Synthesis, Reactivity, and *X*-ray Crystal Structure of $[Ag\{Rh(CO)(PPh_3)(\eta^5\text{-}C_5H_5)\}_2]$-$[PF_6]$.toluene: A Silver-stabilised Radical Cation

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Summary $AgPF_6$ and $[Rh(CO)(PPh_3)Cp]$ ($Cp = \eta^5\text{-}C_5H_5$) afford $[Ag\{Rh(CO)(PPh_3)Cp\}_2][PF_6]$ which contains direct Ag–Rh bonds and is a stable source of the highly reactive radical cation $[Rh(CO)(PPh_3)Cp]^+$.

Electrochemical studies[1] show that many diamagnetic organotransition-metal complexes undergo one-electron oxidation or reduction to radical species. Such species have rarely been exploited[2] as chemical reagents; most have only transient existence. We now show that stable adducts, formed between silver(I) salts and neutral, diamagnetic organometallics, function as controlled sources of highly reactive radical cations.

Addition of $AgPF_6$ to $[Rh(CO)(PPh_3)Cp]$ (**1**) (1 : 2 ratio) in toluene affords good yields (>70%) of an air-stable, yellow solid [**2**; $\bar{\nu}$(CO) 1 984 cm^{-1} (CH_2Cl_2), $\bar{\nu}$(PF) 835 cm^{-1} (Nujol)] which elemental analysis (C,H,P, and Ag) suggests to be $[Ag\{Rh(CO)(PPh_3)Cp\}_2][PF_6]$.toluene. In the absence of further spectral characterisation the full molecular structure of (**2**) has been established by a single crystal *X*-ray diffraction study.

Crystal data: $C_{48}H_{40}AgO_2P_2Rh_2.[F_6P].C_7H_8$, monoclinic, $a = 11{\cdot}078(1)$, $b = 24{\cdot}375(3)$, $c = 18{\cdot}604(3)$ Å, $\beta = 92{\cdot}90(1)^\circ$, $U = 5016{\cdot}3$ Å^3, space group $P2_1/c$, $M = 1260{\cdot}6$, $Z = 4$, $D_c = 1{\cdot}67$ g cm^{-3}, $F(000) = 2\ 520$, μ(Mo-K_α) = $10{\cdot}8$ cm^{-1}, Mo-K_α radiation, $\lambda = 0{\cdot}710\ 69$ Å. The structure was solved by Patterson and Fourier methods and refined using 6 158 unique observed intensities [$F_0 > 3\sigma(F_0)$] measured on a Nonius CAD4 diffractometer ($2\theta_{max}$ 50°). The current *R* value is 0·058.†

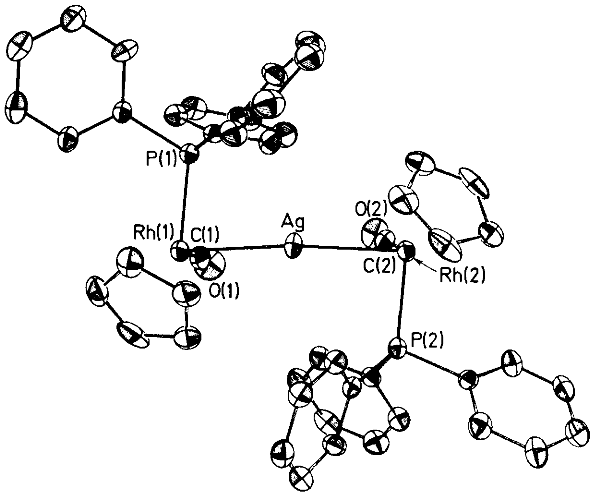

Figure. The structure of the $[Ag\{Rh(CO)(PPh_3)Cp\}_2]$ cation (hydrogen atoms omitted for clarity). Rh(1)–Ag, 2·651(1); Rh(2)–Ag, 2·636(1) Å.

The crystal structure determination of (**2**) reveals the presence of discrete $[Ag\{Rh(CO)(PPh_3)Cp\}_2]^+$ (Figure) and $[PF_6]^-$ ions and one molecule of toluene of crystallisation

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

per formula unit. In the cation, the silver atom is directly bonded to the two rhodium atoms with a near-linear Rh(1)–Ag–Rh(2) bond angle [171·0(0)°]; the two phosphine ligands are mutually *trans*-disposed with respect to the trimetallic skeleton. Somewhat surprisingly the arrangement of the PPh_3, CO, and Cp ligands about the rhodium atom in each $Rh(CO)(PPh_3)Cp$ group is only slightly distorted from that found in $[Ir(CO)(PPh_3)Cp]$[3] [which is likely to be isostructural with (**1**)], despite the additional co-ordination of the silver atom. For the iridium complex, the metal, carbonyl carbon, phosphorus atoms, and the centroid, X, of the Cp ring are co-planar. A comparison of the bond angles around Ir with those about Rh(1) and Rh(2) (Table) reveals little deviation from co-planarity in silver adduct formation. The structure of (**2**) is strikingly different from that of the adduct $[\{WI(CO)_3Cp\}_4Ag][BF_4]$[4] in which the silver atom is bound to the four iodine atoms; in this case Ag–W bonds are absent.

TABLE. Bond angles (°) at the rhodium atoms of (**2**) and at the iridium atom of $[Ir(CO)(PPh_3)Cp]$,[a] (X = centroid of Cp ring).

M	P–M–C(O)	P–M–X	X–M–C(O)	Σ[b]
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

[a] Data from ref. 3. [b] Sum of the angles P–M–C(O), P–M–X, and X–M–C(O).

Despite the structural similarities between the two $Rh(CO)(PPh_3)Cp$ groups, (**2**) may be regarded formally, on the basis of its reactions with radicals, as shown in equation (1). That is, (**2**) is a stable and controlled source of the highly reactive‡ radical cation, $[Rh(CO)(PPh_3)Cp]^+$ (**3**),

$$\underset{\mathbf{(2)}}{[Ag\{Rh(CO)(PPh_3)Cp\}_2]^+} \rightleftharpoons Ag + \underset{\mathbf{(1)}}{[Rh(CO)(PPh_3)Cp]} + \underset{\mathbf{(3)}}{[Rh(CO)(PPh_3)Cp]^+} \qquad (1)$$

which is implicated[5] in the formation of the rhodium–rhodium-bonded fulvalene complex $[Rh_2(CO)_2(PPh_3)_2(\eta^5,\eta^5\text{-}C_{10}H_8)]^{2+}$ from (**1**) and oxidants such as $[N_2C_6H_4F\text{-}p]^+$ and $[FeCp_2]^+$. Thus, mixing CH_2Cl_2 solutions of NO gas and (**2**) at room temperature instantly yields equimolar quantities of silver metal, (**1**), and $[Rh(NO)(PPh_3)Cp][PF_6]$ (**4**).[6] The nitrosyl complex is formed from (**3**) as (**1**) does not react with NO gas. With NO_2 a similar rapid reaction occurs to give silver metal and (**4**). Although the product of direct radical–radical coupling, $[Rh(NO_2)(CO)(PPh_3)Cp]^+$, is not detected, oxygen transfer from co-ordinated NO_2 to CO, and CO_2 elimination,[7] yields the observed product (**4**); the direct reaction between (**1**) and NO_2 gives $[Rh(NO_3)_2(PPh_3)Cp]$.

The stable adducts $[Ag\{Mn(CN)(NO)(PPh_3)Cp\}_2][BF_4]$ and $[Ag\{M(CO)_4(L\text{–}L)\}_2][PF_6]$ (M = Mo or W, L–L = $Ph_2P[CH_2]_nPPh_2$, n = 1 or 2) have also been prepared. Their reactivity and that of (**2**) are under further investigation.

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‡ Cyclic voltammetric studies on (**1**) allow the lifetime of (**3**) to be estimated as no longer than 3·0 ms at room temperature.

[1] *E.g.*, R. E. Dessy, R. B. King, and M. Waldrop, *J. Am. Chem. Soc.*, 1966, **88**, 5112; J. D. L. Holloway and W. E. Geiger, Jnr., *ibid.*, 1979, **101**, 2038; N. G. Connelly and R. L. Kelly, *J. Organomet. Chem.*, 1976, **120**, C16, and references therein.
[2] M. F. Lappert and C. R. C. Milne, *J. Chem. Soc., Chem. Commun.*, 1978, 925; P. K. Baker, K. Broadley, and N. G. Connelly, *ibid.*, 1980, 775.
[3] M. J. Bennett, J. L. Pratt, and R. M. Tuggle, *Inorg. Chem.*, 1974, **13**, 2408.
[4] T. N. Salnikova, V. G. Adrianov, and Y. T. Struchkov, *Koord. Khim.*, 1976, **2**, 707.
[5] R. J. McKinney, *J. Chem. Soc., Chem. Commun.*, 1980, 603; N. G. Connelly and J. D. Payne, unpublished results.
[6] N. G. Connelly and J. D. Davies, *J. Organomet. Chem.*, 1972, **38**, 385.
[7] D. T. Doughty, G. Gordon, and R. P. Stewart, Jnr., *J. Am. Chem. Soc.*, 1979, **101**, 2645; R. D. Feltham and J. C. Kriege, *ibid.*, p. 5064.