Novel Compounds with Gold–Transition-metal Bonds; Crystal and Molecular Structure of Bis(triphenylphosphine)iminium Bis(tetracarbonylcobaltio)aurate(I)

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The tetrahydrothiophen group (tht) in $[Au(C_6F_5)_3(tht)]$ can readily be replaced by carbonylmetallate anions $[M(CO)_n]^-$ (M = Co, *n* = 4; M = Mn, *n* = 5) or $[M(cp)(CO)_3]^-$ (M = Mo or W; cp = η-C_5H_5) to give a novel type of anionic complex of general formula $[N(PPh_3)_2][(C_6F_5)_3Au–M(CO)_n]$ or $[NBu^n_4][(C_6F_5)_3Au–M(cp)(CO)_3]$ whose reactivity with PPh_3 depends upon M. Thus, for M = Mo or W the reaction leads to the cleavage of the metal–metal bond, for M = Mn no reaction is observed at room temperature, whilst substitution of one CO group takes place for M = Co. Reaction of the carbonylmetallates with $[Au(C_6F_5)(tht)]$ gives rise to disproportionations affording $Q[Au(C_6F_5)_2]$ [Q = $N(PPh_3)_2{}^+$ or $NBu^n{}_4{}^+$] and $[N(PPh_3)_2][Au\{M(CO)_n\}_2]$ or $[NBu^n_4][Au\{M(cp)(CO)_3\}_2]$ which are stable at room temperature. The presence of the linear unit Co–Au–Co in $[N(PPh_3)_2][Au\{Co(CO)_4\}_2]$ has been established by a single-crystal structure determination; space group $P\bar{1}$, *a* = 9.610(4), *b* = 9.978(4), *c* = 11.506(5) Å, α = 97.70(2), β = 97.84(2), γ = 90.97(2)°, and *Z* = 1. The structure has been refined to *R* = 0.032 for 2 475 unique observed reflections. Both the anion and cation lie on crystallographic centres of symmetry, hence the Co–Au–Co and P–N–P moieties are linear. The Au–Co bond length is 2.509(2) Å.

BINUCLEAR complexes of the types $[LAu–M(CO)_n]$ and $[LAu–M(CO)_nL_m]$ (M being a transition metal) resulting from reactions between [AuClL] and the corresponding carbonylmetallates have been known [1–5] for some time. The preparation of trimetallic systems M–Au–M by treating $[AuX_2]^-$ (X = Cl or Br) with carbonylmetallate has also been reported [6] and the compound $[NEt_4][(OC)_4Co–Au–Co(CO)_4]$ was stated to decompose after *ca.* 30 min at −79 °C. No complex of general formula $[LX_2Au–M(CO)_n]$ or $[X_3Au–M(CO)_n]^-$ (X = halide or organic radical) has been reported until now.

Recently we discussed [7–9] a general method for synthesising gold(I) and gold(III) organo-anions by the replacement of tetrahydrothiophen (tht) in $[Au(C_6F_5)(tht)]$ or $[Au(C_6F_5)_3(tht)]$ by anionic ligands such as halides, pseudohalides, or organic radicals. Here we describe the results obtained on treating these tht complexes with the carbonylates $[Mn(CO)_5]^-$, $[Co(CO)_4]^-$, $[Mo(cp)(CO)_3]^-$, or $[W(cp)(CO)_3]^-$ (cp = η-C_5H_5), leading to compounds of the types $[(C_6F_5)_3Au–M(CO)_n]^-$, $[(C_6F_5)_3Au–M(cp)(CO)_3]^-$, $[Au\{M(CO)_n\}_2]^-$, and $[Au\{M(cp)(CO)_3\}_2]^-$.

RESULTS AND DISCUSSION

If dichloromethane solutions containing equimolar amounts of $[Au(C_6F_5)_3(tht)]$ and QM* {Q = $[N(PPh_3)_2]^+$; M* = $[Co(CO)_4]^-$ or $[Mn(CO)_5]^-$} are mixed, the rapid replacement of tht by carbonylate anions with formation of a metal–metal bond can be observed [equation (1)]. This reaction is soon complete; after 5 min,

$$[Au(C_6F_5)_3(tht)] + QM^* \longrightarrow Q[(C_6F_5)_3Au–M^*] + tht \qquad (1)$$

ν(CO), characteristic for the carbonylate anion, cannot be observed. For QM* = $[NBu^n_4][Mo(cp)(CO)_3]$ or $[NBu^n_4][W(cp)(CO)_3]$, however, after stirring for 1 h at room temperature the solution still shows ν(CO) of the free carbonylate, along with absorption corresponding to a compound with Au–M bonds. Since the relative intensities of these vibrations do not change even after 24 h, process (1) must be an equilibrium. In fact, the yield of $Q[(C_6F_5)_3Au–M^*]$ can be increased by twice evaporating the solution to dryness and by washing the residue with n-hexane in order to remove the free tht. For QM* = $Na[Fe(cp)(CO)_2]$ and $Na_2[Fe(CO)_4]$ no reaction could be observed in tetrahydrofuran (thf) and, after stirring for 8 h at room temperature, unchanged $[Au(C_6F_5)_3(tht)]$ was recovered.

Complexes (1)—(4) (see Table 1) are isolated as cream or yellow crystals, which are air- and moisture-stable in the solid state, and in solution in oxygen-free solvents. In acetone they show conductivities characteristic of 1 : 1 electrolytes. Their i.r. spectra in the carbonyl region are in good agreement with the expected pattern and the vibrations due to ν(CO) are in every case shifted towards higher energies relative to those of the carbonylmetallates. The derivatives of Co, Mo, and W show only two instead of the three predicted bands ($2a_1 + e$ for Co,[10] and $2a' + a''$ for Mo and W [3]), probably because the broad band at lower energies embraces two of these vibrations ($a_1 + e$ for Co and $a' + a''$ for Mo and W). The manganese compound exhibits three bands which, in decreasing order, are assignable to the vibrations a_1, e, and a_1. In all the cases the vibrations due to ν(CO) show shifts towards higher energies relative to those of the corresponding complexes $[(Ph_3P)Au–M(CO)_n]$ [1,10] or $[(Ph_3P)Au–M(cp)(CO)_3]$.[3]

Although this reaction can be extended to other gold complexes, only in the case of $[Au(C_6F_5)_3(tht)]$ does it lead to the smooth formation of bimetallic complexes.

Reactions of *cis*-$[\mathrm{Au(C_6F_5)_2Cl(PPh_3)}]$,[11] $[\mathrm{AuCl_3(tht)}]$,[7] $[\{\mathrm{Au(C_6F_5)_2Cl}\}_2]$,[12] or *trans*-$[\mathrm{N(PPh_3)_2}][\mathrm{Au(C_6F_5)_2Cl_2}]$ [8] with $[\mathrm{N(PPh_3)_2}][\mathrm{M(CO)}_n]$ (M = Co, $n = 4$; M = Mn, $n = 5$) cause the reduction of gold(III) to gold(I) and even to metallic gold, and only if the moiety $\mathrm{Au(C_6F_5)_3}$ [13] is formed during the process can the complexes $[\mathrm{N(PPh_3)_2}][(\mathrm{C_6F_5})_3\mathrm{Au{-}M(CO)}_n]$ be isolated, although in low yields (10—15%).

At room temperature and in 1 : 1 mol ratio, $\mathrm{PPh_3}$ reacts with complexes (1)—(4) in a selective way. Thus, reaction with complexes (3) and (4) leads to cleavage of the Au–M bond, according to equation (2), and the

$$[\mathrm{NBu^n_4}][\mathrm{R_3Au{-}M(cp)(CO)_3}] + \mathrm{PPh_3} \longrightarrow [\mathrm{AuR_3(PPh_3)}] + [\mathrm{NBu^n_4}][\mathrm{M(cp)(CO)_3}] \tag{2}$$

resulting compounds can easily be separated by evaporation to dryness and extraction of $[\mathrm{AuR_3(PPh_3)}]$ with diethyl ether (in which the carbonylate is insoluble).

TABLE 1

Physical data

	Complex	Colour	M.p. (decomp.) (θ_c/°C)	Λ_M [a] ohm^{-1} cm^2 mol^{-1}	ν(CO) [b]/cm^{-1}
(1)	$[\mathrm{N(PPh_3)_2}][(\mathrm{C_6F_5})_3\mathrm{Au{-}Co(CO)_4}]$	Yellow	118	88	2 059s, 1 975s,br
(2)	$[\mathrm{N(PPh_3)_2}][(\mathrm{C_6F_5})_3\mathrm{Au{-}Mn(CO)_5}]$	Pale cream	115	96	2 070m, 1 978, 1 957 (sh)
(3)	$[\mathrm{NBu^n_4}][(\mathrm{C_6F_5})_3\mathrm{Au{-}Mo(cp)(CO)_3}]$	Pale brown	93	110	1 955s, 1 909s,br
(4)	$[\mathrm{NBu^n_4}][(\mathrm{C_6F_5})_3\mathrm{Au{-}W(cp)(CO)_3}]$	Pale cream	103	94	1 955s, 1 904s,br
(5)	$[\mathrm{N(PPh_3)_2}][(\mathrm{C_6F_5})_3\mathrm{Au{-}Co(CO)_3(PPh_3)}]$	Yellow	114	110	2 000mw, 1 940s, 1 919s
(6)	$[\mathrm{N(PPh_3)_2}][(\mathrm{C_6F_5})_3\mathrm{Au{-}Co(CO)_3\{P(OPh)_3\}}]$	Yellow	107	100	2 019mw, 1 954s, 1 936s
(7)	$[\mathrm{N(PPh_3)_2}][\mathrm{Au\{Co(CO)_4\}_2}]$	Pale cream	105	103	2 020s, 1 954vs,br
(8)	$[\mathrm{N(PPh_3)_2}][\mathrm{Au\{Mn(CO)_5\}_2}]$	Pale cream	126	115	2 030m, 1 945vs, 1 920 (sh)
(9)	$[\mathrm{NBu^n_4}][\mathrm{Au\{Mo(cp)(CO)_3\}_2}]$	Pale cream	114	98	1 932s, 1 910s, 1 823s,br
(10)	$[\mathrm{NBu^n_4}][\mathrm{Au\{W(cp)(CO)_3\}_2}]$	Pale cream	120	94	1 931m, 1 905s, 1 815s,br

[a] In acetone. [b] In dichloromethane.

No reaction takes place with complex (2), whilst the reaction with complex (1) (with equimolar or excess of $\mathrm{PPh_3}$ at room temperature or under reflux) causes the displacement of only one CO group without cleavage of the Au–Co bond and leads to the formation of complex (5) [equation (3)]. Similarly, complex (1) reacts with $\mathrm{P(OPh)_3}$ to give complex (6).

$$[\mathrm{N(PPh_3)_2}][\mathrm{R_3Au{-}Co(CO)_4}] + \mathrm{PPh_3} \longrightarrow [\mathrm{N(PPh_3)_2}][\mathrm{R_3Au{-}Co(CO)_3(PPh_3)}] + \mathrm{CO} \tag{3}$$

The yellow complexes (5) and (6) are air- and moisture-stable and do not decompose in solution. Their conductivities in acetone are characteristic of 1 : 1 electrolytes. Their i.r. spectra in the carbonyl region show three bands, the absorption at higher energies (a_1) being much weaker than the other two (assigned to a split e mode); this suggests, in accordance with literature data,[10] that the substitution has taken place *trans* to the gold atom.

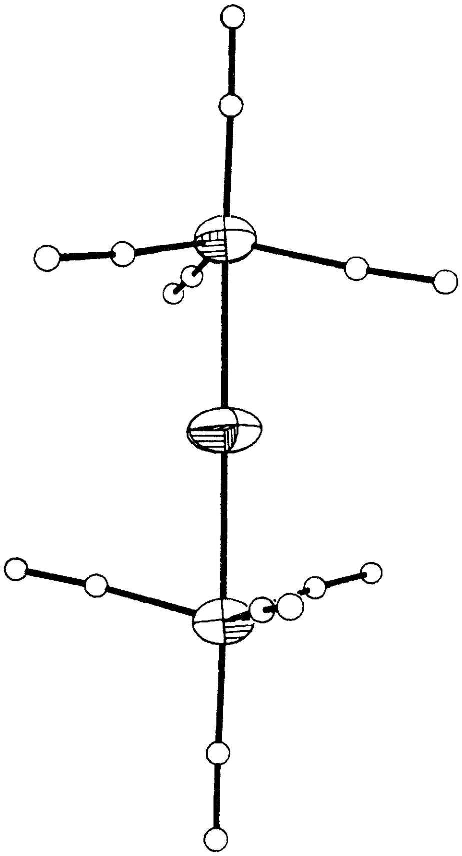
The reaction (at room temperature) of the gold(I) complex $[\mathrm{Au(C_6F_5)(tht)}]$ with equimolar amounts of QM* {QM* = $[\mathrm{N(PPh_3)_2}][\mathrm{Co(CO)_4}]$, $[\mathrm{N(PPh_3)_2}][\mathrm{Mn(CO)_5}]$, $[\mathrm{NBu^n_4}][\mathrm{Mo(cp)(CO)_3}]$, or $[\mathrm{NBu^n_4}][\mathrm{W(cp)(CO)_3}]$} takes a different course and leads finally to a mixture of the anionic complexes $[\mathrm{AuM^*_2}]^-$ and $[\mathrm{Au(C_6F_5)_2}]^-$ [equation (4)], which can be separated by making use of their different solubilities in diethyl ether. The first step of this process is probably the replacement of the tht group by the carbonylates, although the presence of the intermediates could not be detected, presumably because of their rapid disproportionation. These reactions are always fast and after 5 min all the carbonylate of the starting compound has disappeared from the solution. A similar process is observed with $[\mathrm{AuCl(tht)}]$, but in this case $[\mathrm{AuCl_2}]^-$ is obtained instead of pentafluorophenyl derivatives.

$$[\mathrm{Au(C_6F_5)(tht)}] + \mathrm{M^*} \longrightarrow [(\mathrm{C_6F_5})\mathrm{Au{-}M^*}]^- \longrightarrow \tfrac{1}{2}[\mathrm{AuM^*_2}]^- + \tfrac{1}{2}[\mathrm{Au(C_6F_5)_2}]^- \tag{4}$$

At room temperature the complexes $\mathrm{Q[AuM^*_2]}$ (7)—(10) are stable in the solid state under nitrogen and also in oxygen-free solvents. Their conductivities in acetone (Table 1) are characteristic of 1 : 1 electrolytes. It is noteworthy that $[\mathrm{NEt_4}][\mathrm{Au\{Co(CO)_4\}_2}]$ has been reported[6] to decompose above −79 °C, whereas our $[\mathrm{N(PPh_3)_2}]^+$ salt is stable up to 105 °C.

According to its symmetry (D_{3d}) (see below) complex (7) should exhibit three i.r.-active vibrations due to ν(CO), but only two of these bands can be observed (Table 1), probably because two of them overlap to form a broad band (lower frequency). The manganese derivative shows three bands in the ν(CO) region in accordance with its supposed structure[14] (D_{4d}). The i.r. spectra of complexes (9) and (10) are similar to those of the isoelectronic compounds[14] $[\mathrm{Hg\{M(cp)(CO)_3\}_2}]$ for which a structure with two mutually *trans* cp groups was proposed (C_{2h}), although more recent studies[15,16] do not rule out a possible skew configuration (C_2) in solution.

The structure of complex (7) has been determined by a single-crystal *X*-ray diffraction study. The anion is shown in the Figure. The gold atom lies on a crystallographic centre of symmetry and the Co–Au–Co unit is thus exactly linear. The Au–Co bond length [2.509(2) Å] is not significantly different from the 2.50(1) Å in $[\mathrm{(Ph_3P)AuCo(CO)_4}]$.[17] The corresponding manganese derivative $[\mathrm{(Ph_3P)AuMn(CO)_5}]$ shows an Au–Mn bond of 2.52(3) Å,[18] although the refinement was unsatisfactory due to pseudo-symmetry. The Co–CO groups are staggered (imposed by the centre of symmetry) and the anion possesses approximate D_{3d} symmetry. The idealised trigonal-bipyramidal geometry at cobalt is distorted by the bending of the carbonyl groups towards the gold atom (mean Au–Co–C angle 78.1°). The same effect has been noted to a lesser extent in $[Hg\{Co(CO)_4\}_2]$ [19] [which is isoelectronic with the present anion and also possesses a staggered conformation, with Hg–Co bonds of 2.50(1) Å] and in $[(Ph_3P)AuCo(CO)_4]$.[17]



Perspective view of the $[Au\{Co(CO)_4\}_2]^-$ ion

The $[N(PPh_3)_2]^+$ cation is also constrained to be centrosymmetric and is thus linear at the nitrogen atom. This is a known, but uncommon geometry for $[N(PPh_3)_2]^+$; the short P–N bond length [1.547(2) Å] is similar to the 1.539(2) Å in the other reported example, $[N(PPh_3)_2][V(CO)_6]$.[20]

EXPERIMENTAL

Infrared spectra in dichloromethane solution were recorded on a Perkin-Elmer 577 spectrophotometer. Conductivities were measured in 5×10^{-4} mol dm^{-3} acetone solutions with a Philips 9501/01 apparatus. Carbon, H, and N analyses were carried out with a Perkin-Elmer 240 microanalyser. All solvents were dried and distilled under nitrogen and all the operations were conducted in oxygen-free dry nitrogen.

Reactions of Tris(pentafluorophenyl)(tetrahydrothiophen)-gold(III).—(*a*) *With* $[N(PPh_3)_2][Co(CO)_4]$. The salt $[N(PPh_3)_2][Co(CO)_4]$ [21] (0.177 g, 0.25 mmol) in dichloromethane was added to $[Au(C_6F_5)_3(tht)]$ [9] (0.197 g, 0.25 mmol) in the same solvent at room temperature. The solution quickly turned orange-yellow and the reaction ceased after 5 min. Evaporation under reduced pressure rendered solid (1) which was recrystallised from diethyl ether–hexane, 91% yield (Found: C, 49.45; H, 2.45; N, 1.05. $C_{58}H_{30}AuCoF_{15}NO_4P_2$ requires C, 49.5; H, 2.15; N, 1.00%).

TABLE 2

Atom co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Au	0	0	0
Co	1 570(1)	1 924(1)	−296(1)
P	4 954(1)	1 549(1)	5 002(1)
N	5 000	0	5 000
C(1)	747(7)	1 295(5)	−1 749(6)
O(1)	259(6)	952(4)	−2 706(4)
C(2)	2 677(7)	3 210(5)	−582(5)
O(2)	3 438(5)	4 031(4)	−762(4)
C(3)	2 796(7)	881(5)	388(5)
O(3)	3 660(6)	254(5)	842(5)
C(4)	475(7)	2 786(6)	640(5)
O(4)	−214(5)	3 404(5)	1 242(5)
C(12)	2 113(5)	1 519(5)	4 348(5)
C(13)	773(6)	2 000(7)	4 369(6)
C(14)	552(6)	3 101(7)	5 146(6)
C(15)	1 638(6)	3 735(6)	5 894(5)
C(16)	2 979(5)	3 266(5)	5 890(4)
C(11)	3 227(4)	2 154(4)	5 102(3)
C(22)	6 889(4)	3 582(4)	6 124(4)
C(23)	7 774(5)	4 254(5)	7 078(5)
C(24)	7 879(6)	3 795(5)	8 148(5)
C(25)	7 130(7)	2 670(6)	8 264(4)
C(26)	6 232(6)	1 972(5)	7 310(4)
C(21)	6 103(4)	2 441(4)	6 227(3)
C(32)	4 855(5)	3 104(4)	3 161(4)
C(33)	5 330(6)	3 534(5)	2 200(4)
C(34)	6 437(6)	2 890(5)	1 741(4)
C(35)	7 042(6)	1 847(5)	2 226(4)
C(36)	6 589(5)	1 411(4)	3 202(4)
C(31)	5 487(4)	2 050(4)	3 682(3)

(*b*) *With* $[N(PPh_3)_2][Mn(CO)_5]$. Reaction of $[N(PPh_3)_2][Mn(CO)_5]$ [22] (0.183 g, 0.25 mmol) with $[Au(C_6F_5)_3(tht)]$ (0.197 g, 0.25 mmol) in dichloromethane led after similar work up to complex (2), 70% yield (Found: C, 49.7; H, 2.20; N, 1.05. $C_{59}H_{30}AuF_{15}MnNO_5P_2$ requires C, 49.5; H, 2.10; N, 1.00%).

(*c*) *With* $[NBu^n_4][Mo(cp)(CO)_3]$. A solution of $[Au(C_6F_5)_3(tht)]$ (0.393 g, 0.5 mmol) and $[NBu^n_4][Mo(cp)(CO)_3]$ (0.244 g, 0.5 mmol) in dichloromethane (40 cm^3), prepared as described elsewhere for the tungsten derivative,[23] was stirred for 1 h at room temperature and evaporated to dryness under reduced pressure. The resulting solid was washed with hexane (3 × 10 cm^3) to remove the remaining tht, extracted with dichloromethane (30 cm^3), and stirred for 1 h, whereafter it was again evaporated to dryness and

TABLE 3

Selected bond lengths (Å) and angles (°)

Au–Co	2.509(2)	N–P	1.547(2)
C(1)–Co	1.776(7)	C(1)–O(1)	1.141(8)
C(2)–Co	1.746(7)	C(2)–O(2)	1.147(9)
C(3)–Co	1.760(7)	C(3)–O(3)	1.157(9)
C(4)–Co	1.761(7)	C(4)–O(4)	1.150(9)
Au–Co–C(1)	76.0(3)	Au–Co–C(2)	176.6(3)
Au–Co–C(3)	78.8(3)	Au–Co–C(4)	79.6(3)
C(1)–Co–C(2)	101.1(4)	C(1)–Co–C(3)	116.8(3)
C(1)–Co–C(4)	115.6(4)	C(2)–Co–C(3)	101.0(4)
C(2)–Co–C(4)	103.4(4)	C(3)–Co–C(4)	115.3(4)
Co–C(1)–O(1)	175.9(7)	Co–C(2)–O(2)	177.9(7)
Co–C(3)–O(3)	176.1(7)	Co–C(4)–O(4)	176.9(7)

complex (3) was obtained after recrystallisation from diethyl ether–hexane, 40% yield (Found: C, 42.1; H, 3.35; N, 1.45. $C_{42}H_{41}AuF_{15}MoNO_3$ requires C, 42.3; H, 3.45; N, 1.15%).

(*d*) *With* $[NBu^n_4][W(cp)(CO)_3]$. Reaction of $[Au(C_6F_5)_3(tht)]$ (0.197 g, 0.25 mmol) with $[NBu^n_4][W(cp)(CO)_3]$ [23] (0.144 g, 0.25 mmol) in dichloromethane (30 cm^3) and work-up as for (*c*) led to complex (4), 38% yield (Found: C, 39.95; H, 3.35; N, 1.25. $C_{42}H_{41}AuF_{15}NO_3W$ requires C, 39.6; H, 3.25; N, 1.10%).

(*e*) *With* $Na[Fe(cp)(CO)_2]$ *and* $Na_2[Fe(CO)_4]$. No reaction was observed when $Na[Fe(cp)(CO)_2]$ [23] (0.5 mmol) or $Na_2[Fe(CO)_4]$ [24] (0.25 mmol) was added to a solution of $[Au(C_6F_5)_3(tht)]$ (0.393 g, 0.5 mmol) in thf (40 cm^3); after stirring for 8 h at room temperature the unchanged gold(III) complex was recovered.

Reactions of Bis(triphenylphosphine)iminium Tris(pentafluorophenyl)(tetracarbonylcobaltio)aurate(III).—(*a*) *With triphenylphosphine*. Triphenylphosphine (0.026 g, 0.1 mmol) was added to a solution of complex (1) (0.141 g, 0.1 mmol) in dichloromethane (25 cm^3) which was stirred for 24 h at room temperature and then filtered. The filtrate was concentrated under reduced pressure to *ca.* 5 cm^3 and complex (5) was precipitated by addition of hexane, 87% yield (Found: C, 54.85; H, 2.85; N, 1.05. $C_{75}H_{45}AuCoF_{15}NO_3P_3$ requires C, 54.85; H, 2.75; N, 0.85%).

No reaction was observed with equimolar amounts of complex (2) and PPh_3 in dichloromethane at room temperature. Under the same conditions complexes (3) and (4) both gave a mixture of $[AuR_3(PPh_3)]$ and $[NBu^n_4][M(cp)(CO)_3]$.

(*b*) *With triphenyl phosphite*. Triphenyl phosphite (0.032 g, 0.1 mmol) was added to a dichloromethane solution of complex (1) (0.141 g, 0.1 mmol) which was stirred for 9 h at room temperature and then evaporated to dryness. The residue was washed with hexane (3 × 10 cm^3). Treatment with diethyl ether (20 cm^3) dissolved most of the residue, whilst the remaining white solid (8%) was identified as $[N(PPh_3)_2][Au(C_6F_5)_3Cl]$. The ether solution was evaporated to dryness and complex (6) was recrystallised from diethyl ether–hexane, 72% yield (Found: C, 53.2; H, 2.75; N, 1.10. $C_{75}H_{45}AuCoF_{15}NO_6P_3$ requires C, 53.3; H, 2.70; N, 0.85%).

Reactions of Pentafluorophenyl(tetrahydrothiophen)gold(I).—(*a*) *With* $[N(PPh_3)_2][Co(CO)_4]$. The salt $[N(PPh_3)_2][Co(CO)_4]$ [21] (0.355 g, 0.5 mmol) was added to a solution of $[Au(C_6F_5)(tht)]$ [7] (0.266 g, 0.5 mmol) in dichloromethane (30 cm^3) at room temperature and the reaction was complete after 5 min (i.r. spectra). The solution was evaporated to dryness and addition of diethyl ether (10 cm^3) led to the precipitation of a white solid, $[N(PPh_3)_2][Au(C_6F_5)_2]$ [7] (33% yield). The filtrate was evaporated to *ca.* 5 cm^3 and complex (7) was obtained upon addition of hexane (20 cm^3), 46% yield (Found: C, 49.5; H, 2.80; N, 1.50. $C_{44}H_{30}AuCo_2NO_8P_2$ requires C, 49.05; H, 2.80; N, 1.30%).

(*b*) *With* $[N(PPh_3)_2][Mn(CO)_5]$. A dichloromethane solution of $[Au(C_6F_5)(tht)]$ (0.226 g, 0.5 mmol) and $[N(PPh_3)_2][Mn(CO)_5]$ [22] (0.376 g, 0.5 mmol) was stirred for 10 min at room temperature then concentrated to 5 cm^3. Addition of hexane led to the precipitation of complex (8), 35% yield (Found: C, 49.15; H, 2.70; N, 1.40. $C_{46}H_{30}AuMn_2NO_{10}P_2$ requires C, 49.1; H, 2.70; N, 1.25%). The filtrate was evaporated to dryness and addition of diethyl ether led to a white solid which was identified as $[N(PPh_3)_2][Au(C_6F_5)_2]$,[7] 40% yield.

(*c*) *With* $[NBu^n_4][Mo(cp)(CO)_3]$. A solution of $[Au(C_6F_5)(tht)]$ (0.226 g, 0.5 mmol) and $[NBu^n_4][Mo(cp)(CO)_3]$ [23] (0.244 g, 0.5 mmol) in dichloromethane (30 cm^3) was stirred for 10 min at room temperature and then evaporated to dryness. The residue was washed with diethyl ether (5 × 20 cm^3) leaving the insoluble complex (9), which was filtered off and recrystallised from dichloromethane–hexane, 42% yield (Found: C, 41.65; H, 5.00; N, 1.60. $C_{32}H_{46}AuMo_2NO_6$ requires C, 41.35; H, 5.00; N, 1.50%). The ether solution contains $[NBu^n_4][Au(C_6F_5)_2]$ [7] which was isolated upon evaporation, 37% yield.

(*d*) *With* $[NBu^n_4][W(cp)(CO)_3]$. Reaction of $[Au(C_6F_5)(tht)]$ (0.226 g, 0.5 mmol) and $[NBu^n_4][W(cp)(CO)_3]$ (0.288 g, 0.5 mmol) and work-up as above led to complex (10), 40% yield (Found: C, 34.6; H, 4.20; N, 1.35. $C_{32}H_{46}AuNO_6W_2$ requires C, 34.75; H, 4.20; N, 1.25%), and $[NBu^n_4][Au(C_6F_5)_2]$, 37% yield.

Crystal Data.—$C_{44}H_{30}AuCo_2NO_8P_2$, $M = 1\,077.51$, Triclinic, space group $P\bar{1}$, $a = 9.610(4)$, $b = 9.978(4)$, $c = 11.506(5)$ Å, $\alpha = 97.70(2)$, $\beta = 97.84(2)$, $\gamma = 90.97(2)°$, $U = 1\,082$ Å^3, $Z = 1$, $D_c = 1.653$ g cm^{-3}, $F(000) = 527.9$, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 43 cm^{-1}.

A plate-shaped yellow crystal (0.3 × 0.3 × 0.1 mm) was used to collect 3 396 reflections with $7 < 2\theta < 45°$ (Stoe four-circle diffractometer, monochromated Mo-K_α radiation). After application of Lorentz, polarisation, and empirical absorption corrections, averaging equivalent reflections gave 2 818 unique reflections, 2 476 with $F > 4\sigma(F)$. The structure was solved by the heavy-atom method and refined to $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o| = 0.034$, $R = 0.032$. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0005F^2$. All non-hydrogen atoms were refined anisotropically; hydrogen atoms (riding on C atoms with C–H 0.96 Å) were assigned isotropic temperature factors equal to 1.2 times the equivalent isotropic temperature factor of their respective C atoms. A final difference map showed no peaks >0.35 e Å^{-3}. Calculations were performed using the SHELXTL system of programs (written by G.M.S.).

Final atomic co-ordinates are given in Table 2, with selected bond lengths and angles in Table 3. Hydrogen-atom co-ordinates, thermal parameters, and structure-factor tables are available as Supplementary Publication No. SUP 22959 (20 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

REFERENCES

[1] E. C. Coffey, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1964, 1741.

[2] E. W. Abel and G. V. Hutson, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2339.

[3] R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc. A*, 1968, 46.

[4] A. S. Kasenally, J. Lewis, A. R. Manning, J. R. Miller, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 1965, 3404.

[5] M. Casey and A. R. Manning, *J. Chem. Soc. A*, 1971, 2989.

[6] P. Braunstein and J. Dehand, *J. Organomet. Chem.*, 1975, **88**, C24.

[7] R. Usón, A. Laguna, and J. Vicente, *J. Chem. Soc., Chem. Commun.*, 1976, 353; *J. Organomet. Chem.*, 1977, **131**, 471.

[8] R. Usón, A. Laguna, J. Garcia, and M. Laguna, *Inorg. Chim. Acta*, 1979, **37**, 201.

[9] R. Usón, A. Laguna, M. Laguna, and E. Fernandez, *Inorg. Chim. Acta*, 1980, **45**, L177.

[10] L. M. Bower and M. H. B. Stiddard, *J. Chem. Soc. A*, 1968, 706.

[11] R. S. Nyholm and P. Royo, *Chem. Commun.*, 1969, 421.

[12] R. Usón, A. Laguna, M. Laguna, and M. Abad, unpublished work.

[13] L. G. Vaughan and W. A. Sheppard, *J. Organomet. Chem.*, 1970, **22**, 739.

[14] P. M. Brier, A. A. Chalmers, J. Lewis, and S. B. Wild, *J. Chem. Soc. A*, 1967, 1889.

[15] R. D. Fischer and K. Noack, *J. Organomet. Chem.*, 1969, **16**, 125.

[16] R. D. Adams and F. A. Cotton, *Inorg. Chim. Acta*, 1973, **7**, 153.

[17] T. L. Blundell and H. M. Powell, *J. Chem. Soc. A*, 1971, 1685.

[18] H. M. Powell, K. A. I. F. M. Mannan, B. T. Kilbourne, and P. Porta, Int. Conf. Coord. Chem., Vienna, 1964, Springer-Verlag, Vienna, New York, 1964, vol. 8, p. 155; K. A. I. F. M. Mannan, *Acta Crystallogr.*, 1967, **23**, 649.

[19] G. M. Sheldrick and R. N. F. Simpson, *J. Chem. Soc. A*, 1968, 1005.

[20] R. D. Wilson and R. Bau, *J. Am. Chem. Soc.*, 1974, **96**, 7601 and refs. therein.

[21] J. K. Ruft and W. J. Schlientz, *Inorg. Synth.*, 1974, **15**, 84.

[22] D. N. Duffy and B. K. Nicholson, *J. Organomet. Chem.*, 1979, **164**, 227.

[23] J. M. Burlitch, M. E. Leonowiez, R. B. Petersen, and R. E. Hughes, *Inorg. Chem.*, 1979, **18**, 1097.

[24] J. K. Ruff, *Inorg. Chem.*, 1968, **7**, 1499.