Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 15.[1] Synthesis, Electrochemistry, and Reactivity of the Radical Cations $[Co(CO)_{2-n}L_n(\eta\text{-}C_5R_5)]^+$ (n = 1 or 2, L = phosphine, R = H or Me)

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Cyclic voltammetric studies show that the complexes $[Co(CO)L(\eta\text{-}C_5H_5)]$ [1; L = $P(C_6H_{11})_3$ or PPh_3] undergo one-electron oxidation to the radical cations $[Co(CO)L(\eta\text{-}C_5H_5)]^+$. Chemical oxidation of (1) with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ gives $[Co(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ (2) and the bis(phosphine) salt $[Co(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (3). The latter is also prepared directly from $[Co(CO)_2(\eta\text{-}C_5H_5)]$ and PPh_3 in the presence of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$, but $[Co(CO)_2(\eta\text{-}C_5Me_5)]$ gives $[Co(CO)(PPh_3)(\eta\text{-}C_5Me_5)][PF_6]$ (4). Complex (2) undergoes substitution reactions to give paramagnetic $[CoL\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ (L = PPh_3 or pyridine) and diamagnetic $[Co\{P(OMe)_3\}_3(\eta\text{-}C_5H_5)][PF_6]_2$. With halogens, X_2, with $Me_2NC(S)SSC(S)NMe_2$, and with NO gas, (2)—(4) undergo radical-coupling reactions to give $[CoX(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ (X = Br or I), $[CoL(S_2CNMe_2)(\eta\text{-}C_5H_5)][PF_6]$ [L = $P(C_6H_{11})_3$ or PPh_3], and $[Co(NO)(PPh_3)(\eta\text{-}C_5R_5)][PF_6]$ (R = H or Me) respectively. With *ortho*-quinones, (2) gives $[Co(O\text{–}O)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ (5; O–O = *o*-chloranil, 1,2-naphthoquinone, or phenanthrenequinone) the e.s.r. spectra of which suggest the unpaired electron to be localised mainly on the quinone ligand.

We have recently shown [2] that the one-electron oxidation of $[Fe(CO)_3(PPh_3)_2]$ gives the isolable radical cation $[Fe(CO)_3(PPh_3)_2]^+$, a precursor to otherwise inaccessible iron(II) carbonyl complexes.[3] The cation is also formed in the first step of the oxidative-elimination reaction between $[Fe(CO)_3(PPh_3)_2]$ and iodine. It then reacts with I^- to give a paramagnetic adduct whose identity is uncertain but may be formulated either as the 19-electron metal halide $[FeI(CO)_3(PPh_3)_2]$ [2] or, perhaps more likely, the 17-electron iodo-acyl $[Fe(COI)(CO)_2(PPh_3)_2]$.[3] Clearly, e.s.r. spectroscopic studies of analogous systems containing a central metal atom with non-zero nuclear spin ($I > 0$) might lead to a direct distinction between the 19- and 17-electron configurations. We have, therefore, studied the one-electron oxidation reactions of $[M(CO)L(\eta\text{-}C_5H_5)]$ (1) which are known to undergo oxidative-elimination reactions with halogens to give $[MI_2L(\eta\text{-}C_5H_5)]$ (M = Co [4] or Rh,[5] L = P-donor). We,[6] and others,[7] have described preliminary findings on the rhodium complexes. We now give details of the synthesis, electrochemistry, and reactivity of the cobalt radical cations $[Co(CO)_{2-n}L_n(\eta\text{-}C_5R_5)]^+$ [n = 1 or 2, L = PPh_3 or $P(C_6H_{11})_3$, R = H or Me]. During this work complementary synthetic studies were carried out by McKinney.[8]

Results and Discussion

Chemical and Electrochemical Oxidation of $[Co(CO)_{2-n}L_n(\eta\text{-}C_5R_5)]$ (1).—Cyclic voltammetry shows that $[Co(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)]$ undergoes reversible one-electron oxidation in CH_2Cl_2 at a platinum electrode. As with the other electrochemical processes studied in this work, electron transfer was diffusion controlled with the anodic current function ($i_{pa}/v^{\frac{1}{2}}$) independent of scan rate (v) over the range 200—5 000 mV s^{-1}. The ratio of cathodic to anodic currents was unity over the same scan range, establishing the chemical reversibility of the redox couple. The peak separation at v = 50 mV s^{-1} was 65 mV, very close to that measured for the oxidation of ferrocene under the same conditions. Hence, the one-electron oxidation seems reversible in both the chemical and electrochemical sense.

Table 1. Cyclic voltammetric [a] data for $[Co(CO)_{2-n}L_n(\eta\text{-}C_5H_5)]^z$

n	L	Z	$E^\ominus$/V [b]
1	$P(C_6H_{11})_3$	0	−0.04 [c]
1	$P(C_6H_{11})_3$	+1	−0.04 [c]
			−0.10 [d]
1	PPh_3	0	0.13 [c]
			0.21 [d]
2	PPh_3	+1	−0.71 [c]
			−0.55 [d]

[a] At a platinum electrode. [b] *vs.* An aqueous saturated calomel electrode; $E^\ominus$ for $[Fe(\eta\text{-}C_5H_5)_2]$ = 0.43 V. [c] In CH_2Cl_2. [d] In thf.

The other compounds studied were similarly well behaved except for $[Co(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ which displayed a tendency to deposit a film on the platinum electrode during oxidation in CH_2Cl_2. For this compound the electrode had to be cleaned after every scan; the oxidation potential, $E^\ominus$, was estimated at 0.13 V. In tetrahydrofuran (thf) the voltammetry was cleaner ($E^\ominus$ = 0.21 V) but the oxidation was not as chemically reversible having a ratio i_c/i_a = 0.73 at v = 32 mV s^{-1}. In addition there was a second, irreversible wave, with a peak potential of 0.75 V, which was not present in CH_2Cl_2. Because the new wave is peculiar to thf we believe it to be due to the oxidation of the solvated radical cation $[Co(CO)(PPh_3)(thf)(\eta\text{-}C_5H_5)]^+$ to the diamagnetic dication. In this context we will refer later to the further oxidation of $[CoL_2(\eta\text{-}C_5H_5)]^+$ by silver(I) ions in thf.

The oxidation potentials for $[Co(CO)L(\eta\text{-}C_5H_5)]$ [1; L = $P(C_6H_{11})_3$ or PPh_3], summarised in Table 1, show the expected dependence of $E^\ominus$ on the donor ability of L but also, by comparison with $[Fe(CO)_3L_2]$,[2] that the cobalt complexes are far more readily oxidised.

Chemical oxidation might be expected to be effected by

Table 2. Infrared and analytical data for cyclopentadienylcobalt derivatives

Compound	Colour	$\tilde{\nu}$(CO) [a]/cm^{-1}	Analysis [b] (%) C	H	N
$[Co(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$	Green	2 045	49.9 (49.9)	6.5 (6.6)	—
$[Co(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$	Yellow-brown	—	61.5 (62.0)	4.3 (4.4)	—
$[Co(CO)(PPh_3)(\eta\text{-}C_5Me_5)][PF_6]$	Red	2 033	54.8 (55.3)	4.7 (4.8)	—
$[Co\{P(C_6H_{11})_3\}(PPh_3)(\eta\text{-}C_5H_5)][PF_6]$	Yellow-brown	—	56.8 (56.4)	5.7 (6.1) [c]	—
$[Co(NC_5H_5)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$	Pink	—	52.8 (53.5)	6.8 (6.8)	3.0 (2.2)
$[Co\{P(OMe)_3\}_3(\eta\text{-}C_5H_5)][PF_6]_2$	Pale yellow	—	21.5 (21.4)	4.3 (4.1)	—
$[CoBr(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$	Yellow-green	2 085	43.3 (43.8)	5.9 (5.8)	—
$[CoI(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$	Olive-green	2 077	40.7 (40.9)	5.4 (5.4)	—
$[Co\{P(C_6H_{11})_3\}(S_2CNMe_2)(\eta\text{-}C_5H_5)][PF_6]$	Brown-purple	—	44.6 (44.8)	6.5 (6.6)	2.2 (2.1)
$[Co(PPh_3)(S_2CNMe_2)(\eta\text{-}C_5H_5)][PF_6]$	Brown-purple	—	47.2 (47.8)	4.1 (4.0)	2.3 (2.2)
$[Co(NO)(PPh_3)(\eta\text{-}C_5Me_5)][PF_6]$	Brown	1 817 [d]	50.4 (50.8)	5.0 (4.6)	2.0 (2.1) [e]
$[Co(O_2C_6Cl_4)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ [f]	Blue	—	44.7 (44.7)	5.8 (5.2)	—
$[Co(O_2C_{14}H_8)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ [g]	Brown	—	60.6 (61.2)	7.4 (7.1)	—

[a] In CH_2Cl_2. [b] Calculated values in parentheses. [c] Including 1.0 CH_2Cl_2. [d] $\tilde{\nu}$(NO). [e] Including 0.5 CH_2Cl_2. [f] $O_2C_6Cl_4$ = *o*-chloranil, including 0.5 OEt_2. [g] $O_2C_{14}H_8$ = phenanthrenequinone, including 1.0 hexane.

Table 3. E.s.r. data for paramagnetic cyclopentadienylcobalt derivatives

Compound	$g_{av.}$	A_{iso} (^{59}Co) [a]/G
$[Co(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$	2.134	—
$[Co(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$	2.167	—
$[Co(CO)(PPh_3)(\eta\text{-}C_5Me_5)][PF_6]$	2.118	—
$[Co\{P(C_6H_{11})_3\}(PPh_3)(\eta\text{-}C_5H_5)][PF_6]$	2.167	—
$[Co(NC_5H_5)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$	2.147	—
$[Co(O_2C_6Cl_4)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$	2.000	14.3
$[Co(O_2C_{14}H_8)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$	2.004	10.7
$[Co(O_2C_{10}H_6)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ [b]	1.997	11.5

[a] 1 G = 10^{-4} T. Identical values were obtained for A_{iso} (^{31}P). [b] $O_2C_{10}H_6$ = 1,2-naphthoquinone.

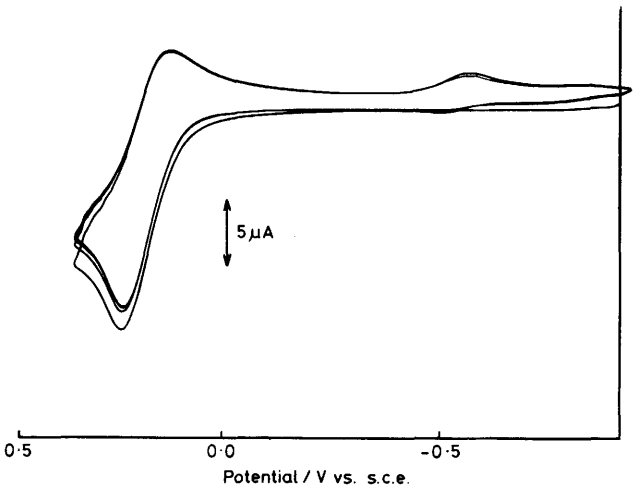


Figure 1. Multiple-scan cyclic voltammogram, at 264 mV s^{-1}, of $[Co(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ in the presence of PPh_3 in thf. Potentials are *vs.* the s.c.e., with 0.1 mol dm^{-3} $[NBu^n_4][PF_6]$ as base electrolyte

weak one-electron oxidants such as the ferricinium ion for which the reduction potential, $E^{\ominus}$, is 0.43 V in CH_2Cl_2. Accordingly, [1; L = $P(C_6H_{11})_3$] was treated with an equimolar quantity of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ in CH_2Cl_2 to give a green solution from which the radical cation $[Co(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)]^+$ (2) was isolated in good yield. The complex was readily characterised by elemental analysis and i.r. spectroscopy (Table 2) and by cyclic voltammetry which revealed a diffusion-controlled, reversible one-electron reduction in CH_2Cl_2 with $E^{\ominus}$ identical to that measured for the oxidation of [1; L = $P(C_6H_{11})_3$]. The e.s.r. spectrum (Table 3) verifies the paramagnetism of (2) but disappointingly the single broad line in CH_2Cl_2 shows coupling neither to the ^{59}Co ($I = \frac{7}{2}$) nor to the ^{31}P ($I = \frac{1}{2}$) nucleus.

By contrast, the one-electron oxidation of (1; L = PPh_3) with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ in thf gives yellow-brown crystals of the bis(phosphine) complex $[Co(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (3), yields of which are increased to 79% in the presence of equimolar quantities of PPh_3.

The carbonyl ligand of neutral $[Co(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ is not substituted by PPh_3 either thermally or by u.v. photolysis. However, the oxidation of (1; L = PPh_3) to $[Co(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ leads both to a weakening of the Co–CO bond and to an increase in the susceptibility of the metal towards attack by the nucleophilic phosphine ligand; substitution is therefore facilitated.

The formation of (3) from (1; L = PPh_3) and PPh_3, *via* $[Co(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$, can be monitored by multiple-scan cyclic voltammetry in thf (Figure 1). On the first scan, from −0.94 to 0.38 V, only the wave for the one-electron oxidation of (1; L = PPh_3) is detectable. On subsequent scans, however, a small, reversible wave is found at −0.55 V due to the couple $[Co(PPh_3)_2(\eta\text{-}C_5H_5)]^+$–$[Co(PPh_3)_2(\eta\text{-}C_5H_5)]$. Although $[Co(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ is insoluble in thf, precluding direct verification of the above, cyclic voltammetric studies in CH_2Cl_2 show a diffusion-controlled, reversible, one-electron reduction with $E^{\ominus} = -0.71$ V. A comparison of $E^{\ominus}$ values in CH_2Cl_2 and thf, for example for (1; L = PPh_3) and (2) (Table 1), shows that the reduction of (3) in thf might reasonably be expected to occur at −0.55 V.

The very negative potential for the reduction of (3) testifies to the ease with which $[Co(PPh_3)_2(\eta\text{-}C_5H_5)]$ undergoes one-electron oxidation. The $E^{\ominus}$ value is a measure of the 'electron-richness' of the neutral complex, and Werner and co-workers [9] have described many reactions in which $[CoL_2(\eta\text{-}C_5H_5)]$, formally a cobalt(I) complex, readily yields cobalt(III) derivatives. The redox potentials of $[CoL_2(\eta\text{-}C_5H_5)]$ (L = PMe_3, *etc.*) and of reagents such as halogens and alkyl halides are such that one-electron transfer reactions may well be implicated in this chemistry. It is known, for example, that $[Cr(\eta\text{-}C_6H_6)_2]$ ($E^{\ominus} = -0.83$ V) is oxidised by alkyl or aryl halides to $[Cr(\eta\text{-}C_6H_6)_2]^+$.[10]

$$[Co(CO)_2(\eta\text{-}C_5H_5)] + PPh_3 \rightleftharpoons [Co(CO)(PPh_3)(\eta\text{-}C_5H_5)] + CO \quad (i)$$

$$[Co(CO)(PPh_3)(\eta\text{-}C_5H_5)] \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Co(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+ \quad (ii)$$

$$[Co(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+ + PPh_3 \longrightarrow [Co(PPh_3)_2(\eta\text{-}C_5H_5)]^+ + CO \quad (iii)$$

Scheme 1

The oxidation potential for $[Co(CO)_2(\eta\text{-}C_5H_5)]$ cannot easily be determined experimentally in CH_2Cl_2. Nevertheless, $E^\ominus$ may be estimated at *ca.* 0.97 V assuming a linear relationship between n and $E^\ominus$ for $[Co(CO)_{2-n}(PPh_3)_n(\eta\text{-}C_5H_5)]$ (n = 0—2); such a relationship has been found previously for several series of complexes, including $[Mn(CO)_{6-n}(CNMe)_n]^+$ (n = 1—6) and $[Cr(CO)_{6-n}(CNMe)_n]$ (n = 1—3).[11]

No reaction occurs when $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ is added to $[Co(CO)_2(\eta\text{-}C_5H_5)]$ in CH_2Cl_2, as expected on the basis of $E^\ominus$ values. In the presence of PPh_3, however, rapid oxidation occurs at room temperature to give (3). Neither the ferricinium ion nor the dicarbonyl undergoes detectable reactions with PPh_3 at room temperature. The formation of (3) must, therefore, occur *via* the mechanism shown in Scheme 1. One-electron oxidation of $[Co(CO)(PPh_3)(\eta\text{-}C_5H_5)]$, present in low concentration, and subsequent carbonyl substitution of $[Co(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ to give (3) forces equilibrium (i) to the right.

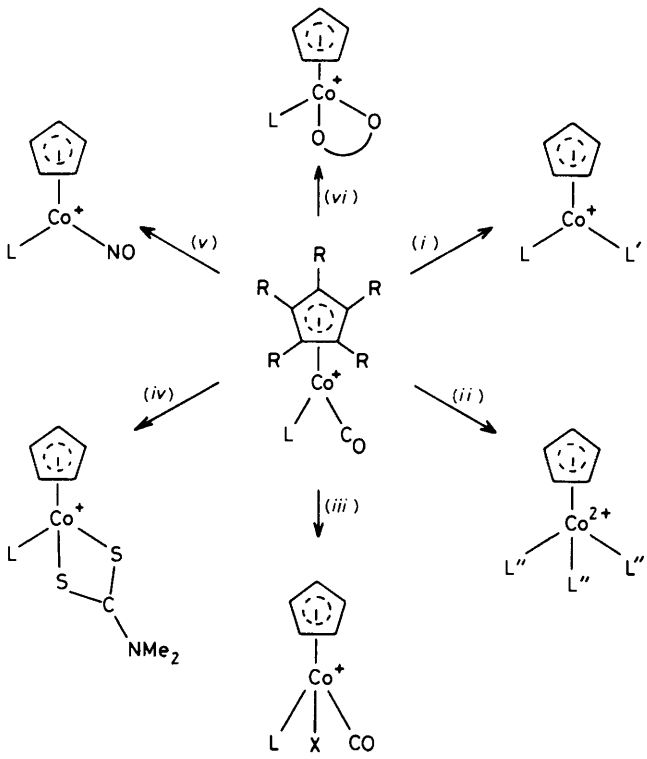
The oxidative-substitution reaction described above may also be applied to $[Co(CO)_2(\eta\text{-}C_5Me_5)]$. Although neither carbonyl ligand is substituted by PPh_3 in boiling hexane, good yields of red crystalline $[Co(CO)(PPh_3)(\eta\text{-}C_5Me_5)][PF_6]$ (4) (Table 2) are isolable from the rapid, room-temperature reaction between $[Co(CO)_2(\eta\text{-}C_5Me_5)]$, $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$, and an excess of PPh_3. The salt is air-sensitive and in CH_2Cl_2 rapidly gives an intense blue solution from which an uncharacterised, but diamagnetic, blue solid can be precipitated on hexane addition.

Other radical cations of the formula $[CoL_2(\eta\text{-}C_5H_5)]^+$ (L = phosphine or phosphite) have been independently prepared by McKinney,[8] either by the direct oxidation of $[CoL_2(\eta\text{-}C_5H_5)]$ with silver(I) salts in thf, or by the reaction between $[CoX_2L_2]$ (X = halide) and $Tl[C_5H_5]$ to give $[CoXL(\eta\text{-}C_5H_5)]$, followed by $Tl[BF_4]$ giving $[CoL_2(\eta\text{-}C_5H_5)][BF_4]$.

Reactions of $[Co(CO)_{2-n}L_n(\eta\text{-}C_5R_5)]^+$.—The lack of hyperfine coupling in the e.s.r. spectra of (2)—(4) has prevented studies designed to shed further light on the mechanism of the oxidative-addition reactions of (1) and $[Fe(CO)_3(PPh_3)_2]$. However, we have found alternative uses for the radical cations (2)—(4), in the synthesis of a range of cationic cyclopentadienylcobalt complexes. The substitution and radical-coupling reactions of (2) are summarised in Scheme 2.

Unlike $[Fe(CO)_3(PPh_3)_2]^+$,[3] the isoelectronic cobalt cation $[Co(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)]^+$ undergoes carbonyl-substitution reactions with Group 5 donor ligands. For example, PPh_3 gives the mixed phosphine derivative $[Co\{P(C_6H_{11})_3\}(PPh_3)(\eta\text{-}C_5H_5)]^+$ and pyridine gives the pink, paramagnetic salt $[Co(NC_5H_5)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ (Tables 2 and 3).

By contrast, $P(OMe)_3$ gives high yields of the diamagnetic, formally cobalt(III) derivative $[Co\{P(OMe)_3\}_3(\eta\text{-}C_5H_5)][PF_6]_2$. Presumably, in this case, the paramagnetic bis(phosphite) complex undergoes further oxidation after co-ordination of a third $P(OMe)_3$ ligand. In this context the electrochemistry of $[Co(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ in CH_2Cl_2 and thf (see above) is relevant. Only in the donor solvent thf is a second oxidation wave observed, attributable to the oxidation of $[Co(CO)(PPh_3)(thf)(\eta\text{-}C_5H_5)]^+$ to the cobalt(III) dication $[Co(CO)(PPh_3)(thf)(\eta\text{-}C_5H_5)]^{2+}$.



Scheme 2. L = $P(C_6H_{11})_3$, R = H, unless stated. (*i*) L′ = PPh_3 or pyridine; (*ii*) L″ = $P(OMe)_3$; (*iii*) 0.5 X_2; X = Br or I; (*iv*) $Me_2NC(S)SSC(S)NMe_2$; (*v*) NO gas, L = PPh_3, R = Me; (*vi*) O–O = *o*-quinone

We might also comment here on McKinney's observation[8] that $[Co(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ is further oxidised to the air-stable, yellow $[Co(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]_2$, by Ag[$BF_4$] in thf. Because the cyclic voltammogram of $[Co(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ in CH_2Cl_2 shows no oxidation wave up to +1.8 V we believe that the formation of an air-stable dication is not possible. Should silver(I) ions be capable of oxidation at potentials more positive than 1.8 V in thf, and this is most unlikely,[12] the product would be extremely prone to reduction, and air-sensitive. We have, however, been unable to characterise further the yellow solid prepared from $[Co(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ and Ag[PF_6] in thf.

The complexes (2) and (3) undergo radical-coupling reactions similar to those of $[Fe(CO)_3(PPh_3)_2]^+$.[3] With bromine or iodine, (2) gives good yields of the green, crystalline, cobalt(III) complexes $[CoX(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ (X = Br or I) (Tables 2 and 4). Similarly, $Me_2NC(S)SSC(S)NMe_2$, as a source of S_2CNMe_2 radicals, and (2) or (3) afford the diamagnetic, purple-brown salts $[CoL(S_2CNMe_2)(\eta\text{-}C_5H_5)][PF_6]$ [L = $P(C_6H_{11})_3$ or PPh_3] *via* coupling and subsequent loss of CO or PPh_3. The dithiocarbamate complexes may also be made from (2) or (3) and $Na[S_2CNMe_2]\cdot 2H_2O$, presumably *via* a similar mechanism to that of the reaction with $[Fe(CO)_3(PPh_3)_2]^+$.[3]

Table 4. Proton n.m.r. data for diamagnetic cyclopentadienylcobalt derivatives

Compound	δ/p.p.m.
$[Co\{P(OMe)_3\}_3(\eta\text{-}C_5H_5)][PF_6]_2$ [a]	6.10 (5 H, s, C_5H_5), 4.12 [27, m, $P(OMe)_3$]
$[CoBr(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ [b]	6.16 (5 H, s, C_5H_5), 1.7 [33 H, m, br, $P(C_6H_{11})_3$]
$[CoI(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ [b]	6.15 (5 H, s, C_5H_5), 1.8 [33 H, m, br, $P(C_6H_{11})_3$]
$[Co\{P(C_6H_{11})_3\}(S_2CNMe_2)(\eta\text{-}C_5H_5)][PF_6]$ [b]	5.52 (5 H, s, C_5H_5), 3.23 (6 H, s, S_2CNMe_2), 1.8 [33 H, m, br, $P(C_6H_{11})_3$]
$[Co(PPh_3)(S_2CNMe_2)(\eta\text{-}C_5H_5)][PF_6]$ [a]	7.60 (15 H, m, br, PPh_3), 5.47 (5 H, s, C_5H_5), 2.78 (6 H, s, S_2CNMe_2)

[a] In $[^2H_6]$acetone. [b] In CD_3NO_2.

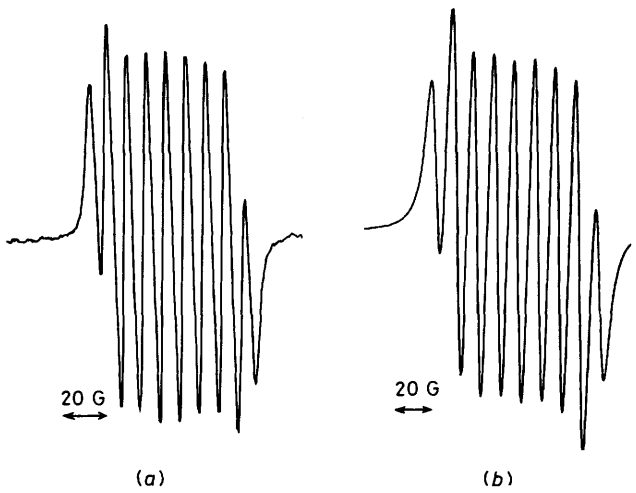


Figure 2. Observed (*a*) and simulated (*b*) CH_2Cl_2 solution e.s.r. spectra of $[Co(O_2C_{14}H_8)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$

Nitric oxide also reacts with (3) to give $[Co(NO)(PPh_3)(\eta\text{-}C_5H_5)][PF_6]$, a complex previously prepared [13] from $[NO][PF_6]$ and $[Co(CO)(PPh_3)(\eta\text{-}C_5H_5)]$. More significantly, NO gas and (4) give brown $[Co(NO)(PPh_3)(\eta\text{-}C_5Me_5)][PF_6]$ which is not preparable directly from $[NO][PF_6]$ due to the absence of a route to $[Co(CO)(PPh_3)(\eta\text{-}C_5Me_5)]$.

The final set of reactions paralleling those of $[Fe(CO)_3(PPh_3)_2]^+$ [3] involves the formation of paramagnetic quinone derivatives $[Co(O\text{–}O)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ (5; O–O = *ortho*-quinone). The addition of a quinone to (2) in CH_2Cl_2 gives high yields of the dark blue *o*-chloranil (3,4,5,6-tetrachloro-*o*-benzoquinone) or the brown phenanthrenequinone derivative; the 1,2-naphthoquinone analogue has also been generated in solution.

Although complexes (2)—(4) show only broad, single-line e.s.r. spectra, the quinone compounds (5) show nine-line e.s.r. spectra (Table 3) of relative intensity 1 : 2 : 1 . . . 2 : 2 : 1. The measured and computer-simulated spectra of (5; O–O = phenanthrenequinone) are shown in Figure 2; for all three examples of (5), $A_{iso}(^{31}P)$ is coincidentally equal to $A_{iso}(^{59}Co)$. The $g_{av.}$ values of (5) (Table 3) are very different from those of (2)—(4). Their close proximity to 2.00, together with the small ^{31}P and ^{59}Co hyperfine couplings, suggests the unpaired electron density to be largely localised on the quinone ligand. In this respect (5) are similar to $[Fe(CO)_2(O\text{–}O)(PPh_3)_2]^+$.

The use of *o*-quinone ligands as e.s.r. probes of electron density in organotransition-metal radicals has been applied to the cobalt and iron cations described above as well as to neutral manganese [14] and rhenium [15] carbonylphosphines. Recent work [16] suggests that highly reactive organorhodium radicals such as $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$, otherwise inaccessible to synthetic and spectroscopic study, may also be stabilised by quinone-complex formation.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Unless stated otherwise the complexes are air-stable, dissolving in polar solvents such as acetone, CH_2Cl_2, and nitromethane to give air-sensitive solutions. The complexes $[Co(CO)L(\eta\text{-}C_5H_5)]$ [17] and $[Co(CO)_2(\eta\text{-}C_5Me_5)]$ [18,19] were prepared by literature methods, *o*-quinones were purchased from Aldrich Chemical Co., and NO gas was purified by passage through a cold trap (−78 °C) before use.

Cyclic voltammetric measurements were made under a purge of prepurified nitrogen using solvents containing 0.5×10^{-3} mol dm^{-3} complex and either 0.1 mol dm^{-3} $[NBu^n_4][PF_6]$ or $[NBu^n_4][BF_4]$ as supporting electrolyte. Dichloromethane was purified by distillation from CaH_2, and thf was distilled from $Li[AlH_4]$. The reference was an aqueous saturated calomel electrode (s.c.e.) and was separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. All potentials are standardised and quoted *vs.* the s.c.e. with $[NBu^n_4][PF_6]$ as the supporting electrolyte. Under these conditions, $E^\ominus$ for the couple $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ is 0.43 V. A small platinum bead served as the working electrode, and a platinum wire as auxiliary. Either the AMEL [20] or Princeton Applied Research [21] equipment was employed.

Infrared spectra were recorded on Perkin-Elmer PE 257 or PE 457 spectrometers and calibrated against the absorption band of polystyrene at 1 601 cm^{-1}. Proton n.m.r. spectra were obtained on a Varian Associates T60 instrument and calibrated against $SiMe_4$ as internal reference. *X*-Band e.s.r. spectra were recorded on a Varian Associates 4502/15 instrument and were calibrated against a solid sample of the diphenylpicrylhydrazyl radical. The e.s.r. spectra were simulated on an Apple Microcomputer, using a PASCAL program written [22] by Dr. J. P. Maher and Mr. A. P. Grigg of the Department of Inorganic Chemistry, University of Bristol. Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Carbonyl(η-cyclopentadienyl)(tricyclohexylphosphine)-cobalt Hexafluorophosphate, $[Co(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$.—The compounds $[Co(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)]$ (0.30 g, 0.69 mmol) and $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (0.23 g, 0.69 mmol) were stirred in CH_2Cl_2 (10 cm^3) for 5 min. The resulting green solution was filtered, and n-hexane added to precipitate the product as a green *solid*, yield 0.20 g (50%).

(η-Cyclopentadienyl)bis(triphenylphosphine)cobalt Hexafluorophosphate, $[Co(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$.—*Method* (*a*). To a solution of $[Co(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (0.30 g, 0.73 mmol) and PPh_3 (0.19 g, 0.73 mmol) in thf (10 cm^3) was added $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (0.24 g, 0.73 mmol). On stirring, CO was

evolved and the yellow-brown *product* was precipitated. After 5 min it was filtered off, washed with toluene to remove ferrocene, and dried, yield 0.44 g (79%).

Method (*b*). The compounds $[Co(CO)_2(\eta\text{-}C_5H_5)]$ (0.34 g, 1.89 mmol) and PPh_3 (0.98 g, 3.74 mmol) were dissolved in CH_2Cl_2 (15 cm^3). On addition of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (0.59 g, 1.78 mmol) vigorous evolution of CO occurred and the solution became dark brown. After filtration, n-hexane (50 cm^3) was added to precipitate the crude product as a pale brown solid, yield 1.22 g (81%).

The compound $[Co(CO)(PPh_3)(\eta\text{-}C_5Me_5)][PF_6]$ was prepared similarly as red, air-sensitive *crystals*, yield (72%).

(η-*Cyclopentadienyl*)(*tricyclohexylphosphine*)(*triphenylphosphine*)*cobalt Hexafluorophosphate*, $[Co\{P(C_6H_{11})_3\}(PPh_3)(\eta\text{-}C_5H_5)][PF_6]$.—On adding PPh_3 (0.08 g, 0.31 mmol) to $[Co(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ (0.17 g, 0.30 mmol) in CH_2Cl_2 (15 cm^3) CO gas was evolved. After 15 min n-hexane was added to give the product as a yellow-brown solid, yield 0.10 g (42%).

Pink $[Co(NC_5H_5)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ was prepared in 70% yield by a similar method but in this case the reaction was complete almost immediately. The *product* was precipitated rapidly to avoid decomposition in solution.

(η-*Cyclopentadienyl*)*tris*(*trimethyl phosphite*)*cobalt Bis*(*hexafluorophosphate*), $[Co\{P(OMe)_3\}_3(\eta\text{-}C_5H_5)][PF_6]_2$.—To $[Co(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ (0.15 g, 0.26 mmol) in CH_2Cl_2 (10 cm^3) was added $P(OMe)_3$ (0.09 cm^3, 0.76 mmol); CO was evolved and the solution became yellow. On addition of diethyl ether the product was precipitated as a pale yellow solid, yield 0.08 g (80%).

Carbonyl(η-*cyclopentadienyl*)*iodo*(*tricyclohexylphosphine*)*cobalt Hexafluorophosphate*, $[CoI(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$.—A solution of I_2 (0.04 g, 0.16 mmol) in CH_2Cl_2 (15 cm^3) was added dropwise to solid $[Co(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ (0.2 g, 0.35 mmol). After stirring for 5 min, n-hexane (35 cm^3) was added to give olive-green crystals of the *product*, yield 0.19 g (79%).

The compound $[CoBr(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ was prepared similarly as a yellow-green solid, yield (79%).

(η-*Cyclopentadienyl*)(*dimethyldithiocarbamato*)(*tricyclohexylphosphine*)*cobalt Hexafluorophosphate*, $[Co\{P(C_6H_{11})_3\}(S_2CNMe_2)(\eta\text{-}C_5H_5)][PF_6]$.—*Method* (*a*). To a stirred solution of $[Co(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ (0.20 g, 0.35 mmol) in CH_2Cl_2 (10 cm^3) was added $Me_2NC(S)SSC(S)NMe_2$ (0.04 g, 0.17 mmol). n-Hexane was added to the resultant purple solution to precipitate the product as a brown-purple *solid*, yield 0.13 g (57%).

Method (*b*). The salts $Na[S_2CNMe_2]\cdot 2H_2O$ (0.03 g, 0.17 mmol) and $[Co(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ (0.2 g, 0.35 mmol) were stirred in CH_2Cl_2 (10 cm^3) for 20 min. Treatment of the solution as in method (*a*) gave the product, yield 0.03 g (27% based on $[S_2CNMe_2]^-$).

The compound $[Co(PPh_3)(S_2CNMe_2)(\eta\text{-}C_5H_5)][PF_6]$ may be made by either method (*a*) (75%) or method (*b*) (88%) as a brown-purple *solid*.

Nitrosyl(η-*pentamethylcyclopentadienyl*)(*triphenylphosphine*)*cobalt Hexafluorophosphate*, $[Co(NO)(PPh_3)(\eta\text{-}C_5Me_5)][PF_6]$.—A solution of NO gas in CH_2Cl_2 (20 cm^3) was added slowly to $[Co(CO)(PPh_3)(\eta\text{-}C_5Me_5)][PF_6]$ (0.37 g, 0.59 mmol) in CH_2Cl_2 (10 cm^3). Diethyl ether was then added to the resulting brown solution to precipitate the product as a brown *solid*, yield 0.27 g (73%). The solid complex becomes purple on exposure to air.

(o-*Chloranil*)(η-*cyclopentadienyl*)(*tricyclohexylphosphine*)*cobalt Hexafluorophosphate*, $[Co(O_2C_6Cl_4)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$.—To $[Co(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)][PF_6]$ (0.10 g, 0.17 mmol) in CH_2Cl_2 (10 cm^3) was added *o*-chloranil (0.04 g, 0.16 mmol). The dark blue solution was filtered and n-hexane added to give the product as a dark blue *solid*, yield 0.10 g (73%).

The phenanthrenequinone analogue was prepared similarly as a brown *solid*, yield (76%).

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