Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 17.[1] The Reaction of $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ with One-electron Oxidants: Fulvalene Complex and Silver Adduct Formation, and the *X*-Ray Crystal Structure of $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2][PF_6]\cdot C_6H_5Me$ †

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Cyclic voltammetry shows that $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (1) undergoes irreversible one-electron oxidation to the reactive radical cation $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ (2); chemical oxidation of (1), with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ or $[N_2C_6H_4F\text{-}p][PF_6]$, or controlled potential electrolysis gives the fulvalene complex $[Rh_2(CO)_2(PPh_3)_2(\eta^5{:}\eta'^5\text{-}C_{10}H_8)]^{2+}$ (3). Cyclic voltammetry shows that (3) undergoes a reversible two-electron reduction, and sodium amalgam or bulk electrolysis affords the complex $[Rh_2(CO)_2(PPh_3)_2(\eta^5{:}\eta'^5\text{-}C_{10}H_8)]$ (4). The reaction of (1) with $AgPF_6$ in toluene gives the adduct $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2][PF_6]\cdot C_6H_5Me$ (5), *X*-ray structural studies on which reveal a near linear Rh–Ag–Rh framework. Complex (5) acts as a stabilised source of (2), reacting with NO gas to give $[Rh(PPh_3)(NO)(\eta\text{-}C_5H_5)][PF_6]$, $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$, and silver metal.

Many cyclopentadienyl metal carbonyl derivatives are now known to undergo one-electron oxidation reactions, giving isolable radical cations such as $[V(CO)_{4-n}L_n(\eta\text{-}C_5H_5)]^+$ ($n = 1$, L = PPh_3; $n = 2$, $L_2 = Ph_2PCH_2CH_2PPh_2$),[2] $[Mn(CO)_{3-n}L_n(\eta\text{-}C_5H_5)]^+$ ($n = 1$ or 2, L = P-donor),[3] and $[FeXL_2(\eta\text{-}C_5H_5)]^+$ (X = SPh or $SnPh_3$, L = PMe_3; X = halide, H, Me, $SnMe_3$, CN, NCS, or SPh, $L_2 = Ph_2PCH_2CH_2PPh_2$).[4] Recently we,[5] and others,[6] have investigated the electron-transfer reactions of $[M(CO)_{2-n}L_n(\eta\text{-}C_5R_5)]$ (M = Co or Rh, $n = 1$ or 2, R = H or Me) and reported the isolation of stable, paramagnetic cobalt salts of the type $[Co(CO)_{2-n}L_n(\eta\text{-}C_5H_5)]X$ ($n = 1$ or 2, L = P-donor, X = BF_4 or PF_6). We now present details of chemical and electrochemical studies which show that the oxidation of $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (1) gives the radical cation $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ (2) which rapidly dimerises to the fulvalene complex $[Rh_2(CO)_2(PPh_3)_2(\eta^5{:}\eta'^5\text{-}C_{10}H_8)]^{2+}$ (3). By contrast (1) and silver(I) ions give the adduct $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2]^+$ which acts as a stable source of (2) and which has been characterised by an *X*-ray structural study.

Results and Discussion

Cyclic voltammetry shows that $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (1) undergoes one-electron oxidation to the radical cation $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ (2) at the platinum-bead electrode. For scan rates, v, between 42 and 410 mV s^{-1} and even at -40 °C the process is irreversible showing (2) to have a maximum lifetime of *ca.* 0.5 s; the oxidation peak potential, E_p^{ox}, is 0.43 V [*vs.* a saturated calomel electrode (s.c.e.), at $v = 204$ mV s^{-1}]. The electron transfer is, however, diffusion controlled with $i_p^{ox}/v^{\frac{1}{2}}$ constant over the range of scan rates used.

A multiple-scan cyclic voltammogram of (1), from -0.2 to $+0.8$ V in CH_2Cl_2, is shown in Figure 1. Not only is the irreversible oxidation wave apparent, but on the second and subsequent scans a product wave centred at *ca.* 0.0 V is observed. The nature of this product has been elucidated by both electrochemical and chemical methods.

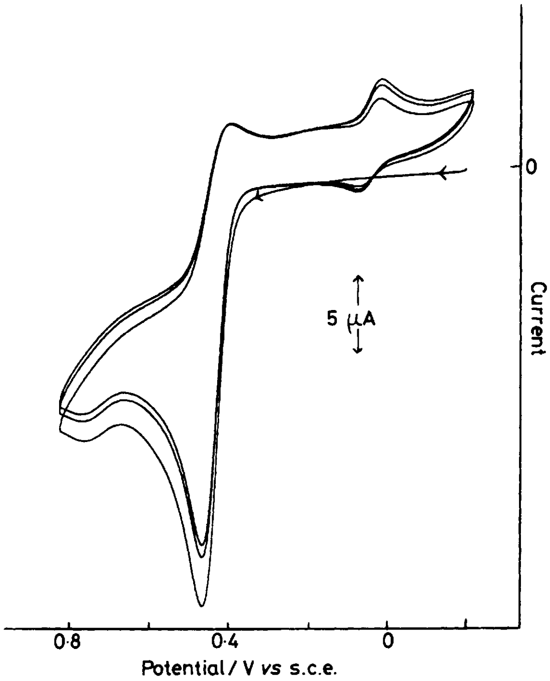

Figure 1. The cyclic voltammogram, at 198 mV s^{-1}, of $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (1) at a platinum-bead electrode in CH_2Cl_2. Potentials are *vs.* the s.c.e., with 0.1 mol dm^{-3} $[NBu^n_4][PF_6]$ as base electrolyte

Controlled potential electrolysis of a solution of $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ in CH_2Cl_2, for 30 min at 0.5 V, gave an orange-brown solution which cyclic voltammetry showed to

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† Bis[carbonyl-η-cyclopentadienyl(triphenylphosphine)rhodio]silver hexafluorophosphate-toluene (1/1).

Supplementary data available (No. SUP 23643, 44 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Analytical, and i.r. and ^{1}H n.m.r. spectral data

Compound	$\tilde{\nu}$(CO) [a]/cm^{-1}	Analysis (%) [b] C	Analysis (%) [b] H	δ/p.p.m.
(3) $[Rh_2(CO)_2(PPh_3)_2(\eta^5:\eta'^5\text{-}C_{10}H_8)][PF_6]_2$	2 069, 2 049	47.8 (47.8)	3.4 (3.2)	7.66 (30 H, m, PPh_3), 7.26 (2 H, m, C_5H_4), 6.72 (2 H, m, C_5H_4), 5.12 (2 H, m, C_5H_4), 4.00 (2 H, m, C_5H_4) [c]
(4) $[Rh_2(CO)_2(PPh_3)_2(\eta^5:\eta'^5\text{-}C_{10}H_8)]$	1 937 1 959 [d]	63.4 (63.0)	4.6 (4.2)	7.58 (5 H, m, PPh_3), 6.98 (10 H, m, PPh_3), 5.11 (2 H, m, C_5H_4), 4.99 (2 H, m, C_5H_4) [e]
(5) $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2][PF_6]\cdot C_6H_5Me$	1 984	52.5 (52.4)	3.9 (3.8) [f]	7.50 (15 H, m, PPh_3), 5.10 (5 H, s, C_5H_5) [g]

[a] In CH_2Cl_2, unless otherwise stated. [b] Calculated values in parentheses. [c] In $(CD_3)_2CO$. [d] In hexane. [e] In [$^2H_8$]toluene. [f] Silver analysis 8.8 (8.6)%. Phosphorus analysis 7.2 (7.4)%. [g] In CD_2Cl_2, toluene resonances omitted.

contain only the product referred to above ($E^\ominus = 0.01$ V). A plot of ln *i vs. t* for the electrolysis was linear, showing the oxidation to be diffusion controlled, and a value of $n = 0.93$ electron was determined by coulometry, verifying the one-electron oxidation process.

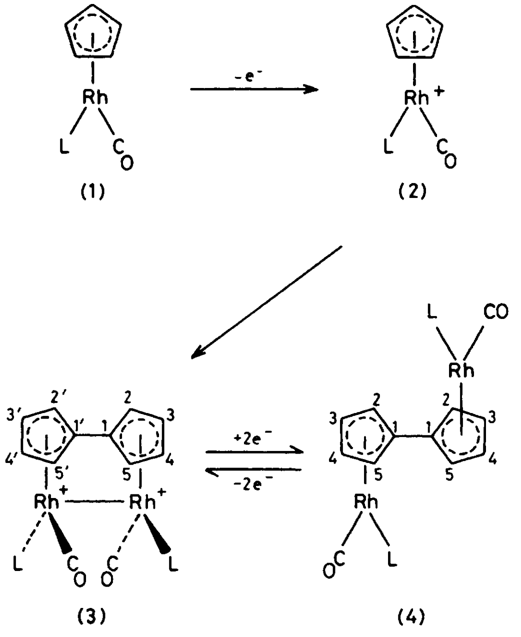
The product was fully identified when formed by chemical oxidation. The E_p^{ox} value of *ca.* 0.43 V for (1) suggested that a mild oxidant would effect the reaction and accordingly (1) was stirred at room temperature in CH_2Cl_2 with an equimolar quantity of either $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ or $[N_2C_6H_4F\text{-}p]X$ ($X = BF_4$ or PF_6). In all cases, an orange-brown solution was formed from which the orange air-stable salts $[Rh_2(CO)_2(PPh_3)_2(\eta^5:\eta'^5\text{-}C_{10}H_8)]X_2$ (3; $X = BF_4$ or PF_6) were isolated.

The i.r. spectrum of (3) showed absorptions due to the anion, X^-, and two closely spaced carbonyl bands (Table 1) at high energy indicative of a cationic carbonyl complex. The elemental analysis was in good agreement with the formulation given above for (3), and the field-desorption mass spectrum of (3; $X = PF_6$) showed a parent ion at *m/e* 914 for the dication. The ^{1}H n.m.r. spectrum (Table 1) was, however, most informative, showing the presence of the fulvalene ligand, $C_{10}H_8$.

Many fulvalene complexes are now known,[7] among the simplest being the bis(fulvalene) derivatives $[M_2(\eta^5:\eta'^5\text{-}C_{10}H_8)_2]^{z+}$ ($z = 0$, M = V,[8] Mo,[9] or Fe;[10] $z = 2$, M = Co [11]). The latter, when diamagnetic, commonly show two multiplets in the ^{1}H n.m.r. spectrum due to two equivalent sets of four ring protons. By contrast, complex (3) shows four multiplets because of the presence of two different ligands in each $Rh(CO)(PPh_3)$ unit (Scheme 1).

The metal–metal bond, required to account for the diamagnetism of (3), restrains the $Rh(CO)(PPh_3)$ groups to a *cis* configuration with respect to the $C_{10}H_8$ ligand. Whether the carbonyl ligands are mutually *cis* or *trans* is, however, unclear although the latter is more likely on steric grounds.

Cyclic voltammetry of (3) showed conclusively that the products of chemical and electrochemical oxidation of (1) are identical. In CH_2Cl_2, at a platinum-bead electrode, (3) shows a fully reversible, diffusion-controlled reduction with $E^\ominus = 0.01$ V, with i_p^{ox}/i_p^{red} unity, and with $i_p^{red}/v^{\frac{1}{2}}$ constant for the scan rates $v = 55$—483 mV s^{-1}. That this reduction involves two electrons was established by both cyclic voltammetry and coulometry. The cyclic voltammogram of a dilute (*ca.* 5×10^{-5} mol dm^{-3}) solution of (3) in CH_2Cl_2, at a slow scan rate (14 mV s^{-1}), and using a Luggin probe, showed a peak separation, $E_p^{ox} - E_p^{red}$, of 38 mV, a value consistent with a reversible, two-electron process in CH_2Cl_2. In addition, controlled potential electrolysis of (3) at -0.3 V gave an orange solution with the consumption of 1.73 electrons per dication. Again, a plot of ln *i vs. t* was linear, verifying the reduction of (3) to be diffusion controlled. A cyclic voltammogram of the product solution showed complete conversion of (3) to $[Rh_2(CO)_2(PPh_3)_2(\eta^5:\eta'^5\text{-}C_{10}H_8)]$ (4) with only the two-electron wave at $E^\ominus = 0.01$ V for the couple (3)—(4) in the range ±1.6 V.



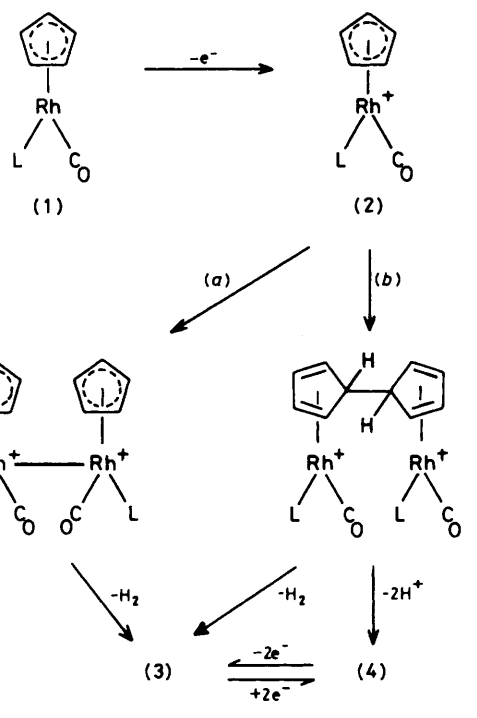
Scheme 1. L = PPh_3

Complex (4) was isolated by reducing (3) chemically with sodium amalgam in tetrahydrofuran (thf). In contrast to (3), the orange-red solid shows only one carbonyl absorption in the i.r. spectrum (Table 1), and only two multiplets for the fulvalene ring protons. Whereas complex (3) contains a metal–metal bond its absence in (4) allows rotation of the $Rh(CO)(PPh_3)$ groups with respect to the C_5H_4 rings. Hence, protons H^2 and H^5, and H^3 and H^4 (Scheme 1), can become equivalent.

Preliminary *X*-ray diffraction studies [12] have shown that (4) is structurally similar to $[Co_2(CO)_4(\eta^5:\eta'^5\text{-}C_{10}H_8)]$[13] in that the two metal atoms are bonded on opposite sides of the fulvalene ligand. Thus, the reversible electron-transfer reaction relating (3) to (4) not only involves Rh–Rh bond breaking and making but also *cis–trans* isomerisation *via* rotation about the C(1)–C(1′) bond (Scheme 1). Such an isomerisation might seem unlikely in view of the *X*-ray structure [14] of $[Ni_2(\eta^5:\eta'^5\text{-}C_{10}H_8)_2]$, which showed multiple character in the C(1)–C(1′) bond, and because of the close similarity between the $E^\ominus$ values of (3) (see above) and (4) ($E^\ominus = 0.01$ V; $E_p^{ox} - E_p^{red} = 42$ mV at a scan rate of 50 mV s^{-1}). However, although the *cis* and *trans* isomers of $[M(CO)_2(L\text{–}L)_2]$ (M = Cr, Mo, or W; L–L = $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH_2PPh_2$[15]), the *fac* and *mer* isomers of $[MX(CO)_3L_2]$ (M = Mn or Re, X = Br or Cl, L = P-donor),[16] and the 1—4-η- and 1—2-η:5—6-η-bonded isomers of $[Co(\eta^4\text{-}R)(\eta\text{-}C_5H_5)]$ (R = cyclo-octatetraene or cyclo-octadiene) [17] have very different redox potentials, those of *cis*- and *trans*-$[Mo(CO)_4(PBu^n{}_3)_2]$ differ by no more than 50 mV.[18]

Two other aspects of the chemistry of (3) and (4) are worthy of note. First, the $E^{\ominus}$ value for the oxidation of (4) (0.01 V) is very much lower than the potential at which (1) is oxidised ($E_p{}^{ox}$ = 0.43 V) despite the observation that (4) might be regarded simply as a ring-substituted derivative of (1). A comparison of the electrochemistry of ferrocene with that of $[Fe_2(\eta^5:\eta'^5\text{-}C_{10}H_8)_2]$ shows a similar difference with the latter oxidised to the monocation at a potential 0.28 V more negative than for the formation of $[Fe(\eta\text{-}C_5H_5)_2]^+$.[19] Whereas the oxidation of (1) (and of ferrocene) involves the removal of an electron from an orbital predominantly metal bonding in character, the oxidation of the binuclear species may well involve electron removal from an orbital antibonding with respect to the dimetal centre.

Secondly, the mechanism by which (1) is converted to (3) is by no means clear. The first step is undoubtedly the formation of the radical cation $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ (2). Two possible routes from (2) to (3) are shown in Scheme 2 although neither is intuitively satisfactory. First, the formation of a rhodium–rhodium bond [path (a)] seems unlikely if the positive charge of (2) is localised on the metal. Second, the formation of the $\eta^4:\eta'^4$-dihydrofulvalene ligand [path (*b*)] would render each metal atom electron deficient until loss of H_2 or two protons gave (3) or (4) respectively.



Scheme 2. L = PPh_3

Of the two mechanisms, the latter seems the more likely, and certainly (3) is formed from (4) on addition of HBF_4. However, further study is required and in this light the recent synthesis [20] of the radical $[RhL(PPh_3)(\eta\text{-}C_5H_5)]^+$ (L = tetrachloro-*o*-benzoquinone), stable enough at room temperature for the e.s.r. spectrum to be detectable, may be of help.

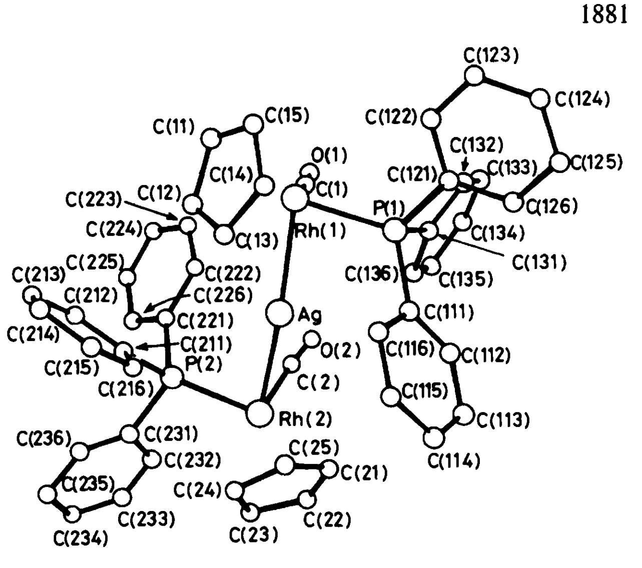


Figure 2. The *X*-ray structure of the cation $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2]^+$ (hydrogen atoms omitted for clarity)

Reaction of $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ *with Silver*(I) *Ions.*— Although silver(I) salts are potentially strong oxidants,[21] (1) and $AgPF_6$ do not afford (3); in toluene the reactants gave a yellow precipitate, but little or no silver metal. Recrystallisation of the solid from CH_2Cl_2–n-hexane gave yellow crystals of the toluene-solvated adduct $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2][PF_6]\cdot C_6H_5Me$ [(5), Table 1] which, in the absence of further spectroscopic data, was fully characterised by single-crystal *X*-ray diffraction methods.

The *X*-ray diffraction analysis (Tables 2 and 3) confirmed the chemical identity of the crystals and the presence of the toluene of crystallisation; there are no significant interactions between the cation, the anion, and the solvent.

The overall structure of the cation is shown in Figure 2 together with the crystallographic atom-numbering scheme. The silver atom is directly bonded to the rhodium atoms of two crystallographically independent $Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)$ groups with slightly different Rh–Ag bond lengths, 2.651(1) and 2.636(1) Å; the sum of the single-bond metallic radii [22] of rhodium and silver (2.591 Å) suggests little or no multiple metal-metal bond character.

The Rh–Ag–Rh backbone is nearly linear [171.0(0)], and the structures of the two $Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)$ groups, with regard to the angles about the metal atoms (Table 4), differ very little from each other and from that of $[Ir(CO)(PPh_3)(\eta\text{-}C_5H_5)]$.[23] However, the rhodium, carbonyl carbon, phosphorus atom, and X, the centroid of the cyclopentadienyl ring, deviate from coplanarity in that the distances Rh(1) and Rh(2) to the planes P(1)C(1)X(1) and P(2)C(2)X(2) are 0.13 and 0.19 Å respectively; in each case the rhodium ligands are moved away from the silver atom.

Interestingly, the orientations of the two $Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)$ groups relative to the trimetallic skeleton are somewhat different. The angles in Table 5 show that in both cases the $Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)$ group is orientated so as to place the cyclopentadienyl ligand away from the silver atom. In so doing, the carbonyl group moves toward the silver and, in the case of CO(2), the Ag–C(2) non-bonding distance is relatively short [2.86 Å; *cf.* Ag–C(1) = 3.08 Å].

The different orientations of the two $Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)$ groups with respect to the silver atom, the non-linearity of the Rh(1)–Ag–Rh(2) chain, and the small difference between the two silver-rhodium bond lengths presumably occur as a result of the minimisation of steric interactions between the bulky PPh_3 ligands.

Table 2. Interatomic distances (Å) and angles (°) for $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2][PF_6]\cdot C_6H_5Me$ (5)

(*a*) Cation

Ag-Rh(1)	2.651(1)	Ag-Rh(2)	2.636(1)	C(112)-C(113)	1.402(10)	C(212)-C(213)	1.397(10)
Rh(1)-P(1)	2.277(2)	Rh(2)-P(2)	2.266(2)	C(113)-C(114)	1.348(13)	C(213)-C(214)	1.388(10)
Rh(1)-C(1)	1.852(8)	Rh(2)-C(2)	1.845(6)	C(114)-C(115)	1.387(12)	C(214)-C(215)	1.360(10)
Rh(1)-C(11)	2.231(9)	Rh(2)-C(21)	2.219(7)	C(115)-C(116)	1.388(11)	C(215)-C(216)	1.389(9)
Rh(1)-C(12)	2.251(8)	Rh(2)-C(22)	2.258(9)	C(111)-C(116)	1.392(9)	C(211)-C(216)	1.379(8)
Rh(1)-C(13)	2.278(7)	Rh(2)-C(23)	2.245(7)	C(121)-C(122)	1.383(9)	C(221)-C(222)	1.399(8)
Rh(1)-C(14)	2.239(7)	Rh(2)-C(24)	2.196(8)	C(122)-C(123)	1.386(10)	C(222)-C(223)	1.393(10)
Rh(1)-C(15)	2.278(8)	Rh(2)-C(25)	2.238(8)	C(123)-C(124)	1.374(11)	C(223)-C(224)	1.372(11)
P(1)-C(111)	1.833(6)	P(2)-C(211)	1.832(6)	C(124)-C(125)	1.369(11)	C(224)-C(225)	1.390(11)
P(1)-C(121)	1.822(8)	P(2)-C(221)	1.831(6)	C(125)-C(126)	1.380(10)	C(225)-C(226)	1.394(10)
P(1)-C(131)	1.824(6)	P(2)-C(231)	1.834(6)	C(121)-C(126)	1.399(9)	C(221)-C(226)	1.372(9)
C(1)-O(1)	1.141(10)	C(2)-O(2)	1.138(8)	C(131)-C(132)	1.404(8)	C(231)-C(232)	1.415(9)
C(11)-C(12)	1.445(12)	C(21)-C(22)	1.400(12)	C(132)-C(133)	1.377(10)	C(232)-C(233)	1.380(10)
C(12)-C(13)	1.377(12)	C(22)-C(23)	1.345(13)	C(133)-C(134)	1.399(11)	C(233)-C(234)	1.375(10)
C(13)-C(14)	1.396(11)	C(23)-C(24)	1.418(14)	C(134)-C(135)	1.373(11)	C(234)-C(235)	1.377(12)
C(14)-C(15)	1.403(11)	C(24)-C(25)	1.357(11)	C(135)-C(136)	1.372(10)	C(235)-C(236)	1.392(10)
C(11)-C(15)	1.386(13)	C(21)-C(25)	1.363(11)	C(131)-C(136)	1.392(9)	C(231)-C(236)	1.367(9)
C(111)-C(112)	1.362(10)	C(211)-C(212)	1.394(8)				

(*b*) Anion

P(3)-F(1)	1.500(9)
P(3)-F(2)	1.523(9)
P(3)-F(3)	1.524(9)
P(3)-F(4)	1.507(8)
P(3)-F(5)	1.582(6)
P(3)-F(6)	1.570(6)

(*c*) Toluene of crystallisation

C(10)-C(20)	1.43(2)
C(20)-C(30)	1.40(2)
C(30)-C(40)	1.33(2)
C(40)-C(50)	1.41(2)
C(50)-C(60)	1.36(2)
C(10)-C(60)	1.38(1)
C(60) C(70)	1.50(1)

(*a*) Cation

Rh(1)-Ag-Rh(2)	171.0(0)			P(1)-C(121)-C(126)	119.3(6)	P(2)-C(221)-C(226)	122.3(4)
Ag-Rh(1)-C(1)	84.3(2)	Ag-Rh(2)-C(2)	77.1(2)	P(1)-C(131)-C(132)	120.5(5)	P(2)-C(231)-C(232)	118.1(4)
Ag-Rh(1)-P(1)	82.3(0)	Ag-Rh(2)-P(2)	87.4(0)	P(1)-C(131)-C(136)	120.8(5)	P(2)-C(231)-C(236)	122.4(5)
Ag-Rh(1)-C(11)	119.9(2)	Ag-Rh(2)-C(21)	95.0(2)	C(111)-C(112)-C(113)	120.1(7)	C(211)-C(212)-C(213)	120.1(6)
Ag-Rh(1)-C(12)	84.2(2)	Ag-Rh(2)-C(22)	130.9(2)	C(112)-C(113)-C(114)	121.7(8)	C(212)-C(213)-C(214)	120.0(6)
Ag-Rh(1)-C(13)	79.9(2)	Ag-Rh(2)-C(23)	144.2(3)	C(113)-C(114)-C(115)	118.8(7)	C(213)-C(214)-C(215)	119.8(6)
Ag-Rh(1)-C(14)	110.7(2)	Ag-Rh(2)-C(24)	109.5(2)	C(114)-C(115)-C(116)	120.0(8)	C(214)-C(215)-C(216)	120.4(6)
Ag-Rh(1)-C(15)	139.9(2)	Ag-Rh(2)-C(25)	84.6(2)	C(115)-C(116)-C(111)	120.7(7)	C(215)-C(216)-C(211)	121.1(6)
C(1)-Rh(1)-P(1)	90.5(2)	C(2)-Rh(2)-P(2)	93.3(2)	C(112)-C(111)-C(116)	118.6(6)	C(212)-C(211)-C(216)	118.5(3)
C(1)-Rh(1)-C(11)	102.9(3)	C(2)-Rh(2)-C(21)	108.5(3)	C(121)-C(122)-C(123)	121.6(6)	C(221)-C(222)-C(223)	119.9(6)
C(1)-Rh(1)-C(12)	112.9(3)	C(2)-Rh(2)-C(22)	107.0(3)	C(122)-C(123)-C(124)	118.6(6)	C(222)-C(223)-C(224)	120.9(6)
C(1)-Rh(1)-C(13)	145.6(3)	C(2)-Rh(2)-C(23)	132.6(3)	C(123)-C(124)-C(125)	121.1(7)	C(223)-C(224)-C(225)	119.5(7)
C(1)-Rh(1)-C(14)	161.2(3)	C(2)-Rh(2)-C(24)	166.6(3)	C(124)-C(125)-C(126)	120.3(7)	C(224)-C(225)-C(226)	119.5(7)
C(1)-Rh(1)-C(15)	125.2(3)	C(2)-Rh(2)-C(25)	138.0(3)	C(125)-C(126) C(121)	119.9(6)	C(225) C(226)-C(221)	121.5(6)
P(1)-Rh(1)-C(11)	154.7(2)	P(2)-Rh(2)-C(21)	158.0(2)	C(122)-C(121)-C(126)	118.4(6)	C(222)-C(221)-C(226)	118.6(5)
P(1)-Rh(1)-C(12)	151.5(2)	P(2)-Rh(2)-C(22)	139.2(2)	C(131)-C(132)-C(133)	120.4(6)	C(231)-C(232)-C(233)	119.5(6)
P(1)-Rh(1)-C(13)	117.1(2)	P(2)-Rh(2)-C(23)	106.8(2)	C(132)-C(133)-C(134)	120.5(6)	C(232)-C(233)-C(234)	120.3(7)
P(1)-Rh(1)-C(14)	102.4(2)	P(2)-Rh(2)-C(24)	98.5(2)	C(133)-C(134)-C(135)	118.5(7)	C(233)-C(234)-C(235)	120.3(7)
P(1)-Rh(1)-C(15)	119.4(2)	P(2)-Rh(2)-C(25)	123.5(2)	C(134)-C(135)-C(136)	121.9(7)	C(234)-C(235)-C(236)	120.2(7)
Rh(1)-C(1)-O(1)	175.9(6)	Rh(2)-C(2)-O(2)	176.9(6)	C(135)-C(136)-C(131)	120.2(7)	C(235)-C(236)-C(231)	120.1(6)
Rh(1)-P(1)-C(111)	116.3(2)	Rh(2)-P(2)-C(211)	117.9(2)	C(132)-C(131)-C(136)	118.4(6)	C(232)-C(231)-C(236)	119.5(5)
Rh(1)-P(1)-C(121)	115.0(3)	Rh(2)-P(2)-C(221)	119.0(2)	C(11)-C(12)-C(13)	108.0(7)	C(21)-C(22)-C(23)	108.8(8)
Rh(1)-P(1)-C(131)	112.4(2)	Rh(2)-P(2)-C(231)	109.1(2)	C(12)-C(13)-C(14)	107.4(7)	C(22)-C(23)-C(24)	106.9(7)
P(1)-C(111)-C(112)	123.7(5)	P(2)-C(211)-C(212)	119.6(4)	C(13)-C(14)-C(15)	109.9(7)	C(23)-C(24)-C(25)	107.9(7)
P(1)-C(111)-C(116)	117.5(5)	P(2)-C(211)-C(216)	121.8(4)	C(11)-C(15)-C(14)	106.9(7)	C(21)-C(25)-C(24)	108.7(7)
P(1)-C(121)-C(122)	121.7(6)	P(2)-C(221)-C(222)	118.8(5)	C(12)-C(11)-C(15)	107.7(8)	C(22)-C(21)-C(25)	107.4(7)

(*b*) Anion

F(1)-P(3)-F(2)	175.6(6)
F(3)-P(3)-F(4)	179.2(5)
F(5)-P(3)-F(6)	178.7(4)
F(1)-P(3)-F(3)	88.3(5)
F(1)-P(3)-F(4)	92.1(6)
F(1)-P(3)-F(5)	90.3(4)
F(1)-P(3)-F(6)	88.6(4)
F(2)-P(3)-F(3)	87.3(5)
F(2)-P(3)-F(4)	92.3(5)
F(2)-P(3)-F(5)	89.5(4)
F(2)-P(3)-F(6)	91.6(4)
F(3)-P(3)-F(5)	90.1(4)
F(3)-P(3)-F(6)	90.6(4)
F(4)-P(3)-F(5)	89.1(4)
F(4)-P(3)-F(6)	90.2(4)

(*c*) Toluene of crystallisation

C(10)-C(20)-C(30)	120.6(11)
C(20)-C(30)-C(40)	119.8(11)
C(30)-C(40)-C(50)	120.5(12)
C(40)-C(50)-C(60)	120.6(11)
C(50)-C(60)-C(70)	120.(10)
C(10)-C(60)-C(70)	119.2(9)
C(10)-C(60)-C(50)	120.8(9)
C(20)-C(10)-C(60)	117.6(9)

Table 3. Final atomic positions (fractional co-ordinates, Ag and Rh × 10^5, others × 10^4), with estimated standard deviations in parentheses, for $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2][PF_6]\cdot C_6H_5Me$ (5)

Atom	*x*	*y*	*z*
(*a*) Cation			
Ag	30 250(4)	12 829(2)	19 895(3)
Rh(1)	7 440(4)	13 083(2)	23 557(3)
Rh(2)	51 905(4)	11 232(2)	15 021(3)
P(1)	847(1)	2 180(1)	1 923(1)
P(2)	4 991(1)	228(1)	1 805(1)
C(111)	2 231(5)	2 563(3)	2 167(3)
C(112)	2 803(6)	2 894(3)	1 703(4)
C(113)	3 816(7)	3 200(3)	1 945(5)
C(114)	4 252(7)	3 176(3)	2 634(5)
C(115)	3 669(7)	2 846(3)	3 115(5)
C(116)	2 673(6)	2 537(3)	2 880(4)
C(121)	−311(5)	2 650(2)	2 227(3)
C(122)	−1 263(5)	2 468(3)	2 618(4)
C(123)	−2 115(6)	2 828(3)	2 868(4)
C(124)	−1 992(6)	3 378(3)	2 730(4)
C(125)	−1 068(7)	3 570(3)	2 337(4)
C(126)	−218(6)	3 212(3)	2 088(4)
C(131)	675(5)	2 207(2)	944(3)
C(132)	−444(6)	2 342(3)	601(4)
C(133)	−615(6)	2 298(3)	−135(4)
C(134)	318(8)	2 110(3)	−551(4)
C(135)	1 414(8)	1 988(3)	−210(4)
C(136)	1 609(6)	2 040(3)	521(4)
C(211)	4 537(5)	70(2)	2 716(3)
C(212)	4 132(6)	−455(3)	2 873(3)
C(213)	3 838(6)	−588(3)	3 574(4)
C(214)	3 929(6)	−194(3)	4 112(4)
C(215)	4 329(6)	318(3)	3 958(3)
C(216)	4 640(5)	450(3)	3 265(3)
C(221)	3 962(5)	−207(2)	1 256(3)
C(222)	2 751(5)	−49(3)	1 154(4)
C(223)	1 930(6)	−392(3)	783(4)
C(224)	2 288(7)	−889(3)	521(4)
C(225)	3 484(7)	−1 053(3)	631(4)
C(226)	4 309(6)	−705(3)	990(3)
C(231)	6 458(5)	−114(2)	1 756(3)
C(232)	7 051(6)	−84(3)	1 101(4)
C(233)	8 139(6)	−351(3)	1 038(4)
C(234)	8 659(6)	−634(3)	1 614(5)
C(235)	8 100(6)	−651(3)	2 258(5)
C(236)	6 989(5)	−394(3)	2 235(4)
C(11)	37(8)	647(4)	3 048(5)
C(12)	1 340(7)	648(4)	3 141(4)
C(13)	1 689(7)	1 140(4)	3 450(4)
C(14)	642(7)	1 446(3)	3 541(4)
C(15)	−379(7)	1 136(4)	3 323(4)
C(21)	5 762(7)	1 993(3)	1 613(4)
C(22)	6 660(8)	1 724(4)	1 245(5)
C(23)	7 158(6)	1 332(3)	1 673(6)
C(24)	6 574(7)	1 357(4)	2 333(5)
C(25)	5 771(6)	1 778(3)	2 290(4)
C(1)	412(6)	1 043(3)	1 434(4)
O(1)	171(5)	855(2)	884(3)
C(2)	4 188(5)	1 057(3)	684(4)
O(2)	3 609(4)	1 026(2)	162(3)
X(1) *	666	1 003	3 301
X(2) *	6 385	1 637	1 831
(*b*) Anion			
P(3)	5 745(2)	1 926(1)	4 669(1)
F(1)	6 696(7)	1 671(5)	4 230(4)
F(2)	4 794(6)	2 226(4)	5 082(5)
F(3)	5 972(6)	2 468(3)	4 288(5)
F(4)	5 501(9)	1 391(3)	5 039(5)
F(5)	4 741(5)	1 774(3)	4 067(3)
F(6)	6 756(5)	2 066(3)	5 262(3)
(*c*) Toluene of crystallisation			
C(10)	1 136(9)	3 738(4)	294(5)
C(20)	2 378(10)	3 892(6)	376(5)
C(30)	2 708(10)	4 409(7)	645(6)
C(40)	1 861(13)	4 770(5)	794(6)
C(50)	625(12)	4 629(5)	709(5)
C(60)	284(8)	4 124(4)	465(4)
C(70)	−1 036(9)	3 985(6)	357(6)

* X(1) and X(2) are the calculated centroids of the C_5H_5 rings bonded to Rh(1) and Rh(2) respectively.

Table 4. Bond angles (°) within the $Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)$ groups of $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2]^+$ and at the iridium atom of $[Ir(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (X = centroid of C_5H_5 ring)

M	P-M-C(O)	P-M-X	X-M-C(O)	Σ [a]
Rh(1)	90.5(2)	133.8	134.3	358.6
Rh(2)	93.3(2)	129.0	134.7	357.0
Ir	89.2(3)	135.0(2)	135.7(3)	359.9 [b]

[a] Sum of the angles P-M-C(O), P-M-X, and X-M-C(O). [b] Data from ref. 21.

Table 5. Bond angles (°) at the rhodium atoms of $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2]^+$ (X = centroid of C_5H_5 ring)

M	Ag-M-C(O)	Ag-M-P	Ag-M-X
Rh(1)	84.3	82.3	108.4
Rh(2)	77.1	87.4	115.0

Complex (5) may be regarded as an adduct between the Lewis acid Ag^+ and the base $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$. Other complexes containing silver–transition metal bonds have been prepared [24] from silver halides and metal carbonyl anions such as $[M(CO)_3(\eta\text{-}C_5H_5)]^-$ (M = Cr, Mo, or W) and $[Co(CO)_4]^-$. Thus $[LAgCo(CO)_4]$ [L = $Me_2AsC_6H_4As(Me)C_6H_4AsMe_2$] [Ag–Co = 2.50(1) Å] [25] may be regarded as having an electron-pair shared bond and thus superficially different from that of (5).

The variable co-ordination of silver to alkenes and alkynes, with respect to co-ordination number and geometry, is well documented,[26] and we have noted previously [21] the several different ways in which silver(I) will react with organometallic substrates. Recent *X*-ray structural studies have revealed addition of Ag^+ across an iron–iron bond, in $[AgFe_2(CO)_6(\mu\text{-}PPh_2)\{(\mu\text{-}CHC(Ph)NHMe\}][ClO_4]$,[27] and to an osmium–carbyne bond to give the mixed dimetallacyclopropene $[ClAg\{\mu\text{-}C(C_6H_4Me\text{-}p)\}OsCl(CO)(PPh_3)_2]$.[28]

While the *X*-ray structural study of (5) revealed no gross difference between the two $Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)$ groups it is useful, for the purpose of synthetic applications, to visualise the cation as a silver(0)-stabilised source of the radical cation (2) (see below). This description of (5) allows a rationalisation of the reactions with the radicals NO and NO_2.

$$(5) = Ag^0 + \underset{(2)}{[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+} + \underset{(1)}{[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]}$$

Whereas pure NO does not react with (1), the dropwise addition of a solution of the gas in CH_2Cl_2 to (5) in the same solvent gave a precipitate of silver metal and equivalent quantities of (1) and $[Rh(NO)(PPh_3)(\eta\text{-}C_5H_5)]^+$.[29] Coupling of NO with the isolable radical cation $[Co(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)]^+$ has been shown [5] to give $[Co(NO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)]^+$, implying that the reaction between (5) and NO indeed involves (2).

Nitrogen dioxide and (5) also give Ag metal and $[Rh(NO)(PPh_3)(\eta\text{-}C_5H_5)]^+$, together with $[Rh(NO_3)_2(PPh_3)(\eta\text{-}C_5H_5)]$ the product of the reaction between (1) and NO_2. In this case the complex $[Rh(NO_2)(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ has not been detected, but by analogy with the reaction between NO_2 and the radical cation $[Fe(CO)_3(PPh_3)_2]^+$,[30] coupling between (2) and NO_2 is followed by oxygen transfer and CO_2 elimination to give $[Rh(NO)(PPh_3)(\eta\text{-}C_5H_5)]^+$. Other examples of such transfer reactions are well documented.[31]

Conclusions

The radical cations $[M(CO)(PR_3)(\eta\text{-}C_5H_5)]^+$ (M = Co or Rh) differ drastically in their reactivity; the isolation of $[Co(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ contrasts markedly with the spontaneous dimerisation of $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ (2).

The formation of $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2]^+$ (5) from $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (1) and Ag^+, despite the redox potentials involved favouring oxidation, again highlights the complexities inherent in the use of this particular oxidant. However, the behaviour of (5) towards NO and NO_2 illustrates the potential use of silver(I) adducts as stable sources of organotransition-metal radicals.

Experimental

The preparation and purification of the complexes described were carried out under an atmosphere of dry nitrogen. Solvents were dried by standard methods and deoxygenated before use. Unless otherwise stated, the solid complexes are moderately stable in air and dissolve in polar solvents such as CH_2Cl_2 or acetone to give solutions which slowly decompose in air.

The compounds $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ [32] and $[N_2C_6H_4F\text{-}p]X$ (X = BF_4 or PF_6) [33] were prepared by published methods, and silver(I) salts and NO gas were purchased from Fluorochem Ltd., Glossop, Derbyshire, and B.O.C. Ltd., respectively.

Infrared spectra were recorded on a Perkin-Elmer PE 257 spectrophotometer and calibrated against the absorption of polystyrene at 1 601 cm^{-1}. Electrochemical studies were made as described previously,[5] and potentials are recorded *vs.* an aqueous saturated calomel electrode with $[NBu^n_4][PF_6]$ as base electrolyte. Under these conditions, $E^{\ominus}$ for the one-electron oxidation of ferrocene is 0.43 V. Proton and ^{13}C n.m.r. spectra were recorded on JEOL PS100 and on JEOL PFT100 or FX90Q instruments respectively and calibrated against $SiMe_4$ as internal reference. Field-desorption mass spectra were recorded on an AEI MS902 spectrometer. Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol or by Drs. F. and A. Pascher, Bonn, West Germany.

(μ-1—5-η:1′—5′-η-*Bicyclopentadienediyl*)*dicarbonylbis*(*triphenylphosphine*)*dirhodium*(Rh–Rh) *Bis*(*hexafluorophosphate*), $[Rh_2(CO)_2(PPh_3)_2(\eta^5\text{:}\eta'^5\text{-}C_{10}H_8)][PF_6]_2$ (3).—To $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (0.25 g, 0.55 mmol) in CH_2Cl_2 (20 cm^3) was added $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (0.18 g, 0.54 mmol). After 5 min n-hexane was added to the red solution to give an orange precipitate. Recrystallisation from CH_2Cl_2–n-hexane gave the *product* as an orange solid, yield 0.26 g (79%).

The complex is only moderately soluble in polar solvents.

(μ-1—5-η:1′—5′-η-*Bicyclopentadienediyl*)*dicarbonylbis*(*triphenylphosphine*)*dirhodium*, $[Rh_2(CO)_2(PPh_3)_2(\eta^5\text{:}\eta'^5\text{-}C_{10}H_8)]$ (4).—A solution of $[Rh_2(CO)_2(PPh_3)_2(\eta^5\text{:}\eta'^5\text{-}C_{10}H_8)][PF_6]_2$ (3) (0.21 g, 0.17 mmol) in thf (60 cm^3) was stirred with sodium (0.15 g, 6.5 mmol) in mercury (8 cm^3) for 5 min. The dark brown solution was then separated from excess amalgam and evaporated to dryness. Chromatography of a toluene solution of the residue on an alumina–hexane column gave an orange band eluted with toluene. Evaporation of the eluate to dryness, and recrystallisation from toluene–n-hexane gave the *product* as an orange-red solid, yield 0.096 g (60%).

The compound is stable when stored in the solid state under nitrogen, and is soluble in diethyl ether and in toluene.

Bis[*carbonyl*-η-*cyclopentadienyl*(*triphenylphosphine*)*rhodio*]-*silver Hexafluorophosphate–toluene* (1/1) $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2][PF_6]\cdot C_6H_5Me$ (5).—To a rapidly stirred solution of $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (0.20 g, 0.44 mmol) in toluene (30 cm^3) was added $AgPF_6$ (0.11 g, 0.44 mmol) in toluene (5 cm^3). The yellow precipitate was filtered off, and purified by dissolution in CH_2Cl_2 (5 cm^3) and addition to rapidly stirred toluene (100 cm^3), yield 0.20 g (72%).

Structure Determination.—The crystal of $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2][PF_6]\cdot C_6H_5Me$ chosen for intensity measurements (0.25 × 0.25 × 0.13 mm) was mounted and aligned on an Enraf-Nonius CAD4 diffractometer; data were collected using an $\omega/2\theta$ scan technique. Each reflection was given a fast prescan (6.67° min^{-1} in ω) and only those considered significant were rescanned so that their net intensities had $I > 3.3\sigma$, with a maximum measuring time of 60 s. Those reflections which had satisfied this condition on the prescan were not remeasured. Because of the low value of the linear absorption coefficient, μ, no absorption correction was applied. Of 9 485 independent observations ($2\theta < 25°$), 6 158 satisfied the criterion $F_o > 3\sigma(F_o)$ and only these were used in the solution and refinement of the structure.

Crystal data. $C_{48}H_{40}AgF_6O_2P_3Rh_2\cdot C_6H_5CH_3$, M = 1 261.6, Monoclinic, space group $P2_1/c$ (no. 14), a = 11.078(1), b = 24.375(3), c = 18.604(3) Å, β = 92.90(1)°, U = 5 016.8 Å^3, D_m = 1.66, Z = 4, D_c = 1.67 g cm^{-3}, $F(000)$ = 2 520, Mo-K_α X-radiation (graphite monochromator), λ = 0.710 69 Å, μ(Mo-K_α) = 10.8 cm^{-1}.

Structure analysis and refinement. The positions of the metal atoms were found from a Patterson map, computed using the SHELX [34] program. After several cycles of least-squares refinement of the metal atom positions, the non-hydrogen atoms were located from successive difference maps, and their positional and thermal parameters improved by several cycles of isotropic least-squares refinement. Because of the large number of parameters, anisotropic refinement was carried out in three blocks, with the silver atom being refined in each. The first and second blocks each contained one rhodium and those groups of atoms bonded to it, while the third contained the toluene and hexafluorophosphate molecules. At this stage a weighting scheme $\{w = [\sigma^2(F_o) + 0.0006\,F_o^2]^{-1}\}$ was applied and this gave flat analyses of variance. All hydrogen atoms (excepting those of the toluene, which were ignored) were now inserted into calculated positions with a fixed carbon–hydrogen distance of 1.08 Å and suitable interatomic angles. These were refined with a common thermal parameter. Owing to the large number of atoms, final refinement was carried out in two halves, and it converged at R_1 = 0.0578 and R_2 = 0.0557. The highest peak remaining in the final difference map represented an electron density of 0.9 e Å^{-3}.

Atomic scattering factors for neutral atoms were taken from ref. 35 with corrections for anomalous dispersion for the heavier atoms from ref. 36. All computations were carried out at Queen Mary College on the ICL 2980 computer, and the final stages of refinement were completed on the University of Cambridge IBM 370/165 computer.

Acknowledgements

We thank the S.E.R.C. for a Research Studentship (to J. D. P.), for funds to purchase electrochemical equipment (to N. G. C.), and *via* the single-crystal *X*-ray data collection service at Queen Mary College, London. We also thank N.A.T.O. for a Research Grant (to N. G. C. and W. E. G.) and the National Science Foundation for financial support. We gratefully acknowledge Johnson Matthey for a generous loan of rhodium trichloride, and Professor M. D. Rausch for the results of *X*-ray studies on $[Co_2(CO)_4(\eta^5:\eta'^5-C_{10}H_8)]$.

References

1 Part 16, N. G. Connelly, J. D. Payne, and W. E. Geiger, *J. Chem. Soc., Dalton Trans.*, 1983, 295.
2 N. G. Connelly and M. D. Kitchen, *J. Chem. Soc., Dalton Trans.*, 1976, 2165.
3 N. G. Connelly and M. D. Kitchen, *J. Chem. Soc., Dalton Trans.*, 1977, 931; P. M. Treichel, K. P. Wagner, and H. J. Mueh, *J. Organomet. Chem.*, 1975, **86**, C13; L. I. Denisovich, N. V. Zakurin, S. P. Gubin, and A. G. Ginzburg, *ibid.*, 1975, **101**, C43.
4 P. M. Treichel, D. C. Molzahn, and K. P. Wagner, *J. Organomet. Chem.*, 1979, **174**, 191; P. M. Treichel and D. A. Komar, *ibid.*, 1981, **206**, 77.
5 K. Broadley, N. G. Connelly, and W. E. Geiger, *J. Chem. Soc., Dalton Trans.*, 1983, 121; N. G. Connelly, A. R. Lucy, and A. M. R. Galas, *J. Chem. Soc., Chem. Commun.*, 1981, 43.
6 R. J. McKinney, *Inorg. Chem.*, 1982, **21**, 2051; *J. Chem. Soc., Chem. Commun.*, 1980, 603.
7 L. J. Guggenberger and F. N. Tebbe, *J. Am. Chem. Soc.*, 1973, **95**, 7870; A. Davison and S. S. Wreford, *ibid.*, 1974, **96**, 3017; M. Berry, N. J. Cooper, M. L. H. Green, and S. J. Simpson, *J. Chem. Soc., Dalton Trans.*, 1980, 29; D. A. Lemenovskii, V. P. Fedin, Yu. L. Slovohotov, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1982, **228**, 153; D. A. Lemenovskii, S. A. Konde, and E. G. Perevalova, *ibid.*, 1982, **226**, 223.
8 J. C. Smart and B. L. Pinsky, *J. Am. Chem. Soc.*, 1980, **102**, 1009.
9 J. C. Smart and C. J. Curtis, *J. Am. Chem. Soc.*, 1977, **99**, 3518.
10 F. L. Hedberg and H. Rosenberg, *J. Am. Chem. Soc.*, 1969, **91**, 1258.
11 A. Davison and J. C. Smart, *J. Organomet. Chem.*, 1973, **49**, C43.
12 M. Freeman, A. G. Orpen, S. J. Raven, and N. G. Connelly, unpublished work.
13 M. D. Rausch, personal communication; see also ref. 76, in D. W. Macomber, W. P. Hart, and M. D. Rausch, *Adv. Organomet. Chem.*, 1982, **21**, 29.
14 P. R. Sharp, K. N. Raymond, J. C. Smart, and R. J. McKinney, *J. Am. Chem. Soc.*, 1981, **103**, 753.
15 A. M. Bond, R. Colton, and J. J. Jackowski, *Inorg. Chem.*, 1975, **14**, 274, 2526; F. L. Wimmer, M. R. Snow, and A. M. Bond, *ibid.*, 1974, **13**, 1617.
16 A. M. Bond, R. Colton, and M. E. McDonald, *Inorg. Chem.*, 1978, **17**, 2842; A. M. Bond, B. S. Grabaric, and Z. Grabaric, *ibid.*, 1978, **17**, 1013; A. M. Bond, R. Colton, and M. J. McCormick, *ibid.*, 1977, **16**, 155.
17 J. Moraczewski and W. E. Geiger, jun., *J. Am. Chem. Soc.*, 1981, **103**, 4779.
18 A. M. Bond, D. J. Darensbourg, E. Mocellin, and B. J. Stewart, *J. Am. Chem. Soc.*, 1981, **103**, 6827.
19 W. H. Morrison, jun., S. Krogsrud, and D. N. Hendrickson, *Inorg. Chem.*, 1973, **12**, 1998.
20 N. G. Connelly and I. Manners, unpublished work.
21 P. K. Baker, K. Broadley, N. G. Connelly, B. A. Kelly, M. D. Kitchen, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1980, 1710.
22 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 256.
23 M. J. Bennett, J. L. Pratt, and R. M. Tuggle, *Inorg. Chem.*, 1974, **13**, 2408.
24 A. S. Kasenally, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 1965, 5343; P. Chini, S. Martinengo, and G. Longoni, *Gazz. Chim. Ital.*, 1975, **105**, 203; P. Hackett and A. R. Manning, *J. Chem. Soc., Dalton Trans.*, 1975, 1606.
25 T. L. Blundell and H. M. Powell, *J. Chem. Soc. A*, 1971, 1685.
26 C. D. M. Beverwijk, G. J. M. Van der Kerk, A. J. Leusink, and J. G. Noltes, *Organomet. Chem. Rev., Sect. A*, 1970, **5**, 215.
27 A. J. Carty, G. N. Mott, and N. J. Taylor, *J. Am. Chem. Soc.*, 1979, **101**, 3131.
28 G. R. Clark, C. M. Cochrane, W. R. Roper, and L. J. Wright, *J. Organomet. Chem.*, 1980, **199**, C35.
29 N. G. Connelly and J. D. Davies, *J. Organomet. Chem.*, 1972, **38**, 385.
30 P. K. Baker, K. Broadley, and N. G. Connelly, *J. Chem. Soc., Dalton Trans.*, 1982, 471.
31 D. T. Doughty, G. Gordon, and R. P. Stewart, jun., *J. Am. Chem. Soc.*, 1979, **101**, 2645; R. D. Feltham and J. C. Kriege, *ibid.*, p. 5064.
32 A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, 1970, **9**, 2658.
33 A. Roe, *Org. React.*, 1949, **5**, 193.
34 SHELX, Program for crystal structure determination, G. M. Sheldrick, University of Cambridge, 1975.
35 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
36 D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

Received 10th January 1983; *Paper* 3/036