Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 25.[1] The One-electron Reduction of Cationic Cyclopentadienyl–Cobalt and –Rhodium Nitrosyl Derivatives *

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The complexes $[ML(NO)(\eta\text{-}C_5R_5)][PF_6]$ [M = Co or Rh, R = H, L = PPh_3; R = Ph, L = $P(OMe)_3$ or $P(OPh)_3$] undergo diffusion-controlled, one-electron reduction at a platinum-bead electrode in CH_2Cl_2 or tetrahydrofuran (thf). Reduction of the cobalt complexes either chemically with $[Co(\eta\text{-}C_5H_5)_2]$ or by controlled potential electrolysis leads to P-donor ligand elimination, and dimerisation, to give $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]$ (R = H or Ph). The primary reduction products, namely $[CoL(NO)(\eta\text{-}C_5Ph_5)]$ [L = $P(OMe)_3$ or $P(OPh)_3$], have been detected by e.s.r. spectroscopy at −196 °C; the rhodium analogues, $[RhL(NO)(\eta\text{-}C_5Ph_5)]$ [L = $P(OMe)_3$ or $P(OPh)_3$] are stable at room temperature and have been isolated from the reaction between $[RhL(NO)(\eta\text{-}C_5Ph_5)][PF_6]$ and $[Co(\eta\text{-}C_5H_5)_2]$. The dimer $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2]$ undergoes two reversible, one-electron oxidations and one irreversible, one-electron reduction; the paramagnetic salt $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2][PF_6]$ has been isolated *via* $[N_2C_6H_4F\text{-}p][PF_6]$ oxidation of the neutral precursor. The rhodium dimer $[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2]$, prepared by the reductive nitrosylation of $[\{RhBr_2(\eta\text{-}C_5Ph_5)\}_2]$ with NO gas and $[Co(\eta\text{-}C_5H_5)_2]$ in thf, or by the $[Co(\eta\text{-}C_5H_5)_2]$ reduction of $[RhI(NO)(\eta\text{-}C_5Ph_5)]$, undergoes reversible one-electron oxidation and reduction and a second, irreversible, one-electron oxidation.

We have recently shown that the one-electron oxidation of $[\{M(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]$ (M = Co, R = H or Me;[2] M = Rh, R = H[3]) results in the activation of the metal–metal (M = Co) bond towards cleavage by nucleophiles. Thus, for example, $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]^+$ and PPh_3 give $[ML(NO)(\eta\text{-}C_5R_5)]^+$ (**1**, M = Co, L = PPh_3, R = H) according to equation (**1**).

$$2[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]^+ + 2PPh_3 \longrightarrow [\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2] + 2[Co(PPh_3)(NO)(\eta\text{-}C_5H_5)]^+ \quad (1)$$

We now demonstrate that one-electron reduction reconverts the cations $[ML(NO)(\eta\text{-}C_5R_5)]^+$ (**1**, M = Co, L = phosphine or phosphite, R = H or Ph) to the dimers $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]$ *via* the radicals $[CoL(NO)(\eta\text{-}C_5R_5)]$, stable rhodium analogues of which have been isolated and fully characterised. We also describe the synthesis of $[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2]$, the cyclic voltammetry of $[\{M(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2]$ (M = Co and Rh) and the isolation of $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2][PF_6]$.

Results and Discussion

Cyclic Voltammetry of $[ML(NO)(\eta\text{-}C_5R_5)]^+$ (**1**, *M* = Co *or* Rh, *L* = *Phosphine or Phosphite*, *R* = H *or* Ph).—The cyclic voltammogram of $[ML(NO)(\eta\text{-}C_5R_5)][PF_6]$ (**1**, M = Co, L = PPh_3, R = H), from 0.6 to −0.7 V, is shown in Figure 1. The one-electron (see below) reduction wave (E_{red} = −0.42 V, at a scan rate, v, of 200 mV s^{-1}) is diffusion controlled† but chemically irreversible, and corresponds to the formation of the radical $[ML(NO)(\eta\text{-}C_5R_5)]$ (**2**, M = Co, L = PPh_3, R = H), whose lifetime is no greater than several hundred ms at room temperature. The reversible oxidation wave (E° = 0.37 V), which is only observed if the reduction wave is scanned first,‡ is

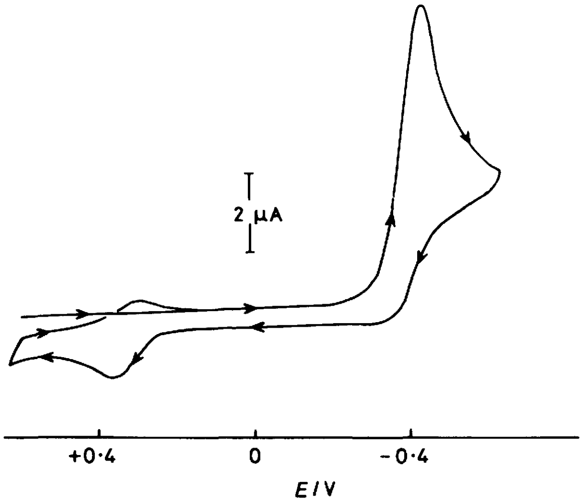

Figure 1. The cyclic voltammogram of $[Co(PPh_3)(NO)(\eta\text{-}C_5H_5)][PF_6]$ at a platinum-bead electrode in CH_2Cl_2. Potentials are *vs.* s.c.e. with 0.1 mol dm^{-3} $[NBu^n_4][PF_6]$ as supporting electrolyte

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* *Non-S.I. unit employed:* G = 10^{-4} T.

† Throughout this paper, diffusion-controlled waves show $i/v^{\frac{1}{2}}$ constant for scan rates 50 < v < 500 mV s^{-1}; chemical reversibility is characterised by i_{ox}/i_{red} = 1 (over the same range of scan rates). Reversible waves show a peak-to-peak separation similar to that observed for the one-electron oxidation of $[Fe(\eta\text{-}C_5H_5)_2]$, under identical conditions. Numerical data are given only when necessary.

‡ The diminished peak height of the new product couple (E° = 0.37 V) is as expected under the conditions. During the time the potential is scanned from *ca.* −0.4 to 0.2 V, no electrolysis is occurring and the product of the reduction at −0.42 V is diffusing away from the electrode surface.

identical[2] to that of $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$ implying that (**2**, M = Co, L = PPh_3, R = H) undergoes loss of phosphine and dimerisation. Futher evidence for this reaction is provided by scanning the cyclic voltammogram of (**1**, M = Co, L = PPh_3, R = H) to more negative potentials. Thus, a second irreversible reduction wave is observed at $E_{pk} = -1.4$ V, again identical to that observed[2] for the reduction of $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$.

The electrochemical behaviour (Table 1) of [**1**, M = Co, L = $P(OMe)_3$ or $P(OPh)_3$, R = Ph], prepared from $[Co(CO)L(\eta\text{-}C_5Ph_5)]$ and $[NO][PF_6]$ in CH_2Cl_2 and characterised by elemental analysis and i.r. spectroscopy (Table 2), is very similar to that of (**1**, M = Co, L = PPh_3, R = H). The potential of the first reduction wave is dependent on L, as expected for the formation of [**2**, M = Co, L = $P(OMe)_3$ or $P(OPh)_3$, R = Ph], but the product waves are identical for both of the phosphite derivatives and correspond to the oxidation and reduction waves of the dimer (**3**, M = Co, R = Ph) (see below).

Table 1. Cyclic voltammetric data for nitrosyl complexes

Complex	Process[a]	E° or E_{pk}[b]/V
$[Co(PPh_3)(NO)(\eta\text{-}C_5H_5)][PF_6]$	$+1 \longrightarrow 0$	−0.42 (I)
$[Co\{P(OMe)_3\}(NO)(\eta\text{-}C_5Ph_5)][PF_6]$	$+1 \longrightarrow 0$	−0.27 (I)
$[Co\{P(OPh)_3\}(NO)(\eta\text{-}C_5Ph_5)][PF_6]$	$+1 \longrightarrow 0$	−0.16 (I)
$[Rh(PPh_3)(NO)(\eta\text{-}C_5H_5)][PF_6]$	$+1 \longrightarrow 0$	−0.38 (I)
$[Rh\{P(OMe)_3\}(NO)(\eta\text{-}C_5Ph_5)][PF_6]$	$+1 \longrightarrow 0$	−0.18 (R)
	$0 \longrightarrow -1$	−1.07 (I)
$[Rh\{P(OPh)_3\}(NO)(\eta\text{-}C_5Ph_5)][PF_6]$	$+1 \longrightarrow 0$	−0.02 (R) (0.14)[c]
	$0 \longrightarrow -1$	−0.94 (I) (−0.90)[c]
$[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2]$	$0 \longrightarrow -1$	−1.40 (I)
	$0 \longrightarrow +1$	0.46 (R)
	$+1 \longrightarrow +2$	1.25 (R)
$[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$	$0 \longrightarrow -1$	−1.4 (I)[d]
	$0 \longrightarrow +1$	0.37 (R)
	$+1 \longrightarrow +2$	1.22 (R)
$[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2][PF_6]$	$0 \longrightarrow -1$	−1.7 (I)[d]
	$+1 \longrightarrow 0$	−0.11 (R)
	$+1 \longrightarrow +2$	0.72 (R)
$[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2]$	$0 \longrightarrow -1$	−1.08 (R)
	$0 \longrightarrow +1$	0.71 (R)
	$+1 \longrightarrow +2$	1.18 (I)
$[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$	$0 \longrightarrow -1$	−1.13 (R)[e]
	$0 \longrightarrow +1$	0.7 (I)[e]

[a] All processes are diffusion-controlled and one-electron, obeying the criterion $i/v^{\frac{1}{2}}$ = constant for scan rates, v, in the range 50—500 mV s^{-1}. [b] E° values are reported for reversible (R) processes, calculated as the average of the cathodic and anodic peak potentials. Peak potentials, E_{pk}, are reported for irreversible (I) processes, at v = 200 mV s^{-1}. [If the heterogeneous charge transfers are rapid, the E° value of an irreversible wave will be *ca.* 0.03 V positive of E_{pk}(oxidation) or *ca.* 0.03 V negative of E_{pk}(reduction).] All potentials are *versus* the aqueous saturated calomel electrode, at a platinum-bead electrode in CH_2Cl_2 with 0.1 mol dm^{-3} $[NBu^n_4][PF_6]$ as supporting electrolyte. Under these conditions, the E° values for the couples $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ and $[Fe(\eta\text{-}C_5Me_5)_2]^+$–$[Fe(\eta\text{-}C_5Me_5)_2]$ are 0.47 and −0.07 V respectively. [c] In thf. [d] Data taken from ref. 2. [e] Data taken from ref. 3.

The cyclic voltammetry of (**1**, M = Rh) is rather different from that of the cobalt analogues, and provides evidence for the increased stability of the radicals (**2**, M = Rh). In CH_2Cl_2, at scan rates in excess of 300 mV s^{-1}, the diffusion-controlled reduction of (**1**, M = Rh, L = PPh_3, R = H) is reversible with $E^\circ = -0.38$ V (at slower scan speeds, $i_{ox}/i_{red} < 1$). A second, diffusion-controlled reduction wave at *ca.* −1.2 V is also partially reversible ($0.72 < i_{ox}/i_{red} < 0.89$ for $44 < v < 438$ mV s^{-1}), but the value of $i_{red}/v^{\frac{1}{2}}$ is approximately half that of the first wave, and the formation of $[Rh(PPh_3)(NO)(\eta\text{-}C_5H_5)]^-$ is not certain. In tetrahydrofuran (thf), the second reduction wave is very poorly defined. However, the first is reversible at scan rates as slow as 78 mV s^{-1}, implying that (**2**, M = Rh, L = PPh_3, R = H) is more stable in thf than in CH_2Cl_2.

The most stable examples of (**2**) are formed from the pentaphenylcyclopentadienylrhodium cations [**1**, M = Rh, L = $P(OMe)_3$ or $P(OPh)_3$, R = Ph] (Table 2). For example, the first reduction wave of $[Rh\{P(OPh)_3\}(NO)(\eta\text{-}C_5Ph_5)][PF_6]$ in CH_2Cl_2 or thf (Table 1) is fully reversible for all scan rates used. In addition, the ratio of the height of the second reduction wave to that of the first is closer to one than for the C_5H_5 analogue suggesting, perhaps, that the anions $[RhL(NO)(\eta\text{-}C_5Ph_5)]^-$ [L = $P(OMe)_3$ or $P(OPh)_3$] *do* result from the second reduction reaction.

The Controlled Potential Reduction of (**1**).—The cyclic voltammetric studies described above suggested that the one-electron reduction of (**1**) would provide routes to $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]$ and $[RhL(NO)(\eta\text{-}C_5Ph_5)]$. These suggestions were borne out by controlled potential electrolysis, coulometry, and voltammetry.

On bulk electrolysis at −0.6 V, an orange-brown solution of $[Co(PPh_3)(NO)(\eta\text{-}C_5H_5)][PF_6]$ in CH_2Cl_2 became dark brown during the consumption of 0.96 F mol^{-1}. The cyclic voltammogram of the product solution then showed only the reversible one-electron oxidation ($E^\circ = 0.37$ V) and irreversible reduction ($E_{red} \approx -1.4$ V) waves diagnostic of $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$ (see above). Similarly, the electrolytic reduction of [**1**, M = Co, L = $P(OMe)_3$, R = Ph ($E_{app} = -0.6$ V; 0.93 F mol^{-1})] gave a green solution of $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2]$. The synthesis, by chemical reduction of [**1**, M = Co, L = $P(OPh)_3$, R = Ph], and characterisation of this previously unknown dimer are described below.

The cation (**1**, M = Rh, L = PPh_3, R = H) was also reduced ($E_{app} = -0.6$ V) in a one-electron step (0.91 F mol^{-1}) but the cyclic voltammogram of the product solution showed only ill defined waves; no products were identifiable. By contrast, the

Table 2. Infrared spectroscopic and analytical data for nitrosyl complexes

Complex	Colour	Yield (%)	$\tilde{v}(NO)$[a]/cm^{-1}	Analysis[b] (%) C	H	N
$[Co\{P(OMe)_3\}(NO)(\eta\text{-}C_5Ph_5)][PF_6]$	Green	85	1 836	56.7 (56.8)	4.2 (4.3)	1.9 (1.7)
$[Co\{P(OPh)_3\}(NO)(\eta\text{-}C_5Ph_5)][PF_6]$	Green	80	1 840	63.7 (64.3)	3.9 (4.0)	1.4 (1.4)
$[Rh\{P(OMe)_3\}(NO)(\eta\text{-}C_5Ph_5)][PF_6]$	Red	91	1 819	53.7 (53.9)	4.2 (4.0)	1.3 (1.6)
$[Rh\{P(OPh)_3\}(NO)(\eta\text{-}C_5Ph_5)][PF_6]$	Red	85	1 825	61.4 (61.6)	4.0 (3.9)	1.2 (1.3)
$[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2]$	Green-brown	94	1 580, 1 520[c]	78.7 (78.6)	4.9 (4.7)	2.3 (2.6)
$[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2][PF_6]$[d]	Dark green	76	1 595[c]	67.1 (67.4)	4.2 (4.1)	2.1 (2.2)
$[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2]$	Black	24	1 566, 1 524[c]	73.0 (72.7)	4.7 (4.4)	2.2 (2.4)
$[Rh\{P(OMe)_3\}(NO)(\eta\text{-}C_5Ph_5)]$	Dark brown	45		66.0 (65.0)	4.9 (4.7)	2.0 (1.8)

[a] In CH_2Cl_2 unless otherwise stated. [b] Calculated values are given in parentheses. [c] In Nujol. [d] Analysed as a $0.5CH_2Cl_2$ solvate.

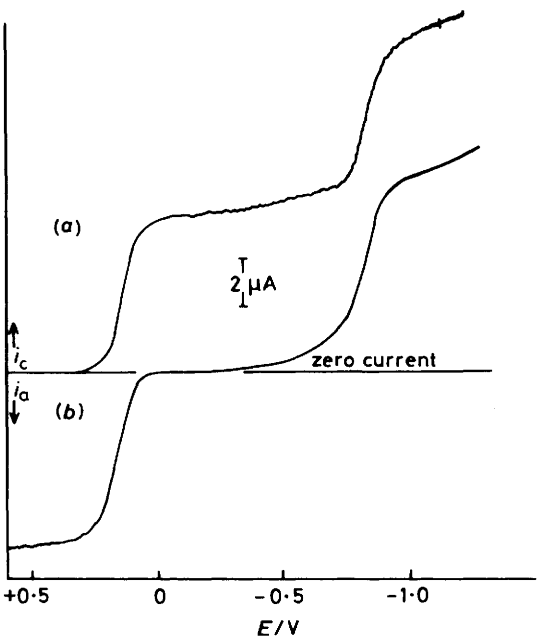

Figure 2. (*a*) The voltammogram of $[Rh\{P(OPh)_3\}(NO)(\eta\text{-}C_5Ph_5)][PF_6]$, in thf at a rotating platinum-bead electrode, and (*b*) after controlled potential reduction at −0.1 V

controlled potential reduction of [**1**, M = Rh, L = $P(OPh)_3$, R = Ph] in thf provided unequivocal evidence for the stable radical $[Rh\{P(OPh)_3\}(NO)(\eta\text{-}C_5Ph_5)]$.

The voltammogram of [**1**, M = Rh, L = $P(OPh)_3$, R = Ph], in thf at a rotating platinum electrode, is shown in Figure 2(*a*); the observation of two reduction waves of nearly equal height is in agreement with the cyclic voltammetric study described above. After electrolysis at −0.1 V (0.95 F mol^{-1}), the voltammogram [Figure 2(*b*)] is identical except that the wave at 0.14 V corresponds to the oxidation of [**2**, M = Rh, L = $P(OPh)_3$, R = Ph]; the quantitative nature of the reduction may be deduced from the constancy of the wave height associated with the couple (**1**)–(**2**).

The Chemical Reduction of (**1**).—The reduction reactions described above may also be carried out by chemical methods. Thus, the addition of $[Co(\eta\text{-}C_5H_5)_2]$ to a suspension of [**1**, M = Co, L = $P(OPh)_3$, R = Ph] in thf gave a green solution from which an excellent yield of $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2]$ was isolated *via* column chromatography on alumina. The dimer, which could not be prepared directly from $[Co(CO)_2(\eta\text{-}C_5Ph_5)]$ and NO gas (*cf.* $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$[4]), was characterised by elemental analysis and i.r. spectroscopy (Table 2); two i.r. absorptions at 1 580 and 1 520 cm^{-1} (Nujol) were assigned to the bridging nitrosyl ligands by analogy with $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$ [$\tilde{\nu}$(NO) (KBr) = 1 585 and 1 525 cm^{-1}].[4]

The reaction of a suspension of [**1**, M = Rh, L = $P(OPh)_3$ or $P(OMe)_3$, R = Ph] with $[Co(\eta\text{-}C_5H_5)_2]$ in benzene gave a dark brown solution and a precipitate of $[Co(\eta\text{-}C_5H_5)_2][PF_6]$. After filtration, $[RhL(NO)(\eta\text{-}C_5Ph_5)]$ [L = $P(OMe)_3$ or $P(OPh)_3$] were readily isolated in low yield as dark brown solids which decompose in air.

Only the $P(OMe)_3$ derivative, which is the more thermally stable, has been characterised by elemental analysis (Table 2) but both give well defined e.s.r. spectra at room temperature. Figure 3 shows the spectrum of [**2**, M = Rh, L = $P(OPh)_3$, R = Ph] in thf.* It is deceptively simple in showing four lines (g_{av} = 1.97) but is consistent with equal hyperfine coupling (A = 15 G) to the nitrosyl nitrogen atom (^{14}N, I = 1) and to a second atom with $I = \frac{1}{2}$ (either ^{31}P or ^{103}Rh). The anisotropic spectrum (in frozen thf, at −196 °C) will be discussed in detail elsewhere, but each component shows *inequivalent* coupling to nitrogen and the second spin-active nucleus.

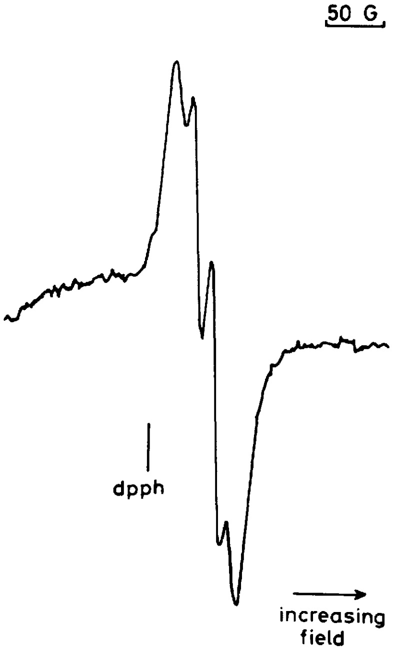

Figure 3. The room-temperature e.s.r. spectrum of $[Rh\{P(OPh)_3\}(NO)(\eta\text{-}C_5Ph_5)]$ in thf

The ^{14}N hyperfine coupling in the e.s.r. spectra of [**2**, M = Rh, L = $P(OMe)_3$ or $P(OPh)_3$, R = Ph] suggests that the reduction of (**1**) results in partial localisation of the unpaired electron on the nitrosyl nitrogen atom. Such localisation has previously been observed[5] when $[W(PR_3)(NO)_2(\eta\text{-}C_5H_5)]^+$ (R = Ph, OMe, or OPh) is reduced to paramagnetic $[W(PR_3)(NO)_2(\eta\text{-}C_5H_5)]$ [$A(^{14}N)$ = 7.0 G]. In this case a drastic lowering of $\tilde{\nu}$(NO) (by *ca.* 160—175 cm^{-1}) and a bending of the W–N–O bond angle (*ca.* 5—10°) occurs. Unfortunately, no band attributable to $\tilde{\nu}$(NO) was detected in the i.r. spectrum of (**2**). However, a large decrease similar to that found for the tungsten dinitrosyls would place $\tilde{\nu}$(NO) for (**2**) in a region obscured by bands associated with the C_5Ph_5 ligand.

The characterisation of [**2**, M = Rh, L = $P(OMe)_3$ or $P(OPh)_3$] leads us to propose that $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]$ is formed from (**1**, M = Co) *via* the route (2).

$$\begin{tikzcd}
{[CoL(NO)(\eta\text{-}C_5R_5)]^+} \arrow[r, "+e^-"] & {[CoL(NO)(\eta\text{-}C_5R_5)]} \arrow[d, "-L"] \\
& \frac{1}{2}[\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]
\end{tikzcd} \qquad (2)$$

As further evidence for this proposal, it is noteworthy that addition of CH_2Cl_2 to a solid mixture of $[Co(\eta\text{-}C_5H_5)_2]$ and [**1**, M = Co, L = $P(OMe)_3$ or $P(OPh)_3$, R = Ph], followed by rapid cooling to −196 °C, results in the observation of anisotropic e.s.r. spectra qualitatively similar to those of (**2**, M = Rh). Not only do these spectra provide excellent evidence

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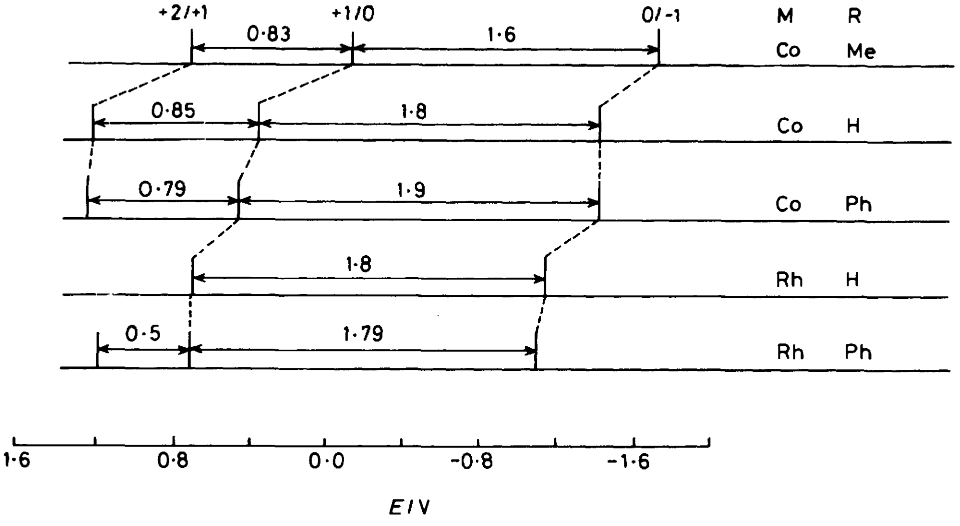
* The spectrum is identical whether the complex is prepared using $[Co(\eta\text{-}C_5H_5)_2]$ in benzene or generated by controlled potential electrolysis in thf.



Scheme. The differences (V) between two reversible waves and between one reversible and one irreversible wave, given to two and one decimal place respectively, for $[\{M(\mu\text{-}NO)(\eta\text{-}C_5R_5)_2\}]$

for [2, M = Co, L = P(OMe) or $P(OPh)_3$, R = Ph] but also suggest that the hyperfine coupling is due to ^{14}N and ^{31}P, rather than to the metal, for both cobalt and rhodium radicals (see above). This conclusion is, however, tentative and corroboration must await a more complete analysis of the frozen-solution spectra.

The Synthesis of $[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2]$.—In order to compare the redox properties of $[\{M(NO)(\eta\text{-}C_5R_5)\}_2]$ (3, M = Co or Rh) we have devised new routes to (3, M = Rh, R = Ph); the established[6] synthesis for (3, M = Rh, R = H) gives a very poor yield and we have, therefore, previously been restricted in our electrochemical studies of nitrosyl-bridged rhodium dimers.[3]

The addition of $[NBu^n_4]I$ to $[Rh\{P(OPh)_3\}(NO)(\eta\text{-}C_5Ph_5)][PF_6]$ in CH_2Cl_2 gave a dark green solution [$\tilde{\nu}$(NO) = 1 798 cm^{-1}] which we assume contains $[RhI(NO)(\eta\text{-}C_5Ph_5)]$. Precipitating the products with n-hexane, redissolving the solid in thf, and treatment with $[Co(\eta\text{-}C_5H_5)_2]$ gave a black solution from which $[\{Rh(NO)(\eta\text{-}C_5Ph_5)\}_2]$ was isolated *via* column chromatography. Alternatively, (3, M = Rh, R = Ph) may be prepared by the reductive nitrosylation of $[\{RhBr_2(\eta\text{-}C_5Ph_5)\}_2]$. Thus, addition of $[Co(\eta\text{-}C_5H_5)_2]$ to a suspension of the bromo-bridged dimer in NO-saturated thf gave a black solution from which $[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2]$ was isolated as above.

The second route is, unfortunately, inapplicable to the synthesis of the C_5H_5 analogue. It is known that $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$ reacts further with NO gas to give the unstable dinitrosyl $[Co(NO)_2(\eta\text{-}C_5H_5)]$[7] and it seems likely that any $[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$ initially formed is rapidly destroyed *via* a similar pathway.

Redox Properties of $[\{M(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2]$ (M = Co *or* Rh).—The cyclic voltammogram of $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2]$ is similar to those of $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]$ (R = H or Me),[2] with two reversible one-electron oxidation waves at 0.46 and 1.25 V and one irreversible reduction wave at −1.40 V (all of which are diffusion controlled). The data are compared with related dimers in Table 1 and in the Scheme.

The first trend to note involves the effect of R on $E°$. The shift to more positive potentials, when R = H is replaced by R = Ph, is as expected[8,9] but is small (*ca.* 50—100 mV) compared, for example, with the effect of R = Me. Thus, permethylation of the C_5 rings shifts the redox potentials to markedly more negative values (*ca.* 500 mV), greatly increasing the chemical accessibility of the more oxidised species. The C_5Ph_5 ring, then, appears to stabilise the paramagnetic products of both one-electron oxidation and reduction *via* steric rather than electronic effects.

The second trend revealed in the Scheme involves the separations between the two oxidation waves, Δ_1, and between the reduction and first oxidation waves, Δ_2, of the cobalt complexes. That these separations are nearly independent of R ($\Delta_1 \approx 0.8$, $\Delta_2 = 1.6$—1.9 V) suggests that the C_5 ring substituent has very little effect on any structural changes accompanying electron transfer. The *X*-ray structures of $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]^z$ ($z = 0$[10] or $+1$[11]) and $[\{Co(\mu\text{-}CO)(\eta\text{-}C_5Me_5)\}_2]$[12] (which is isoelectronic with $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]^{2+}$) show the $Co_2(\mu\text{-}X)_2$ (X = N or C) cores to be essentially planar with the C_5 rings parallel, and orthogonal to the cobalt–cobalt vectors. Thus, one might well expect even the bulky phenyl substituents to have little steric effect on the core structure. No structural data exist for $[\{M(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]^-$, or any analogues, but the constancy of Δ_2 again suggests that the $M_2(\mu\text{-}N)_2$ core of the neutral complex may not pucker on reduction.

The low potential for the first oxidation of (3, M = Co, R = Ph) results in the ready synthesis of the monocation. Thus, addition of $[N_2C_6H_4F\text{-}p][PF_6]$ to the neutral dimer in CH_2Cl_2 gave a high yield of dark green $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2][PF_6]$ (Table 2). The isotropic e.s.r. [15 lines, $g_{av} = 2.048$, $A(^{59}Co) = 37.8$ G] and i.r. [$\tilde{\nu}$(NO) (Nujol) = 1 595 cm^{-1}] spectra are very similar to those of the C_5R_5 (R = H or Me) analogues.[2]

The cyclic voltammogram of (3, M = Rh, R = Ph) is different both from the cobalt analogues and from (3, M = Rh, R = H) (Table 1). Like its C_5H_5 analogue, (3, M = Rh, R = Ph) undergoes a *reversible* one-electron reduction (*cf.* M = Co). However, the C_5Ph_5 rhodium complex shows *two* oxidation waves, the first of which is reversible and the second irreversible; the complex (3, M = Rh, R = H) shows only one, irreversible oxidation wave. Here again, the separation between the reduction and first oxidation waves is *ca.* 1.8 V, but that between the two oxidation waves is reduced to *ca.* 0.5 V.

Unfortunately, we have been unable to detect the e.s.r. spectra of either the monocation or monoanion of (3, M = Rh, R = Ph). However, the stability of $[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]^-$

(R = H or Ph), at least on the cyclic voltammetric time-scale, suggests that one-electron transfer precedes cleavage when $[Co(NO)(\eta\text{-}C_5H_5)]^-$ is prepared by sodium-amalgam reduction of $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5H_5)\}_2]$.[13]

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 CH_2Cl_2 to give moderately air-sensitive solutions. The compounds $[M(CO)L(\eta\text{-}C_5Ph_5)]$ [M = Co or Rh, L = $P(OMe)_3$ or $P(OPh)_3$],[9] $[\{RhBr_2(\eta\text{-}C_5Ph_5)\}_2]$,[9] $[M(PPh_3)(NO)(\eta\text{-}C_5H_5)][PF_6]$ (M = Co or Rh),[14] $[Co(\eta\text{-}C_5H_5)_2]$,[15] and $[N_2C_6H_4F\text{-}p][PF_6]$[16] were prepared by published methods. The salt $[NO][PF_6]$ was purchased from Flurochem, Ltd. (Glossop, Derbyshire).

Infrared spectra were recorded on a Nicolet MX-5 spectrometer, or a Perkin-Elmer PE257 spectrometer with calibration against the absorption band of polystyrene at 1 601 cm^{-1}. Hydrogen-1 n.m.r. spectra were recorded on a JEOL PMX60 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 (dpph).

Electrochemical studies were carried out using AMEL Electrochemolab or PAR 170 instruments in conjunction with a three-electrode cell. For cyclic voltammetry the auxiliary and working electrodes were platinum wires and the reference was an aqueous saturated calomel electrode (s.c.e.) separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. A similar configuration was used for controlled potential electrolysis but with a platinum gauze basket as the working electrode and a platinum spiral as auxiliary electrode. Voltammetry used a platinum-bead electrode rotated at 600 revolutions min^{-1}. Solutions were 0.5×10^{-3} and 1.0×10^{-3} mol dm^{-3} in complex for voltammetry and controlled potential electrolysis respectively; in both cases the solutions were 0.1 mol dm^{-3} in $[NBu^n_4][PF_6]$ as supporting electrolyte. Under these conditions, E° for the couples $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ and $[Fe(\eta\text{-}C_5Me_5)_2]^+$–$[Fe(\eta\text{-}C_5Me_5)_2]$ are 0.47 and −0.07 V respectively. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Nitrosyl(η-pentaphenylcyclopentadienyl)(trimethyl phosphite)rhodium Hexafluorophosphate, $[Rh\{P(OMe)_3\}(NO)(\eta\text{-}C_5Ph_5)][PF_6]$.—To a stirred solution of $[Rh(CO)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$ (0.19 g, 0.27 mmol) in CH_2Cl_2 (60 cm^3) was added $[NO][PF_6]$ (0.056 g, 0.32 mmol). After 1 h the red solution was filtered through Celite and n-hexane was added to precipitate the product. The red crystals were washed with toluene (2 × 40 cm^3) and n-hexane (2 × 40 cm^3) and air dried, yield 0.21 g (91%). ^1H N.m.r., 3.70 [9 H, d, J(MeP) 10 Hz, $P(OMe)_3$], 7.00 (25 H, m, C_5Ph_5).

The compounds $[ML(NO)(\eta\text{-}C_5Ph_5)][PF_6]$ [M = Co, L = $P(OMe)_3$ or $P(OPh)_3$; M = Rh, L = $P(OPh)_3$] were prepared similarly.

Di-μ-nitrosyl-bis(η-pentaphenylcyclopentadienyl)dicobalt, $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2]$.—To a suspension of $[Co\{P(OPh)_3\}(NO)(\eta\text{-}C_5Ph_5)][PF_6]$ (0.16 g, 0.16 mmol) in thf (40 cm^3) was added $[Co(\eta\text{-}C_5H_5)_2]$ (0.03 g, 0.16 mmol). After stirring for 20 min, the green solution was filtered through Celite and hexane (80 cm^3) was added to give a green solid. The solid was redissolved in benzene and chromatographed on an alumina–n-hexane column, elution with benzene giving a green solution. Addition of n-heptane and partial removal of the solvent *in vacuo* gave the product as a green-brown precipitate, yield 82 mg (94%).

The complex is moderately soluble in benzene or toluene giving green solutions.

Di-μ-nitrosyl-bis(η-pentaphenylcyclopentadienyl)dicobalt Hexafluorophosphate, $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2][PF_6]$.—The addition of solid $[N_2C_6H_4F\text{-}p][PF_6]$ (0.03 g, 0.12 mmol) to a stirred solution of $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2]$ (0.13 g, 0.12 mmol) in CH_2Cl_2 (70 cm^3) immediately gave a dark green solution. After filtration through Celite, and reduction of the volume of solvent *in vacuo*, addition of n-hexane gave a dark green solid. The product was washed with toluene (40 cm^3) and then n-hexane (40 cm^3) and air dried, yield 0.11 g (75%).

Di-μ-nitrosyl-bis(η-pentaphenylcyclopentadienyl)dirhodium, $[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5Ph_5)\}_2]$.—*Method A*. Solid $[NBu^n_4]I$ (0.16 g, 0.42 mmol) was added to a stirred solution of $[Rh\{P(OPh)_3\}(NO)(\eta\text{-}C_5Ph_5)][PF_6]$ (0.43 g, 0.42 mmol) in CH_2Cl_2 (15 cm^3). After 5 min, the dark green solution was filtered, and n-hexane (60 cm^3) was added to give a dark green precipitate. The solid was then dissolved in thf (30 cm^3), $[Co(\eta\text{-}C_5H_5)_2]$ (0.08 g, 0.42 mmol) was added, and the black solution filtered after stirring for 10 min. The filtrate was then reduced to low volume *in vacuo*, and chromatographed on an alumina–n-hexane column. Elution with thf–n-hexane (2:3) gave a black band from which the product was isolated as a black solid by partial removal of the solvent *in vacuo*, yield 60 mg (25%). The complex is moderately soluble in benzene or toluene giving black solutions.

Method B. To a stirred suspension of $[\{RhBr_2(\eta\text{-}C_5Ph_5)\}_2]$ (0.40 g, 0.28 mmol), in thf (60 cm^3) saturated with NO gas, was added $[Co(\eta\text{-}C_5H_5)_2]$ (0.20 g, 1.06 mmol). After 5 min the black solution was filtered, reduced to low volume *in vacuo*, and chromatographed as above, yield 50 mg (16%).

Nitrosyl(η-pentaphenylcyclopentadienyl)(trimethyl phosphite)rhodium, $[Rh\{P(OMe)_3\}(NO)(\eta\text{-}C_5Ph_5)]$.—To a stirred solution of $[Rh\{P(OMe)_3\}(NO)(\eta\text{-}C_5Ph_5)][PF_6]$ (0.21 g, 0.22 mmol) in benzene (20 cm^3) was added $[Co(\eta\text{-}C_5H_5)_2]$ (0.04 g, 0.21 mmol). After 10 min the brown solution was filtered, and n-heptane (40 cm^3) was added. Partial evaporation *in vacuo* gave the product as a dark brown solid, yield 80 mg (45%).

$[Rh\{P(OPh)_3\}(NO)(\eta\text{-}C_5Ph_5)]$ was prepared similarly; both complexes slowly decompose in the solid state, and are soluble in benzene, toluene, or thf to give air-sensitive brown solutions.

Acknowledgements

We thank the S.E.R.C. for a Research Studentship (to S. J. R.), the National Science Foundation and N.A.T.O. for financial support, and Johnson Matthey for a generous loan of rhodium trichloride.

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Recieved 16*th April* 1986; *Paper* 6/736