Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 31.[1] Reductive Elimination, Oxidative Addition and Substitution, and Migratory Insertion in Pentaphenylcyclopentadienylruthenium Nitrosyl Chemistry

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The complexes [RuBr(CO)L(η-C_5Ph_5)] [**1**; L = PPh_3, PEt_3, $P(OMe)_3$, or $P(OPh)_3$] react with [NO][PF_6] in CH_2Cl_2 to give [RuBrL(NO)(η-C_5Ph_5)][PF_6] [**2**; L = PPh_3, PEt_3, $P(OMe)_3$, or $P(OPh)_3$]; an excess of [NO][PF_6] with (**1**; L = PEt_3) yields [Ru(CO)(PEt_3)(NO)(η-C_5Ph_5)][PF_6]$_2$ (**3**). The chemical reduction of (**2**) with [Co(η-C_5H_5)$_2$] gives [RuL(NO)(η-C_5Ph_5)] [**4**; L = PEt_3, $P(OMe)_3$, or $P(OPh)_3$], but electrolytic reduction gives (**4**) and [RuX_2(NO)(η-C_5Ph_5)] (**5**; X = Br), the latter *via* the reaction of (**2**) with Br^- ions. Cyclic voltammetry shows that [**4**, L = $P(OPh)_3$] is reversibly oxidised, but in the presence of PPh_3 oxidative substitution gives (**4**; L = PPh_3). Complex (**4**) also undergoes oxidative addition with halogens to give (**5**; X = Br or I). The reaction between [RuMe(CO)L(η-C_5Ph_5)] [**6**; L = PEt_3, $P(OMe)_3$, $P(OPh)_3$, or $CNBu^t$] and [NO][PF_6] results in migratory insertion, giving [Ru(COMe)L(NO)(η-C_5Ph_5)][PF_6] [**7**; L = PEt_3, $P(OMe)_3$, $P(OPh)_3$, or $CNBu^t$]. The one-electron reduction of (**7**) gives the neutral radicals [Ru(COMe)L(NO)(η-C_5Ph_5)] [**8**; L = PEt_3, $P(OMe)_3$, $P(OPh)_3$, or $CNBu^t$] the e.s.r. spectra of which show extensive localisation of the unpaired electron on the nitrosyl ligand.

During recent studies[2] of the redox reactions of pentaphenylcyclopentadienylruthenium carbonyls we observed that competitive nitrosyl substitution appeared to occur if [NO][PF_6] was used as an oxidant. We now show that such substitution does indeed occur giving [RuBrL(NO)(η-C_5Ph_5)]$^+$ from [RuBr(CO)L(η-C_5Ph_5], and [Ru(COMe)L(NO)(η-C_5Ph_5)]$^+$, *via* nitrosyl-induced migratory insertion, from [RuMe(CO)L(η-C_5Ph_5)] (L = phosphine, phosphite, or isocyanide). Both types of cationic complex are reduced, the bromides to [RuL(NO)(η-C_5Ph_5)] *via* redox-induced reductive elimination, and the acyls to 19-electron radicals [Ru(COMe)L(NO)(η-C_5Ph_5)].

Results and Discussion

Reaction of [NO]$^+$ *with* [RuBr(CO)L(η-C_5Ph_5)].—When [RuBr(CO)L(η-C_5Ph_5)] (**1**; L = PEt_3) and [NO][PF_6] were treated with CH_2Cl_2 and the resulting mixture was cooled rapidly to −196 °C the e.s.r. spectrum of the radical cation [RuBr(CO)(PEt_3)(η-C_5Ph_5)]$^+$ was readily detected.[2] At room temperature, however, the reaction between [NO][PF_6] and [**1**; L = PEt_3, PPh_3, $P(OMe)_3$, or $P(OPh)_3$] in CH_2Cl_2 gave brown solutions* from which the diamagnetic nitrosyl complexes [RuBrL(NO)(η-C_5Ph_5)][PF_6] [**2**; L = PEt_3, PPh_3, $P(OMe)_3$, or $P(OPh)_3$] were isolated in 40—75% yield; the salts were characterised by elemental analysis and by i.r. and n.m.r. spectroscopy (Table 1). In the case of (**1**; L = PEt_3) the reaction with an excess of [NO][PF_6] resulted in the slow deposition of an air-sensitive orange precipitate. Although the solid could not be recrystallised without decomposition, it was washed with toluene and then diethyl ether to give a product whose elemental analysis (C, H, and N) and i.r. spectrum (Table 1) are in agreement with the formula [Ru(CO)(PEt_3)(NO)(η-C_5Ph_5)][PF_6]$_2$ (**3**). The very high carbonyl-stretching frequency [$\tilde{\nu}$(CO)(Nujol) = 2 118 cm^{-1}] is consistent with the dipositive charge, and the nitrosyl stretching frequency [$\tilde{\nu}$(NO) = 1 882 cm^{-1}] is very similar to that of [Ru(PMe_3)$_2$(NO)(η-C_5H_5)]$^{2+}$, a complex prepared[3] from [NO][PF_6] and [RuCl(PMe_3)$_2$(η-C_5H_5)].

Despite the high carbonyl-stretching frequency of complex (**3**), implying a labile Ru–CO bond, carbonyl substitution to give an analogue of [Ru(PMe_3)$_2$(NO)(η-C_5H_5)]$^{2+}$ could not be effected. However, the dication rapidly reacted in tetrahydrofuran (thf) with 2 equivalents of the one-electron reductant [Co(η-C_5H_5)$_2$] to give [Co(η-C_5H_5)$_2$][PF_6] and an air-sensitive brown solid with an i.r. carbonyl band at 1 931 cm^{-1} but no peak due to the [PF_6]$^-$ anion. That the brown solid was uncharged was also implied by the ready observation of an electron-impact mass spectrum; peaks assignable to the ions [*M* − CO]$^+$, [*M* − PEt_3]$^+$, [*M* − CO − PEt_3]$^+$, and [*M* − CO − PEt_3 − NO]$^+$ suggest the formula [Ru(CO)(PEt_3)(NO)(η-C_5Ph_5)]. For this formula to be correct, the two-electron reduction of (**3**) must result in the conversion of the nitrosyl ligand from a three- into a one-electron donor, with concurrent bending of the Ru–N–O bond angle from linear to *ca.* 120°. However, no i.r. absorption could be reliably assigned to the nitrosyl stretching frequency [expected at a much lower energy than that of the nitrosyl band of (**3**)] and no further characterisation was possible.

Reduction of [RuBrL(NO)(η-C_5Ph_5)]$^+$ (**2**).—The addition of 2 equivalents of [Co(η-C_5H_5)$_2$] to [**2**; L = PEt_3 or $P(OMe)_3$] in CH_2Cl_2 gave a brown solution from which the air-sensitive neutral compound [RuL(NO)(η-C_5Ph_5)] [**4**; L = PEt_3 or $P(OMe)_3$] was isolated in high yield. Both complexes were fully characterised by elemental analysis, and by i.r. and ^{1}H n.m.r. spectroscopy (Table 1); in the case of [**4**; L = $P(OMe)_3$] a parent ion was observed in the mass spectrum. The air-stable complex [**4**; L = $P(OPh)_3$] can also be isolated using this method but was usually prepared from [Ru(COMe){$P(OPh)_3$}(NO)(η-C_5Ph_5)]$^+$ (see below); the complex (**4**; L = PPh_3) was too air-sensitive to characterise fully but was identified in

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* In the early stages of the reactions of [NO][PF_6] with [**1**; L = PEt_3, PPh_3, or $P(OMe)_3$], i.r. carbonyl absorptions attributable[2] to (**1**$^+$) were detectable.

Table 1. Analytical and i.r. and ^{1}H n.m.r. spectral data for pentaphenylcyclopentadienylruthenium nitrosyl complexes

Complex	Colour	Yield (%)	Analysis^a (%) C	H	N	$\tilde{\nu}$(NO)^b/cm^{-1}	$\tilde{\nu}$(CO)^b/cm^{-1}	^{1}H(δ)^c	^{31}P(δ/p.p.m.)^c
[RuBr(PEt$_3$)(NO)(η-C$_5$Ph$_5$)][PF$_6$] (**2**; L = PEt$_3$)	Red-brown	44	53.4(53.5)	4.4(4.4)	2.0(1.5)	1 817	—	1.27 (9 H, m, PEt$_3$), 2.33 (6 H, m, PEt$_3$)	—
[RuBr(PPh$_3$)(NO)(η-C$_5$Ph$_5$)][PF$_6$] (**2**; L = PPh$_3$)	Yellow-brown	75	59.8(59.8)	3.9(3.8)	1.2(1.3)	1 819	—	—	—
[RuBr{P(OMe)$_3$}(NO)(η-C$_5$Ph$_5$)][PF$_6$] [**2**; L = P(OMe)$_3$]	Red-brown	66	48.8(49.3)	4.0(3.7)	1.7(1.5)	1 827	—	4.05 [9 H, d, *J*(HP) 12, P(OMe)$_3$]	—
[RuBr{P(OPh)$_3$}(NO)(η-C$_5$Ph$_5$)][PF$_6$] [**2**; L = P(OPh)$_3$]	Light brown	63	56.6(57.3)	3.8(3.6)	2.0(1.3)	1 840	—	—	—
[Ru(CO)(PEt$_3$)(NO)(η-C$_5$Ph$_5$)][PF$_6$]$_2$ (**3**)	Orange	60	49.6(49.8)	4.0(4.0)	1.6(1.4)	1 882	2 118		—
[Ru(PEt$_3$)(NO)(η-C$_5$Ph$_5$)] (**4**; L = PEt$_3$)	Light brown	74	70.2(70.9)	5.5(5.8)	1.6(2.0)	1 665	—	1.06 (9 H, m, PEt$_3$), 1.52 (6 H, m, PEt$_3$)	32.41
[Ru{P(OMe)$_3$}(NO)(η-C$_5$Ph$_5$)][**4**; L = P(OMe)$_3$]	Light brown	83	65.3(65.1)	4.7(4.9)	1.7(2.0)	1 690	—	3.50 [9 H, d, *J*(HP) 13, P(OMe)$_3$]	160.22
[Ru{P(OPh)$_3$}(NO)(η-C$_5$Ph$_5$)][**4**; L = P(OPh)$_3$]	Yellow-brown	55	71.6(71.8)	4.7(4.6)	1.6(1.6)	1 705	—	—	—
[RuBr$_2$(NO)(η-C$_5$Ph$_5$)] (**5**; X = Br)	Olive green	70	57.1(57.1)	3.4(3.4)	2.2(1.9)	1 828	—	—	—
[RuI$_2$(NO)(η-C$_5$Ph$_5$)] (**5**; X = I)	Dark brown	66	49.1(48.9)	3.1(3.0)	1.8(1.6)^d	1 823	—	—	—
[Ru(COMe)(PEt$_3$)(NO)(η-C$_5$Ph$_5$)][PF$_6$] (**7**; L = PEt$_3$)	Brown-red	71	57.1(57.9)	4.8(4.8)	1.8(1.6)	1 799	1 690^e	1.22 (9 H, m, PEt$_3$), 2.13 (6 H, m, PEt$_3$), 3.01 (3 H, s, COMe)^f	—
[Ru(COMe){P(OMe)$_3$}(NO)(η-C$_5$Ph$_5$)][PF$_6$] [**7**; L = P(OMe)$_3$]	Light brown	63	54.1(54.1)	4.4(4.2)	1.5(1.6)	1 812	1 711^e	2.97 (3 H, s, COMe), 3.85 [9 H, d, *J*(HP) 12, P(OMe)$_3$]^e	—
[Ru(COMe){P(OPh)$_3$}(NO)(η-C$_5$Ph$_5$)][PF$_6$] [**7**; L = P(OPh)$_3$]	Light brown	65	61.2(61.5)	4.1(4.0)	1.2(1.3)	1 819	1 709^e	2.97 (3 H, s, COMe)^f	—
[Ru(COMe)(CNBu^t)(NO)(η-C$_5$Ph$_5$)][PF$_6$] (**7**; L = CNBu^t)	Light brown	35	59.1(59.5)	4.7(4.4)	3.2(3.3)	1 821	1 715^e 2 214^g	1.47 (9 H, s, CNBu^t) 3.06 (3 H, s, COMe)	—

[a] Calculated values in parentheses. [b] In CH$_2$Cl$_2$. [c] In CDCl$_3$ unless otherwise stated, *J* values in Hz. Complex multiplets at *ca.* δ7.0 (having the correct integrated intensities) due to the phenyl groups of the C$_5$Ph$_5$ and other ligands are omitted. [d] Calculated for 0.5 CH$_2$Cl$_2$ solvate. [e] Acyl carbonyl. [f] In CD$_2$Cl$_2$. [g] $\tilde{\nu}$(CN).

Table 2. Cyclic voltammetric[a] data for the reduction of $[RuXL(NO)(\eta\text{-}C_5Ph_5)]$ [X = Br, (**2**); or COMe (**7**) and $[RuX_2(NO)(\eta\text{-}C_5Ph_5)]$ (**5**)

Complex	X	L	E^1_{red}/V	E^2_{red}[b]/V	E_{ox}[c]/V
(**2**)	Br	PEt_3	−0.27	−0.50	0.26
(**2**)	Br	PPh_3	−0.15	−0.47	0.36
(**2**)	Br	$P(OMe)_3$	−0.16	−0.54	0.47
(**2**)	Br	$P(OPh)_3$	−0.18	−0.51	0.68
(**7**)	COMe	PEt_3	−0.45[d]	−1.42[e]	—
(**7**)	COMe	$P(OMe)_3$	−0.34[d]	−1.39[e]	—
(**7**)	COMe	$P(OPh)_3$	−0.23[d]	−1.29[e]	—
(**7**)	COMe	$CNBu^t$	−0.29[d]	−1.30[e]	—
(**5**)	Br	—	−0.42[f]	—	—
(**5**)	I	—	−0.45	—	—

[a] Potentials are *versus* the aqueous saturated calomel electrode, measured at a platinum bead 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 −0.09V respectively. Unless stated otherwise, all of the processes are irreversible with E_{red} and E_{ox}, reduction and oxidation peak potentials respectively, measured at a scan rate of 200 mV s^{-1}. [b] Product reduction wave unless stated otherwise. [c] Product oxidation wave. [d] Reversible; E_{red} is the average of the reduction and oxidation peak potentials. [e] Second reduction wave corresponding to the formation of $[Ru(COMe)L(NO)(\eta\text{-}C_5Ph_5)]^-$. [f] This reduction process corresponds to the product reduction process observed for (**2**) (see text).

Table 3. Cyclic voltammetric data[a] for the oxidation of $[RuL(NO)(\eta\text{-}C_5Ph_5)]$ (**4**)

L	E_{ox}/V
PEt_3	0.32
$P(OMe)_3$	0.60
$P(OPh)_3$	0.67[b]

[a] See footnote *a* in Table 2. [b] Reversible process; E_{ox} is the average of the oxidation and reduction peak potentials.

solution by its i.r. nitrosyl stretching absorption at 1 681 cm^{-1}.

Complex (**2**) is converted into (**4**) by a redox-induced reductive-elimination reaction; the decrease in oxidation state by two (formally, at least, from Ru^{II} to Ru^0) is mirrored in the lowering of $\tilde{\nu}$(NO) by *ca.* 150 cm^{-1}. The elimination reaction is readily reversed in that the addition of a solution of bromine in CH_2Cl_2, or of solid iodine, to [**4**; L = $P(OPh)_3$] in CH_2Cl_2 gave good yields of $[RuX_2(NO)(\eta\text{-}C_5Ph_5)]$ (**5**; X = Br or I) (Table 2). These dihalides, analogues of $[RuX_2(NO)(\eta\text{-}C_5R_5)]$ (X = Cl, Br, or I, R = H or Me)[4–6] show i.r. bands which are similar in energy to those of (**2**) confirming the reformation of the ruthenium(II) oxidation state. The proposal[5] of Ru^{IV} as the oxidation state of the metal in $[RuI_2(NO)(\eta\text{-}C_5H_5)]$ would require the nitrosyl ligand to act as $[NO]^-$, leading to $\tilde{\nu}$(NO) at much lower energy.

Electrochemistry of Complexes (**2**), (**4**), *and* (**5**).—The synthetic studies described above show that complexes (**2**), (**4**), and (**5**) are related by reductive-elimination and oxidative-addition reactions. Electrochemical studies imply that these reactions involve a series of electron-transfer steps.

The cyclic voltammograms (c.v.s) of complexes (**2**) have the same general appearance; those of (**2**; L = PPh_3 and PEt_3) are shown in Figure 1(*a*) and 1(*b*) respectively. Each complex is irreversibly reduced, the c.v. showing a wave with a peak potential, E^1_{red}, in the rather limited range of −0.15 to −0.30 V (Table 2). Each c.v. also shows two product waves, the first due to an oxidation process with E_{ox} dependent on L and in the wider potential range of 0.26—0.68V; the second is due to a reduction reaction, with E^2_{red} essentially independent of L, at *ca.* −0.5V.

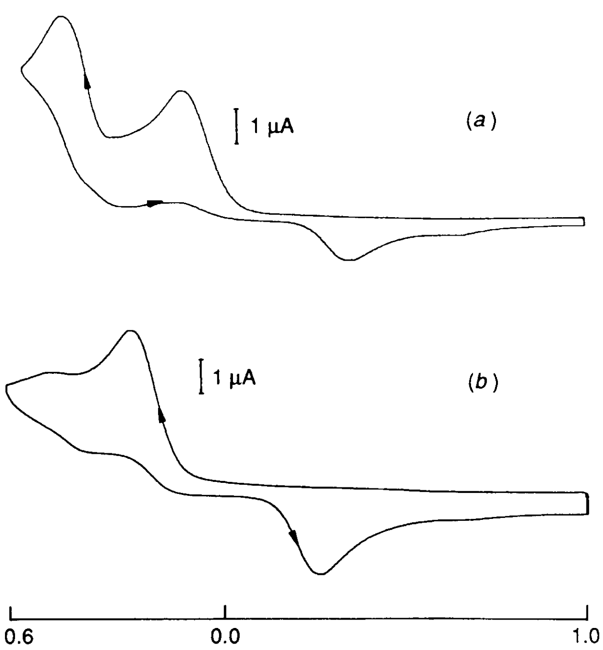


Figure 1. The cyclic voltammograms of (*a*) $[RuBr(NO)(PPh_3)(\eta\text{-}C_5Ph_5)]^+$ and (*b*) $[RuBr(NO)(PEt_3)(\eta\text{-}C_5Ph_5)]^+$, from 1.0 to −0.6V in CH_2Cl_2 at a platinum-bead electrode

In order to identify the products detected by c.v., and to compare them with those found in the chemical reductions described above, [**2**; L = $P(OPh)_3$] was subjected to controlled-potential reduction ($E_{applied}$ = −0.3V) at a cylindrical platinum-gauze electrode in CH_2Cl_2 at 0 °C. After electrolysis for 45 min, a green-brown solution was obtained and a total of 1.3 F mol^{-1} of current had been consumed. The c.v. of the solution then showed the absence of starting material but the presence of two irreversible waves of near equal height; the potentials of these waves, 0.7 [$(E_p)_{ox}$] and −0.4V [$(E_p)_{red}$], correspond approximately to those of the product waves in the c.v. of [**2**; L = $P(OPh)_3$]. The i.r. spectrum of the electrolysed solution showed two nitrosyl stretching absorptions, again of approximately equal height, at 1 828 and 1 705 cm^{-1}. Thus, both the cyclic voltammetric and i.r. spectroscopic results suggest that the electrochemical reduction of [**2**; L = $P(OPh)_3$] gives $[RuBr_2(NO)(\eta\text{-}C_5Ph_5)]$ as well as $[Ru\{P(OPh)_3\}(NO)(\eta\text{-}C_5Ph_5)]$.

Further evidence that the reduction of complex (**2**) gives both (**4**) and (**5**) was provided by cyclic voltammetry of the neutral nitrosyl complexes themselves. Each of the compounds [**4**; L = PEt_3, $P(OMe)_3$, or $P(OPh)_3$] shows a diffusion-controlled oxidation wave the potential of which is dependent on L such that an increase in donor ability leads to a more negative potential [*i.e.* $(E_p)_{ox}$ = $P(OPh)_3$ > $P(OMe)_3$ > PEt_3] (Table 3); the wave is (*a*) reversible for L = $P(OPh)_3$ at scan rates, ν in excess of 50 mV s^{-1}, (*b*) partially reversible for L = PEt_3 (i_{red}/i_{ox} = 0.86, ν = 200 mV s^{-1}), and (*c*) completely irreversible for L = $P(OMe)_3$ (no reduction peak was observed even for ν = 500 mV s^{-1}).

The oxidation process probably involves the loss of one electron in that exhaustive electrolysis of [**4**; L = $P(OPh)_3$] at 0.85V in CH_2Cl_2 led to the passage of 0.85 F mol^{-1} of current. In this case, the c.v. of the brown product solution showed no evidence of (4^+) and this radical cation is therefore unstable on the time-scale of the electrolysis (but stable on the much shorter

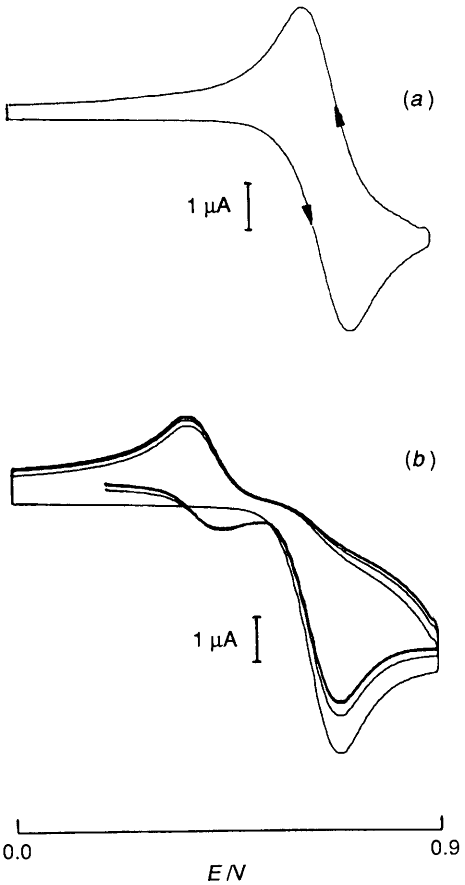


Figure 2. The c.v. of $[Ru\{P(OPh)_3\}(NO)(\eta\text{-}C_5Ph_5)]$ from 0.0 to 0.9V in CH_2Cl_2 at a platinum-bead electrode: (a) single scan and (b) multiple scan in the presence of PPh_3 (1:1)

time-scale of c.v.). Interestingly, the addition of $AgPF_6$ to [4; L = $P(OPh)_3$] in CH_2Cl_2 at room temperature resulted in the appearance of a new i.r. nitrosyl band at 1 760 cm^{-1}, and freezing this solution (−196 °C) resulted in the observation of an axial e.s.r. spectrum (g_1 = 2.060, g_2 = 2.006; $g_{av.}$ = 2.024) which might be assigned to $[Ru(NO)\{P(OPh)_3\}(\eta\text{-}C_5Ph_5)]^+$. Isoelectronic paramagnetic carbonyls, $[Rh(CO)L(\eta\text{-}C_5Ph_5)]^+$ (L = PPh_3, $AsPh_3$, *etc.*), are stable in solution at room temperature when generated[7] by one-electron oxidation of $[Rh(CO)L(\eta\text{-}C_5Ph_5)]$.

The cyclic voltammogram of [4; L = $P(OPh)_3$] is altered in the presence of bromide ion in that the oxidation wave not only becomes completely irreversible, implying a rapid reaction between [4^+; L = $P(OPh)_3$] and Br^-, but is also shifted to more negative potentials. For example, $(E_p)_{ox}$ is shifted from 0.73 to 0.62 V on the addition of 0.5 equivalent of $[PPr^nPh_3]Br$ to the c.v. cell. This last observation accounts for the small differences observed between the $(E_p)_{ox}$ values of pure (4) and those measured for (4) when it is produced during the cyclic voltammetry or electrolysis of (2) (where, of course, bromide ion is also a product of reduction).

The oxidation wave of complex [4; L = $P(OPh)_3$], shown in Figure 2(*a*), also becomes irreversible in the presence of PPh_3, and a new wave, apparently reversible, appears at a more negative potential [Figure 2(*b*)]. The potential of the new wave is similar to that of the product wave (oxidation) observed in the c.v. of (2; L = PPh_3), a product wave we have assigned to (4; L = PPh_3). It seems, therefore, that substitution of $P(OPh)_3$ by PPh_3 occurs on oxidation, giving (4; L = PPh_3) from [4; L = $P(OPh)_3$].

The dihalides (5) also undergo irreversible reduction (Table 2) at a potential (*ca.* −0.5V) very similar to those of the product waves (reductions) of (2) described above. The c.v. of (5; X = Br) also shows a product wave, possibly reversible and at a potential very similar to that for the reduction of (5; X = Br) itself.

The chemistry following electron addition to (2) is clearly complex but the characterisation of the products of electrolysis as (4) and (5) means that the overall reaction can be summarised by equation (1). Thus, although the formation of complex

$$\underset{(2)}{2[RuBrL(NO)(\eta\text{-}C_5Ph_5)]^+} + 2e^- \longrightarrow \underset{(4)}{[RuL(NO)(\eta\text{-}C_5Ph_5)]} + \underset{(5)}{[RuBr_2(NO)(\eta\text{-}C_5Ph_5)]} + L \quad (1)$$

(4) from (2) requires two-electron reduction, the overall stoicheiometry requires only one electron per cation for the complete consumption of (2) (*i.e.* a coulometric *n* value of 1.0 is to be expected). The observed *n* value of 1.3 may result from partial electrolytic reduction of (5) [$(E_p)_{red}$ = −0.42 V].

This stoicheiometry, for the electrolytic reduction, seems to contradict the results of the chemical reduction in that (2) reacts with 2 equivalents of $[Co(\eta\text{-}C_5H_5)_2]$ to give (4), in high yield, and none of complex (5; X = Br). This apparent contradiction is resolved, however, when it is realised that complex (5; X = Br) rapidly and quantitatively reacts with $P(OPh)_3$ in the presence of 2 equivalents of $[Co(\eta\text{-}C_5H_5)_2]$ to give (4) [equation (2)].

$$[RuBr_2(NO)(\eta\text{-}C_5Ph_5)] + L + 2[Co(\eta\text{-}C_5H_5)_2] \longrightarrow [RuL(NO)(\eta\text{-}C_5Ph_5)] + 2[Co(\eta\text{-}C_5H_5)_2]Br \quad (2)$$

This reaction will occur in the chemical reduction of (2) by cobaltocene as the latter has a reduction potential (E° = −0.86V well negative of the potential required to reduce (5). However, the potential applied to reduce (2) electrochemically (−0.3V) is insufficient to reduce (5) rapidly, and (4) will only slowly be formed by the secondary route [*i.e.* by a reaction similar to that given by equation (2)].

Various mechanisms, involving electrochemical-electrochemical-chemical (e.e.c.) or electrochemical-chemical-electrochemical (e.c.e.) processes, for the formation of complex (4) from (2) can be proposed but none can be confirmed by the relatively simple c.v. studies presented here; a more detailed analysis of the electrochemistry of this system is beyond the scope of this work. The formation of (5) from (2), however, undoubtedly involves reaction (3); the addition of $[PPr^nPh_3]Br$ to $[RuBr(PEt_3)(NO)(\eta\text{-}C_5Ph_5)]^+$ in CH_2Cl_2 immediately gave (5), providing a second synthetic route to the dibromide.

$$[RuBrL(NO)(\eta\text{-}C_5Ph_5)]^+ + Br^- \longrightarrow [RuBr_2(NO)(\eta\text{-}C_5Ph_5)] + L \quad (3)$$

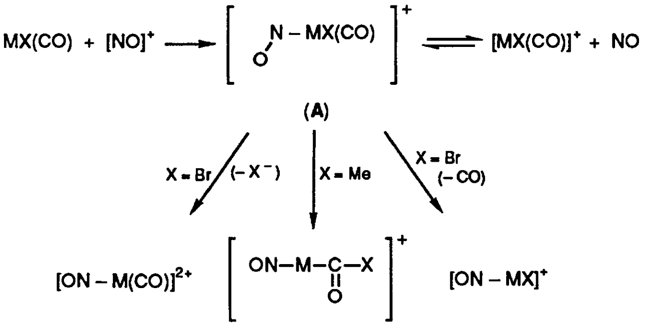
Reaction of $[NO]^+$ *with* $[RuMe(CO)L(\eta\text{-}C_5Ph_5)]$, *and a General Mechanism for the Reaction of the Nitrosonium Ion with Metal Carbonyls.*—The complexity of the redox chemistry of (2) is largely due to the lability of the Ru–Br bond on reduction. An attempt was therefore made to study the electron-transfer reactions of analogues of (2) in which the bromide ligand was replaced, *i.e.* of complexes containing the rather more inert Ru–Me bond. However, this simple modification resulted in markedly different chemistry.

The reaction between $[RuMe(CO)L(\eta\text{-}C_5Ph_5)]$ [6; L = PEt_3,[2] $P(OMe)_3$, $P(OPh)_3$, or $CNBu^t$ (Table 4)] and $[NO][PF_6]$ in CH_2Cl_2 gave moderate (L = $CNBu^t$) to good yields of pale brown solids which were characterised by elemental analysis and i.r. and n.m.r. spectroscopy (Table 1) as

Table 4. Analytical and i.r. spectroscopic data for $[RuMe(CO)L(\eta\text{-}C_5Ph_5)]$

L	Colour	Yield/%	Analysis^a/% C	H	N	$\tilde{\nu}(CO)^b/cm^{-1}$
$P(OMe)_3$	Pale yellow	76	67.3(67.3)	5.6(5.2)	—	1 931
$P(OPh)_3$	Cream	87	73.3(73.4)	5.0(4.8)	—	1 944
$CNBu^t$	Cream	45	74.9(75.0)	5.7(5.5)	2.1(2.1)	1 935 (2 130)^c

^{a} Calculated values in parentheses. ^{b} In CH_2Cl_2. ^{c} $\tilde{\nu}(CN)$.



Scheme. M = $RuL(\eta\text{-}C_5Ph_5)$

$[Ru(COMe)L(NO)(\eta\text{-}C_5Ph_5)][PF_6]$ (7; L = PEt_3, $P(OMe)_3$, $P(OPh)_3$, or $CNBu^t$]; the unexpected acyl group was readily identified by a ketonic carbonyl band in the i.r. spectrum at *ca.* 1 710 cm^{-1}and by a ^1H n.m.r. singlet resonance at *ca.* δ 3.0.

The formation of (7), rather than the expected alkyl cations $[RuMe(NO)L(\eta\text{-}C_5Ph_5)]^+$, shows that $[NO]^+$ can react with $[RuX(CO)L(\eta\text{-}C_5Ph_5)]$ to give *four* different types of product, *i.e.* *via* one-electron oxidation [giving (1^+)], direct carbonyl substitution [giving (2)], nitrosyl-induced migratory insertion [giving (7)], and halide displacement [giving (3)].

We have previously presented[8] a general mechanism to account for the observed competition between nitrosyl substitution and one-electron oxidation during the reaction of $[NO]^+$ with metal carbonyls. We now suggest that this mechanism can accommodate all four reaction pathways, with all of the observed products able to form from one common intermediate. The Scheme shows this mechanism for the reaction between $[NO]^+$ and $[RuX(CO)L(\eta\text{-}C_5Ph_5)]$. The common intermediate here is the simple 18-electron adduct $[RuX(CO)(NO)L(\eta\text{-}C_5Ph_5)]^+$ (**A**) in which the Ru–N–O linkage is bent; the nitrosyl ligand, formulated as $[NO]^-$, acts as a one-electron donor. As described before,[8] nitrosyl substitution *vs.* one-electron oxidation is explained in terms of the equilibrium reaction (4) and the irreversible decarbonylation (5). However, (**A**) can also undergo migratory insertion when X

$$(\mathbf{A}) \rightleftharpoons NO + [RuX(CO)L(\eta\text{-}C_5Ph_5)]^+ \qquad (4)$$

$$(\mathbf{A}) \longrightarrow [RuXL(NO)(\eta\text{-}C_5Ph_5)]^+ + CO \qquad (5)$$

is Me [to give (7)], or lose bromide ion (possibly removed as NOBr *via* the reaction between Br^- and excess of $[NO]^+$) to give the carbonylnitrosyl dication (3). This mechanism only rationalises the observed products and as yet the many factors (including co-ordination number and geometry of M, donor–acceptor properties of ancillary ligands, *etc.*) which influence the formation and stability of (**A**) and the routes by which it reacts further are not understood.

Comments on the Nitrosyl-induced Migratory Insertion Reaction forming Complex (7).—That migratory insertion can be induced by treating a carbonylmethyl complex with $[NO]^+$ is of interest in its own right {and, in particular, the formation of (7) contrasts markedly with our failure to observe[2] an oxidatively induced migration when (6) was treated with Ag^+ under CO, *cf.* the electron-transfer catalysed reaction[9] of $[FeMe(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ with $[Fe(\eta\text{-}C_5H_5)_2]^+$ and CO to give $[Fe(COMe)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$}. However, the formation of (7) also suggests a more important general possibility, namely that $[NO]^+$ may induce coupling of ligands X and Y *in* $[MX(Y)L_n]$ to give $[M(XY)(NO)L_n]^+$. Clearly the ligands X and Y must be chosen so that in total they donate two more electrons than the coupled group XY. In this way, the 18-electron configuration is retained. Alternatively, one of the two-electron ligands, L, might be lost.

Legzdins *et al.*[10] have recently reported one such reaction where $[NO]^+$ and $[CrR(NO)_2(\eta\text{-}C_5H_5)]$ give $[Cr\{N(O)R\}(NO)_2(\eta\text{-}C_5H_5)]^+$ (R = Me, CH_2SiMe_3 or Ph); R (a one-electron donor) and one of the nitrosyls (a three-electron donor) are linked in the nitroso group (two-electron donor) of the final product. Similarly, Geoffroy and co-workers,[11] have shown that $[NO]^+$ and $[Mn(COR)(CO)_2(\eta\text{-}C_5H_4Me)]^-$ give the novel α-ketoacyl (one-electron donor) complex $[Mn\{C(O)C(O)R\}(CO)(NO)(\eta\text{-}C_5H_4Me)]$ in which acyl (one-electron) and carbonyl (two-electron) fragments have been joined. In this case, yields of the insertion product are relatively low, possibly because equilibrium (6) lies well to the right (favouring loss of

$$[Mn(COR)(CO)_2(NO)(\eta\text{-}C_5H_4Me)] \rightleftharpoons NO + [Mn(COR)(CO)_2(\eta\text{-}C_5H_4Me)] \qquad (6)$$

NO from the reaction medium). Oxidation of $[Mn(COR)(CO)_2(\eta\text{-}C_5H_4Me)]^-$ by $[Fe(\eta\text{-}C_5H_5)_2]^+$, to give the 17-electron radical $[Mn(COR)(CO)_2(\eta\text{-}C_5H_4Me)]$, followed by bubbling NO gas (*i.e.* presumably an excess) through the reaction solution provides a much higher yield of the ketoacyl product.

One-electron Reduction of $[Ru(COMe)L(NO)(\eta\text{-}C_5Ph_5)]^+$ (7).—The cyclic voltammetry of complex (7) is very different from that of (2) in that each acyl complex undergoes *reversible* diffusion-controlled one-electron reduction, in the potential range −0.2 to −0.5V (Table 2); a typical c.v., for [7; L = $P(OMe)_3$] (Figure 3), also shows a second, irreversible wave at a potential *ca.* 1.0V more negative than the first.

The controlled-potential reduction of complex [7; L = $P(OMe)_3$], at −0.6V in CH_2Cl_2 at 0 °C, resulted in the formation of a dark green-brown solution and the passage of 1.13 F mol^{-1} over a period of 45 min. Cyclic voltammetry and voltammetry at a rotating platinum electrode then showed the solution contained $[Ru(COMe)L(NO)(\eta\text{-}C_5Ph_5)]$, [**8**; L = $P(OMe)_3$], characterised by a reversible *oxidation* wave at the same potential (−0.30 V) observed for the reduction of [7; L = $P(OMe)_3$]. The height of the oxidation wave was somewhat smaller (*ca.* 85%) than that of the reduction wave of [7; L = $P(OMe)_3$], and it further diminished with time as the electrolysed solution was allowed to stand at room temperature.

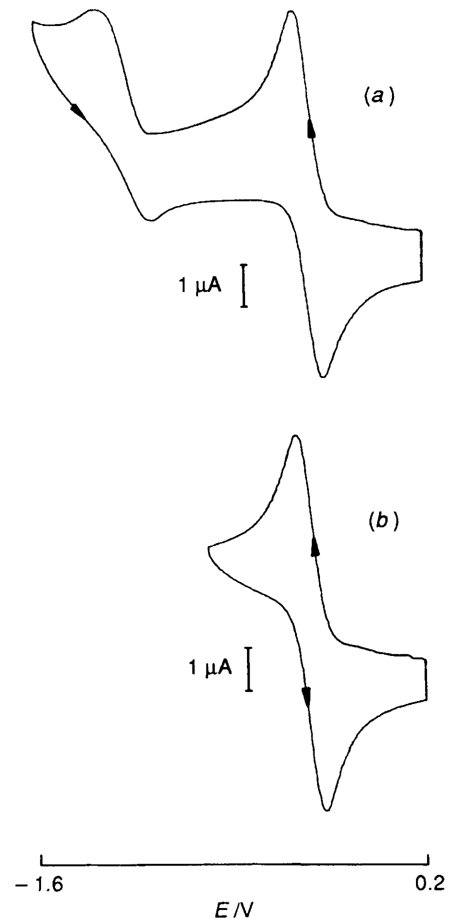


Figure 3. The c.v. of $[Ru(COMe)(NO)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]^+$ in CH_2Cl_2 at a platinum-bead electrode: (*a*) from 0.2 to −1.6 and (*b*) from 0.2 to −0.8V

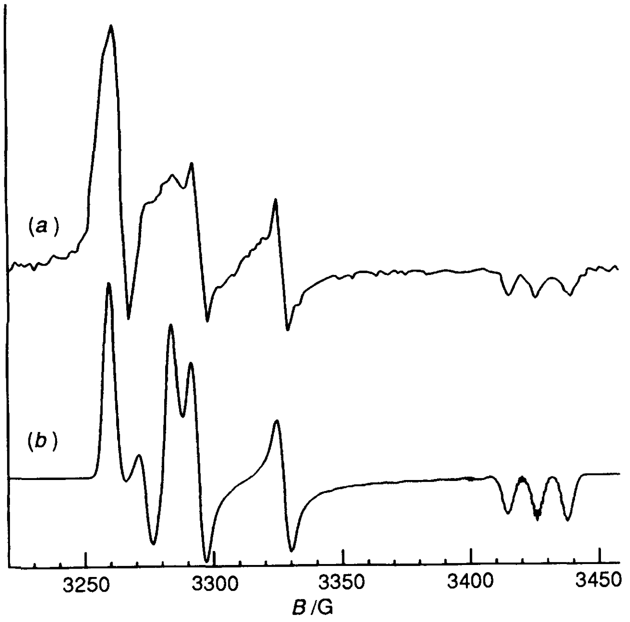


Figure 4. The e.s.r. spectrum of complex ($\mathbf{8}$; L = $CNBu^t$) in thf–CH_2Cl_2 (2:1) at −196 °C: (*a*) experimental spectrum, (*b*) computer-simulated spectrum using the parameters of Table 5. G = 10^{-4} T

The chemical reduction of [**7**; L = $P(OMe)_3$] was readily achieved using 1 equivalent of $[Co(\eta\text{-}C_5H_5)_2]$ [*cf.* the reduction of (**2**)] in toluene. After 5 min, filtration of the brown solution to separate precipitated $[Co(\eta\text{-}C_5H_5)_2][PF_6]$, removal of the toluene *in vacuo*, and recrystallisation from thf-n-hexane gave the radical [**8**; L = $P(OMe)_3$] as a green-brown powder. As implied by the results of the electrolytic reduction of [**7**; L = $P(OMe)_3$], the radical is unstable, decomposing in air so that no satisfactory elemental analysis was obtained. However, a freshly prepared sample showed the expected oxidation wave at −0.33V, due to the formation of [**7**; L = $P(OMe)_3$], and an e.s.r. spectrum (see below) consistent with the paramagnetism expected for (**8**).

Interestingly, an attempt to purify complex [**8**; L = $P(OMe)_3$] by chromatography on alumina led to the isolation of 30—40% yields of $[RuMe(CO)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$, and the cobaltocene reduction of (**7**; L = PEt_3) directly gave a 25% isolated yield of (**6**; L = PEt_3) (without chromatography). The formation of (**6**) may result from the loss of NO gas from (**8**) and then carbonyl extrusion to regenerate the methyl from the acyl. The behaviour of [**8**; L = $P(OMe)_3$] on alumina is in marked contrast to that of the cation [**7**; L = $P(OPh)_3$]. For the latter, where the nitrosyl ligand is bound as a strong π acceptor (*i.e.* formally as NO^+), preferential acyl loss occurs to give [**4**; L = $P(OPh)_3$] in 55% yield.

E.S.R. Spectra of Complex (**8**).—The room-temperature e.s.r. spectra of complex (**8**) in CH_2Cl_2, and the frozen-solution anisotropic spectra [at −196 °C, in thf–CH_2Cl_2 (2:1)] were obtained by adding the solvent to a solid mixture of (**7**) and $[Co(\eta\text{-}C_5H_5)_2]$ in an e.s.r. tube and cooling when appropriate. Representative spectra of (**8**; L = $CNBu^t$) are shown in Figure 4.

The e.s.r. spectrum of (**8**; L = $CNBu^t$) is qualitatively similar to those of $[M(CO)_2(NO)(\eta\text{-}C_5H_5)]^-$ (M = Cr or Mo) reported by Geiger *et al.*[12] The liquid solution spectrum consists of a 1:1:1 triplet due to hyperfine coupling of the nitrosyl nitrogen; parameters are given in Table 5. The frozen-solution spectrum can be understood as arising from approximately axial *g* and ^{14}N hyperfine tensors with nearly perpendicular parallel axes; thus three sets of triplets are observed corresponding to $g_\perp$, $A_\parallel$, $g_\perp$, $A_\perp$, and $g_\parallel$, $A_\perp$. The tensor principal axes are not quite coincident, leading to unequal spacings of the high-field triplet ($g_\parallel$, $A_\perp$). Analysis of the frozen-solution spectrum assuming an axial hyperfine tensor gives the parameters shown in Table 5, together with $g_y = 2.004$, $A_\perp = 9.2 \times 10^{-4}$ cm^{-1}, and $\beta = 99°$ (the angle between parallel axes). Because of only partial resolution in the $g_\perp$ region, the values of $A_\perp$ and β are rather uncertain; a somewhat better fit can be obtained if the hyperfine tensor is not assumed axial, but $A_\parallel$ and the *g*-tensor components are essentially unchanged.

The isotropic e.s.r. spectra of complexes [**8**; L = PEt_3, $P(OMe)_3$, or $P(OPh)_3$] show partially resolved triplets corresponding to ^{14}N hyperfine couplings; the spectra are apparently broadened by unresolved ^{31}P hyperfine splittings ($\langle A^P \rangle < \langle A^N \rangle/2$). The frozen-solution spectra of these radicals are poorly resolved so that only the $g_\perp$, $A_\parallel$ features could be interpreted; the resulting parameters are given in Table 5. In the case of [**8**; L = $P(OPh)_3$] there is evidence for a second, unidentified radical.

Since $A_\parallel$ and $\langle A \rangle$ are reasonably well established, we can estimate the nitrogen *p*-electron spin densities. Using equations given by Geiger *et al.*,[12] and the dipolar coupling parameter, $P = 46.3 \times 10^{-4}$ cm^{-1},[13] we obtain the values given in Table 5. Since there is a small nitrogen 2*s* contribution and some spin density on the nitrosyl oxygen, it appears that about half the unpaired electron density resides on the nitrosyl ligand. On the other hand it is clear from the

Table 5. E.s.r. spectral data[a] for [Ru(COMe)L(NO)(η-C_5Ph_5)] (**8**)

L	$\langle g \rangle$	$\langle A^N \rangle$	$g_{\parallel}$	g_x	$A_{\parallel}^N$	$A_{\parallel}^P$	ρ_P^N [b]
PEt_3	1.962	19	1.91	1.996	36	7	0.44
$P(OMe)_3$	1.968	18	1.91	1.996	32	10	0.37
$P(OPh)_3$	1.979	16.5	1.925	1.997	30	—	0.36
CNBu^t	1.974	17	1.921	1.998	32	—	0.41

[a] Hyperfine couplings in units of 10^{-4} cm^{-1}. [b] ρ_P^N is the *p*-electron spin density on nitrogen.

relatively large *g*-tensor anisotropy that there is also a significant metal contribution.

Conclusion

(1) The bromide complexes [RuBrL(NO)(η-C_5Ph_5)]$^+$ (**2**) undergo electron-transfer-initiated reductive elimination to give [RuL(NO)(η-C_5Ph_5)] (**4**). The latter undergoes one-electron oxidation, and oxidative addition with halogens.

(2) Migratory insertion of CO into a metal–methyl bond is induced by nitrosyl substitution of [RuMe(CO)L(η-C_5Ph_5)] (**6**), giving [Ru(COMe)L(NO)(η-C_5Ph_5)]$^+$ (**7**). The latter undergoes reversible one-electron reduction to the radical [Ru(COMe)L(NO)(η-C_5Ph_5)] (**8**) e.s.r. spectroscopic studies on which show the unpaired electron localised extensively on the nitrosyl ligand.

(3) A general mechanism for the reactions of [NO]$^+$ with metal carbonyl substrates, featuring a 'bent' nitrosyl adduct as the key intermediate, is discussed.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Where necessary the progress of a reaction was monitored by i.r. carbonyl spectroscopy. Unless stated otherwise, products (*i*) were purified by dissolving in CH_2Cl_2, filtration, addition of n-hexane, and partial evaporation of the solvent mixture *in vacuo* to induce precipitation, and (*ii*) are air-stable in the solid state and dissolve in polar solvents such as CH_2Cl_2, acetone, or thf to give solutions which only slowly decompose in air.

The complexes [RuBr(CO)L(η-C_5Ph_5)] [L = PEt_3, PPh_3, $P(OMe)_3$, or $P(OPh)_3$], [RuMe(CO)(PEt_3)(η-C_5Ph_5)],[2] and [Co(η-C_5H_5)$_2$][14] were prepared by published methods or by minor modifications thereof. The salt [NO][PF_6] was purchased from Fluorochem Ltd.

Infrared spectra were recorded on a Nicolet 5ZDX FT spectrometer, proton n.m.r. spectra on a JEOL GX270 instrument and calibrated against tetramethylsilane as internal reference, and phosphorus-31 n.m.r. spectra on a JEOL FX90Q instrument using 85% H_3PO_4 as external reference. Mass spectra were recorded on an AEI MS 902 spectrometer. *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 (dpph) radical.

Electrochemical studies were carried out as described previously[15] using AMEL or E.G. and G. PAR 273 potentiostats. Solutions were 1.0 × 10^{-3} mol dm^{-3} in complex and 0.1 mol dm^{-3} in [NBu^n_4][PF_6] as supporting electrolyte. Under these conditions, E° for the couples [Fe(η-C_5H_5)$_2$]$^+$–[Fe(η-C_5H_5)$_2$] and [Fe(η-C_5Me_5)$_2$]$^+$–[Fe(η-C_5Me_5)] are 0.47 and −0.09V respectively.

Bromocarbonyl(η-*pentaphenylcyclopentadienyl*)(*t-butyl isocyanide*)*ruthenium*, [RuBr(CO)(CNBu^t)(η-C_5Ph_5)].—To a suspension of [RuBr(CO)$_2$(η-C_5Ph_5)] (0.50 g, 0.73 mmol) in acetone (50 cm^3) was added CNBu^t (0.062 g, 0.74 mmol) and $ONMe_3 \cdot 2H_2O$ (0.081 g, 0.73 mmol). After heating the mixture under reflux for 15 min, n-hexane (50 cm^3) was added and the solution cooled to −10 °C to give a yellow precipitate. The precipitate was dissolved in a minimum volume of CH_2Cl_2 and the solution was placed on an alumina–n-hexane column. Elution with CH_2Cl_2–n-hexane (2:3) gave a yellow solution from which the product was isolated as a bright yellow powder on partial removal of the solvent *in vacuo*, yield 0.23 g (43%) (Found: C, 66.5; H, 4.7; N, 1.9. $C_{41}H_{34}BrNORu$ requires C, 66.8; H, 4.7; N, 1.9%), $\tilde{\nu}$(CO)(CH_2Cl_2) 1 981 cm^{-1}, $\tilde{\nu}$(CN) 2 164 cm^{-1}; E_{ox} (for reversible one-electron oxidation) 1.24V.

Further elution, with CH_2Cl_2, gave small quantities of [RuBr(CNBu^t)$_2$(η-C_5Ph_5)] [$\tilde{\nu}$(CN) = 2 143 and 2 114 cm^{-1}].

Carbonyl(*methyl*)(η-*pentaphenylcyclopentadienyl*)(*trimethyl phosphite*)*ruthenium*, [RuMe(CO){$P(OMe)_3$}(η-C_5Ph_5)].—To [RuBr(CO){$P(OMe)_3$}(η-C_5Ph_5)] (1.0 g, 1.28 mmol), partially dissolved in thf (50 cm^3) at 0 °C, was added LiMe (2.0 mmol) in diethyl ether (5 cm^3 of 0.4 mol dm^{-3} solution). After 10 min, the excess of LiMe was destroyed by the addition of a few drops of water. The brown solution was then filtered, evaporated to smaller volume (*ca.* 20 cm^3) *in vacuo*, and transferred to an alumina–n-hexane chromatography column (20 × 3 cm). Elution with thf gave a yellow solution from which the pale yellow product was precipitated on addition of n-hexane and partial removal of the solvent *in vacuo*, yield 0.7 g (76%).

The complexes [RuMe(CO)L(η-C_5Ph_5)] [L = $P(OPh)_3$ or CNBu^t] were prepared similarly, the first by using Li[$CuMe_2$] in place of LiMe and the second by using a 1:2 mixture of thf and n-hexane for elution from the chromatography column. All of the complexes dissolve in solvents such as CH_2Cl_2, thf, or toluene to give pale yellow solutions.

Bromo(*nitrosyl*)(η-*pentaphenylcyclopentadienyl*)(*trimethyl phosphite*)*ruthenium Hexafluorophosphate*, [RuBr{$P(OMe)_3$}(NO)(η-C_5Ph_5)][PF_6].—To a stirred solution of [RuBr(CO){$P(OMe)_3$}(η-C_5Ph_5)]$\cdot$0.5CH_2Cl_2 (0.35 g, 0.43 mmol) in CH_2Cl_2 (35 cm^3) was added [NO][PF_6] (0.09 g, 0.51 mmol). After 3 h the brown solution was filtered through Kieselguhr and reduced in volume to 15 cm^3 *in vacuo*. Addition of n-hexane (80 cm^3) precipitated the product as a brown solid, yield 0.6 g (66%).

The complexes [RuBrL(NO)(η-C_5Ph_5)][PF_6] [L = PEt_3 or $P(OPh)_3$] were prepared similarly. All of the complexes dissolve to give red-brown or brown solutions.

Carbonyl(*nitrosyl*)(η-*pentaphenylcyclopentadienyl*)(*triethylphosphine*)*ruthenium Bis*(*hexafluorophosphate*), [Ru(CO)(PEt_3)(NO)(η-C_5Ph_5)][PF_6]$_2$.—To a stirred solution of [RuBr(CO)(PEt_3)(η-C_5Ph_5)] (0.37 g, 0.48 mmol) in CH_2Cl_2 (20 cm^3) was added a large excess of [NO][PF_6] (0.31 g, 1.77 mmol). After 15 min the orange precipitate was removed by filtration, washed with toluene (2 × 25 cm^3) and diethyl ether (4 × 25 cm^3), and dried *in vacuo* to give the orange solid product, yield 0.9 g (60%).

The complex decomposes in all solvents in which it is soluble, such as thf and acetone.

Reaction of [Ru(CO)(PEt_3)(NO)(η-C_5Ph_5)][PF_6]$_2$ *with* [Co(η-C_5H_5)$_2$].—To a stirred solution of [Co(η-C_5H_5)$_2$] (44 mg, 0.23 mmol) in thf (20 cm^3) was added [Ru(CO)(PEt_3)(NO)(η-C_5Ph_5)][PF_6]$_2$ (91 mg, 0.09 mmol). After 5 min the brown solution was filtered through a 5 cm thick pad of alumina. Addition of n-hexane (50 cm^3), followed by reduction of the solvent volume *in vacuo*, gave a brown precipitate. Purification from CH_2Cl_2–n-hexane gave [Ru(CO)(PEt_3)-

(NO)(η-C_5Ph_5)] as an impure brown solid, yield 50 mg. The complex is air-sensitive.

Acetyl(nitrosyl)(η-pentaphenylcyclopentadienyl)(trimethyl phosphite)ruthenium Hexafluorophosphate, [Ru(COMe){P(OMe)$_3$}(NO)(η-C_5Ph_5)][PF_6].—To a stirred solution of [RuMe(CO){P(OMe)$_3$}(η-C_5Ph_5)] (0.70 g, 0.98 mmol) in CH_2Cl_2 (50 cm^3) was added solid [NO][PF_6] (0.17 g, 0.98 mmol). After 20 min the red-brown solution was filtered, n-hexane was added, and the volume of solvent was reduced *in vacuo* to give a pale brown precipitate. Purification from CH_2Cl_2–n-hexane gave the product, yield 0.55 g (63%).

The complexes [Ru(COMe)L(NO)(η-C_5Ph_5)][PF_6] [L = PEt_3, P(OPh)$_3$, or CNBu^t] were prepared similarly; the P(OPh)$_3$ derivative was purified from CH_2Cl_2–diethyl ether. All dissolve to give brown solutions.

Preparation of [Ru{P(OMe)$_3$}(NO)(η-C_5Ph_5)] *from* [RuBr{P(OMe)$_3$}(NO)(η-C_5Ph_5)][PF_6].—To a stirred solution of [RuBr{P(OMe)$_3$}(NO)(η-C_5Ph_5)][PF_6] (0.38 g, 0.41 mmol) in CH_2Cl_2 (25 cm^3) was added [Co(η-C_5H_5)$_2$] (0.15 g, 0.79 mmol). After 10 min the brown solution was filtered through a 3 cm thick pad of alumina. Addition of n-hexane (80 cm^3) followed by reduction of the solvent volume *in vacuo* gave a brown precipitate. Purification from CH_2Cl_2–n-hexane afforded the product as a brown solid, yield 0.4 g (83%).

The complex [Ru(PEt_3)(NO)(η-C_5Ph_5)] was prepared by the same method. Both compounds are air-sensitive in the solid state, and dissolve in solvents such as CH_2Cl_2, thf, *etc.* to give brown air-sensitive solutions.

Preparation of [Ru{P(OPh)$_3$}(NO)(η-C_5Ph_5)] *from* [Ru(COMe){P(OPh)$_3$}(NO)(η-C_5Ph_5)][PF_6].—The complex [Ru(COMe){P(OPh)$_3$}(NO)(η-C_5Ph_5)][PF_6] (1.0 g, 0.93 mmol) was dissolved in a minimum volume of CH_2Cl_2 and then placed onto an alumina–n-hexane column. Elution of the yellow-brown band with CH_2Cl_2, addition of n-hexane, and partial evaporation of the solvent *in vacuo* gave a yellow-brown solid. The solid was then dissolved in toluene (200 cm^3) and the resulting solution was filtered to remove small quantities of the starting material. Evaporation of the toluene *in vacuo* followed by purification from CH_2Cl_2–n-hexane gave the product as a yellow-brown powder, yield 0.47 g (55%). The complex dissolves in solvents such as CH_2Cl_2, thf, and toluene to give yellow-brown solutions.

Di-iodo(nitrosyl)(η-pentaphenylcyclopentadienyl)ruthenium, [RuI_2(NO)(η-C_5Ph_5)].—To a stirred solution of [Ru{P(OPh)$_3$}(NO)(η-C_5Ph_5)] (0.10 g, 0.11 mmol) in CH_2Cl_2 (20 cm^3) was added solid I_2 (0.029 g, 0.114 mmol). The dark red-brown solution was filtered, n-hexane was added, and the volume of the solvent was reduced *in vacuo*. The resulting precipitate was purified from CH_2Cl_2–n-hexane to give the dark brown solid product, yield 0.062 g (66%).The complex dissolves in solvents such as CH_2Cl_2, acetone, and toluene to give red-brown solutions.

Dibromo(nitrosyl)(η-pentaphenylcyclopentadienyl)ruthenium, [$RuBr_2$(NO)(η-C_5Ph_5)].—To a stirred solution of [Ru{P(OPh)$_3$}(NO)(η-C_5Ph_5)] (0.26 g, 0.29 mmol) in CH_2Cl_2 (40 cm^3) was added dropwise a dilute solution of bromine in CH_2Cl_2 until the i.r. spectrum showed the absence of starting material. Filtration, evaporation of the solution to low volume *in vacuo*, and addition of n-hexane gave an olive-green powder which was purified from CH_2Cl_2–n-hexane, yield 0.15 g (70%). The complex dissolves in solvents such as CH_2Cl_2, acetone, and toluene to give green solutions.

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