Synthesis and Reactivity of Binuclear Cyclopentadienylrhodium Nitrosyl Cations, and the *X*-Ray Structure of $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$ *

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The complex $[Rh(CO)_2(cp)]$ (cp = $\eta^5\text{-}C_5H_5$) reacts with $[NO][PF_6]$ in CH_2Cl_2 to give $[Rh_2(CO)_2(\mu\text{-}NO)(cp)_2][PF_6]$ (1) which is cleaved by ligands, L, to yield $[Rh(NO)L(cp)][PF_6]$ (2; L = PPh_3, cyclo-octene, or cyclohexa-1,3-diene) and $[Rh(CO)_2(cp)]$; the related reaction of (1) with ethylene is reversible. With RC≡CR, complex (1) affords $[Rh_2(CO)\{\mu\text{-}N(O)C(R)CR\}(cp)_2][PF_6]$ (3; R = Ph or $C_6H_4OMe\text{-}p$) *via* alkyne insertion into a metal–nitrosyl bond. Slow, thermal decarbonylation of (1) gives $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(cp)_2][PF_6]$ (4), but $[NO][PF_6]$ and $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ directly afford $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$ (5), *X*-ray studies on which revealed a short rhodium–rhodium bond [2.577(1) Å] symmetrically bridged by the nitrosyl [Rh–N(O) 1.95(1) Å] and carbonyl [Rh–C(O) 2.00(2) Å] ligands; the $[PF_6]^-$ anion is disordered. Crystals of (5) are monoclinic, space group *A*2, and the structure has been refined to *R* 0.034 for 1 519 reflections [$I \geqslant 1.5\sigma(I)$]. Complex (5) forms a 1 : 1 adduct with PPh_3, namely $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(PPh_3)(\eta\text{-}C_5Me_5)_2][PF_6]$ (6), and reacts with a second equivalent of $[NO][PF_6]$ to yield $[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2][PF_6]_2$ (7). At a platinum electrode, in CH_2Cl_2, (5) undergoes reversible one-electron reduction to $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2]$. Similarly, $[\{Rh(\mu\text{-}NO)(cp)\}_2]$ is reduced in tetrahydrofuran to the monoanion $[\{Rh(\mu\text{-}NO)(cp)\}_2]^-$.

We have recently described[1] the synthesis and electrochemistry of the binuclear cyclopentadienyl complexes $[Co_2(\mu\text{-}NO)(\mu\text{-}L)(\eta\text{-}C_5R_5)_2]^z$ (L = CO, R = Me, z = 0 or 1; L = NO, R = H or Me, z = 0, 1, or 2). We now present details[2] of related rhodium chemistry which allows a comparison to be made of $[Rh_2(CO)_2(\mu\text{-}NO)(cp)_2][PF_6]$ (cp = $\eta^5\text{-}C_5H_5$), $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5R_5)_2][PF_6]$ (R = H or Me), and $[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2][PF_6]_2$ not only with the cobalt analogues referred to above but also with the well known and synthetically important isoelectronic carbonyls $[Rh_2(CO)_2(\mu\text{-}CO)(\eta\text{-}C_5R_5)_2]$ and $[\{Rh(\mu\text{-}CO)(\eta\text{-}C_5R_5)\}_2]$.

Previous reports of nitrosyl-bridged cyclopentadienylrhodium complexes have been confined to those of the low-yield syntheses of $[\{Rh(\mu\text{-}NO)(cp)\}_2]$, $[Rh_2(\mu\text{-}NO)(\mu\text{-}NO_2)(cp)_2]$, and $[Rh_3(\mu_3\text{-}NO)_2(cp)_3]$,[3] and, while the present work was in progress, the independent preparation of $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][BF_4]$.[4]

Results and Discussion

The addition of $[NO][PF_6]$ to a solution of $[Rh(CO)_2(cp)]$ in CH_2Cl_2 resulted in the deposition of an air-sensitive, orange solid, and the formation of a red-brown solution from which a moderate yield of $[Rh_2(CO)_2(\mu\text{-}NO)(cp)_2][PF_6]$ (1) was isolated by adding hexane. The air-sensitive, orange solid shows one carbonyl band in the i.r. spectrum, at *ca.* 2 110 cm^{-1}, but has not been characterised further. The identity of complex (1) was fully established by elemental analysis and by i.r. and n.m.r. spectroscopy (Tables 1 and 2). The low nitrosyl and high carbonyl stretching frequencies show that the NO ligand bridges in preference to the carbonyls, and the single resonance in the ^1H n.m.r. spectrum, even at −90 °C, reveals the equivalence of the two cyclopentadienyl rings. The structure of complex (1) is, therefore, likely to be very similar to those crystallographically determined for $[Rh_2(CO)_2(\mu\text{-}L)(\eta\text{-}C_5H_4R)_2]$ (R = H, L = CO,[5] SO_2,[6] or CH_2;[7] R = Me, L = CH_2[8]) and $[Rh_2(CO)_2(\mu\text{-}CR_2)(\eta\text{-}C_5Me_5)_2]$ (R = CO_2Me);[9] the carbonyls are *trans*-disposed about the metal-metal bond. By contrast to $[Rh_2(CO)_2(\mu\text{-}CO)(cp)_2]$, which undergoes bridge–terminal carbonyl exchange above −80 °C,[10] and $[Rh_2(CNBu^t)_2(\mu\text{-}CNBu^t)(\eta^5\text{-}C_9H_7)_2]$ in which the isocyanide ligands interchange,[11] complex (1) is not fluxional.

When treated with donor ligands, L, cation (1) yields $[Rh(NO)L(cp)]^+$ (2) according to the stoicheiometry (i).

$$[Rh_2(CO)_2(\mu\text{-}NO)(cp)_2]^+ + L \longrightarrow [Rh(CO)_2(cp)] + [Rh(NO)L(cp)]^+ \quad \text{(i)}$$

Cleavage results not only in bridge–terminal nitrosyl transfer but also in the migration of one carbonyl ligand between the two metal atoms. Although complex (2; L = PPh_3) is readily prepared directly[12] from $[Rh(CO)(PPh_3)(cp)]$ and $[NO]^+$, the cleavage reactions of (1) provide a route to hitherto undiscovered alkene derivatives. Thus, complex (1) and an excess of cyclo-octene in CH_2Cl_2 give an orange solution from which good yields of (2; L = C_8H_{14}) (Table 1) can be isolated after removal of $[Rh(CO)_2(cp)]$. The ^1H n.m.r. spectrum of (2; L = C_8H_{14}) (Table 2) is fully consistent with the presence of the η^2-bonded alkene, and is very similar to that of $[Rh(CO)(\eta^2\text{-}C_8H_{14})(cp)]$.[13]

The related η^2-cyclohexa-1,3-diene complex (2; L = C_6H_8) is also isolable, but ethylene and propylene react with (1) reversibly. Thus, on bubbling gaseous C_2H_4 through complex (1) in CH_2Cl_2 an orange solution is rapidly formed; the i.r. spectrum shows carbonyl bands only at 2 041 and 1 973 cm^{-1}, due to $[Rh(CO)_2(cp)]$, and one terminal nitrosyl absorption at 1 859 cm^{-1} assignable to $[Rh(\eta^2\text{-}C_2H_4)(NO)(cp)]^+$ by analogy with (2; L = C_6H_8 or C_8H_{14}) (Table 2). On adding n-hexane to the reaction mixture, or on partial evaporation of the solvent at reduced pressure, complex (1) is rapidly and quantitatively regenerated, and the cycle can be repeated without loss of (1). The reversible co-ordination of alkenes by

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* μ-Carbonyl-μ-nitrosyl-bis[(η-pentamethylcyclopentadienyl)-rhodium] (*Rh–Rh*) hexafluorophosphate.

Supplementary data available (No. SUP 23956, 16 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Infrared and analytical data for cyclopentadienylrhodium nitrosyl derivatives

Complex	Colour	Yield (%)	$\tilde{\nu}$(CO) [a]/cm^{-1}	$\tilde{\nu}$(NO)/cm^{-1}	Analysis [b] (%)		
					C	H	N
(1) $[Rh_2(CO)_2(\mu\text{-}NO)(cp)_2][PF_6]$	Orange-brown	54	2 074, 2 048	1 636	25.6 (25.4)	1.9 (1.8)	2.5 (2.5)
(2; L = C_8H_{14}) $[Rh(NO)(\eta^2\text{-}C_8H_{14})(cp)][PF_6]$	Yellow-brown	95	—	1 863 [c]	34.4 (34.4)	4.2 (4.2)	4.5 (3.1)
(2; L = C_6H_8) $[Rh(NO)(\eta^2\text{-}C_6H_8)(cp)][PF_6]$	Khaki	63	—	1 850 [c]	29.9 (31.2)	2.7 (3.1)	3.1 (3.3)
(3; R = Ph) $[Rh_2(CO)\{\mu\text{-}N(O)C(R)CR\}(cp)_2][PF_6]$	Dark red	86	2 038	—	41.7 (41.8)	3.0 (2.8)	1.7 (2.0)
(3; R = C_6H_4OMe-*p*) $[Rh_2(CO)\{\mu\text{-}N(O)C(R)CR\}(cp)_2][PF_6]$	Dark red	62	2 035	—	41.7 (41.7)	3.2 (3.1)	1.5 (1.8)
(4) $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(cp)_2][PF_6]$	Dark blue	46	1 897 [c]	1 582	24.6 (24.5)	1.9 (1.9)	3.1 (2.6)
(5) $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$	Dark blue	98	1 846 [c]	1 524	37.4 (37.1)	4.3 (4.4)	2.1 (2.1)
(6) $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(PPh_3)(\eta\text{-}C_5Me_5)_2][PF_6]$	Brown	79	1 840	1 520	47.1 (46.8)	4.8 (4.6)	1.5 (1.4) [d]
(7) $[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2][PF_6]_2$	Dark blue	71	—	1 587 [c]	29.0 (29.1)	3.8 (3.6)	2.6 (3.4)

[a] In CH_2Cl_2 unless otherwise stated. [b] Calculated values are in parentheses. [c] In Nujol. [d] Analysed as a 1 : 1 CH_2Cl_2 solvate. For the 1 : 1 $CHCl_3$ solvate: C, 45.2 (45.3); H, 4.7 (4.4); N, 1.2 (1.3)%.

Table 2. Proton and ^{13}C n.m.r. data [a] for cyclopentadienylrhodium nitrosyl derivatives

Complex	^1H (δ/p.p.m.) [b]
(1) $[Rh_2(CO)_2(\mu\text{-}NO)(cp)_2][PF_6]$	6.70 [c]
(2; L = C_8H_{14}) $[Rh(NO)(\eta^2\text{-}C_8H_{14})(cp)][PF_6]$	6.06 (5 H, s, cp), 5.91 (2 H, m, H^1), 2.40 (4 H, m, H^2), 1.70 (8 H, m, H^3 and H^4)
(2; L = C_6H_8) $[Rh(NO)(\eta^2\text{-}C_6H_8)(cp)][PF_6]$	6.28 (2 H, m, H^1 and H^2), 5.92 (5 H, s, cp), 5.52 (2 H, m, H^3 and H^4), 3.30 (4 H, m, H^5 and H^6)
(3; R = Ph) $[Rh_2(CO)\{\mu\text{-}N(O)C(R)CR\}(cp)_2][PF_6]$	7.15 (10 H, m, Ph), 6.17 (5 H, s, cp), 5.90 (5 H, s, cp) [d]
(3; R = C_6H_4OMe-*p*) $[Rh_2(CO)\{\mu\text{-}N(O)C(R)CR\}(cp)_2][PF_6]$ [e]	6.90 (4 H, $[AB]_2$, C_6H_4), 6.59 (4 H, br s, C_6H_4), 6.22 [5 H, d, *J*(^{103}RhH) 0.5, cp], 5.98 [5 H, d, *J*(^{103}RhH) 0.5, cp], 3.77 (3 H, s, OMe), 3.66 (3 H, s, OMe)
(4) $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(cp)_2][PF_6]$	5.85
(5) $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$	1.75 [f]
(6) $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(PPh_3)(\eta\text{-}C_5Me_5)_2][PF_6]$	7.5 (15 H, m, PPh_3), 1.70 (15 H, s, C_5Me_5), 1.56 [15 H, d, *J*(^{31}PH) 3.5, C_5Me_5] [f]
(7) $[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2][PF_6]_2$	1.53

[a] Numbering as in Scheme 1. [b] Downfield from $SiMe_4$, *J* values in Hz. In CD_2Cl_2 unless stated otherwise. [c] In $(CD_3)_2CO$. [d] In CD_3NO_2. [e] ^{13}C N.m.r.: [b] δ 55.68 (OMe), 55.90 (OMe), 94.47 [d, *J*(^{103}RhC) 5, cp], 96.31 [d, *J*(^{103}RhC) 5, cp], 113.75, 114.30 (C^4, $C^{4'}$), 128.16, 132.28 (C^5, $C^{5'}$), 147.12 (C^6, $C^{6'}$), 160.01, 160.88 (C^3, $C^{3'}$), 185.26 [d, *J*(^{103}RhC) 5, C^1], 190.57 [t, *J*(^{103}RhC) 39, CO], 230.92 [d, *J*(^{103}RhC) 32, C^2]. [f] In $CDCl_3$.

metal nitrosyls has obvious implications for homogeneous catalysis.

The reaction of complex (1) with alkynes is very different from that with alkenes. Although dialkylacetylenes yield complex and inseparable mixtures, (1) and RC_2R (R = Ph or *p*-$MeOC_6H_4$) in CH_2Cl_2 give deep red solutions from which good yields of dark red, air-stable solids (3) are isolable. Elemental analysis (C, H, and N) (Table 1) suggests the empirical formula $[Rh_2(CO)(RC_2R)(NO)(cp)_2][PF_6]$ for (3), with one carbonyl ligand replaced by the alkyne. However, spectroscopic studies militate against simple substitution. The i.r. spectrum of complex (3; R = C_6H_4OMe-*p*) shows one terminal carbonyl absorption at 2 035 cm^{-1}, but the lack of other peaks between 2 100 and 1 500 cm^{-1} suggests the absence of either terminal or bridging nitrosyl ligands. The ^1H and ^{13}C n.m.r. spectra of (3) (Table 2) show the cyclopentadienyl ligands to be inequivalent and, for (3; R = C_6H_4OMe-*p*), the inequivalence of the two *p*-methoxy-substituents. Of particular note in the ^{13}C n.m.r. spectrum of (3; R = C_6H_4OMe-*p*) is the difference between the chemical shifts of the acetylenic carbon atoms C^1 and C^2 (185.3 and 230.9 p.p.m.) and the very different rhodium–carbon couplings [*J*($^{103}Rh^{13}C$) = 5 and 32 Hz respectively].

On the basis of the data presented above, and in Tables 1 and 2, a structure is proposed for complex (3) (Scheme 1) in which the nitrosyl group and the alkyne are linked to form a bridging C-nitroso-ligand. Although alkyne insertion into a metal–nitrosyl bond is unprecedented, $[\{Co(NO)(cp)\}_2]$ and olefins (R_2CCR_2) give $[Co\{N(O)CR_2CR_2N(O)\}(cp)]$ [14] and $[Co(NO)(cp)]^-$ reacts with alkyl iodides in the presence of phosphines to give [15] nitrosoalkane derivatives such as $[Co\{N(O)Me\}(PPh_3)(cp)]$. In addition, the structure of $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C(Ph)CPh\}(cp)_2]$, which arises [16] from alkyne insertion into one Ru–CO bond of $[\{Ru(CO)_2(cp)\}_2]$, is very similar to that proposed for (3).

To date, all attempts to crystallise complex (3) have failed,* precluding single-crystal *X*-ray structural studies. Similarly, ^{15}NO-labelling studies have been of limited help in the location of the NO moiety within (3). The reaction between $[Rh(CO)_2(cp)]$ and $[^{15}NO][BF_4]$ gave $[Rh_2(CO)_2(\mu\text{-}^{15}NO)(cp)_2][BF_4]$ [$\tilde{\nu}$(CO) (CH_2Cl_2) = 2 080 and 2 050 cm^{-1}, $\tilde{\nu}$(^{15}NO) = 1 586 cm^{-1}] which reacted with RC_2R to afford $[Rh_2(CO)\{\mu\text{-}^{15}N(O)C(R)CR\}(cp)_2][BF_4]$ [R = C_6H_4MeO-*p*, $\tilde{\nu}$(CO) = 2 037 cm^{-1}]. However, a comparison of the Nujol and hexachlorobutadiene i.r. spectra of the ^{14}N and ^{15}N isomers revealed only

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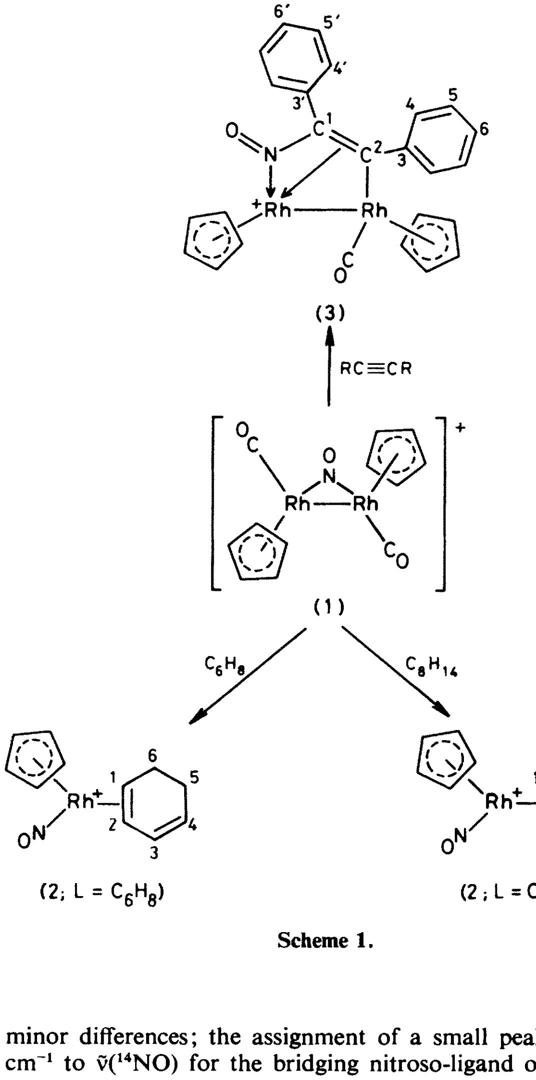
* On one occasion, small quantities of black crystals were obtained but an *X*-ray diffraction study revealed them to be $[Rh_3(\mu_3\text{-}NO)(\mu_3\text{-}PhC_2Ph)(cp)_3][PF_6]$.[17] We have, as yet, been unable to synthesise this species directly from (3; R = Ph).

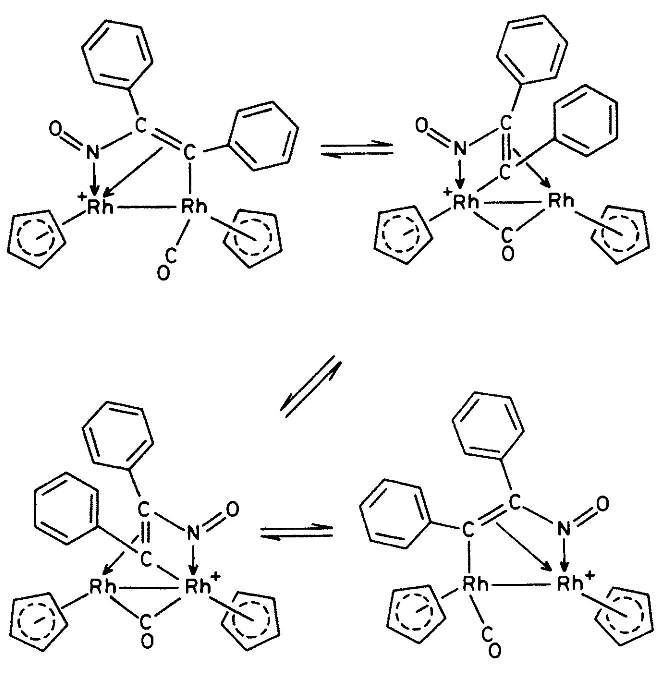


Scheme 1.

minor differences; the assignment of a small peak at 1 430 cm^{-1} to $\tilde{\nu}(^{14}NO)$ for the bridging nitroso-ligand of (3; R = C_6H_4OMe-*p*) is tentative at best. Unfortunately, the small quantities available of the ^{15}N-labelled derivative did not allow the detection of the signals due to C^1 and C^2 in the ^{13}C n.m.r. spectrum. Informative $^{13}C^{15}N$ coupling might reasonably be expected.

One further aspect of the ^{13}C n.m.r. spectrum of complex (3; R = C_6H_4OMe-*p*) is of interest. The resonance due to the single carbonyl ligand has a chemical shift (190.57 p.p.m.) typical of terminal bonding to rhodium.[10,18] However, the signal is observed as a triplet, with the coupling constant [$J(^{103}Rh^{13}C)$ = 39 Hz] approximately half that usually found. Thus, the ^{13}C n.m.r. data suggest a fluxional process for (3), similar to that observed [16] for $[Ru_2(CO)(\mu\text{-}CO)\{\mu C(O)C(Ph)CPh\}(cp)_2]$. The intermediate in this process, shown in Scheme 2, is structurally related to $[W_2(CO)_4\{\mu\text{-}C(O)C(R)CR\}(cp)_2]$ (R = CO_2Me).[19]

At room temperature, a solution of complex (1) in CH_2Cl_2 slowly darkens and new absorptions at 1 897 and 1 586 cm^{-1} appear in the i.r. spectrum. On heating the mixture under reflux, a deep blue solution is formed from which $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(cp)_2][PF_6]$ (4) is isolable after repeated fractional crystallisation. The decarbonylation of (1), giving (4), was confirmed not only by elemental analysis and i.r. and ^1H n.m.r. spectroscopy (Tables 1 and 2) but also by the field-desorption mass spectrum which showed a parent ion for $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(cp)_2]^+$ at *m*/*e* = 394.



Scheme 2.

Complex (4), which can also be prepared from $[\{Rh(CO)(cp)\}_3]$ and $[NO]^+$, is isoelectronic with the, as yet, unknown carbonyl $[\{Rh(\mu\text{-}CO)(cp)\}_2]$. The ease with which (1) is decarbonylated, relative to $[Rh_2(CO)_2(\mu\text{-}CO)(cp)_2]$, is no doubt due to the weakening of the Rh–CO(terminal) bonds by the strong π-accepting nitrosyl ligand and by the overall positive charge on the complex. Attempts to increase the yield of complex (4) from (1), either by thermolysis in CH_2ClCH_2Cl or by adding Me_3NO to the reaction mixture, were unsuccessful so that the chemistry of (4) remains largely undeveloped. However, PhC_2Ph and (4) give (3; R = Ph), thereby confirming the latter to be a monocarbonyl, and PPh_3 causes bridge cleavage and the formation of $[Rh(CO)(PPh_3)(cp)]$ and $[Rh(NO)(PPh_3)(cp)]^+$.[12]

The replacement of cp by C_5Me_5 in $[Rh_2(CO)_2(\mu\text{-}CO)(cp)_2]$ leads to decarbonylation and to the isolation of $[\{Rh(CO)(\eta\text{-}C_5Me_5)\}_2]$.[20,21] Similarly, blue-black $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$ (5) is readily prepared in quantitative yield by the addition of solid $[NO][PF_6]$ to $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ (1 : 2 ratio) in CH_2Cl_2, or in a methanol–benzene mixture;[4] no evidence was found for an intermediate analogous to (1). Complex (5) can also be prepared *via* the nitrosyl-transfer reaction between $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ and $[Rh(\eta^2\text{-}C_8H_{14})(NO)(cp)]^+$. Although the mixed-ligand species $[Rh_2(CO)_2(\mu\text{-}NO)(cp)(\eta\text{-}C_5Me_5)]^+$ was anticipated by analogy with the reaction between $[Rh(CO)_2(cp)]$ and $[Rh(\eta^2\text{-}C_2H_4)(NO)(cp)]^+$ (see above), the formation of (5) is described by equation (ii).

$$2[Rh(CO)_2(\eta\text{-}C_5Me_5)] + [Rh(\eta^2\text{-}C_8H_{14})(NO)(cp)]^+ \longrightarrow [Rh(CO)_2(cp)] + [Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2]^+ + C_8H_{14} + CO \quad (ii)$$

The identity of complex (5) was established by the data given in Tables 1 and 2, and by *X*-ray crystallography. The results of the single-crystal diffraction study are summarised in Table 3, and the structure of $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2]^+$ is illustrated (with the crystallographic numbering) in the Figure. The cation is crystallographically well defined and comprises two $Rh(\eta\text{-}C_5Me_5)$ groups linked by a metal–metal double bond [2.577(1) Å] and by symmetrical nitrosyl

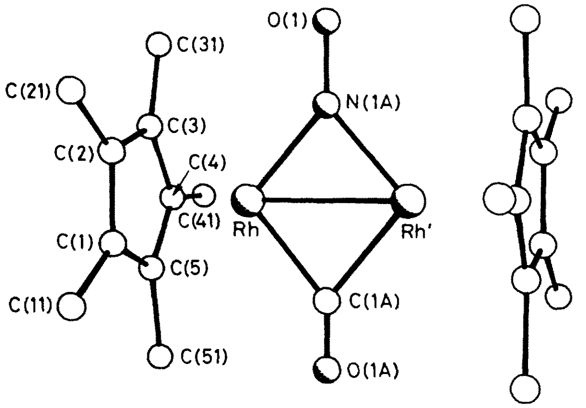


Figure. The configuration of the cation $[Rh_2(\mu\text{-CO})(\mu\text{-NO})(\eta\text{-}C_5Me_5)_2]^+$ (5) showing the crystallographic numbering. The methyl hydrogen atoms are omitted for clarity

[Rh–N(O) 1.95(1) Å] and carbonyl [Rh–C(O) 2.00(2) Å] bridges; the angles subtended at the bridging carbon and nitrogen atoms by the two rhodium atoms are 80.2 and 82.6° respectively. The $Rh_2(\mu\text{-C})(\mu\text{-N})$ core is constrained to be planar by a crystallographic two-fold axis which passes through the carbon and nitrogen bridges; the geometry of the core compares with that of the $Rh_2(\mu\text{-C})_2$ atoms of the isoelectronic carbonyl $[\{Rh(\mu\text{-CO})(\eta\text{-}C_5Me_5)\}_2]$ for which Rh–Rh 2.564(2) Å and Rh–C(O) 1.97(1) Å (average).[22]

The ring-carbon atoms of the pentamethylcyclopentadienyl ligand were refined as a rigid, planar, pentagon (C–C 1.42 Å) but with anisotropic thermal parameters. Although any perturbation of the ring from five-fold symmetry cannot, therefore, be discussed, the Rh–C distances vary noticeably, from 2.169(7) to 2.232(8) Å. The plane of the C_5 ring is almost perpendicular to the metal–metal vector (88.2°), and the metal-to-ring centroid distance is 1.833 Å. The methyl substituents on the ring are bent away from the metal atom by a mean distance of 0.06 Å. The $[PF_6]^-$ anion is disordered, with the phosphorus atom situated on, or very close to, a crystallographic two-fold axis.

The isoelectronic complexes $[\{Co(\mu\text{-CO})(\eta\text{-}C_5Me_5)\}_2]$ [23] and $[Co_2(\mu\text{-CO})(\mu\text{-NO})(\eta\text{-}C_5Me_5)_2]^+$ [1] are known to undergo one-electron reduction to isolable monoanionic and neutral radicals respectively. Although the electrochemistry of $[\{Rh(\mu\text{-CO})(\eta\text{-}C_5Me_5)\}_2]$ has not yet been published, and paramagnetic organorhodium complexes are relatively rare,[24] (5) is reversibly reduced in a one-electron step to $[Rh_2(\mu\text{-CO})(\mu\text{-NO})(\eta\text{-}C_5Me_5)_2]$.

A voltammogram of complex (5), at a rotating platinum electrode in CH_2Cl_2, shows two reduction waves, at $E_{\frac{1}{2}} = -0.56$ and -1.50 V, with approximately equal diffusion currents ($i_d/c = 12.0$ and 10.6 μA l mmol^{-1}, respectively). Although the second wave is close to the base electrolyte curve, the first is well defined and a plot of E *vs.* ln $(i/i_L - i)$ (i_L = limiting current) is a straight line with slope −71 mV, similar to that found for the reversible one-electron oxidation of ferrocene under the same experimental conditions. The implication of the reversible formation of $[Rh_2(\mu\text{-CO})(\mu\text{-NO})(\eta\text{-}C_5Me_5)_2]$ from (5) was borne out by cyclic voltammetry and controlled-potential electrolysis.

The first wave in the cyclic voltammogram of complex (5) ($E^\circ = -0.57$ V) is reversible for scan rates, v, in excess of 91 mV s^{-1} ($i_{ox}/i_{red} = 1.0$), and diffusion controlled ($i_d/\sqrt{v}$ constant) for $23 < v < 454$ mV s^{-1}; the second wave is irreversible at all scan rates used. On electrolytic reduction at −0.7 V an air-sensitive turquoise solution was formed after the passage of 1.10 electrons per cation, and voltammetry of the product, both cyclic and at the rotating electrode, confirmed the quantitative formation of neutral $[Rh_2(\mu\text{-CO})(\mu\text{-NO})(\eta\text{-}C_5Me_5)_2]$. Further characterisation of the product proved impossible. An e.s.r. spectrum taken of the electrolysed solution showed one narrow line at $g = 2.003$, but some evidence for decomposition in the sample precluded assignment of the signal to $[Rh_2(\mu\text{-CO})(\mu\text{-NO})(\eta\text{-}C_5Me_5)_2]$. By comparison, $[Co_2(\mu\text{-CO})(\mu\text{-NO})(\eta\text{-}C_5Me_5)_2]$ shows a 15-line signal [$A_{iso}(^{59}Co)$ = 43.5 G (4.35 mT)] centred at $g = 2.054$.[1]

Table 3. Selected bond lengths (Å) and angles (°) for $[Rh_2(\mu\text{-CO})(\mu\text{-NO})(\eta\text{-}C_5Me_5)_2][PF_6]$ (5) *

Rh–Rh′	2.577(1)	Rh–N(1A)	1.952(12)
Rh–C(1A)	2.00(2)	Rh–C(1)	2.169(7)
Rh–C(2)	2.212(7)	Rh–C(3)	2.232(8)
Rh–C(4)	2.202(7)	Rh–C(5)	2.162(8)
C(1A)–O(1)	1.06(3)	N(1A)–O(1A)	1.28(3)
Rh′–Rh–N(1A)	48.7(3)	Rh′–Rh–C(1A)	49.9(4)
Rh′–Rh–C(1)	145.8(2)	Rh′–Rh–C(2)	145.1(2)
Rh′–Rh–C(3)	146.4(2)	Rh′–Rh–C(4)	148.0(2)
Rh′–Rh–C(5)	147.7(2)	Rh–C(1A)–O(1)	139.9(4)
Rh–C(1A)–Rh′	80.2(8)	Rh–N(1A)–O(1A)	138.7(3)
Rh–N(1A)–Rh′	82.6(6)	C(1A)–Rh–N(1A)	98.6(5)

* Atom Rh′ is related to atom Rh by the two-fold axis of symmetry.

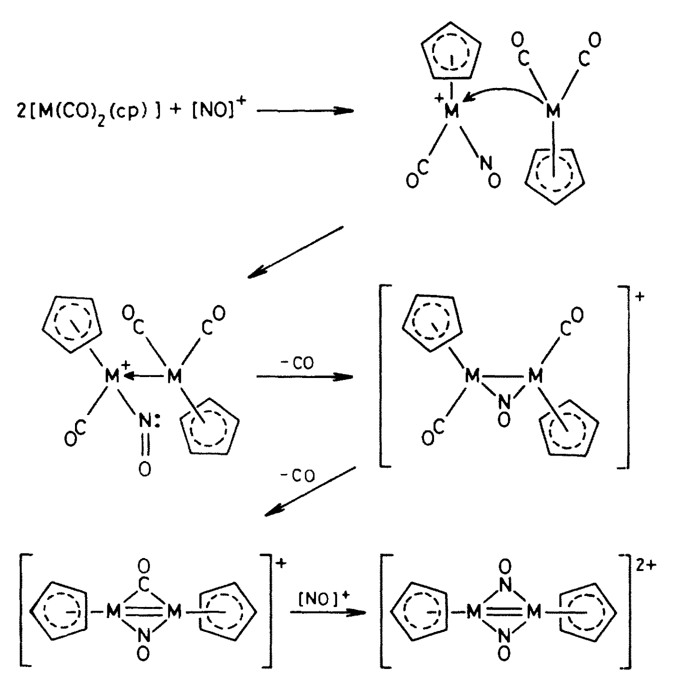
The chemical reduction of complex (5) with $K[BH(CHMeEt)_3]$ in tetrahydrofuran (thf) (successfully employed in the synthesis of the cobalt analogue [1]) gave a transient turquoise solution which rapidly became red. On evaporation of the mixture to dryness, and recrystallisation from n-hexane at −78 °C, a red-brown solid was obtained which showed one bridging carbonyl absorption in the i.r. spectrum [ṽ(CO) (n-hexane) = 1 819 cm^{-1}] but no band attributable to the nitrosyl ligand. Further characterisation proved impossible although chromatography of the red-brown solid on alumina regenerated small quantities of (5).

The reaction of (5) with PPh_3 (1 : 1 ratio) in CH_2Cl_2 differs from those of (1) and (4) in giving good yields of the dark brown, *binuclear* adduct $[Rh_2(\mu\text{-CO})(\mu\text{-NO})(PPh_3)(\eta\text{-}C_5Me_5)_2][PF_6]$ (6). The structure of (6) is simply assigned on the basis of the i.r. and ^1H n.m.r. spectra. The carbonyl and nitrosyl absorptions (Table 1) are lowered by only 5 cm^{-1}, showing the retention of both bridges, and the two C_5Me_5 resonances (Table 2), one split into a doublet by ^{31}P coupling, show that the PPh_3 ligand is bound to one rhodium atom. Similar phosphine and phosphite adducts of $[\{M(\mu\text{-CO})(\eta\text{-}C_5R_5)\}_2]$ (M = Co, R = H;[25] M = Rh, R = Me;[26,27] M_2 = CoRh, R = Me[27]) have been prepared, and *X*-ray studies show $[Rh_2(\mu\text{-CO})_2(PMe_2Ph)(\eta\text{-}C_5Me_5)_2]$ [27] and $[Co_2(\mu\text{-CS})_2(PMe_3)(cp)_2]$ [28] to be isostructural with (6).

Although complex (6) is not cleaved when heated under reflux in CH_2Cl_2 for 3 d with an excess of PPh_3, the reaction with $P(OMe)_3$ initially yields the adduct $[Rh_2(\mu\text{-CO})(\mu\text{-NO})\{P(OMe)_3\}(\eta\text{-}C_5Me_5)_2][PF_6]$ [ṽ(CO) (CH_2Cl_2) = 1 853 cm^{-1}, ṽ(NO) = 1 530 cm^{-1}] followed by white $[Rh\{P(OMe)_3\}_3(\eta\text{-}C_5Me_5)][PF_6]_2$.[29]

Disappointingly, complex (5) does not react with alkenes or RC_2R (R = Ph or Me). However, diazoalkanes give the carbene-bridged cations $[Rh_2(\mu\text{-}CR^1R^2)(\mu\text{-NO})(\eta\text{-}C_5Me_5)_2][PF_6]$ (R^1 = H, R^2 = H, Me, or Ph; $R^1 = R^2$ = Ph),[4] and $[Pt(\eta\text{-cod})_2]$ (cod = cyclo-octa-1,5-diene) adds to the formal rhodium–rhodium double bond affording the cluster $[Rh_2Pt(\mu_3\text{-CO})(\mu_3\text{-NO})(\eta\text{-cod})(\eta\text{-}C_5Me_5)_2][PF_6]$.[30]

The reaction of $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ with an excess of $[NO][PF_6]$ resulted in further carbonyl substitution and the



Scheme 3. M = Co or Rh

isolation of the deep blue dinitrosyl dication $[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2][PF_6]_2$ (7). The latter may be separated from (5), if necessary, by fractional crystallisation from CH_2Cl_2–n-hexane; the dication is the less soluble. Although fully characterised by elemental analysis and by i.r. and ^1H n.m.r. spectroscopy (Tables 1 and 2), complex (7) is very air- and water-sensitive; hydrolysis yields the orange μ-difluorophosphato-complex $[Rh_2(\mu\text{-}O_2PF_2)_3(\eta\text{-}C_5Me_5)_2][PF_6]$.[31]

Neglecting ring substituents, complex (7) differs from $[\{Rh(\mu\text{-}NO)(cp)\}_2]$[3] (8) solely by two electrons, and it is noteworthy that all three members of the redox series $[\{Co(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2]^z$ (z = 0, 1, or 2) are well authenticated.[1] Although the high reactivity of (7) has prevented satisfactory electrochemical studies, voltammetry has shown that (8) does not undergo reversible one-electron oxidation in either CH_2Cl_2 or thf. Somewhat surprisingly, however, complex (8) is reversibly reduced to the monoanion $[\{Rh(\mu\text{-}NO)(cp)\}_2]^-$.

In CH_2Cl_2, at a rotating platinum electrode, complex (8) shows a one-electron reduction wave with $E_{\frac{1}{2}} = -1.17$ V; a linear plot of E vs. ln $(i/i_L - i)$ has a slope of −79 mV. Cyclic voltammetry confirmed that the electron transfer was diffusion controlled, with $i_c/\sqrt{v}$ constant for $255 < v < 510$ mV s^{-1}, but the process is reversible only at v = 500 mV s^{-1}. In thf, however, the reduction ($E^\circ = -1.17$ V) is reversible at all scan rates used, with $i_{ox}/i_{red} = 1.0$ for $47 < v < 376$ mV s^{-1} implying stability of the monoanion $[\{Rh(\mu\text{-}NO)(cp)\}_2]^-$. The cyclic voltammogram of complex (8) in thf also shows a diffusion-controlled oxidation wave which, however, shows no reversibility even at −25 °C (E_{ox} = 0.7 V at v = 213 mV s^{-1}). Thus, the transient existence of $[\{Rh(\mu\text{-}NO)(cp)\}_2]^+$ is in stark contrast to the air-stability of the isolable salt $[\{Co(\mu\text{-}NO)(cp)\}_2][PF_6]$.[1]

The Mechanism of Formation of Complexes (1), (4), (5), *and* (7).—The mechanism of formation of complexes (1), (4), (5), and (7), and of the cobalt analogues,[1] is shown in Scheme 3. Although the first step in the sequence, namely the formation of $[M(CO)(NO)(\eta\text{-}C_5R_5)]^+$, is ill defined for rhodium, the very reactive cobalt complexes can be readily prepared [*e.g.* M = Co, R = H, $\tilde{\nu}$(CO) (CH_2Cl_2) = 2 130 cm^{-1}, $\tilde{\nu}$(NO) = 1 900 cm^{-1}; R = Me, $\tilde{\nu}$(CO) = 2 090 cm^{-1}, $\tilde{\nu}$(NO) = 1 861 cm^{-1}]. For example, the dropwise addition of a solution of $[Co(CO)_2(cp)]$ in CH_2Cl_2 to a suspension of $[NO][PF_6]$ in the same solvent gave, on careful monitoring by i.r. spectroscopy, a deep brown solution containing $[Co(CO)(NO)(cp)][PF_6]$. The very high stretching frequency, $\tilde{\nu}$(CO), suggests the carbonyl ligand should be readily displaced and, indeed, the addition of $[Co(CO)_2(cp)]$ to the solution of $[Co(CO)(NO)(cp)]^+$ rapidly yields $[Co_2(CO)_2(\mu\text{-}NO)(cp)_2]^+$. The formation of the latter, *via* initial electron-pair donation from $[Co(CO)_2(cp)]$ to the electron-poor mononuclear nitrosyl cation (Scheme 3), is supported by the well known ability of $[ML_2(cp)]$ (M = Co or Rh, L = CO or phosphine) to act as a Lewis base.[32]

Intermediates such as $[M_2(CO)_3(NO)(\eta\text{-}C_5R_5)_2]^+$, which contain terminal, but 'bent,' one-electron NO ligands are widely invoked in the chemistry of nitrosyl complexes;[33] decarbonylation to $[M_2(CO)_2(\mu\text{-}NO)(\eta\text{-}C_5R_5)_2]^+$, further carbonyl loss to $[M_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5R_5)_2]^+$, and nitrosyl substitution to give $[\{M(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]^{2+}$ require no further comment.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Unless otherwise stated, the solid complexes are air-stable, dissolving in polar solvents such as acetone and CH_2Cl_2 to give moderately air-sensitive solutions. The compounds $[M(CO)_2(\eta\text{-}C_5R_5)]$ (M = Co, R = H[34] or Me;[35] M = Rh, R = H[36] or Me[37]) and $[^{15}NO][BF_4]$[38] were prepared by published methods. The salt $[NO][PF_6]$ was purchased from Fluorochem Ltd., Glossop, Derbyshire.

Cyclic voltammetry was carried out as previously described,[39] and voltammetry used a platinum-bead electrode rotated at 600 revolutions min^{-1}. Infrared spectra were recorded on Perkin-Elmer PE257 or PE457, or Nicolet MX-1 spectrometers. Proton n.m.r. spectra were recorded on a JEOL PS100 spectrometer and ^{13}C n.m.r. spectra on JEOL FX90-Q or FX200 instruments, calibrated against $SiMe_4$ as internal reference. Field-desorption mass spectra were obtained with an AEI MS902 instrument. X-Band e.s.r. spectra were recorded on a Varian Associates 4502/15 spectrometer and were calibrated against a solid sample of the diphenylpicrylhydrazyl radical.

Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Dicarbonylbis(η-*cyclopentadienyl*)-μ-*nitrosyl-dirhodium Hexafluorophosphate*, $[Rh_2(CO)_2(\mu\text{-}NO)(cp)_2][PF_6]$, (1).—To a well stirred solution of $[Rh(CO)_2(cp)]$ (0.45 g, 2.01 mmol) in CH_2Cl_2 (30 cm^3) was added solid $[NO][PF_6]$ (0.35 g, 2.00 mmol). After 1.5 h a further portion of $[NO][PF_6]$ (0.10 g, 0.57 mmol) was added and after a further 2.5 h the brown solution was filtered to remove an orange solid. Addition of n-hexane (75 cm^3) to the filtrate gave a brown precipitate which was recrystallised from CH_2Cl_2–diethyl ether to yield the orange-brown solid *product*, yield 0.31 g (54%). The compound slowly decomposes in air and is best stored under nitrogen.

(η^2-*Cyclo-octene*)(η-*cyclopentadienyl*)*nitrosylrhodium Hexafluorophosphate*, $[Rh(NO)(\eta^2\text{-}C_8H_{14})(cp)][PF_6]$ (2; L = *cyclo-octene*).—To $[Rh_2(CO)_2(NO)(cp)_2][PF_6]$ (1) (0.11 g, 0.19 mmol) in CH_2Cl_2 (25 cm^3) was added an excess of cyclo-octene (1.5 g, 13.6 mmol). The orange solution was filtered, and n-hexane added to give a brown solid. After washing with n-hexane (2 × 15 cm^3) the product was recrystallised from

Table 4. Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses for $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$ (5)

Atom *	x	y	z	Atom *	x	y	z
Rh	−0.105 31(7)	0.000 00	0.036 67(3)	O(1A)	0.000 00	−0.233 3(15)	0.000 00
P	0.500 00	−0.001 2(10)	0.500 00	C(1)	−0.316 1(7)	0.056 4(9)	−0.004 2(5)
F(1)	0.666 6(13)	−0.006(3)	0.600 6(11)	C(2)	−0.317 3(7)	−0.064 3(9)	−0.003 2(5)
F(2)	0.500 00	−0.131(2)	0.500 00	C(3)	−0.236 1(7)	−0.101 1(9)	0.119 9(5)
F(3)	0.508 9(11)	0.116 5(9)	0.440 8(9)	C(4)	−0.184 7(7)	−0.003 1(9)	0.195 0(5)
F(4)	0.375 6(9)	0.015 5(12)	0.380 8(8)	C(5)	−0.234 1(7)	0.094 2(9)	0.118 2(5)
F(5)	0.429(2)	0.089 3(15)	0.574 5(15)	C(11)	−0.394 8(9)	0.131 0(10)	−0.114 0(9)
F(6A)	0.414(3)	0.019(3)	0.595(3)	C(21)	−0.392 8(7)	−0.136 2(6)	−0.112 7(6)
F(6B)	0.419(2)	−0.056(2)	0.595(2)	C(31)	−0.213(2)	−0.218 1(13)	0.162(2)
O(1)	0.000 00	0.219 9(7)	0.000 00	C(41)	−0.100 5(8)	−0.005(3)	0.334 2(6)
C(1A)	0.000 00	0.130(2)	0.000 00	C(51)	−0.212(2)	0.222 0(10)	0.163 0(12)
N(1A)	0.000 00	−0.124 7(15)	0.000 00				

* For the disordered PF_6 anion: site occupancies F(1)—F(5) 0.5; F(6A), F(6B) 0.25.

CH_2Cl_2–n-hexane to give a yellow-brown *solid*, yield 0.084 g [95%, based on the stoicheiometry (i), see text].

The complex $[Rh(NO)(\eta^2\text{-}C_6H_8)(cp)][PF_6]$ was prepared in a similar manner, as a khaki solid in 63% yield. In this case, however, the pure product was only obtained after several recrystallisations in the presence of cyclohexa-1,3-diene.

The Reaction of Complex (1) *with p*-$MeOC_6H_4C{\equiv}CC_6H_4OMe$-*p; Synthesis of* $[Rh_2(CO)\{\mu\text{-}N(O)C(R)CR\}(cp)_2][PF_6]$ (3; R = C_6H_4OMe-*p*).—To a stirred solution of complex (1) (0.15 g, 0.26 mmol) in CH_2Cl_2 (25 cm^3) was added *p*-$MeOC_6H_4C{\equiv}CC_6H_4OMe$-*p* (0.06 g, 0.26 mmol). After 15 min the red solution was filtered, and n-hexane added to give a dark red oil. Recrystallisation from CH_2Cl_2–diethyl ether gave a dark red *solid*, yield 0.13 g, (62%).

The complex $[Rh_2(CO)\{\mu\text{-}N(O)C(Ph)CPh\}(cp)_2][PF_6]$ was prepared similarly, in 86% yield.

µ-*Carbonyl-bis*(η-*cyclopentadienyl*)-µ-*nitrosyl-dirhodium Hexafluorophosphate*, $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(cp)_2][PF_6]$ (4).—A solution of $[Rh_2(CO)_2(\mu\text{-}NO)(cp)_2][PF_6]$ (1) (0.16 g, 0.28 mmol) in CH_2Cl_2 (25 cm^3) was heated under reflux until the reaction was adjudged complete by i.r. spectroscopy (*ca.* 2 h). Addition of n-hexane (120 cm^3) to the filtered blue solution gave a precipitate which was fractionally crystallised four times from CH_2Cl_2–n-hexane mixtures to give a dark blue *solid*, yield 0.07 g (46%). The complex is air-sensitive in the solid state, and is decomposed by acetone or MeCN.

µ-*Carbonyl*-µ-*nitrosyl-bis*(η-*pentamethylcyclopentadienyl*)-*dirhodium Hexafluorophosphate*, $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$ (5).—To $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ (0.23 g, 0.77 mmol) in CH_2Cl_2 (25 cm^3) was added $[NO][PF_6]$ (0.067 g, 0.38 mmol). After gas evolution had ceased, n-hexane (75 cm^3) was added to the filtered, dark blue solution. The precipitate was recrystallised from CH_2Cl_2–n-hexane to give a dark blue *solid*, yield 0.26 g (98%).

µ-*Carbonyl*-µ-*nitrosyl-bis*(η-*pentamethylcyclopentadienyl*)-(*triphenylphosphine*)*dirhodium Hexafluorophosphate–Dichloromethane* (1/1), $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(PPh_3)(\eta\text{-}C_5Me_5)_2][PF_6]\cdot CH_2Cl_2$ (6).—A mixture of $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$ (0.15 g, 0.22 mmol) and PPh_3 (58 mg, 0.22 mmol) in CH_2Cl_2 (20 cm^3) was stirred at −20 °C for 5 min. Filtration of the mauve solution and addition of n-hexane (50 cm^3) gave a dark brown precipitate which was recrystallised from CH_2Cl_2–n-hexane as a brown *solid*, yield 0.17 g (79%).

Di-(µ-*nitrosyl*)-*bis*(η-*pentamethylcyclopentadienyl*)*dirhodium Bis*(*hexafluorophosphate*), $[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5Me_5)\}_2][PF_6]_2$ (7).—A mixture of $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ (0.02 g, 0.07 mmol) and $[NO][PF_6]$ (0.02 g, 0.11 mmol) in CH_2Cl_2 (25 cm^3) was stirred until i.r. spectroscopy showed the reaction to be complete (*ca.* 0.5 h). The dark blue solution was filtered and n-hexane (40 cm^3) was added to give a dark blue, water-sensitive *solid*, yield 20 mg (71%).

Carbonyl(η-*cyclopentadienyl*)*nitrosylcobalt Hexafluorophosphate*, $[Co(CO)(NO)(cp)][PF_6]$.—A CH_2Cl_2 (20 cm^3) solution of $[Co(CO)_2(cp)]$ (0.31 g, 1.72 mmol) was added dropwise to a suspension of $[NO][PF_6]$ (0.50 g, 2.86 mmol) in the same solvent (20 cm^3). The brown solution was filtered and n-hexane (75 cm^3) added to precipitate a dark brown solid. Recrystallisation from CH_2Cl_2–diethyl ether gave a brown *solid*, yield 0.18 g (33%). The salt is very air- and water-sensitive, both in the solid state and in solution.

Crystal Structure Determination of $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$ (5).—Black crystals of complex (5) grow as regular prisms from CH_2Cl_2–n-hexane. Intensities were measured for a crystal of dimensions 0.1 × 0.36 × 0.45 mm at 293 K in the range $2.9 \leqslant 2\theta \leqslant 60°$ using ω—2θ scans on a Nicolet *P*3/*m* automated four-circle diffractometer; attempts to cool the crystals appeared to induce a phase change and resulted in a much weaker diffraction pattern. The data were corrected for Lorentz, polarisation, and *X*-ray absorption effects [μ(Mo-K_α) = 7.78 cm^{-1}], before merging to give 1 672 unique measurements of which 1 519 satisfied the criterion $I \geqslant 1.5\sigma(I)$.

Crystal data. $C_{21}H_{30}F_6NO_2PRh_2$, M = 679.3, monoclinic, a = 10.325(7), b = 11.760(10), c = 11.258(5) Å, β = 110.00(4)°, U = 1 285(1) Å^3, Z = 2, D_c = 1.76 g cm^{-3}, F(000) = 676, space group *A*2 (non-standard setting of *C*2, no.5), Mo-K_α *X*-radiation (graphite monochromator), λ = 0.710 69 Å.

The structure was solved using Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Tests were carried out to exclude the other enantiomer from that given by the atomic co-ordinates in Table 4, and the possibility that the bridging carbon and nitrogen atoms might be interchanged, or even disordered between the two sites, was checked exhaustively. Refinement in the space group *A*2/*m*, which places a mirror plane through the molecule perpendicular to the two-fold axis, converged at $R(R')$ 0.05 (0.06), whereas a parallel refinement in *A*2 resulted in $R(R')$ 0.034 (0.034). The higher-symmetry space group would also require chemically unnecessary constraints, for example, that the bond lengths Rh–N(O) and Rh–C(O) must be equal and the C and N sites disordered. The atoms Rh, C, N, O, and P were refined anisotropically but such a refinement for the fluorine atoms resulted in exceedingly large thermal parameters. The hydrogen atoms were refined as members of rigid methyl groups (C–H 0.96 Å), with isotropic thermal parameters fixed at *ca.* 1.2 times the equivalent isotropic thermal parameter of the attached carbon atom. Weights were ascribed according to the scheme $w = [\sigma^2(F) + 0.00058|F|^2]$. The final Fourier difference map showed peaks ≈ 0.5 e Å^{-3} (or -0.3 e Å^{-3}) only in the region of the disordered anion. Scattering factors were from ref. 40 and were corrected for the effects of anomalous dispersion. Computations were carried out within the laboratory on an Eclipse (Data General) computer with the SHELXTL[41] system of programs. The final atom co-ordinates are listed in Table 4.

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