# Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 9.[1] Silver(I) Adducts of Cyclic Polyeneone Complexes, the *X*-Ray Crystal Structure of $[\{Fe(CO)_3[\eta^5\text{-}C_5Ph_4OAg(OH_2)]\}_2][PF_6]_2$,† and Comments on the Use of the Silver(I) Ion as a One-electron Oxidant

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The tetraphenylcyclopentadienone complexes $[M(CO)_2L(\eta^4\text{-}C_5Ph_4O)]$ [1; M = Fe, L = CO, $PPh_3$, or $P(OMe)_3$; M = Ru, L = CO] and $[Rh(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5Ph_4O)]$ (2) react with $Ag[PF_6]$ to give dimeric oxygen-bonded silver adducts $[\{M(CO)_2L(\eta^5\text{-}C_5Ph_4OAg)\}_2][PF_6]_2$ (3) and $[\{Rh(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Ph_4OAg)\}_2][PF_6]_2$ (4). The *X*-ray crystal structure of (3; M = Fe, L = CO) confirms that the cation contains a central planar asymmetric $Ag_2O_2$ bridge (Ag–O, 2.27 and 2.65 Å) but there is a molecule of water co-ordinated to each Ag atom. The five-membered ring of the $Fe(CO)_3(C_5Ph_4O)$ moiety is best regarded as a substituted cyclopentadienyl although the carbon atom bearing the oxygen is significantly further from the iron atom (Fe–C, 2.31 Å) than are the other four carbon atoms [Fe–C, 2.11 (mean) Å]. There are also weak interactions between the silver atom and the two phenyl rings adjacent to the CO group in the $C_5$ ring. The crystals were of poor quality, due to partial inclusion of molecules of $CH_2Cl_2$ the positions of which were not refined. This is reflected in the relatively poor *R* value and high standard deviations. The crystals are monoclinic, *a* = 13.293(7), *b* = 14.128(6), *c* = 19.805(14) Å, β = 105.75(5)°, space group $P2_1/n$. The structure was solved by heavy-atom methods and refined to *R* 0.115 for 2 847 reflections. The iron complexes (3) react with halide ions to regenerate (1), but form $[FeX(CO)_2L(\eta^4\text{-}C_5Ph_4O)][PF_6]$ [5; X = Br or I, L = CO, $PPh_3$ or $P(OMe)_3$] with halogens. Reaction of $Ag[BF_4]$ with $[Cr(CO)_3(\eta^6\text{-tropone})]$ gives $[Cr(CO)_3\{\eta^7\text{-}C_7H_6(OH)\}][BF_4]$ *via* the decomposition of an adduct related to (3) and (4). A summary is given of the behaviour of $Ag^I$ as a reagent in organometallic chemistry, and a brief comment made on its use as a one-electron oxidant.

The complexes $[M(CO)_3(\eta^4\text{-polyolefin})]$ [M = Fe or Ru; polyolefin = 2,3-dimethylbutadiene, cycloheptatriene (cht), cyclo-octatetraene (cot), *etc.*] [2] and $[Mo(CO)_3(\eta^6\text{-cht})]$,[3] and their Group 5 donor-ligand derivatives, undergo one-electron oxidation at a platinum electrode in $CH_2Cl_2$; silver(I) salts may be used to carry out the chemical oxidation. In certain cases the radical cations which result from oxidation are isolable as salts, such as $[Fe(CO)\{P(OMe)_3\}_2(C_4Ph_4)][BF_4]$,[4] but in most the radicals react further, as shown in Scheme 1. We now describe the reactions of silver(I) salts with $\eta^4$-tetraphenylcyclopentadienone and $\eta^6$-tropone complexes, which give dimeric oxygen-bonded silver adducts such as $[\{M(CO)_2L(\eta^5\text{-}C_5Ph_4OAg)\}_2][PF_6]_2$ [M = Fe, L = CO, $PPh_3$, or $P(OMe)_3$; M = Ru, L = CO], the *X*-ray crystal structure of the tricarbonyliron complex, and the reactions of the adducts with halide ions, halogens, and an excess of silver(I). We also summarise the diverse behaviour of the silver(I) ion as a reagent in organometallic chemistry, and briefly comment on its use as a one-electron oxidant.

TABLE 1

Analytical, i.r., and $^1H$ n.m.r. spectral data for $[\{M(\eta^5\text{-}C_5Ph_4OAg)\}_2][PF_6]_2$

| M | Analysis [a] (%) C | H | $\tilde{\nu}(CO)$ ($cm^{-1}$) [b] | $^1H$ n.m.r. (τ) [c] |
|---|---|---|---|---|
| $Fe(CO)_3$ | 49.3 (49.5) | 2.9 (2.6) | 2 080s, 2 024s,br, 1 535m [d] | 2.77 (10 H, m, $C_6H_5$); 2.52 (10 H, m, $C_6H_5$) |
| $Fe(CO)_2(PPh_3)$ | 57.7 (58.2) | 3.8 (3.5) | 2 009s, 1 960s | |
| $Fe(CO)_2\{P(OMe)_3\}$ | 48.4 (49.0) | 3.4 (3.6) | 2 017s, 1 982s | |
| $Ru(CO)_3$ | 46.5 (46.6) | 2.7 (2.4) | 2 094s, 2 037s,br, 1 505m [d] | 3.53 (10 H, m, $C_6H_5$); 3.20 (10 H, m, $C_6H_5$) |
| $Rh(\eta^5\text{-}C_5H_5)$ | 50.4 (50.7) | 3.5 (3.1) | 1 480m [d] | 4.18 (5 H, s, $C_5H_5$); 2.82 (10 H, m, $C_6H_5$); 2.44 (10 H, m, $C_6H_5$) |

[a] Calculated values are given in parentheses. [b] In $CH_2Cl_2$, unless stated; s = strong, m = medium, br = broad. [c] In $CD_3NO_2$; m = multiplet, s = singlet. [d] Ketonic carbonyl stretch, in Nujol.

## RESULTS AND DISCUSSION

The addition of $Ag[PF_6]$ to $[M(CO)_2L(\eta^4\text{-}C_5Ph_4O)]$ (1; M = Fe, L = CO) (1 : 1 ratio) in toluene results in the deposition of a yellow solid which, after recrystallisation from $CH_2Cl_2$–n-hexane, analyses (C and H) as the adduct $[\{M(CO)_2L(\eta^5\text{-}C_5Ph_4OAg)\}_2][PF_6]_2$ (3; M = Fe, L = CO). The i.r. spectrum confirms (3; M = Fe, L = CO)

$$\text{(i)}\ [Fe(CO)_3(\eta^4\text{-cht})] \xrightarrow{-e^-} [Fe(CO)_3(C_7H_8)]^+ \xrightarrow{+H\cdot} [Fe(CO)_3(\eta^5\text{-}C_7H_9)]^+ \text{ (ref. 2)}$$

$$\text{(ii)}\ [Fe(CO)_3(\eta^4\text{-cot})] \xrightarrow{-e^-} [Fe(CO)_3(C_8H_8)]^+ \longrightarrow [Fe_2(CO)_6(\eta^5,\eta'^5\text{-}C_{16}H_{16})]^{2+} \text{ (ref. 5)}$$

$$\text{(iii)}\ [Mo(CO)_2(PPh_3)(\eta^6\text{-cht})] \xrightarrow{-e^-} [Mo(CO)_2(PPh_3)(C_7H_8)]^+ \xrightarrow{-H\cdot} [Mo(CO)_2(PPh_3)(\eta^7\text{-}C_7H_7)]^+ \text{ (ref. 3)}$$

SCHEME 1

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† μ-1—5-η : 1′—5′-η-[Bis(μ-tetraphenylcyclopentadienediyl-oxo-*O*)-di(aquasilver)]-bis(tricarbonyliron) bis(hexafluorophosphate).

to be a salt, showing the metal carbonyl absorptions of [1; M = Fe, L = CO, $\tilde{\nu}$(CO) ($CH_2Cl_2$) = 2 066, 2 011, and 1 995 cm$^{-1}$] shifted to higher frequency by, on average, 20 cm$^{-1}$ (Table 1), and the presence of the $[PF_6]^-$ anion [$\tilde{\nu}$(PF) (Nujol) = 835 cm$^{-1}$]. In addition, and most significant, is the change associated with the ketonic carbonyl group of the co-ordinated organic ligand. In (1; M = Fe, L = CO) $\nu$(CO) occurs at 1 640 cm$^{-1}$ (Nujol), *ca.* 100 cm$^{-1}$ to higher energy than that of (3; M = Fe, L = CO) (Table 1); co-ordination of the silver(I) ion to the ketonic oxygen atom is strongly implied. In order to establish unequivocally the co-ordination geometry about the silver atom an *X*-ray crystallographic study was carried out on (3; M = Fe, L = CO).

The molecular structure of (3; M = Fe, L = CO) is shown in Figure 1 which also gives the crystallographic numbering system. The asymmetric unit comprises one half of a centrosymmetric dicationic dimer to which a water molecule has been co-ordinated, and one hexafluorophosphate anion. The $Fe(CO)_3(C_5Ph_4O)$ moiety remains intact but the oxygen atom is now co-ordinated to a monohydrated silver ion; the entire $Fe(CO)_3\{C_5Ph_4OAg(OH_2)\}$ unit is centrosymmetrically related to another similar unit in a manner which creates a central (planar) O–Ag–O–Ag ring which is itself approximately coplanar with the $C_5$ ring. The two Ag–O distances, however, differ considerably from one another at 2.27(2) and 2.65(8) Å. The co-ordination state of the silver atom is characteristically irregular. Apart from the two oxygen atoms of the bridge (which subtend an angle of 74° at the silver atom) and the oxygen atom of the water molecule, O(9) [Ag–O(9), 2.67(5) Å; O(9)–Ag–O(8), 102°; O(9)–Ag–O(8)', 117°],* to all of which it can be considered to be directly bonded, the silver atom is also 2.46(5) Å from atom C(42)' and 2.79(6) Å from atom C(43)' of the phenyl ring attached to C(4)' of the

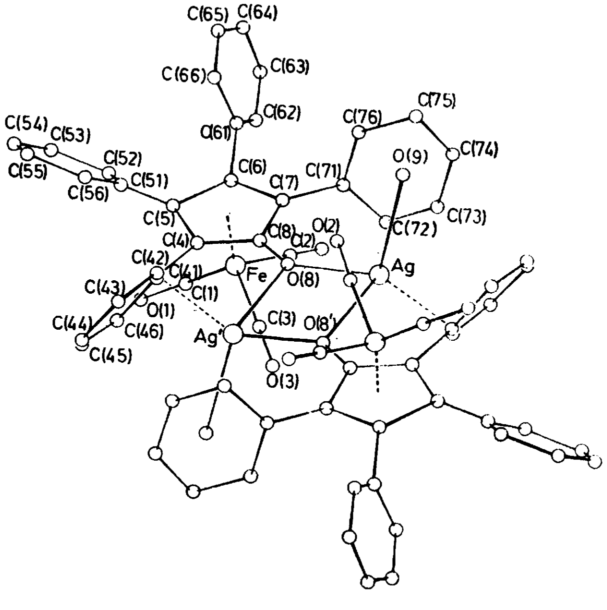

FIGURE 1 The molecular structure of $[\{Fe(CO)_3[\eta^5\text{-}C_5Ph_4OAg(OH_2)]\}_2]^{2+}$

TABLE 2

Atomic positional parameters (fractional co-ordinates) with standard deviations in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Ag | 0.424 9(2) | 0.065 2(1) | −0.086 9(1) |
| Fe | 0.231 8(2) | 0.073 4(2) | 0.089 0(1) |
| C(1) | 0.178 9(19) | 0.024 8(16) | 0.155 5(14) |
| O(1) | 0.145 1(15) | −0.007 0(13) | 0 198 4(10) |
| C(2) | 0.105 0(27) | 0.085 5(14) | 0.025 6(12) |
| O(2) | 0.031 7(15) | 0.097 1(12) | −0.017 8(10) |
| C(3) | 0.257 5(17, | −0.045 1(19) | 0.057 6(11) |
| O(3) | 0.288 1(16) | −0.113 4(13) | 0.043 6(10) |
| C(4) | 0.394 7(15) | 0.099 1(12) | 0.140 0(9) |
| C(5) | 0.330 7(15) | 0.167 1(13) | 0.160 0(9) |
| C(6) | 0.273 0(15) | 0.214 3(12) | 0.098 9(9) |
| C(7) | 0.300 2(15) | 0.177 8(12) | 0.037 8(9) |
| C(8) | 0.387 5(14) | 0.111 7(12) | 0.065 0(9) |
| O(8) | 0.441 3(10) | 0.070 8(10) | 0.030 1(6) |
| C(41) | 0.469 1(16) | 0.032 6(14) | 0.185 1(10) |
| C(42) | 0.575 8(18) | 0.043 8(15) | 0.184 1(11) |
| C(43) | 0.655 3(19) | −0.011 0(16) | 0.226 5(11) |
| C(44) | 0.628 4(21) | −0.079 8(19) | 0.271 3(12) |
| C(45) | 0.526 1(20) | −0.090 6(17) | 0.272 3(12) |
| C(46) | 0.447 4(17) | −0.032 3(14) | 0.230 6(10) |
| C(51) | 0.334 5(16) | 0.195 0(13) | 0.233 2(9) |
| C(52) | 0.244 7(18) | 0.213 7(14) | 0.253 2(11) |
| C(53) | 0.253 8(19) | 0.240 6(16) | 0.324 6(11) |
| C(54) | 0.350 1(18) | 0.248 3(15) | 0.372 5(11) |
| C(55) | 0.435 9(18) | 0.230 9(16) | 0.348 9(11) |
| C(56) | 0.432 3(16) | 0.205 3(13) | 0.281 9(10) |
| C(61) | 0.206 5(15) | 0.305 5(13) | 0.096 3(9) |
| C(62) | 0.100 8(18) | 0.312 6(16) | 0.065 2(11) |
| C(63) | 0.051 7(22) | 0.396 0(19) | 0.066 7(13) |
| C(64) | 0.104 6(23) | 0.475 3(19) | 0.094 0(14) |
| C(65) | 0.202 1(26) | 0.470 9(21) | 0.126 9(15) |
| C(66) | 0.261 2(20) | 0.384 5(18) | 0.127 4(12) |
| C(71) | 0.264 0(15) | 0.210 3(13) | −0.036 4(9) |
| C(72) | 0.229 1(17) | 0.150 4(14) | −0.090 8(10) |
| C(73) | 0.199 7(18) | 0.181 2(15) | −0.161 3(11) |
| C(74) | 0.208 6(19) | 0.274 0(17) | −0.174 3(12) |
| C(75) | 0.247 7(23) | 0.335 7(20) | −0.120 0(14) |
| C(76) | 0.275 6(18) | 0.306 1(16) | −0.049 4(11) |
| O(9) | 0.504 6(14) | 0.232 5(12) | −0.108 8(9) |
| P(1) | 0.375 7(7) | 0.365 4(6) | 0.648 0(5) |
| F(1) | 0.394 3(16) | 0.454 3(13) | 0.697 9(12) |
| F(2) | 0.413 9(18) | 0.421 9(17) | 0.594 3(14) |
| F(3) | 0.259 5(14) | 0.404 3(13) | 0.610 7(11) |
| F(4) | 0.486 7(15) | 0.328 3(15) | 0.685 1(15) |
| F(5) | 0.323 9(20) | 0.308 6(16) | 0.697 5(14) |
| F(6) | 0.356 5(18) | 0.280 6(14) | 0.596 8(14) |
| H(42) | 0.724 7 | −0.041 0 | 0.252 4 |
| H(43) | 0.571 0 | 0.094 4 | 0.143 7 |
| H(44) | 0.368 9 | −0.040 8 | 0.232 4 |
| H(45) | 0.707 4 | −0.085 2 | 0.279 8 |
| H(46) | 0.484 6 | −0.133 4 | 0.297 6 |
| H(52) | 0.169 7 | 0.209 3 | 0.219 3 |
| H(53) | 0.187 9 | 0.253 0 | 0.341 5 |
| H(54) | 0.356 3 | 0.263 5 | 0.423 7 |
| H(55) | 0.507 5 | 0.235 5 | 0.384 8 |
| H(56) | 0.499 6 | 0.194 2 | 0.266 1 |
| H(62) | 0.059 5 | 0.254 3 | 0.043 1 |
| H(63) | −0.028 5 | 0.402 6 | 0.046 2 |
| H(64) | 0.071 8 | 0.538 0 | 0.087 9 |
| H(65) | 0.237 6 | 0.530 4 | 0.154 1 |
| H(66) | 0.343 7 | 0.382 3 | 0.150 0 |
| H(72) | 0.222 9 | 0.080 2 | −0.079 2 |
| H(73) | 0.169 4 | 0.138 9 | −0.201 7 |
| H(74) | 0.192 1 | 0.300 9 | −0.222 5 |
| H(75) | 0.254 9 | 0.409 1 | −0.129 6 |
| H(76) | 0.303 7 | 0.353 2 | −0.009 2 |

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* The centre of inversion relating to the asymmetric unit whose co-ordinates are listed in Table 2 lies at ½, 0, 0. A prime has been used to relate the inverted half of the molecule to the half listed in Table 2.

$C_5$ system. These atoms all lie in one hemisphere if the silver atom is taken as the reference centre of the co-ordination sphere. The silver atom is also at a distance 2.85(6) Å from atom C(72) of the phenyl ring attached to C(7).

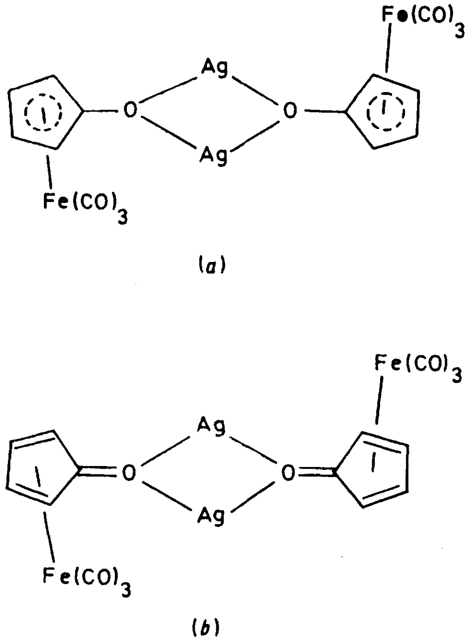

FIGURE 2

The $Fe(CO)_3(C_5Ph_4OAg)$ portion of the ion is perhaps best regarded as containing a substituted cyclopentadienyl ring [Figure 2(*a*)], although the accuracy of the structure determination (see Experimental section) is not sufficiently high to reveal small differences in bonding detail which would distinguish this from the cyclopentadienone form [Figure 2(*b*)]. The low carbonyl stretching frequency (see above) of the CO bond associated with the $C_5$ ring supports structure 2(*a*). The three carbonyl ligands of the $Fe(CO)_3(C_5Ph_4O)$ group are approximately mutually orthogonal (the interbond angles are slightly greater than 90°; Table 3). The carbonyl ligands themselves are almost linear, C(3)–O(3) showing the largest deviation, possibly due to an intermolecular contact [O(3) · · · O(9)] with the water molecule of *ca.* 3.2 Å. The planar $C_5$ ring approximates a regular pentagon, and shows extensive delocalisation, with an exocyclic CO bond of 1.26 Å (Table 3). The carbon atom of the exocyclic CO group is slightly further away from the iron atom [Fe–C(8), 2.31 Å] than are the other four carbon atoms of the ring [Fe–C(4—7)$_{\text{mean}}$, 2.11 Å] but the accuracy of the determination precludes any realistic assessment of bond orders. Incorporation of a water molecule into the co-ordination sphere of a silver atom has been observed in other crystalline complexes, *e.g.* in the silver perchlorate adduct[6] of $[Fe(acac)_3]$ (acac = acetylacetonate).* The hexafluorophosphate ion is, within the accuracy of the determination, ideally octahedral with a mean P–F bond length of 1.56 Å, but the fluorine atoms appear to show high thermal activity, possibly as a result of partial disorder. On the final electron-density difference maps there were two peaks *ca.* 3 Å apart, suggesting the incorporation into the crystals of molecules of solvent $CH_2Cl_2$. The peak heights, however, showed clearly that each site was only partially occupied (*ca.* 50%) and in view of the poor quality of the intensity data it was decided not to attempt least-squares refinement of the atomic positional- and population-parameters for the solvent molecule. It is of interest that the crystals retained their shape and colour over a period of many months, when stored in the absence of sunlight, but then gave even weaker diffraction intensities.

TABLE 3

Bond lengths and interbond angles with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| (*a*) Distances (Å) | | | |
| Fe–C(1) | 1.79(4) | C(8)–O(8) | 1.26(4) |
| Fe–C(2) | 1.82(6) | Ag–O(8)′ | 2.27(2) |
| Fe–C(3) | 1.85(4) | Ag–O(8) | 2.65(8) |
| C(1)–O(1) | 1.16(4) | Ag–O(9) | 2.67(5) |
| C(2)–O(2) | 1.12(5) | P–F(1) | 1.58(4) |
| C(3)–O(3) | 1.11(4) | P–F(2) | 1.52(4) |
| Fe–C(4) | 2.16(6) | P–F(3) | 1.62(5) |
| Fe–C(5) | 2.11(7) | P–F(4) | 1.55(5) |
| Fe–C(6) | 2.06(3) | P–F(5) | 1.56(4) |
| Fe–C(7) | 2.13(5) | P–F(6) | 1.55(4) |
| Fe–C(8) | 2.31(4) | C(4)–C(41) | 1.48(5) |
| C(4)–C(5) | 1.41(4) | C(5)–C(51) | 1.50(3) |
| C(5)–C(6) | 1.41(5) | C(6)–C(61) | 1.55(4) |
| C(6)–C(7) | 1.45(4) | C(7)–C(71) | 1.49(4) |
| C(7)–C(8) | 1.47(5) | | |
| C(8)–C(4) | 1.47(3) | Mean C–C(phenyl) | 1.38(4) |
| (*b*) Angles (°) | | | |
| C(1)–Fe–C(2) | 93.8(12) | Ag–O(8)–Ag′ | 105.9(6) |
| C(1)–Fe–C(3) | 92.6(1) | F(1)–P–F(2) | 89.7(14) |
| C(2)–Fe–C(3) | 94.3(9) | F(1)–P–F(3) | 89.0(11) |
| Fe–C(1)–O(1) | 179.6(22) | F(1)–P–F(4) | 90.3(12) |
| Fe–C(2)–O(2) | 173.0(27) | F(1)–P–F(5) | 92.1(14) |
| Fe–C(3)–O(3) | 169.5(20) | F(1)–P–F(6) | 177.9(14) |
| C(4)–C(5)–C(6) | 108.1(17) | F(3)–P–F(4) | 178.9(16) |
| C(5)–C(6)–C(7) | 110.3(16) | F(3)–P–F(6) | 86.1(13) |
| C(6)–C(7)–C(8) | 105.7(14) | F(4)–P–F(5) | 93.1(14) |
| C(7)–C(8)–C(4) | 105.9(16) | F(5)–P–F(6) | 89.5(14) |
| C(7)–C(8)–O(8) | 126.7(15) | C(4)–C(5)–C(51) | 126.9(15) |
| C(8)–C(4)–C(41) | 122.4(18) | C(5)–C(6)–C(61) | 126.3(16) |
| O(8)–Ag–O(8)′ | 74.1(5) | C(6)–C(7)–C(71) | 128.9(16) |
| (*c*) Some close intra- and inter-molecular contacts (Å) | | | |
| Ag′–C(42) | 2.46(5) | Ag–C(72) | 2.85(6) |
| Ag′–C(41) | 3.03(7) | Ag–C(71) | 3.31(8) |
| Ag′–C(43) | 2.79(6) | Ag–C(73) | 3.38(10) |
| O(3) · · · O(9)′ | 3.19(10) | O(2) · · · O(2)′ | 3.01(5) |
| O(2) · · · F(2)″ | 2.06(7) | O(1) · · · F(4)″ | 3.25(8) |

One prime indicates an inversion, two primes a diagonal glide.

The reactions of $Ag[PF_6]$ with [1; M = Fe, L = $PPh_3$ or $P(OMe)_3$; M = Ru, L = CO] and with $[Rh(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5Ph_4O)]$ (2) give $[\{M(CO)_2L(\eta^5\text{-}C_5Ph_4OAg)\}_2][PF_6]_2$ [3; M = Fe, L = $PPh_3$ or $P(OMe)_3$; M = Ru, L = CO] and $[\{Rh(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Ph_4OAg)\}_2][PF_6]_2$ (4) respectively, analogues of (3; M = Fe, L = CO).

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* The co-ordinated water, in crystals of (3; M = Fe, L = CO), presumably results from the use of a damp sample of $Ag[PF_6]$ although corroborative microanalytical or $^1H$ n.m.r. spectral evidence for the presence of this ligand in vacuum-dried samples of the complex was not obtained.

The tricarbonyl-ruthenium and -iron complexes have similar i.r. carbonyl spectra (Table 1) and the $^{13}C$ n.m.r. spectrum of (4) {156.6 ($C^1$); 132.9, 131.8, 131.3, 130.9, 129.5, 128.9, 128.7 ($C_6H_5$); 98.8 [$C^2$, d, $J(^{103}Rh-^{13}C) = 11$ Hz]; 89.7 [$C_5H_5$, d, $J(^{103}Rh-^{13}C) = 9$ Hz]; 88.6 [$C^3$, d, $J(^{103}Rh-^{13}C) = 9$ Hz]; in $(CD_3)_2CO$, p.p.m. downfield of tetramethylsilane, numbering as in Figure 3} is closely similar to that of {3; M = Fe, L = CO} {209.3 (CO), 169.9 ($C^1$), 132.8, 131.5, 130.7, 129.7, 129.1, 128.8 ($C_6H_5$); 105.3 ($C^3$); 83.4 ($C^2$); in $(CD_3)_2CO$, p.p.m. downfield of $SiMe_4$, $[Cr(acac)_3]$ added}.

Adduct formation between ketonic oxygen and silver(I) is not confined to co-ordinated cyclopentadienones. The addition of $Ag[BF_4]$ to $[Cr(CO)_3(\eta^6\text{-tropone})]$ [$\bar{\nu}(CO)$ $(CH_2Cl_2)$ = 2 009, 1 957, and 1 933 cm$^{-1}$] in toluene or $CH_2Cl_2$ immediately produces an orange precipitate which shows metal carbonyl absorptions at 2 030, 1 990, and 1 950 cm$^{-1}$ (Nujol). In addition, a broad absorption between 1 500 and 1 550 cm$^{-1}$ may be tentatively assigned to the ketonic carbonyl stretching frequency which is shifted, relative to that of the neutral tricarbonyl, by 50—100 cm$^{-1}$ to lower energy. The changes in the carbonyl absorptions, the absence of silver deposition during the reaction, and the presence of the $[BF_4]^-$ anion [$\bar{\nu}(BF)$ (Nujol) = 1 045 cm$^{-1}$] suggest the product formed from $[Cr(CO)_3(\eta^6\text{-tropone})]$ and $Ag[BF_4]$ to be $[\{Cr(CO)_3(\eta^7\text{-}C_7H_6OAg)\}_2][BF_4]_2$, similar to (3) and (4). The adduct $[\{Cr(CO)_3(\eta^7\text{-}C_7H_6OAg)\}_2][BF_4]_2$ slowly dissolves in $CH_2Cl_2$, over a period of 48 h, and silver metal is deposited. Filtration, and addition of n-hexane to the orange filtrate, affords $[Cr(CO)_3\{\eta^7\text{-}C_7H_6(OH)\}][BF_4]$ [7] [i.r.: $\bar{\nu}(CO)$ $(CH_2Cl_2)$ = 2 049, 2 005, and 1 993 cm$^{-1}$; $\bar{\nu}(OH)$ (Nujol) = 3 340 cm$^{-1}$; $^1H$ n.m.r. {$(CD_3)_2CO$}, $\tau$ 3.71 ($H^1$, d, 10 Hz), 3.36 ($H^2$, m), 2.94 ($H^3$, m), 1.90 (O*H*, br, s), numbering as in Figure 4]. The mechanism by which the hydroxytropylium complex is formed from the silver(I) adduct is not clear. It has been shown [8] that $[Cr(CO)_3(\eta^6\text{-tropone})]$ undergoes one-electron oxidation at 0.95 V (*vs.* a calomel electrode, 1 mol dm$^{-3}$ in LiCl), and loss of silver metal from $[\{Cr(CO)_3(\eta^7\text{-}C_7H_6OAg)\}_2]^{2+}$, to give the radical cation $[Cr(CO)_3(C_7H_6O)]^+$, followed by hydrogen radical addition at the oxygen atom, is possible. A similar mechanism is involved in the formation of $[Fe(CO)_3(\eta^5\text{-}C_7H_9)]^+$ from $[Fe(CO)_3(\eta^4\text{-cht})]$ and silver(I) ions [Scheme 1(i)].

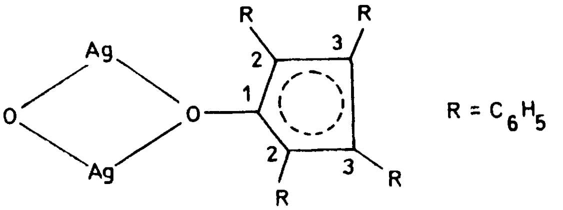

FIGURE 3

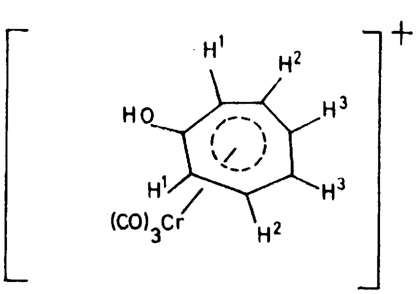

FIGURE 4

Although [3; M = Fe, L = CO, $PPh_3$, or $P(OMe)_3$] is stable in $CH_2Cl_2$ solution to loss of silver metal, it reacts with an excess of $Ag^I$ ions to give two further, uncharacterised products. For example, monitoring the i.r. carbonyl spectrum of a mixture of (3; M = Fe, L = $PPh_3$) and $Ag[PF_6]$ in $CH_2Cl_2$ shows the growth of two bands at 2 014 and 1 969 cm$^{-1}$ followed by their replacement with bands at 2 033 and 1 991 cm$^{-1}$; during the reaction silver metal is deposited. The absorptions at 2 033 and 1 991 cm$^{-1}$ are identical to those of $[Fe(CO)_2(PPh_3)\{\eta^5\text{-}C_5Ph_4(OH)\}][BF_4]$, which may be prepared by the direct protonation of (1; M = Fe, L = $PPh_3$) by $HBF_4$ in thf (tetrahydrofuran). If the hydroxycyclopentadienyl complex is the final product of the reaction between (1; M = Fe, L = $PPh_3$) and $Ag^I$ in $CH_2Cl_2$ it is unlikely to be formed *via* the radical $[Fe(CO)_2(PPh_3)(C_5Ph_4O)]^+$. The complexes [1; L = CO, $PPh_3$, or $P(OMe)_3$] are not oxidised at the platinum electrode in $CH_2Cl_2$ below a potential of 1.5 V (relative to a calomel electrode, 1 mol dm$^{-3}$ in LiCl).

With halide ions, $X^-$, (3) and (4) behave as simple silver(I) salts, giving AgX and (1) and (2) respectively. Similar displacement of the silver(I) ion occurs with $PPh_3$ and (3; M = Fe, L = CO), but no reaction occurs with methyl iodide in $CH_2Cl_2$ at room temperature even after 24 h. With halogens, $X_2$, however, [3; M = Fe, L = CO, $PPh_3$, or $P(OMe)_3$] react to give $[FeX(CO)_2L(\eta^4\text{-}C_5Ph_4O)][PF_6]$ (5). For example, $Br_2$ and (3; M = Fe, L = $PPh_3$) in $CH_2Cl_2$ give AgBr and an orange solution from which [5; X = Br, L = $PPh_3$; i.r.: $\bar{\nu}(CO)$ $(CH_2Cl_2)$ = 2 033 and 1 993 cm$^{-1}$, $\nu(PF)$ (Nujol) = 835 cm$^{-1}$] can be isolated as an orange solid. While bromination of (3) most likely occurs at iron, and (5) is therefore formulated as an $\eta^4$-cyclopentadienone complex, the ketonic carbonyl i.r. absorption is not apparent in the region 1 490—1 700 cm$^{-1}$; the assignment of a band at 1 431 cm$^{-1}$ (hexachlorobutadiene mull) to the ketonic CO stretching vibration is questionable.

The halogenation reactions between $Br_2$ or $I_2$ and (3; M = Fe, L = CO) afford less stable products. The iodo-complex [5; X = I, L = CO; i.r.: $\nu(CO)$ $(CH_2Cl_2)$ = 2 099 and 2 043 cm$^{-1}$] is formed on adding $I_2$ to (3; M = Fe, L = CO) but attempts to isolate the product, once formed, led to dissociation and formation of (1; M = Fe, L = CO). The ready dissociation of (5; X = Br or I, L = CO) is reflected in the absence of a direct reaction between (1; M = Fe, L = CO) and $Br_2$ or $I_2$ in $CH_2Cl_2$, although similar reactions with the more basic, substituted complexes [1; M = Fe, L = $PPh_3$ or $P(OMe)_3$] readily result in the formation of (5).

*The Silver*(I) *Ion as a One-electron Oxidant in Organometallic Chemistry*.—The silver(I) ion is a useful one-electron oxidant in organometallic chemistry, for example, giving radical cations from both $\eta^4$- and $\eta^6$-polyolefin complexes (Scheme 1).[2–5] However, it also undergoes a wide variety of other reactions with organo-transition-metal substrates and must be regarded as a ' non-innocent ' oxidant.

Firstly, silver(I) salts have been widely used to form cationic organometallics *via* halide abstraction from metal–halogen [9] or carbon–halogen [10] bonds. Secondly, direct addition of $Ag^+$ to a metal centre, to form a silver–metal bond, can occur [11,12] [Scheme 2(i)—(iii)]. Thirdly, silver(I) ions will bond to the oxygen (as documented above) or to the sulphur atoms of co-ordinated ligands [13,14] [Scheme 2(iv)—(v)]. It should also be noted that there is an extensive organosilver(I) chemistry [15] involving $\eta^1$- or $\eta^2$-bonding to aryls, acetylides, alkenes, alkynes, and arenes, and silver(I) ions can also be used as catalysts for ring-opening reactions of organic substrates.[16]

(i) $Ag^+ + 2[Mo(CO)_3(cp)]^- \longrightarrow [Ag\{Mo(CO)_3(cp)\}_2]^-$ (ref. 11)

(ii) $Ag^+ + 2[Rh(CO)(PPh_3)(cp)] \longrightarrow [Ag\{Rh(CO)(PPh_3)(cp)\}_2]^+$ (ref. 12)

(iii) $Ag^+ + 2[Mn(CN)(PPh_3)(NO)(cp)] \longrightarrow [Ag\{Mn(CN)(PPh_3)(NO)(cp)\}_2]^+$ (ref. 12)

(iv) $Ag^+ + [W(CO)(CS)(dppe)_2] \longrightarrow [Ag\{W(CO)(dppe)_2(CS)\}_2]^+$ (ref. 13)

(v) $3Ag^+ + 2[Fe_4(cp)_4S_6] \longrightarrow [Ag\{Fe_4(cp)_4S_6\}_2]^{3+} + 2\ Ag$ (ref. 14)

SCHEME 2 cp = $\eta^5$-$C_5H_5$, dppe = 1,2-bis(diphenylphosphino)-ethane

The redox potential of the $Ag^+$–Ag couple is not readily determined in non-aqueous solvents, such as $CH_2Cl_2$, toluene, MeCN, or thf, commonly used in organometallic chemistry. It is clear, however, that the couple will be affected by the solvent in that complexation by toluene, MeCN, or thf would be expected to lower the potential relative to that in $CH_2Cl_2$ (in which $Ag[BF_4]$ or $Ag[PF_6]$, for example, are insoluble). In order to estimate the magnitude of the $Ag^+$–Ag redox potential in various solvents the reactions between $Ag[BF_4]$ and $N(C_6H_4Br\text{-}p)_3$ ($E_p$ = 1.16 V), $NPh_3$ ($E_p$ = 0.88 V), and $[Fe(\eta^5\text{-}C_5H_5)_2]$ ($E_p$ = 0.38 V), in $CH_2Cl_2$, toluene, MeCN, and thf were carried out. Ferrocene is oxidised to the deep blue ferricinium ion in each of the solvents, whereas the amines were only oxidised to the ammonio-cations $[NR_3]^+$ (R = Ph or $C_6H_4Br$-*p*) by $Ag[BF_4]$ suspended in $CH_2Cl_2$. Thus, $Ag^+$ may be regarded as a strong oxidant in $CH_2Cl_2$ but far weaker when dissolved in toluene, MeCN, or thf.

The factors which govern whether oxidation or another reaction will occur between $Ag^+$ and a transition-metal compound * are obviously complex. Perhaps naively one might expect the dominant factor to be the relative redox potentials of the reactants, bearing in mind the solvent dependence of the $Ag^+$–Ag couple discussed above. However, even though the redox potentials are favourable, $[Rh(CO)(PPh_3)(\eta^5\text{-}C_5H_5)]$ [irreversible one-electron oxidation at 0.38 V (cyclic voltammetric scan rate 200 mV $s^{-1}$)] and $[Mn(CN)(NO)(PPh_3)(\eta^5\text{-}C_5H_5)]$ (reversible one-electron oxidation at 0.82 V) each form metal–metal bonded adducts with $Ag[PF_6]$ in $CH_2Cl_2$ [Scheme 2(ii)—(iii)]. It is necessary, therefore to realise that the chemical behaviour of $Ag^I$ ions towards organotransition-metal compounds will be strongly solvent dependent, that in $CH_2Cl_2$ the ion is potentially a strong one-electron oxidant, but that even if the redox potential is favourable, oxidation may not be preferred to one of a variety of other reaction pathways.

## EXPERIMENTAL

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. The complexes $[M(CO)_2L(\eta^4\text{-}C_5Ph_4O)]$ (M = Fe, L = CO or $PPh_3$; [17] M = Ru,[18] L = CO), $[Rh(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5Ph_4O)]$,[19] and $[Cr(CO)_3(\eta^6\text{-}C_7H_6O)]$ [7] were prepared by published methods. Unless stated the complexes described are air-stable in the solid state, and dissolve in polar solvents such as $CH_2Cl_2$ or acetone to give moderately air-sensitive solutions. Nitrosonium and silver(I) salts were purchased from Ozark Mahoning Co., Tulsa, Oklahoma.

Infrared spectra were recorded on Perkin-Elmer PE257 or PE457 spectrometers and were calibrated against the absorption band of polystyrene at 1 601 $cm^{-1}$. Hydrogen-1 and $^{13}C$ n.m.r. spectra were recorded on JEOL PS 100 and PFT 100 instruments respectively. Microanalyses were by the staff of the Microanalytical Laboratory of the School of Chemistry, University of Bristol.

*Dicarbonyl($\eta^4$-tetraphenylcyclopentadienone)(trimethyl phosphite)iron*, $[Fe(CO)_2\{P(OMe)_3\}(\eta^4\text{-}C_5Ph_4O)]$.—A solution of $[Fe(CO)_3(\eta^4\text{-}C_5Ph_4O)]$ (2.0 g, 3.2 mmol) and $P(OMe)_3$ (0.4 $cm^3$, 3.4 mmol) in xylene (100 $cm^3$) was heated under reflux for 24 h. The yellow solution was then evaporated to dryness, and the residue recrystallised from $CH_2Cl_2$–n-hexane to give the product as a yellow solid, yield 2.0 g (84%). The *complex* is partially soluble in n-hexane.

*The Preparation of* $[\{Fe(CO)_3(\eta^5\text{-}C_5Ph_4OAg)\}_2][PF_6]_2$.—To a stirred solution of $[Fe(CO)_3(\eta^4\text{-}C_5Ph_4O)]$ (0.30 g, 0.57 mmol) in toluene (40 $cm^3$) was added $Ag[PF_6]$ (0.15 g, 0.59 mmol). After 1 h the yellow precipitate was removed by filtration and recrystallised from $CH_2Cl_2$–n-hexane at 0 °C to give the *product* as yellow crystals, yield 0.35 g (79%). The solid complex slowly darkens in bright sunlight. Yellow $[\{Fe(CO)_2L(\eta^5\text{-}C_5Ph_4OAg)\}_2][PF_6]_2$ [L = $PPh_3$ (36%) or $P(OMe)_3$ (26%)], white $[\{Ru(CO)_3(\eta^5\text{-}C_5Ph_4OAg)\}_2][PF_6]_2$ (73%), and yellow $[\{Rh(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Ph_4OAg)\}_2][PF_6]_2$ (72%) were prepared similarly.

*Dicarbonyl($\eta^5$-hydroxytetraphenylcyclopentadienyl)(trimethyl phosphite)iron Tetrafluoroborate–Dichloromethane* (2/1), $[Fe(CO)_2\{P(OMe)_3\}\{\eta^5\text{-}C_5Ph_4(OH)\}][BF_4]\cdot0.5CH_2Cl_2$.—An aqueous solution of $HBF_4$ (0.5 $cm^3$, 40% w/w) was added to a stirred solution of $[Fe(CO)_2\{P(OMe)_3\}(\eta^4\text{-}C_5Ph_4O)]$ in thf (30 $cm^3$). After 1 h the yellow solution was evaporated to dryness and the residue recrystallised from $CH_2Cl_2$–n-hexane to give the *product* as pale yellow crystals, yield 0.2 g (88%) [Found: C, 54.7; H, 4.4. $C_{34.5}$-

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* The reactions shown in Scheme 2 all involve metal complexes which have been shown by electrochemical methods to undergo one-electron oxidation.

$H_{31}BClF_4FeO_6P$ requires C, 55.2; H, 4.1%. $\tilde{\nu}$(CO) = 2 041 and 1 998 cm$^{-1}$ ($CH_2Cl_2$), $\tilde{\nu}$(BF) = 1 045 cm$^{-1}$ (Nujol). $^1$H n.m.r. ($CDCl_3$), $\tau$ = 4.64 (1, s, $CH_2Cl_2$), 4.38 {9, d, $J$(PH) = 11 Hz, $P(OMe)_3$}, 3.56 (1, br, s, O*H*), 2.60 (20, m, $C_6H_5$)].

*Bromo(dicarbonyl)($\eta^4$-tetraphenylcyclopentadienone)(triphenylphosphine)iron Hexafluorophosphate*, $[FeBr(CO)_2(PPh_3)(\eta^4\text{-}C_5Ph_4O)][PF_6]$.—A dilute solution of bromine in $CH_2Cl_2$ was added dropwise to $[\{Fe(CO)_2(PPh_3)(\eta^5\text{-}C_5Ph_4OAg)\}_2][PF_6]_2$ (0.10 g, 0.05 mmol) in $CH_2Cl_2$ (40 cm$^3$) until the carbonyl absorptions of the silver complex were absent from the i.r. spectrum. The pale yellow precipitate of AgBr was then removed by filtration, and the orange filtrate reduced in volume. Addition of n-hexane gave the *product* as an orange solid, yield 0.05 g (51%) [Found: C, 60.1; H, 4.0. $C_{49}H_{35}BrF_6FeO_3P_2$ requires C, 59.8; H, 3.6%].

*The Reaction of* $[Cr(CO)_3(\eta^6\text{-}C_7H_6O)]$ *with* $Ag[BF_4]$.—To a stirred solution of $[Cr(CO)_3(\eta^6\text{-}C_7H_6O)]$ (0.20 g, 0.83 mmol) in $CH_2Cl_2$ (20 cm$^3$) was added $Ag[BF_4]$ (0.16 g, 0.83 mmol). An orange precipitate was immediately formed which slowly darkened as silver metal was deposited. After two days the resulting orange solution was filtered, and hexane added to precipitate $[Cr(CO)_3\{\eta^7\text{-}C_7H_6(OH)\}][BF_4]$ as an orange solid, yield 0.10 g {37% based on $[Cr(CO)_3(\eta^6\text{-}C_7H_6O)]$}.

*Structure Determination.*—Crystals of (3; M = Fe, L = CO) grow as pale yellow prisms from $CH_2Cl_2$-n-hexane. A suitable crystal of dimensions 0.20 × 0.35 × 0.18 mm was mounted on a glass fibre on a Syntex $P2_1$ four-circle diffractometer; diffracted intensities were recorded at room temperature for $2\theta \leqslant 60°$ according to methods described earlier.[20] The crystals darken on exposure to light and decompose slowly on exposure to *X*-rays. The intensities were therefore collected only to $2\theta = 45°$, initially, and for the region $2\theta$ = 45—60° the scan speed was increased and the very weak reflections were not measured. During the total exposure time of *ca.* 38 h, 4 677 intensities were recorded, of which 2 847 had $I \geqslant \sigma(I)$ and only these were used in the solution of the structure. By the end of data collection the crystal had decayed some 26%; a correction for this decay was applied, as also for Lorentz and polarisation effects, but in view of the poor quality of the data and the relatively small magnitude of the linear absorption coefficient, no correction for *X*-ray absorption was made [$\mu$(Mo-$K_\alpha$) = 10.6 cm$^{-1}$].

*Crystal Data.*—$C_{32}H_{22}AgF_6FePO_5\cdot xCH_2Cl_2$ with *x ca.* 0.5, $M$ = 794.7 (excluding solvent), Monoclinic, $a$ = 13.293(7), $b$ = 14.128(6), $c$ = 19.805(14) Å, $\beta$ = 105.75(5)° at 297 K, $U$ = 3 579(3) Å$^3$, $D_m$ = 1.54 g cm$^{-3}$, $Z$ = 4, $D_c$ = 1.56 g cm$^{-3}$, $F(000)$ = 1 484 (excluding solvent). Space group $P2_1/n$, Mo-$K_\alpha$ *X*-radiation (graphite monochromator), $\lambda$ = 0.710 69 Å, $\mu$(Mo-$K_\alpha$) = 10.6 cm$^{-1}$.

*Solution and Refinement of the Structure.*—A Patterson synthesis was solved for the positions of the silver and iron atoms, and an electron-density difference map phased on these metal-atom positions revealed the cyclopentadienone ring and, vaguely, the four phenyl groups. Subsequent electron-density difference maps gave reasonable definition of all atoms except hydrogen. The H atoms were not evident on the difference maps and so were incorporated at calculated positions (C–H = 1.0 Å) but were not refined. An extra peak on the electron-density difference map within the co-ordination sphere of the silver atom was identified as the oxygen atom of a water molecule, and was incorporated into block refinement which converged at $R$ 0.115 ($R'$ 0.114). In the final cycles weights were used according to the scheme $w^{-1} = xy$ with $x = F_o/a$ when $F_o > a$, $x = 1$ when $F_o \leqslant a$; $y = b/\sin\theta$ when $\sin\theta < b$, $y = 1$ when $\sin\theta \geqslant b$; with $a$ = 80 and $b$ = 0.31. Anisotropic thermal parameters were allowed for the metal atoms, carbonyl ligands, and hexafluorophosphate ion; the high values for the F atoms are suggestive of possible disorder. As mentioned earlier, two residual peaks on the final electron-density difference map showed fractional incorporation of solvent molecules into the cavities of the structure [approximate atom co-ordinates: Cl(1) 0.56, 0.32, 0.13; Cl(2) 0.67, 0.41, 0.02] but the quality of the data did not permit refinement. Atomic positional parameters are in Table 2, bond lengths and angles and a few significant intermolecular contacts in Table 3. All computational work was carried out at the University of London Computer Centre with the '*X*-Ray System' of programs.[21] Observed and calculated structure factors together with all thermal parameters are listed in Supplementary Publication No. SUP 22788 (15 pp.).*

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

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