# Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 16.[1] Nitrosyl-bridged Dicobalt Complexes $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]^z$ (R = H or Me, $z$ = 0 to +2) and $[Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2]^z$ ($z$ = 0 or +1): Synthesis, Electrochemistry, and Relative Reactivity

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The complex $[Co(CO)_2(\eta\text{-}C_5H_5)]$ reacts with $[NO][PF_6]$ in refluxing $CH_2Cl_2$ to give paramagnetic $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2][PF_6]$ (1), electrochemical studies on which reveal reduction to $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$ and oxidation to $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]^{2+}$; ferrocenium ion oxidation of the neutral dimer provides a second route to (1). With $[Co(CO)_2(\eta\text{-}C_5Me_5)]$, $[NO][PF_6]$ gives $[Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$ (2) which is chemically and electrochemically reduced to paramagnetic $[Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2]$ (3). Complex (2) and NO gas give the complex $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2][PF_6]$ (4) which is reduced to $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2]$ (5) by $K[BH(CHMeEt)_3]$. Electrochemical studies on complex (4) show one-electron reduction to (5) and oxidation to $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2]^{2+}$ (6) which may be made from (2) and $[NO][PF_6]$. Complex (1) reacts with cyclo-octene (L) and $Ag[PF_6]$ to give $[CoL(NO)(\eta\text{-}C_5H_5)][PF_6]$, with $PPh_3$ to give $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$ and $[Co(PPh_3)(NO)(\eta\text{-}C_5H_5)][PF_6]$, and with $CNC_6H_3Me_2\text{-}2,6$ to give $[Co(CNC_6H_3Me_2\text{-}2,6)_3(NO)]$ and $[Co_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}NO)(\eta\text{-}C_5H_5)_2][PF_6]$.

Comparative *X*-ray structural studies on the redox-related complexes $[\{Co(\mu\text{-}CO)(\eta\text{-}C_5Me_5)\}_2]^z$ ($z$ = 0 [2,3] and −1 [3]), on $[\{Co(\mu\text{-}CO)(\eta\text{-}C_5H_5)\}_2]^-$,[3,4] and on $[Co_2(\mu\text{-}X)(\mu\text{-}NO)(\eta\text{-}C_5H_5)_2]$ [5] (X = CO or NO) have been central to the recent development [6] of bonding theories for ligand-bridged bimetallics. We have recently noted the synthesis of a range of cationic, nitrosyl-bridged analogues of these species [7] and now present details of the preparation, electrochemistry, and relative reactivity of $[Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2]^z$ ($z$ = 0 or +1) and $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]^z$ (R = H or Me, $z$ = 0 to +2).

## Results and Discussion

*Synthesis and Electrochemistry of* $[Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2]^z$ ($z$ = 0 *or* +1) *and* $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]^z$ (R = H *or* Me, $z$ = 0 to +2).—The room temperature reaction between $[Co(CO)_2(\eta\text{-}C_5H_5)]$ and $[NO][PF_6]$ in $CH_2Cl_2$ gives several cationic carbonylnitrosyl complexes which may be identified, by analogy with more completely characterised rhodium compounds,[7,8] as $[Co(CO)(NO)(\eta\text{-}C_5H_5)]^+$, $[Co_2(CO)_2(\mu\text{-}NO)(\eta\text{-}C_5H_5)_2]^+$, and $[Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5H_5)_2]^+$. In refluxing $CH_2Cl_2$, however, equimolar quantities of $[Co(CO)_2(\eta\text{-}C_5H_5)]$ and $[NO][PF_6]$ give moderate yields of the paramagnetic dimer $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2][PF_6]$ (1) (Tables 1 and 2). The i.r. spectrum of the dark mauve, air-stable salt shows one band due to the bridging nitrosyl ligands suggesting coplanarity of the $Co_2(NO)_2$ skeleton;† the *X*-ray structure of the isoelectronic anion $[\{Co(\mu\text{-}CO)(\eta\text{-}C_5H_5)\}_2]^-$ has revealed [3,4] such an arrangement for the $Co_2(\mu\text{-}CO)_2$ atoms.

The isotropic e.s.r. spectrum of (1) in $CH_2Cl_2$ shows fifteen lines with relative intensities 1 : 2 : 3 . . . 7 : 8 : 7 . . . 3 : 2 : 1 consistent with the coupling of the free electron to two equivalent cobalt nuclei ($^{59}Co$, $I = 7/2$); no hyperfine coupling to the nitrosyl nitrogen atoms ($^{14}N$, $I = 1$) is observed. The spectrum is qualitatively similar to those of the isoelectronic complexes $[Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5H_5)_2]$ [5] and $[\{Co(\mu\text{-}CO)(\eta\text{-}C_5R_5)\}_2]^-$ (R = H or Me) [3,9] (Table 2).

Electrochemical studies (Table 3) in $CH_2Cl_2$ show that (1) is not only reduced to $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$, but is also oxidised to $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]^{2+}$. Cyclic voltammetry shows that these one-electron transfer reactions, and those described below, are diffusion controlled with $i/v^{\frac{1}{2}}$ constant for scan rates (v) between 50 and 500 mV $s^{-1}$. The one-electron reduction of (1) is fully reversible but the value of $i_{red}/i_{ox}$ for the oxidation to $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]^{2+}$ varies from 0.6 to 0.9 for the scan rates specified and suggests incomplete chemical reversibility. The peak separation, $(E_p)_{ox} - (E_p)_{red}$, for each wave was close to that measured for ferrocene oxidation under the same conditions (70 mV for v = 200 mV $s^{-1}$), showing electrochemical reversibility.

The cyclic voltammogram of (1) also shows a second, irreversible, reduction wave with $(E_p)_{red} = -1.40$ V for v = 196 mV $s^{-1}$. The peak current appears larger than those of the other redox processes described but the wave is close to that of the base electrolyte and may correspond to the initial formation of $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]^-$ (see below). Reduction is most probably followed by metal–metal bond cleavage in that $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$ is known to react chemically with sodium amalgam to give $[Co(NO)(\eta\text{-}C_5H_5)]^-$.[10]

The voltammetry of (1) at a rotating platinum electrode gives results in close agreement with those from cyclic voltammetry; the associated potentials are identical to those given in Table 3.

Cyclic voltammetric studies on $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$ have been made [5] previously in MeCN and the potentials for reversible oxidation to (1), and for the irreversible reduction, are in agreement with those determined for (1); the second oxidation, to $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]^{2+}$, was, however, not reported. We have now studied the electrochemistry of $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$ in $CH_2Cl_2$ (Table 3) and find excellent agreement with the data for (1), both in terms of $E^{\ominus}$ values and reversibility.

The $E^{\ominus}$ value (0.34 V) for the couple $[\{Co(\mu\text{-}NO)(\eta\text{-}$

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† *Note added in proof.* The *X*-ray structure of $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2][BF_4]$ has revealed planarity of the $Co_2(\mu\text{-}NO)_2$ core (F. Wochner, E. Keller, and H. H. Brintzinger, *J. Organomet. Chem.*, 1982, **236**, 267).

**Table 1**. Infrared and analytical data for binuclear cobalt complexes

| Complex | Colour | Yield (%) | $\tilde{\nu}$(CO) [a]/cm$^{-1}$ | $\tilde{\nu}$(NO)/cm$^{-1}$ | Analysis [b] (%) | | |
|---|---|---|---|---|---|---|---|
| | | | | | C | H | N |
| $[\{Co(\mu-NO)(\eta-C_5H_5)\}_2][PF_6]$ (1) | Dark mauve | 67 | — | 1 605 | 26.7<br>(26.5) | 2.2<br>(2.2) | 6.0<br>(6.2) |
| $[Co_2(\mu-CO)(\mu-NO)(\eta-C_5Me_5)_2][PF_6]$ (2) | Green | 85 | 1 857 [c]<br>1 843 | 1 552 | 42.4<br>(42.6) | 5.3<br>(5.1) | 2.8<br>(2.4) |
| $[Co_2(\mu-CO)(\mu-NO)(\eta-C_5Me_5)_2]$ (3) | Black | 75 | 1 813, 1 795 [d]<br>1 803 [c] | 1 508 | 56.1<br>(56.5) | 7.2<br>(6.8) | 3.2<br>(3.1) |
| $[\{Co(\mu-NO)(\eta-C_5Me_5)\}_2][PF_6]$ (4) | Dark red | 87 | — | 1 560 | 40.1<br>(40.5) | 5.5<br>(5.1) | 4.3<br>(4.7) |
| $[Co(CNC_6H_3Me_2-2,6)_3(NO)]$ | Red | 19 | 2 135m,[e]<br>2 065s,<br>2 000m | 1 702s | 66.8<br>(67.2) | 5.8<br>(5.6) | 11.1<br>(11.6) |
| $[Co_2(CNC_6H_3Me_2-2,6)_2(\eta-NO)(\eta-C_5H_5)_2][PF_6]$ | Yellow | 24 | 2 172, 2 140 [e]<br>2 165, 2 137 | 1 655<br>1 660 [c] | 48.6<br>(49.0) | 4.3<br>(4.1) | 5.4<br>(6.1) |
| $[Co_2(\mu-O_2PF_2)_3(\eta-C_5Me_5)_2][PF_6]$ | Blue | 43 | — | — | 29.2<br>(28.7) | 4.1<br>(3.6) | — |

[a] In Nujol unless otherwise stated. [b] Calculated values are in parentheses. [c] In $CH_2Cl_2$. [d] Solid state splitting. [e] $\tilde{\nu}$(CN).

**Table 2**. Room temperature e.s.r. [a] and $^1H$ n.m.r. [b] data

| Complex | $\langle g_{av} \rangle$ | $A_{iso}(^{59}Co)$ [c]/G | δ/p.p.m. |
|---|---|---|---|
| $[\{Co(\mu-NO)(\eta-C_5H_5)\}_2][PF_6]$ (1) | 2.079 | 44.2 | |
| $[Co_2(\mu-CO)(\mu-NO)(\eta-C_5Me_5)_2][PF_6]$ (2) | | | 1.52 [d] |
| $[Co_2(\mu-CO)(\mu-NO)(\eta-C_5Me_5)_2]$ (3) | 2.074 [e] | 43.5 | |
| $[\{Co(\mu-NO)(\eta-C_5Me_5)\}_2][PF_6]$ (4) | 2.061 | 38.4 | |
| $[\{Co(\mu-NO)(\eta-C_5Me_5)\}_2]$ (5) | | | 1.60 [f] |
| $[Co_2(\mu-CO)(\mu-NO)(\eta-C_5H_5)_2]$ | 2.054 [g] | 47.4 | |
| $[\{Co(\mu-CO)(\eta-C_5H_5)\}_2]^-$ | 2.08 [h] | 47.3 | |
| $[\{Co(\mu-CO)(\eta-C_5Me_5)\}_2]^-$ | 2.08 [h] | 44.0 | |
| $[Co_2(\mu-O_2PF_2)_3(\eta-C_5Me_5)_2][PF_6]$ | | | 0.87 |
| $[Co_2(CNC_6H_3Me_2-2,6)_2(\mu-NO)(\eta-C_5H_5)_2][PF_6]$ | | | 6.83 (s, 3 H, $C_6\mathit{H}_3Me_2$), 5.10 (s, 5 H, $C_5\mathit{H}_5$), 2.37 (s, 6 H, $C_6H_3\mathit{Me}_2$) |
| $[Co(CNC_6H_3Me_2-2,6)_3(NO)]$ | | | 6.98 (s, 3 H, $C_6\mathit{H}_3Me_2$), 2.41 (s, 6 H, $C_6H_3\mathit{Me}_2$) |

[a] In $CH_2Cl_2$ unless otherwise stated. [b] In $CDCl_3$ unless otherwise stated. [c] 1 G = $10^{-4}$ T. [d] $[^2H_6]$acetone. [e] In hexane. [f] In $[^2H_8]$toluene. [g] In benzene. From ref. 5. [h] In thf. From ref. 9.

**Table 3**. Cyclic voltammetric data for $[\{Co(\mu-NO)(\eta-C_5R_5)\}_2]^z$ and $[Co_2(\mu-CO)(\mu-NO)(\eta-C_5Me_5)_2]^z$ in $CH_2Cl_2$

| Complex | Process | $E^{\ominus}$/V [a] |
|---|---|---|
| $[\{Co(\mu-NO)(\eta-C_5H_5)\}_2][PF_6]$ (1) | $+1 \rightleftharpoons +2$ | 1.17 |
| | $+1 \rightleftharpoons 0$ | 0.34 |
| $[\{Co(\mu-NO)(\eta-C_5H_5)\}_2]$ | $+1 \rightleftharpoons +2$ | 1.18 |
| | $0 \rightleftharpoons +1$ | 0.33 |
| $[\{Co(\mu-NO)(\eta-C_5Me_5)\}_2][PF_6]$ (4) | $+1 \rightleftharpoons +2$ | 0.68 |
| | $+1 \longrightarrow 0$ | −0.15 |
| | $0 \rightleftharpoons -1$ | *ca.* −1.7 [b] |
| $[Co_2(\mu-CO)(\mu-NO)(\eta-C_5Me_5)_2][PF_6]$ (2) | $+1 \rightleftharpoons 0$ | −0.19 |
| $[Co_2(\mu-CO)(\mu-NO)(\eta-C_5Me_5)_2]$ (3) | $0 \rightleftharpoons +1$ | −0.20 |
| $[\{Co(\mu-CO)(\eta-C_5H_5)\}_2]^-$ | $-1 \rightleftharpoons 0$ | −1.05 [c] |

[a] *Versus* an aqueous saturated calomel electrode, at a platinum bead, with 0.1 mol dm$^{-3}$ $[NBu^n{}_4][PF_6]$ as supporting electrolyte. Under these conditions $E^{\ominus}$ for the couple $[Fe(\eta-C_5H_5)_2]^+$–$[Fe(\eta-C_5H_5)_2]$ is 0.43 V. [b] Estimated value. [c] *Versus* Ag–AgClO$_4$, in MeCN, at mercury. From ref. 4.

$C_5H_5)\}_2]^+$–$[\{Co(\mu-NO)(\eta-C_5H_5)\}_2]$ suggests that the oxidation of the neutral dimer to (1) should be effected by a mild chemical oxidant. Accordingly, the addition of $[Fe(\eta-C_5H_5)_2][PF_6]$ to $[\{Co(\mu-NO)(\eta-C_5H_5)\}_2]$ in $CH_2Cl_2$ provides a second, improved route to (1).

The room temperature reaction between $[Co(CO)_2(\eta-C_5Me_5)]$ and $[NO][PF_6]$ (2 : 1 ratio) in $CH_2Cl_2$ leads to vigorous CO evolution and the formation of a deep green solution from which green crystals of diamagnetic $[Co_2(\mu-CO)(\mu-NO)(\eta-C_5Me_5)_2][PF_6]$ (2) are readily isolated. Elemental analysis, one singlet in the $^1H$ n.m.r. spectrum due to the $C_5Me_5$ ligands, and i.r. absorptions at 1 843 and 1 552 cm$^{-1}$ due to the bridging CO and NO ligands (Tables 1 and 2) fully characterise the salt.

The existence[5] of neutral $[Co_2(\mu-CO)(\mu-NO)(\eta-C_5H_5)_2]$ implies that (2) should be reducible to $[Co_2(\mu-CO)(\mu-NO)(\eta-C_5Me_5)_2]$ (3), an implication borne out by electrochemical and chemical studies.

The cyclic voltammogram of (2) in $CH_2Cl_2$ shows one diffusion-controlled, fully reversible, one-electron reduction wave at $E^{\ominus} = -0.19$ V (Table 3), corresponding to the formation of (3). On treatment of (2) with Na[BH$_4$] in n-hexane–thf (1 : 1), a dark brown solution is formed from which high yields of black, crystalline $[Co_2(\mu-CO)(\mu-NO)(\eta-C_5Me_5)_2]$ (3)

$$[\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]^- \rightleftharpoons [\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]^0 \rightleftharpoons [\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]^+ \rightleftharpoons [\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]^{2+}$$

$$[Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5R_5)_2]^{2-} \rightleftharpoons [Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5R_5)_2]^- \rightleftharpoons [Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5R_5)_2]^0 \rightleftharpoons [Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5R_5)_2]^+$$

$$[\{Co(\mu\text{-}CO)(\eta\text{-}C_5R_5)\}_2]^{3-} \rightleftharpoons [\{Co(\mu\text{-}CO)(\eta\text{-}C_5R_5)\}_2]^{2-} \rightleftharpoons [\{Co(\mu\text{-}CO)(\eta\text{-}C_5R_5)\}_2]^- \rightleftharpoons [\{Co(\mu\text{-}CO)(\eta\text{-}C_5R_5)\}_2]^0$$

**Scheme.**

are isolable. The identity of (3) was readily established by elemental analysis and i.r. spectroscopy (Table 1), by the mass spectrum which shows a parent ion at *m/e* 446, and by the isotropic, 15-line e.s.r. spectrum (Table 2) which is very similar to that of (1). The cyclic voltammogram of (3) is also diagnostic, showing a fully reversible oxidation wave at $E^\ominus = -0.20$ V corresponding to the formation of (2).

The cyclic voltammogram of $[Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5H_5)_2]$ in acetonitrile shows[5] an irreversible oxidation wave (at *ca.* −0.28 V) suggesting that the monocation is unstable. Noting (*i*) the existence of (2), (*ii*) the formation of $[Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5H_5)_2]^+$ {mixed with $[Co_2(CO)_2(\mu\text{-}NO)(\eta\text{-}C_5H_5)_2]^+$} in the room temperature reaction between $[Co(CO)_2(\eta\text{-}C_5H_5)]$ and $NO^+$ in $CH_2Cl_2$, and (*iii*) the rapid reaction of (2) with acetonitrile, it is safe to assume that the irreversibility of the electrochemical oxidation of $[Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5H_5)_2]$ was solely due to the choice of solvent.

Complex (2) reacts with NO gas to give $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2][PF_6]$ (4) analogous to complex (1). The dark red, crystalline compound has one bridging nitrosyl absorption in the i.r. spectrum (Table 1) and a 15-line e.s.r. spectrum similar to those described above (Table 2).

The cyclic votammogram of (4) shows an oxidation wave, and two reduction waves (Table 3), with reduction to the neutral complex $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2]$ (5) and oxidation to the dication $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2]^{2+}$ (6) being fully reversible and diffusion-controlled processes. The second reduction step is not readily quantified in $CH_2Cl_2$; the wave is close to that due to the base electrolyte curve, $[(E_p)_{red}$ *ca.* −1.7 V]. Nevertheless, a comparison of the wave height with those for the formation of (5) and (6) from (4), and the fact that a peak is observed on the reverse sweep for the second reduction step $[(E_p)_{ox}$ *ca.* −1.6 V], suggest that the dimeric anion $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2]^-$ may have some stability. In this context we note that $[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$ undergoes fully reversible, one-electron reduction in thf.[8]

The $E^\ominus$ values for the one-electron reduction and oxidation of (4) suggest that chemical reduction to (5) should occur with ease whereas a strong oxidant might effect the formation of (6). The reaction of (4) with $K[BH(CHMeEt)_3]$ in n-hexane–thf (1 : 1) gave a brown solution from which low yields of air-sensitive (5) were isolated. Satisfactory elemental analyses could not be obtained, but the black solid showed i.r. absorptions at 1 544 and 1 503 cm$^{-1}$, similar to those due to the bridging nitrosyl ligands of $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$ [$\tilde{\nu}$(NO) (KBr) = 1 585 and 1 525 cm$^{-1}$].[11] In addition, the mass spectrum showed a parent ion at *m/e* 448, and the $^1H$ n.m.r. spectrum showed only one singlet, at $\delta$ 1.60, due to the $C_5Me_5$ rings.

Attempts to oxidise (4) to (6), using $Ag[PF_6]$ in $CH_2Cl_2$, resulted in low yields of a dark brown precipitate which showed a weak absorption at 1 623 cm$^{-1}$ in the i.r. spectrum. In addition, complex (2) and $[NO][PF_6]$ in $CH_2Cl_2$ gave a solid with a similar absorption. Recrystallisation of the product, from acetone–diethyl ether, gave complex (4) suggesting that the band at 1 623 cm$^{-1}$ might be assigned to (6). The dication (6) is readily reduced, as expected on the basis of the $E^\ominus$ value for the couple (6)–(4).

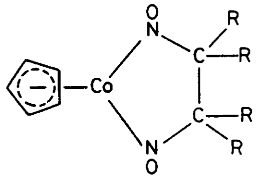
Further attempts to prepare (6), by the reaction of $[Co(CO)_2(\eta\text{-}C_5Me_5)]$ with an excess of $[NO][PF_6]$ in $CH_2Cl_2$, were unsuccessful. The blue reaction mixture yielded, on addition of n-hexane, $[Co_2(\mu\text{-}O_2PF_2)_3(\eta\text{-}C_5Me_5)_2][PF_6]$ (Tables 1 and 2) presumably *via* the catalysed hydrolysis of the $[PF_6]^-$ anion. The analogous rhodium complex has been described previously.[12]

The electrochemical studies described above reveal extensive series of redox-related, binuclear carbonyl- and nitrosyl-bridged complexes. For $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]^z$ (R = H or Me) we have detected species in which $z = 0$ to $+2$, and the existence of the anion, $z = -1$, is suggested by cyclic voltammetric studies of (4) (and confirmed by those on $[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$).[8]

Given that $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]^+$, $[Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5R_5)_2]$, and $[\{Co(\mu\text{-}CO)(\eta\text{-}C_5R_5)\}_2]^-$ are isoelectronic, the Scheme shows the possible four-membered redox series. Obviously not all of the species shown will be isolable for a given substituent, R. However, the replacement of $C_5Me_5$ ligands by $C_5H_5$ causes $E^\ominus$ values to shift to more negative potentials by *ca.* 0.35 V (Table 3), and the use of more electron-withdrawing groups such as $C_5Ph_5$[13] will undoubtedly lead to further stabilisation of the more reduced complexes shown. The isolation of such species, and subsequent *X*-ray structural characterisation, will play an important part in a fuller understanding of the electronic structure of ligand-bridged bimetallic compounds.

*Reactivity of* $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]^z$ (R = H or Me, $z$ = 0 *to* +2) *and* $[Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$ (2).—The existence of $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]^z$ (R = H or Me, $z = -1$, 0, +1, or +2) and $[Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5R_5)_2]^z$ (R = H or Me, $z$ = 0 or +1) has allowed us to show how the one-electron oxidation or reduction of bridged bimetallics leads to major changes in reactivity. The complexes $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]^z$ ($z$ = 0 to +2) well illustrate this point.

The most interesting reaction of the neutral dimer is that with olefins ($R_2CCR_2$) and NO, leading[14] to the *C*-nitroso-complexes shown below. Reduction of these species with Li[AlH$_4$] affords the synthetically important vicinal diamines $NH_2CR_2CR_2NH_2$.[15] By contrast, the monocation (1) reacts with alkenes only in the presence of $Ag[PF_6]$. Thus (1), the silver salt, and an excess of cyclo-octene give, after heating under reflux for 12 h in $CH_2Cl_2$, a purple solution from which a mauve solid was precipitated with hexane. The air-sensitive complex has been characterised as $[CoL(NO)(\eta\text{-}C_5H_5)][PF_6]$ (L = cyclo-octene) [$\tilde{\nu}$(NO) ($CH_2Cl_2$) 1 863 cm$^{-1}$] by analogy with the more stable rhodium complex,[7,8] and by its reaction with $PPh_3$ which gave $[Co(PPh_3)(NO)(\eta\text{-}C_5H_5)][PF_6]$.[16] On the basis of the redox potential shown in Table 3,



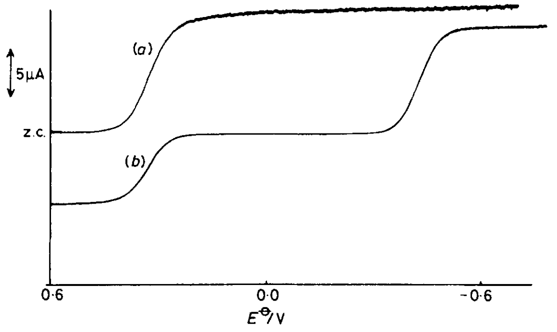


**Figure.** (*a*) The voltammogram of [{Co(μ-NO)(η-$C_5H_5$)}$_2$][$PF_6$] (1), at a rotating platinum bead electrode, from 0.6 to −0.6 V, and (*b*) after the addition of $PPh_3$; z.c. = zero current

the cyclo-octene reacts with [{Co(μ-NO)(η-$C_5H_5$)}$_2$]$^{2+}$, generated *in situ* by $Ag^+$ oxidation of (1).

With $PPh_3$, [{Co(μ-NO)(η-$C_5H_5$)}$_2$] is unreactive but (1) undergoes instant metal-metal bond cleavage to give [Co($PPh_3$)(NO)(η-$C_5H_5$)]$^+$. The exact nature of the cleavage reaction, both in terms of stoicheiometry and full product identification, was revealed by voltammetry at a rotating platinum electrode.

Figure (*a*) shows the voltammogram of (1) in the range 0.6 to −0.6 V. The one-electron reduction of (1) occurs at $E^{\ominus}$ = 0.34 V, with $i_d/c$ = 28.3 μA l $mmol^{-1}$ ($i_d$ = diffusion current); at 0.6 V the bulk of the solution contains (1). On adding one equivalent of $PPh_3$, reaction occurs to give an orange-brown solution, and the voltammogram in Figure (*b*) is obtained. The wave at $E_{\frac{1}{2}}$ = −0.43 V is due [17] to the irreversible one-electron reduction of [Co($PPh_3$)(NO)(η-$C_5H_5$)]$^+$ and the value of $i_d/c$ (24.8 μA l $mmol^{-1}$) confirms the formation of one equivalent of the cation. The wave at $E^{\ominus}$ = 0.34 V corresponds to the couple [{Co(μ-NO)(η-$C_5H_5$)}$_2$]$^+$–[{Co(μ-NO)(η-$C_5H_5$)}$_2$], but now the bulk of the solution contains the neutral dimer. In addition, the value of $i_d/c$ (16.3 μA l $mmol^{-1}$) reveals the presence of only one-half of one equivalent of [{Co(μ-NO)(η-$C_5H_5$)}$_2$].

The overall stoicheiometry of the reaction is given by equation (i). The formation of the neutral dimer does not

$$2\,[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]^+ + 2\,PPh_3 \longrightarrow [\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2] + 2\,[Co(PPh_3)(NO)(\eta\text{-}C_5H_5)]^+ \quad \text{(i)}$$

occur by the direct reduction of (1) by $PPh_3$; the relative redox potentials and reaction stoicheiometry are incorrect.

Initial attack at one cobalt atom of (1), by $PPh_3$, leads to Co–Co bond cleavage and the formation of [Co($PPh_3$)(NO)(η-$C_5H_5$)]$^+$ and [Co(NO)(η-$C_5H_5$)] radicals; subsequent dimerisation of the latter to [{Co(μ-NO)(η-$C_5H_5$)}$_2$] is rapid. There is abundant evidence for equilibria between dimeric carbonyl complexes and the corresponding monomeric radicals. Perhaps the most compelling [18] is that a solution of [{Cr(CO)$_3$(η-$C_5H_5$)}$_2$] in nitrobenzene shows an e.s.r. spectrum due to [Cr(CO)$_3$(η-$C_5H_5$)].

The reaction of (1) with xylyl isocyanide is somewhat different, giving mononuclear [Co($CNC_6H_3Me_2$-2,6)$_3$(NO)] and the yellow, binuclear salt [$Co_2$($CNC_6H_3Me_2$-2,6)$_2$(μ-NO)(η-$C_5H_5$)$_2$][$PF_6$]. The latter, characterised by elemental analysis, one bridging nitrosyl absorption in the i.r. spectrum (Table 1), and one $^1H$ n.m.r. singlet due to equivalent cyclopentadienyl rings, is isoelectronic with [$Rh_2$(CO)$_2$(μ-X)(η-$C_5H_5$)$_2$]$^z$ (X = CO, *z* = 0 [19]; X = NO, *z* = +1).[7,8]

By contrast to (1), [{Co(μ-NO)(η-$C_5Me_5$)}$_2$]$^+$ does not react with $PPh_3$. Cyclic voltammetry of (4) in the presence of one equivalent of $PPh_3$ shows neither a diminution in the height of the reduction wave (at $E^{\ominus}$ = −0.15 V) nor any product waves. However, on scanning to 1.0 V the reversibility of the oxidation wave at $E^{\ominus}$ = 0.68 V is decreased, implying a reaction between [{Co(μ-NO)(η-$C_5Me_5$)}$_2$]$^{2+}$ (6) and $PPh_3$.

Complex (2) which is isoelectronic with (6) does not react with $PPh_3$, in contrast to [$Rh_2$(μ-CO)(μ-NO)(η-$C_5Me_5$)$_2$]$^+$ and [{Co(μ-CO)(η-$C_5H_5$)}$_2$] which yield the 1 : 1 adducts [$Rh_2$(μ-CO)($PPh_3$)(μ-NO)(η-$C_5Me_5$)$_2$]$^+$ (ref. 8) and [$Co_2$(μ-CO)$_2$($PPh_3$)(η-$C_5H_5$)$_2$] [20] respectively. Further comparisons between cobalt and rhodium nitrosyl analogues will be presented elsewhere.

## Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Unless otherwise stated the complexes are air-stable, dissolving in polar solvents such as acetone and $CH_2Cl_2$ to give moderately air-sensitive solutions. The compounds [Co(CO)$_2$(η-$C_5R_5$)] (R = H [21] or Me [22,23]) and [{Co(μ-NO)(η-$C_5H_5$)}$_2$] [11] were prepared by published methods. Nitric oxide gas was purchased from B.O.C. Ltd., and purified by passage through a cold trap (−78 °C), [NO][$PF_6$] was purchased from Fluorochem, Ltd., Glossop, Derbyshire, and K[BH(CHMeEt)$_3$] from Aldrich Chemical Co. Ltd. Cyclic voltammetry was carried out as previously described,[1] and voltammetry used a platinum bead electrode rotated at 600 r.p.m.

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 recorded on a JEOL PS100 spectrometer 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. Mass spectra were obtained with an AEI MS902 instrument. Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

*Bis*(η-*cyclopentadienyl*)*di*-μ-*nitrosyl-dicobalt Hexafluorophosphate*, [{Co(μ-NO)(η-$C_5H_5$)}$_2$][$PF_6$] (1).—*Method A*. To [Co(CO)$_2$(η-$C_5H_5$)] (1.52 g, 8.4 mmol) in $CH_2Cl_2$ (25 $cm^3$) was added solid [NO][$PF_6$] (1.50 g, 8.6 mmol). The mixture was then heated under reflux until the reaction was complete (*ca.* 2 h). The mauve solution was then filtered, and n-hexane (50 $cm^3$) added to precipitate a dark solid. Recrystallisation from $CH_2Cl_2$–n-hexane gave the product as a dark mauve solid, yield 0.75 g (42%).

*Method B*. The complex [Fe(η-$C_5H_5$)$_2$][$PF_6$] (86 mg, 0.26 mmol) was added to [{Co(μ-NO)(η-$C_5H_5$)}$_2$] (80 mg, 0.26 mmol) in $CH_2Cl_2$ (20 $cm^3$) giving a mauve solution. Filtration, and treatment of the filtrate as above, gave a dark mauve powder, yield 80 mg (67%).

μ-*Carbonyl*-μ-*nitrosyl-bis*(η-*pentamethylcyclopentadienyl*)-*dicobalt Hexafluorophosphate*, [$Co_2$(μ-CO)(μ-NO)(η-$C_5Me_5$)$_2$][$PF_6$] (2).—On adding solid [NO][$PF_6$] (0.14 g, 0.80 mmol) to [Co(CO)$_2$(η-$C_5Me_5$)] (0.40 g, 1.60 mmol) in $CH_2Cl_2$ (25 $cm^3$), CO was vigorously evolved. After 5 min, when the reaction was adjudged complete by i.r. spectroscopy, the deep green solution was filtered, and n-hexane (100 $cm^3$) added. Recrystallisation of the precipitate, from $CH_2Cl_2$–n-hexane, gave the product as green crystals, yield 0.41 g (85%).

The complex decomposes slowly in the solid state and more rapidly in $CH_2Cl_2$; it reacts with acetonitrile.

μ-*Carbonyl*-μ-*nitrosyl-bis*(η-*pentamethylcyclopentadienyl*)-*dicobalt*, [$Co_2$(μ-CO)(μ-NO)(η-$C_5Me_5$)$_2$] (3).—A suspension of

$[Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$ (2) (0.25 g, 0.42 mmol) in a 1 : 1 mixture of n-hexane and thf (25 $cm^3$) was stirred with $Na[BH_4]$ (0.15 g, 3.95 mmol) until all the solid had dissolved. The dark brown solution was then filtered and evaporated to dryness. Extraction of the residue with n-hexane (50 $cm^3$) and cooling to −78 °C gave black crystals of the product, yield 0.14 g (75%).

The complex is stable under nitrogen, and is soluble in n-hexane and polar solvents such as $CH_2Cl_2$ to give air-sensitive dark red solutions.

*Di-μ-nitrosyl-bis(η-pentamethylcyclopentadienyl)dicobalt Hexafluorophosphate*, $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2][PF_6]$ (4).—Nitric oxide gas was slowly bubbled through a solution of $[Co_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$ (2) (0.40 g, 0.68 mmol) in $CH_2Cl_2$ (25 $cm^3$) until the green solution became mauve (*ca.* 5 min). Reduction of the solvent volume *in vacuo* and addition of n-hexane (75 $cm^3$) gave a dark red precipitate which was recrystallised from $CH_2Cl_2$–n-hexane as dark red *crystals*, yield 0.35 g (87%).

The complex dissolves in polar solvents to give deep mauve solutions; the solid slowly decomposes even under an atmosphere of dry nitrogen.

*Di-μ-nitrosyl-bis(η-pentamethylcyclopentadienyl)dicobalt*, $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2]$ (5).—Addition of $K[BH(CHMeEt)_3]$ (0.7 $cm^3$ of a 1 mol $dm^{-3}$ solution in thf) to a stirred suspension of $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2][PF_6]$ (4) (0.31 g, 0.52 mmol) in a 1 : 1 mixture of hexane and thf (25 $cm^3$) immediately gave a brown solution which was filtered and evaporated to dryness. Extraction of the residue with n-hexane (10 $cm^3$), filtration, and cooling to −78 °C gave the product as a black solid, yield 23 mg (10%).

The air-sensitive solid dissolves in common organic solvents to give dark red, air-sensitive solutions.

*Synthesis of* $[Co_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}NO)(\eta\text{-}C_5H_5)_2][PF_6]$ *and* $[Co(CNC_6H_3Me_2\text{-}2,6)_3(NO)]$.—Xylyl isocyanide (0.21 g, 1.6 mmol) was added to $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2][PF_6]$ (1) (0.30 g, 0.66 mmol) in $CH_2Cl_2$ (25 $cm^3$). The resulting dark yellow solution was filtered, and n-hexane (75 $cm^3$) added to give a dark yellow solid and a red solution. The precipitate was recrystallised from $CH_2Cl_2$–n-hexane to give dark yellow $[Co_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}NO)(\eta\text{-}C_5H_5)_2][PF_6]$, yield 0.11 g (24%).

The red solution was evaporated to dryness and the residue dissolved in toluene and chromatographed on an alumina–n-hexane column. Elution with toluene gave a brown solution which, on evaporation to dryness, gave $[Co(CNC_6H_3Me_2\text{-}2,6)_3(NO)]$ as red crystals, yield 48 mg (19% based on $CNC_6H_3Me_2$-2,6). The complex is soluble in common organic solvents to give air-stable red solutions.

*Tris(μ-difluorophosphato)-bis(η-pentamethylcyclopentadienyl)dicobalt Hexafluorophosphate*, $[Co_2(\mu\text{-}O_2PF_2)_3(\eta\text{-}C_5Me_5)_2][PF_6]$.—To a rapidly stirred suspension of $[NO][PF_6]$ (0.15 g, 0.86 mmol) in $CH_2Cl_2$ (17 $cm^3$) was added $[Co(CO)_2(\eta\text{-}C_5Me_5)]$ (0.085 g, 0.34 mmol). The blue solution was filtered, and n-hexane (75 $cm^3$) added to give a blue solid. Recrystallisation from $CH_2Cl_2$–n-hexane gave the product, yield 0.12 g (43%).

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