber region showed an intense band at 241 cm^{-1}. The mass spectrum of the product had the following peaks (m/z, relative intensity, assignment): 434, 6.7, $[AuBr_3]^+$; 355, 24.5, $[AuBr_2]^+$; and 276,100, $[AuBr]^+$.

In a control experiment $[Au_2Cl_6]$ (1.29 g, 2.13 mmol) suspended in CCl_4 (50 cm) was treated with HBr (12.9 mmol). After 66 h of stirring the IR spectrum of the supernatant solution showed that the concentration of HBr was at the limits of detection (ε_{HCl} = 43 ± 0.5, ε_{HBr} = 28 ± 3 dm^3 mol^{-1} cm^{-1}): an estimate of the residual concentration gave 0.3 mmol of unreacted HBr, corresponding to a 98% conversion of $[Au_2Cl_6]$ into $[Au_2Br_6]$.

(*b*) *By reaction with* Pr^iBr. In a flask (100 cm^3) containing CH_2Cl_2 (50 cm^3) was introduced $[Au_2Cl_6]$ (9.87 g, 16.27 mmol) together with Pr^iBr (10.0 cm^3, 106.5 mmol). The reaction mixture was stirred for about 24 h at room temperature and then filtered: the black-violet $[Au_2Br_6]$ was dried *in vacuo* (13.0 g, 91% yield) and gave a correct elemental analysis (Au).

The reactions between $[Au_2Cl_6]$ and other alkyl bromides gave the results shown in Table 1.

Reaction between Triphenylmethyl Chloride and Anhydrous Gold(III) *Chloride: Preparation of* $[CPh_3][AuCl_4]$.—Anhydrous gold(III) chloride, $[Au_2Cl_6]$ (2.39 g, 3.94 mmol), was suspended in CH_2Cl_2 (70 cm^3) in a flask (500 cm^3) equipped with a dropping funnel; this suspension was added to a solution of CPh_3Cl (2.28 g, 8.18 mmol) in CH_2Cl_2 (80 cm^3). A yellow solid and an orange solution were obtained; after 30 min of stirring the solvent was partially evaporated under reduced pressure (to a volume of about 100 cm^3). Upon addition of CCl_4 (130 cm^3) more of the yellow solid precipitated. After filtration the triphenylmethylium tetrachloroaurate was dried *in vacuo* (4.14 g, 90% yield) (Found: C, 38.9; H, 2.6; Au, 33.3. Calc. for $C_{19}H_{15}AuCl_4$: C, 39.2; H, 2.6; Au, 33.8%). The solid is sensitive to moisture, decomposes in the presence of oxygen-donor solvents and is readily soluble in halogenated solvents. The ^{1}H NMR spectrum showed resonances at δ 8.30 (t, 1 H, J = 7.2), 7.94 (t, 2 H, J = 7.8) and 7.75 (d, 2 H, J = 7.5 Hz) due to the *para*, *meta* and *ortho* protons, respectively. The spectrum agrees with that in the literature[9] for the triphenylmethyl cation as its $CF_3CO_2^-$ or $CF_3SO_3^-$ derivative. The ^{13}C NMR spectrum has resonances at δ 131.1, 140.3, 143.4, 143.9 and 210.9, the latter being assigned to the central carbon atom, a value of δ 211 being reported[10] for the central carbon atom of CPh_3^+ as the SbF_6^- or the $Sb_2F_{11}^-$ derivative in liquid SO_2. The IR spectrum [Nujol and polychlorotrifluoroethylene mulls] had bands at 3059w, 1580s, 1451s, 1359s, 1291s, 1182s, 992m, 843m, 803m, 771w, 764m, 695s, 614m, 601m, 461s, 422w, 402s, 353s (AuCl) and 315m cm^{-1}.

X-Ray Diffraction Analysis of $[CPh_3][AuCl_4]$.—*Data collection and structure refinement.* The title compound $[CPh_3][AuCl_4]$ was recrystallized by cooling (about −30 °C) a saturated solution in chlorobenzene prepared at room temperature. A rectangular plate-shaped yellow crystal of approximate dimensions 0.08 × 0.28 × 0.96 mm was sealed in a Lindemann capillary. All diffraction work was carried out at room temperature on a computer-controlled single-crystal Siemens AED diffractometer. A monoclinic symmetry was identified *via* a quick search for intense low-angle reflections. The extinctions $h0l$, l = odd, and $0k0$, k = odd, observed during data collection uniquely determined the space group as $P2_1/c$. The unit-cell parameters were determined from the setting angles of 29 reflections, accurately measured.

Crystal data. $C_{19}H_{15}AuCl_4$, M = 582.11, space group $P2_1/c$, a = 8.225(3), b = 14.671(6), c = 16.738(8) Å, β = 97.85(2)°, U = 2001(1) Å^3, Z = 4, D_c = 1.932 g cm^{-3}, Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 78.77 cm^{-1}, $F(000)$ = 1104.

A total of 3819 reflections were collected with Mo-Kα radiation using the θ–2θ scanning mode in the range 2θ 6.0–50.0°. No correction for crystal decomposition was necessary. Peak-profile analysis was performed with a local modification of the Lehmann and Larsen procedure[11] and the intensity data were corrected for Lorentz and polarization factors. After removal of redundant and space-group forbidden data, 1807 reflections with $I \geqslant 2\sigma(I)$ were retained as observed and used in the structure analysis. The method of Walker and Stuart[12] was applied during the refinement to account for absorption effects.[13]

The co-ordinates for the gold atom were obtained from a three-dimensional Patterson map. A Fourier difference synthesis phased on the refined position of this atom led to the location of all non-hydrogen atoms. Refinement was by full-matrix least-squares techniques minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, and assuming anisotropic thermal parameters for Au, Cl and C(1). The phenyl rings were refined isotropically as rigid bodies of D_{6h} symmetry. While a difference map revealed electron density at several of the expected hydrogen-atom positions, it was found to be more convenient to incorporate all the hydrogens at calculated positions, with a refineable overall isotropic thermal parameter for each of the three phenyl rings. A weighting scheme of the type $w = k/[\sigma^2(F_o) + gF_o^2]$ (k = 0.6490 and g = 0.004 096 in the last cycle) was applied in the final stages of refinement. Refinement converged to R' = 0.0605 (R' = 0.0762 and goodness of fit = 0.6687) for 94 variables refined, with the final cycle having shift-to-error ratios less than 0.1. The final difference map had no electron density greater than 1.06 e Å^{-3}.

The analytical forms of the scattering-factor tables for the neutral atoms were used and all non-hydrogen scattering factors were corrected for both the real and imaginary components of the anomalous dispersion.[14] The computing was performed on a GOULD 6040 computer using the SHELX 76 package[15] for solution and refinement, PARST[16] for molecular geometry calculations, and ORTEP[17] and PLUTO[18] for drawings. Atomic coordinates for non-hydrogen atoms are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Table 2 Fractional atomic coordinates (× 10^5 for Au, 10^4 for Cl and C) of $[CPh_3][AuCl_4]$

Atom	*X/a*	*Y/b*	*Z/c*
Au	9 214(8)	25 663(5)	6 888(5)
Cl(1)	3 426(6)	2 263(4)	1 412(4)
Cl(2)	1 275(7)	4 076(4)	960(4)
Cl(3)	−1 521(7)	2 892(4)	−62(4)
Cl(4)	509(8)	1 056(4)	435(5)
C(1)	2 449(21)	2 557(11)	3 459(10)
C(2)	3 085(14)	1 640(7)	3 640(8)
C(3)	4 741(14)	1 484(7)	3 589(8)
C(4)	5 415(14)	622(7)	3 760(8)
C(5)	4 434(14)	−84(7)	3 982(8)
C(6)	2 778(14)	71(7)	4 033(8)
C(7)	2 104(14)	933(7)	3 862(8)
C(8)	3 470(14)	3 326(8)	3 657(7)
C(9)	3 324(14)	4 082(8)	3 148(7)
C(10)	4 369(14)	4 827(8)	3 317(7)
C(11)	5 560(14)	4 815(8)	3 996(7)
C(12)	5 706(14)	4 058(8)	4 505(7)
C(13)	4 661(14)	3 314(8)	4 336(7)
C(14)	751(18)	2 677(8)	3 097(9)
C(15)	−21(18)	2 023(8)	2 572(9)
C(16)	−1 615(18)	2 171(8)	2 190(9)
C(17)	−2 436(18)	2 974(8)	2 333(9)
C(18)	−1 664(18)	3 629(8)	2 858(9)
C(19)	−70(18)	3 480(8)	3 240(9)

Preparation of $[Au_4Cl_8]$ *from* $[Au_2Cl_6]$.—(*a*) *By reaction with* PrCl. In a Schlenk tube were introduced $CDCl_3$ (7.5 cm^3), PrCl (1.5 cm^3, 17.0 mmol) and $[Au_2Cl_6]$ (0.48 g, 0.79 mmol). Over a period of 3 d at room temperature the reaction was monitored by ^1H NMR spectra of the supernatant solution. The black solid, which was filtered off and dried *in vacuo* (0.25 g, 59% yield), analysed correctly for $[Au_4Cl_8]$ (Found: Au, 72.6. Calc.: Au 73.5%). The IR spectrum of the solid (Nujol) was substantially identical to that of an authentic sample.[19] The ^1H NMR spectrum of the solution showed intense peaks due to PrCl (δ 3.6, t; 1.9, m; 1.1, t) and to 1,2-dichloropropane (δ 4.3, m; 1.6, d). A resonance at δ 3.0 (s) was observed, probably due to the MeCl resulting from attack of $[Au_2Cl_6]$ on the silicon grease used as a glassware lubricant.

(*b*) *By reaction with* $SiMe_3Cl$. Anhydrous gold(III) chloride, $[Au_2Cl_6]$ (1.05 g, 1.73 mmol), suspended in CH_2Cl_2 (20 cm^3) was treated with $SiMe_3Cl$ (0.30 cm^3, 2.36 mmol). After stirring for 5 d the resulting suspension was filtered and the black solid was dried *in vacuo* (0.73 g, 79% yield) (Found: Au, 73.5. Calc. for Au_4Cl_8: Au, 73.5%). The same reaction was carried out in a sealed NMR tube (diameter 5 mm) between $[Au_2Cl_6]$ (0.12 g, 0.2 mmol) and $SiMe_3Cl$ (0.06 cm^3, 0.47 mmol) in CD_2Cl_2 (1 cm^3). After 4 d of stirring the NMR spectrum showed resonances at δ 0.4 (s), 3.0 (s) and 0.8 (s) attributed to unreacted $SiMe_3Cl$, MeCl and $SiMe_2Cl_2$, respectively. From the intensity the mixture was calculated to be approximately 42, 31 and 27 (molar %) of the three components.

(*c*) *By reaction with* Bu^tCl *at low temperature*. Anhydrous $[Au_2Cl_6]$ (1.25 g, 2.06 mmol) and Bu^tCl (0.45 cm^3, 4.14 mmol) were stirred for 1 h at a temperature between −20 and −30 °C in a flask (100 cm^3) containing CH_2Cl_2 (30 cm^3). The black solid was filtered off and dried *in vacuo* (0.90 g, 82% yield); it was analysed correctly as $[Au_4Cl_8]$ and had an IR spectrum (Nujol) similar to that of an authentic sample prepared from $[Au_2Cl_6]$ and CO.[19]

(*d*) *By dechlorination of* $[Au_2Cl_8]$ *with cyclohexene at low temperature*.* In a flask (100 cm^3) equipped with a dropping funnel, $[Au_2Cl_6]$ (1.248 g, 2.06 mmol) suspended in CH_2Cl_2 (20 cm^3) was treated dropwise at about −78 °C with a solution of cyclohexene (2.07 mmol) in CH_2Cl_2 (50 cm^3). After stirring for 1 h the temperature was gradually increased to the ambient value. The black precipitate of $[Au_4Cl_8]$ was filtered off and dried *in vacuo* (0.89 g, 81% yield) with the expected elemental (Au) analysis and IR spectrum.

Reaction between $[Au_2Cl_6]$ *and* Pr^iI.—*Preparation of* AuI. Gold(III) chloride, $[Au_2Cl_6]$ (1.43 g, 2.36 mmol), suspended in CH_2Cl_2 (50 cm^3) was treated with Pr^iI (1.60 cm^3, 16.0 mmol). After 20 min the presence of a yellow solid and of an intensely violet supernatant solution was noted. After stirring for 24 h the yellow AuI was recovered by filtration and dried *in vacuo* (1.35 g, 88% yield) with a satisfactory analytical content (Found: Au, 60.6. Calc. for AuI: Au, 60.8%). The IR spectrum did not show any absorption between 600 and 200 cm^{-1}, thus confirming the absence of any detectable impurity of AuCl. An X-ray powder diffraction pattern obtained on a sample of the yellow solid (Guinier method) corresponded to that reported in the literature for AuI[20] prepared by halide exchange from $[AuCl_4]^-$ and I^- in aqueous solution.[21] The interplanar distances (*d*/Å) and the corresponding intensities (in parentheses) were as follows: 6.96 (s), 3.71 (s), 3.10 (m), 3.02 (vs), 2.71 (m), 2.57 (s), 2.30 (m), 2.09 (s), 2.05 (m), 1.88 (m), 1.85 (s), 1.66 (m), 1.54 (m), 1.37 (m) and 1.32 (m).

Reaction of $[Au_2Cl_6]$ *with Anhydrous Iron*(III) *Chloride*.—A suspension of $[Au_2Cl_6]$ (2.35 g, 3.87 mmol) and anhydrous iron(III) chloride, $FeCl_3$ (1.26 g, 7.77 mmol), in $SOCl_2$ (50 cm^3) was stirred for 3 d at room temperature. The resulting brown solid was filtered off and dried *in vacuo* (3.14 g). A similar reaction was carried out in CH_2Cl_2 with analogous results. Table 3 reports the mass spectra of the gold–iron adducts obtained in $SOCl_2$ or CH_2Cl_2, in comparison with an intimate mixture of the two solid halides.

Results and Discussion

Halide-exchange Reactions.—Anhydrous gold(III) chloride, a chloride-bridged dimer,[22] undergoes the halide-exchange reactions (2) and (3). Reaction (2), which was monitored by IR

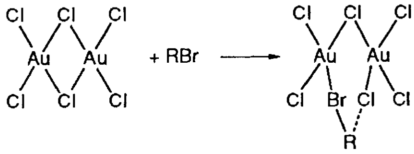
$$[Au_2Cl_6] + 6HBr \longrightarrow 6HCl + [Au_2Br_6] \quad (2)$$

$$[Au_2Cl_6] + 6RBr \longrightarrow 6RCl + [Au_2Br_6] \quad (3)$$

spectra based on the well resolved absorptions of HCl and HBr, was found to be substantially complete, even by using the stoichiometric amount of HBr. The driving force for the reaction clearly arises from the formation of the relatively more stable HCl [ΔG_f°(HCl) = −95, (HBr) = −53 kJ mol^{-1}],[23] in spite of the relatively weaker Au–Br bond being formed.[24]

The use of the more conveniently handled alkyl bromides, see equation (3), was also successfully attempted. Neat 1,2-dibromoethane or Pr^iBr in dichloromethane as reaction medium gave the best results, see Table 1; EtBr gave incomplete exchange and Bu^tBr led to reduction to both AuBr and Au.

In the HBr-promoted exchange, it is believed that the primary attack by HBr, see equation (4), R = H, involves cleavage of a



(4)

R = H or alkyl

---

* Fast addition of cyclohexene at room temperature gave a mixture of $[Au_2Cl_6]$ and AuCl. A mixture of AuCl and $[Au_2Cl_6]$ in a 2:1 molar ratio did not yield any $[Au_4Cl_8]$ after 1 week of stirring at room temperature.

Table 3 Mass spectra of the reaction products of $[Au_2Cl_6]$ and $FeCl_3$ in CH_2Cl_2 (**A** and **A′**) and $SOCl_2$ (**B**) and of an intimate mixture of the two halides (**C**)

		Relative intensity			
Ion	*m/z*	**A**	**B**	**C**	**A′**
$[FeAuCl_6]^+$	463	<0.5	<1		8
$[FeAuCl_5]^+$	428	<0.5	<0.5		4
$[FeAuCl_4]^+$	393	3	3		23
$[FeAuCl_3]^+$	358	2	1		8
$[FeAuCl_2]^+$	323	2	2		12
$[Au_2Cl_6]^+$	604			<0.1	
$[Au_2Cl_4]^+$	534			<0.1	
$[Au_2Cl_3]^+$	499			<0.1	
$[Au_2Cl_2]^+$	464			<0.1	
$[Au_2Cl]^+$	429			<0.1	
Au_2^+	394			<0.1	
$[AuCl_2]^+$	267			2	
$[AuCl]^+$	232	<1	1	3	4
Au^+	197		3	2	
$[Fe_4Cl_{10}]^+$	574	<1			
$[Fe_3Cl_{10}]^+$	518	<0.5			
$[Fe_3Cl_9]^+$	483	<0.5			
$[Fe_3Cl_8]^+$	448	5			
$[Fe_3Cl_7]^+$	413	37	<0.5		
$[Fe_3Cl_6]^+$	378	1			
$[Fe_2Cl_6]^+$	322	3	3	1	9
$[Fe_2Cl_5]^+$	287	23	16	12	47
$[Fe_2Cl_4]^+$	252	65	33	31	100
$[Fe_2Cl_3]^+$	217	10	9	4	11
$[FeCl_3]^+$	161	33	88	28	4
$[FeCl_2]^+$	126	88	100	35	63
$[FeCl]^+$	91	100	78	100	92

The spectra of **A**–**C** were measured at a source temperature of 200 °C and that of **A′** at 70 °C.

Au–Cl_b (Cl_b = bridging chloride) bond, followed by proton transfer to an adjacent chloride and elimination of HCl. This will be repeated up to complete chloride substitution. Although we have no direct evidence of HBr co-ordination to gold(III), support for the proposed mechanism comes from the isolation of co-ordination compounds of HX (X = Cl, Br or I) with the pentacarbonyltungsten(0) fragment.[25]

The reaction with HBr is fast, in spite of the low solubility of both the gold reagent and the product, and complete in about 2 h at room temperature. The X-ray powder diagram suggests that a compound with the same structure as that obtained from the elements at higher temperature[8] was obtained.

In the case of alkyl bromides, an addition of the type (4) may lead to partial charge separation with formation of a R^+ $Au_nCl_{3n}Br^-$ (n = 1 or 2) ion pair (the low relative permittivity of the reaction medium would not probably allow charge separation to take place). In this connection, recently co-ordination compounds of silver(I) with halogenated hydrocarbons, such as CH_2Cl_2 and 1,2-$C_2H_4Cl_2$, have been isolated.[26]

Although the formation of gold(III) bromide by the halide-exchange mechanism within the ion pair is rather speculative, a stable carbocationic species was found to be formed from CPh_3Cl and $[Au_2Cl_6]$, according to equation (5). The product

$$CPh_3Cl + \tfrac{1}{2}[Au_2Cl_6] \longrightarrow [CPh_3][AuCl_4] \quad (5)$$

was completely characterized by conventional methods, including X-ray diffractometry. Triphenylmethylium tetrachloroaurate(III) consists of discrete CPh_3^+ and $AuCl_4^-$ ions. Perspective views of these are provided in Fig. 1. The crystal packing is shown in Fig. 2. All atoms are located in general positions and therefore no crystallographic symmetry is imposed on the complex.

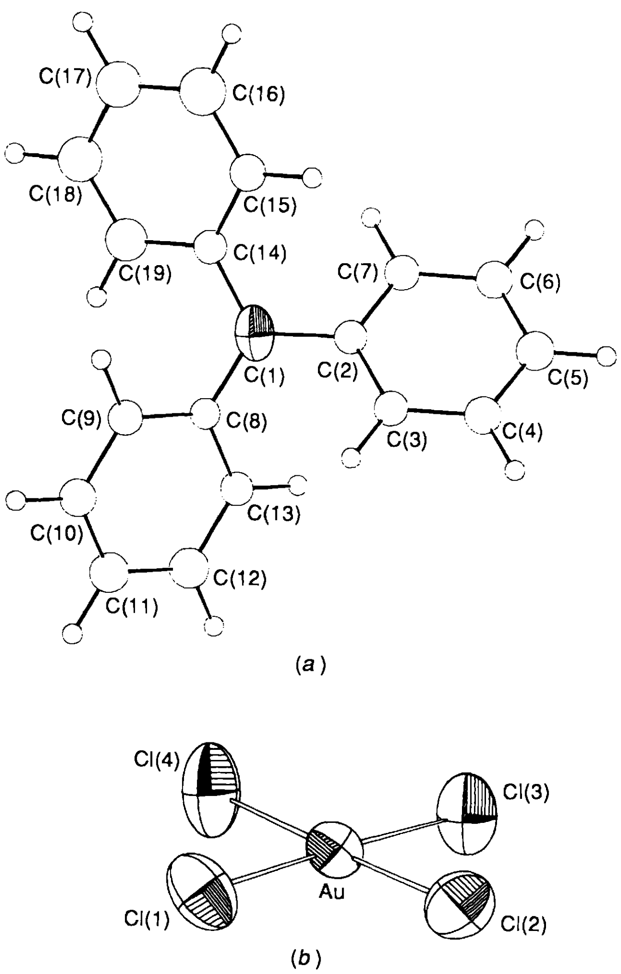


Fig. 1 A perspective ORTEP view of (*a*) the $[CPh_3]^+$ cation and (*b*) the $[AuCl_4]^-$ anion of $[CPh_3][AuCl_4]$. Thermal ellipsoids are drawn at the 50% probability level. Hydrogens of the phenyl groups are represented by arbitrarily small spheres

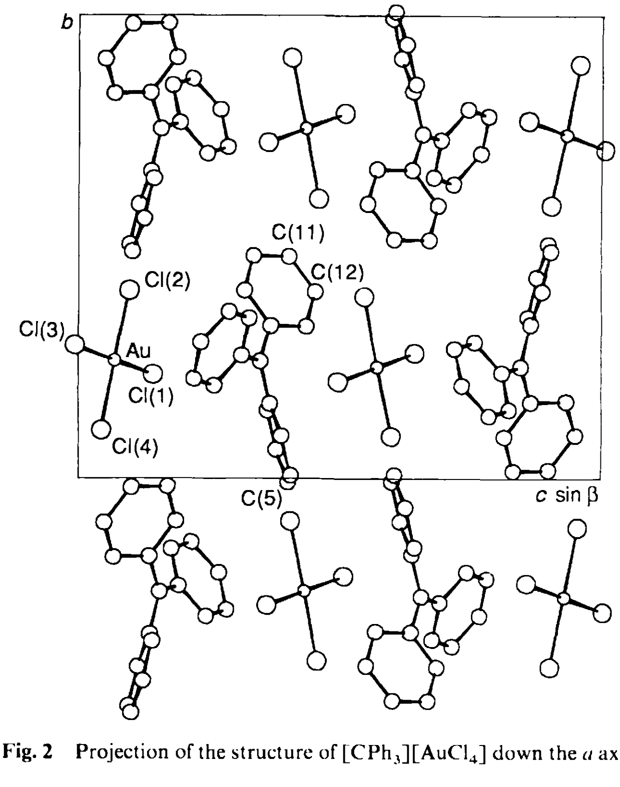


Fig. 2 Projection of the structure of $[CPh_3][AuCl_4]$ down the *a* axis

Table 4 Selected bond distances (Å) and angles (°) of $[CPh_3][AuCl_4]$

Au–Cl(1)	2.286(5)	C(1)–C(2)	1.46(2)
Au–Cl(2)	2.272(6)	C(1)–C(8)	1.42(2)
Au–Cl(3)	2.270(6)	C(1)–C(14)	1.46(2)
Au–Cl(4)	2.273(6)		
Cl(1)–Au–Cl(2)	90.2(2)	C(2)–C(1)–C(8)	120(1)
Cl(1)–Au–Cl(3)	178.0(2)	C(2)–C(1)–C(14)	120(1)
Cl(1)–Au–Cl(4)	90.6(2)	C(8)–C(1)–C(14)	120(1)
Cl(2)–Au–Cl(3)	89.1(2)		
Cl(2)–Au–Cl(4)	178.5(3)		
Cl(3)–Au–Cl(4)	90.2(2)		

The four-co-ordinated chlorine atoms form a very slightly distorted square-planar array about the gold atom, the maximum deviation from the best least-squares plane being less than 0.04 Å. The four Au–Cl distances are virtually identical, the range being 2.270(6)–2.286(5) Å, and fall just in the middle of the range of lengths observed for other $[AuCl_4]^-$ ions (see below). The bond angles at gold differ from those expected for regular square-planar co-ordination by 0.1–2.0° only, see Table 4.

To our knowledge, structural data are available for 20 compounds containing the $[AuCl_4]^-$ ion as a discrete entity (only structures with $R < 0.08$ have been considered). Since two or three crystallographically independent $[AuCl_4]^-$ ions are present in the unit cell of some of these compounds, there are 29 structures of this ion available for comparison. In 25 cases the gold atom is located in a special position (inversion centre, 18 cases,[27] two-fold axis, three cases;[27o,28] four-fold axis, one case;[29] mirror plane, one case;[27i] *mm*2 symmetry, two cases[30]) and only four examples are known in which the gold atom lies on a general position,[17g,28a,31] as found in the present structure. In each case the gold atom is co-ordinated to the four chlorines in square-planar arrangement, typical for compounds of Au^{III}. The Au–Cl distances span a rather small range, 2.253–2.306 Å. With only two exceptions, the angles around the gold atom are all of 90 and 180°, within 2°.

The $[CPh_3]^+$ cation is propeller shaped, as steric constraints prevent the aromatic rings from being coplanar. These rings are twisted by 32.8(5), 35.2(5) and 29.2(5)° out of the plane of the four central carbon atoms. The three bond angles to the central carbon atom total 360°, *i.e.* the hybridization of this atom is pure sp^2. Adjacent phenyl rings are at angles of 56.4(4), 55.0(4) and 54.4(4)°. All these findings are fully comparable with those observed in structural investigations carried out on this ion.[32]

Each ion can be considered to be a discrete entity. The closest atoms to the gold atom other than chlorines are two carbon atoms, C(15) and C(16), belonging to the same phenyl ring, which are 3.44(2) and 3.53(2) Å away, respectively. Even if these values seem to exclude any possibilities of co-ordination to the metal, nevertheless it is noticeable that C(15) occupies approximately one of the potential axial co-ordination sites of the anion. Other interionic interactions of interest are: $Cl(2)\cdots C(4)$ $(1 - x, y + \frac{1}{2}, \frac{1}{2} - z)$ 3.52(1); $Cl(4)\cdots Cl(4)$ $(-x, -y, -z)$ 3.476(9); $C(5)\cdots C(5)$ $(1 - x, -y, 1 - z)$ 3.42(2) and $C(11)\cdots C(12)$ $(1 - x, 1 - y, 1 - z)$ 3.30(2) Å. The last two contacts, which involve two of the three phenyl rings, give rise to chains of cations which run parallel to *b*. The third ring, as mentioned above, is involved in weak interactions with the gold atom.

It is interesting that in this ionic compound the central atoms of both the cation and anion have a planar co-ordination. Complete charge separation is in this case probably due to the relatively low charge density on the flat carbocation. The same type of argument can probably be used to explain the high solubility of this compound in a solvent of relatively low permittivity such as dichloromethane.

With this information available, the mechanistic problems connected with (*a*) the halide-exchange reaction between $[Au_2Cl_6]$ and RBr, and (*b*) the secondary reduction to gold(I) observed with Bu^tBr can now be discussed to a greater extent. However, some additional experimental information was required and, in order to separate the two phenomena, the reactions of $[Au_2Cl_6]$ with some alkyl chlorides, have been taken into consideration.

Reduction of $[Au_2Cl_6]$ occurs with PrCl, $SiMe_3Cl$ and Bu^tCl. In all these cases, $[Au_4Cl_8]$ was observed as the unique reaction product. We believe that the observed facts can be accommodated by a mechanism involving the formation of ion pairs, as shown in equations (6)–(8) for the specific case of PrCl. From this alkyl halide, the $Pr^+Au_nCl_{3n+1}^-$ (n = 1 or 2) pair would be formed, followed by rearrangement to the more stable Me_2CH^+ cation and by dehydrochlorination involving the methyl group. The overall reaction can therefore be regarded as obeying the stoichiometry of (10).

$$2MeCH_2CH_2Cl + [Au_2Cl_6] \longrightarrow 2MeCH_2CH_2{}^+AuCl_4{}^- \quad (6)$$

$$2MeCH_2CH_2{}^+AuCl_4{}^- \longrightarrow 2Me_2CH^+AuCl_4{}^- \quad (7)$$

$$2Me_2CH^+AuCl_4{}^- \longrightarrow 2CH_2ClCHClMe + 2HCl + 2\text{`AuCl'} \quad (8)$$

$$2\text{`AuCl'} + [Au_2Cl_6] \longrightarrow [Au_4Cl_8] \quad (9)$$

$$2MeCH_2CH_2Cl + 2[Au_2Cl_6] \longrightarrow 2CH_2ClCHClMe + 2HCl + [Au_4Cl_8] \quad (10)$$

The gold(I) chloride formulated in equations (8) and (9) is proposed to exist in a soluble form in solution, corresponding to the failure to observe the formation of AuCl(s). It is believed that $[Au_4Cl_8]$ is formed through a concerted process by which 'AuCl' formed in a relatively slow step (8) is trapped by the excess of $[Au_2Cl_6]$ still present in solution to give the observed mixed-valence compound, before it can collapse to AuCl(s). In this connection, it is interesting that AuCl and $[Au_2Cl_6]$ do not react to give $[Au_4Cl_8]$, in agreement with the earlier suggestion that $[Au_4Cl_8]$ is a metastable compound with respect to its gold(I) and gold(III) constituent fragments.[33]

The formation of 1,2-dichloropropane, see step (8), may follow two different paths, namely (8a) and (8b) or (8c)–(8e).

$$Me_2CH^+AuCl_4{}^- \longrightarrow HCl + MeCH{=}CH_2 + AuCl_3 \quad (8a)$$

$$MeCH{=}CH_2 + AuCl_3 \longrightarrow MeCHClCH_2Cl + \text{`AuCl'} \quad (8b)$$

$$Me_2CH^+AuCl_4{}^- \longrightarrow HCl + MeCH^+CH_2AuCl_3{}^- \quad (8c)$$

$$MeCH^+CH_2AuCl_3{}^- \longrightarrow MeCHClCH_2AuCl_2 \quad (8d)$$

$$MeCHClCH_2AuCl_2 \longrightarrow MeCHClCH_2Cl + \text{`AuCl'} \quad (8e)$$

Steps (8a) and (8b) involve an olefin elimination followed by chlorine addition across the double bond. Steps (8c)–(8e) involve deprotonation of a methyl group by $[AuCl_4]^-$ with HCl elimination, followed by collapse of the gold(III) organometallic to 1,2-dichloropropane and gold(I) chloride. In this connection, it is worth mentioning that compounds of the type $[AuRBr_2]$ are known[34] to decompose thermally to AuBr and RBr. Step (8d) involves the formation of a gold(III) carbon-bonded species. Anhydrous gold(III) chloride is an efficient metallating agent for aromatic hydrocarbons and, as has been pointed out earlier in connection with the problem of saturated C–H bond activation, aliphatic C–H bonds are weaker than aromatic ones.[35] Earlier attempts[36] to metallate functionalized hydrocarbons such as aromatic nitriles failed due to the decreased acidity of the gold(III) centre in the primary adduct $AuCl_3{\cdot}RCN$.

We have no data to decide between the two mechanistic proposals. On the other hand, in favour of the olefin intermediacy is the observation that dehalogenation of $[Au_2Cl_6]$ to $[Au_4Cl_8]$ can also be carried out with a halogen abstractor such as cyclohexene in the strictly stoichiometric amount. At low temperature, self-aggregation of 'AuCl' to AuCl(s) is substantially suppressed and $[Au_4Cl_8]$ is thus formed.

Gold(III) iodide is a non-existent compound, being presumably unstable with respect to its decomposition to AuI + I_2.[2] However, it was of interest to verify what the products in the $[Au_2Cl_6]$–RI (R = H or alkyl) system would be if the halide exchange was carried out in the absence of water (AuI is normally prepared in the $AuCl_4^-$–I^- aqueous system[21]).

By operating in halogenated hydrocarbons as medium, anhydrous gold(III) chloride was found promptly to exchange with either Pr^iI or HI at room temperature to give AuI exclusively with I_2 formation [equations (11) and (12)]. The AuI

$$[Au_2Cl_6] + 6Pr^iI \longrightarrow 2AuI + 2I_2 + 6Pr^iCl \quad (11)$$

$$[Au_2Cl_6] + 6HI \longrightarrow 2AuI + 2I_2 + 6HCl \quad (12)$$

obtained is microcrystalline and an X-ray powder diagram had an identical pattern to that of a sample prepared in aqueous solution. We therefore conclude that AuI_3 is intrinsically unstable and also we do not find any definite evidence of gold(I) triiodide.

The mixed-valence chloride $[Au_4Cl_8]$ was shown to have a chair-like chloride-bridged structure with two gold(III) and two gold(I) centres.[37] The question then arose as to whether similar structures could also exist with different halides. However, the reaction of $[Au_2Br_6]$ with Bu^tBr at low temperature led to AuBr and Au and no evidence of a mixed-valence bromide $[Au_4Br_8]$ could be obtained. On the other hand, treatment of $[Au_2Br_6]$ with cyclohexene led to intractable solids and similar results were also obtained in the attempted $[Au_4Cl_8]$–HBr exchange reaction.

Gold(III) chloride is a centrosymmetric chloride-bridged dimer:[22] in principle, it should be possible to consider a non-symmetric heterometallic chloride-bridged dimer by combining $[Au_2Cl_6]$ with another dimeric metal chloride. Anhydrous iron(III) chloride was chosen for this purpose: as in the gas phase it is a chloride-bridged dimer obtained by edge sharing of two $FeCl_4$ tetrahedra,[38] the existence of a $Cl_2Au(\mu\text{-}Cl)_2FeCl_2$ dimer was conceivable, obtained by edge sharing of a gold(III) square with an iron(III) tetrahedron. Mixing a suspension of the two little-soluble chlorides in either $SOCl_2$ or CH_2Cl_2 resulted in the formation of an apparently homogeneous solid containing both gold and iron. Since analytical data are not significant in this case and other physicochemical (magnetic susceptibility, electronic spectra) data would not easily distinguish between a molecular gold–iron mixed species and a mixture of the starting materials, we reasoned that mass spectrometry should be able to provide some insight into this problem. As Table 3 shows, the product of the reaction gave mixed iron–gold fragments which are not present in an intimate mixture of the metal chlorides. Particularly interesting is the fact that a peak corresponding to $AuFeCl_6$ was observed (m/z = 463). This led us to be believe that a mixed molecular species $AuFeCl_6$[39] is actually formed in an essentially entropy-driven reaction, although we are not able to establish to what extent the reaction has occurred. These findings are relevant to the gas-phase transport of metal halides.[40]

Acknowledgements

The authors thank the Consiglio Nazionale delle Ricerche (C.N.R., Roma) and the Ministero dell'Università e della Ricerca Scientifica (M.U.R.S.T.) for financial support, and Dr. G. Del Piero, Eniricerche, S. Donato Milanese, Milano and Mrs. R. Hüpper, Universität Tübingen, for the X-ray powder diagrams.

References

1 E. M. W. Janssen, J. C. W. Folmer and G. A. Wiegers, *J. Less-Common Met.*, 1974, **38**, 71; E. M. W. Janssen and G. A. Wiegers, *J. Less-Common Met.*, 1978, **57**, 47, 59.
2 R. J. Puddephatt, *The Chemistry of Gold*, Elsevier, Amsterdam, 1978.
3 D. Belli Dell'Amico and F. Calderazzo, *Gazz. Chim. Ital.*, 1973, **103**, 1099.
4 W. E. Dasent, *Non-existent Compounds*, Marcel Dekker, New York, 1965; *Handbook of Chemistry and Physics*, 65th edn., CRC Press, Boca Raton, FL, 1985.
5 P. Biagini, F. Calderazzo, G. Pampaloni, and P. F. Zanazzi, *Gazz. Chim. Ital.*, 1987, **117**, 27.
6 D. Beli Dell'Amico, F. Calderazzo, A. Segre and P. Robino, *Gazz. Chim. Ital.*, 1991, **121**, 51.
7 A. R. Pray, *Inorg. Synth.*, 1990, **28**, 321.
8 J. Strähle and K. P. Lörcher, *Z. Naturforsch., Teil B*, 1974, **29**, 266; K. P. Lörcher and J. Strähle, *Z. Naturforsch., Teil B*, 1975, **30**, 662.
9 C. F. Wilcox, D. Hellwinkel, H. Stahl, H. G. Gaa and M. Dörner, *Tetrahedron Lett.*, 1988, **29**, 5501.
10 G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, 1969, **91**, 5801.
11 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.
12 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
13 F. Ugozzoli, ABSORB, *Comput. Chem.*, 1987, **11**, 109.
14 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
15 G. M. Sheldrick, SHELX 76, A program for crystal structure determination, University of Cambridge, 1976.
16 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.
17 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, TN, 1976.
18 W. D. S. Motherwell, PLUTO, University of Cambridge, 1976.
19 D. Belli Dell'Amico, F. Calderazzo and F. Marchetti, *J. Chem. Soc., Dalton Trans.*, 1976, 1829.
20 H. Jagodzinsky, *Z. Kristallogr.*, 1959, **112**, 80.
21 G. Brauer, *Handbuch der präparativen anorganischen Chemie*, Ferdinand Henke, Stuttgart, 1978, Band 2, Dritte Aufl., S.1014.
22 E. S. Clark, D. H. Templeton and C. H. MacGillavry, *Acta Crystallogr.*, 1958, **11**, 284.
23 D. R. Stull, E. F. Westrum and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York, 1973.
24 J. E. Huheey, *Inorganic Chemistry*, Harper and Row, New York, 1978.
25 E. O. Fischer, S. Walz, G. Kreis and F. R. Kreissl, *Chem. Ber.*, 1977, **110**, 1651.
26 M. R. Colsman, T. D. Newbound, L. J. Marshall, M. D. Noirot, M. M. Miller, G. P. Wulfsberg, J. S. Frye, O. P. Anderson and S. H. Strauss, *J. Am. Chem. Soc.*, 1990, **112**, 2349.
27 (*a*) M. S. Hussian and E. O. Schemper, *J. Chem. Soc., Dalton Trans.*, 1982, 751; (*b*) H.-N. Adams and J. Strahle, *Z. Anorg. Allg. Chem.*, 1982, **485**, 65; (*c*) L. S. Hollis and S. J. Lippard, *J. Am. Chem. Soc.*, 1983, **105**, 4293; (*d*) J. Vicente, M.-T. Chicote, M. D. Bermudez, X. Solans and M. Font-Altaba, *J. Chem. Soc., Dalton Trans.*, 1984, 557; (*e*) A. M. Schacter, E. B. Fleischer and R. C. Haltiwanger, *Acta Crystallogr., Sect. C*, 1987, **43**, 1876; (*f*) M. S. Hussain and S. A. A. Al-Hamoud, *J. Chem. Soc., Dalton Trans.*, 1985, 749; (*g*) M. G. B. Drew, L. R. Glaves and M. J. Hudson, *J. Chem. Soc., Dalton Trans.*, 1985, 771; (*h*) H. Kiriyama, N. Matsushita and Y. Yamagata, *Acta Crystallogr., Sect. C*, 1986, **42**, 277; (*i*) J. Vicente, M.-T. Chicote, M. D. Bermudez, M. J. Sanchez-Santano, P. G. Jones, C. Fittschen and G. M. Sheldrick, *J. Organomet. Chem.*, 1986, **310**, 401; (*l*) M. S. Hussain and E. O. Schemper, *J. Chem. Soc., Dalton Trans.*, 1980, 750; (*m*) H. J. Keller, I. Leichert, G. Uhlmann and J. Weiss, *Chem. Ber.*, 1977, **110**, 1684; (*n*) P. G. Jones, R. Schelbach and E. Schwarzmann, *Acta Crystallogr., Sect. C*, 1987, **43**, 1674; (*o*) P. G. Jones, R. Schelbach, E. Schwarzmann and C. Thöne, *Acta Crystallogr., Sect. C*, 1988, **44**, 1198; (*p*) P. G. Jones, A. Olbrich, R. Schelbach and E. Schwarzmann, *Acta Crystallogr., Sect. C*, 1988, **44**, 2201.
28 (*a*) M. Bonamico and G. Dessy, *Acta Crystallogr., Sect. B*, 1973, **29**, 1737; (*b*) P. G. Jones and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1978, **34**, 1353.
29 P. G. Jones, J. J. Guy and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1975, **31**, 2687.

30 C. F. Erdbrügger, P. G. Jones, R. Schelback, E. Schwarzmann and G. M. Sheldrick, *Acta Crystallogr., Sect. C*, 1987, **43**, 1857.

31 M. C. Caira, L. R. Nassimbeni and A. L. Rodgers, *Acta Crystallogr., Sect. B*, 1975, **31**, 1112; M. Sakhawathussain and S. A. A. Al-Hamoud, *Inorg. Chim. Acta*, 1984, **82**, 111.

32 A. H. Gomes de Mesquita, C. H. MacGillavry and K. Eriks, *Acta Crystallogr., Sect B*, 1965, **18**, 437; L. L. Koh and K. Eriks, *Acta Crystallogr., Sect. B*, 1971, **27**, 1405; B. Krebs and V. Paulat, *Z. Naturforsch., Teil B*, 1979, **34**, 900; D. Fenske, R. Kujanek and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1983, **507**, 51.

33 E. M. W. Jansen, F. Pohlmann and G. A. Wiegers, *J. Less-Common Met.*, 1976, **45**, 261; F. Calderazzo and D. Belli Dell'Amico, *Inorg. Chem.*, 1982, **21**, 3639.

34 B. Armer and H. Schmidbaur, *Angew. Chem.*, 1970, **82**, 120.

35 B. B. Wayland, *J. Am. Chem. Soc.*, 1985, **107**, 7941; W. D. Jones, *Acc. Chem. Res.*, 1989, **22**, 91; A. D. Riabov, *Chem. Rev.*, 1990, **90**, 403.

36 F. Calderazzo and D. Belli Dell'Amico, *J. Organomet. Chem.*, 1974, **76**, C59; D. Belli Dell'Amico and W. Hiller, *J. Chem. Soc., Dalton Trans.*, 1987, 1329.

37 D. Belli Dell'Amico, F. Calderazzo, F. Marchetti and S. Merlino, *J. Chem. Soc., Chem. Commun.*, 1977, 31.

38 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., Wiley, New York, 1988.

39 J. P. Hager and R. B. Hill, *Metall. Trans.*, 1970, **1**, 2723.

40 H. Schäfer, *Adv. Inorg. Chem. Radiochem.*, 1983, **26**, 201.

Received 15*th March* 1991; *Paper* 1/01240A