The Chemical and Electrochemical One-electron Oxidation of Diamidonaphthalene-bridged Complexes; Paramagnetic $[Rh_2]^{3+}$-containing A-Frames

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The complexes $[Rh_2L_4\{\mu\text{-}2,3\text{-}(NH)_2C_{10}H_6\}]$ [**1**; L_2 = (CO)(PPh_3) or η^4-cod (cyclo-octa-1,5-diene)] and $[Rh_2L_4\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}]$ [**2**; L_2 = (CO)(PPh_3), η^4-cod, η^4-nbd (norbornadiene), or η^4-tfbb (tetrafluorobenzobarrelene)] undergo two sequential one-electron oxidations at a platinum bead electrode. At −78 °C, the chemical oxidation of compound (**1**; $L_2 = \eta^4$-cod) or (**2**; $L_2 = \eta^4$-cod) in thf, with $[CPh_3][BF_4]$ in CH_2Cl_2, gives the $[Rh_2]^{3+}$-containing salts $[Rh_2(\eta^4\text{-cod})_2(\mu\text{-}L^1)][BF_4]$ [**1**$^+$; $L^1 = 2,3\text{-}(NH)_2C_{10}H_6$ or **2**$^+$; $L^1 = 1,8\text{-}(NH)_2C_{10}H_6$] which, in tetrahydrofuran (thf)-CH_2Cl_2 mixtures at −196 °C, show solvent-dependent e.s.r. spectra implying thf co-ordination at one axial site. The irreversible one-electron reduction of $[Rh_2(NO)(\eta^4\text{-cod})_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}][PF_6]$ (**3**), prepared from (**2**; $L_2 = \eta^4$-cod) and $[NO][PF_6]$ in CH_2Cl_2, leads to the loss of NO and the regeneration of (**2**; $L_2 = \eta^4$-cod).

The face-to-face complexes $[\{Rh(CO)_2(\mu\text{-RNXNR})\}_2]$ (Figure 1; X = CMe, R = Ph; X = N, R = *p*-tolyl) and their phosphine, η^4-diene,[1] and 2,2′-bipyridyl[2,3] derivatives undergo series of sequential one-electron oxidation reactions during which the $[Rh_2]^{Z+}$ core remains intact for Z = 2—5. A combination of *X*-ray structural studies on $[\{Rh(CO)(PPh_3)(\mu\text{-RNNNR})\}_2]^Z$ (Z = 0 or 1, R = *p*-tolyl),[4] molecular orbital (m.o.) calculations,[4,5] and e.s.r. spectroscopic studies on the $[Rh_2]^{3+}$ complexes[2—4,6] has shown that the highest occupied molecular orbital (h.o.m.o.) of the $[Rh_2]^{2+}$ species is comprised of the out-of-phase combination of the $4d_{z^2}$ orbitals on the two metal atoms. Clearly, the bonding in the $[Rh_2]^{Z+}$ core, and in particular the extent of delocalisation in the mixed-valence $[Rh_2]^{3+}$ derivatives, will be affected by changing θ, the angle between the two square-planar rhodium centres.

We have therefore investigated the redox reactions of A-frame diamidonaphthalene-bridged complexes (Figure 2), in which the angle θ is likely to be similar to that found in $[Rh_2(CO)_4\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}]$ (*i.e.* 110.9°),[7] and now report on the isolation and solvent-dependent e.s.r. spectra of the paramagnetic $[Rh_2]^{3+}$-containing complexes $[Rh_2(\eta^4\text{-cod})_2(\mu\text{-}L^1)][BF_4]$ [cod = cyclo-octa-1,5-diene, L^1 = 1,8- or 2,3-$(NH)_2C_{10}H_6$]. We also note the synthesis of $[Rh_2(NO)(\eta^4\text{-cod})_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}][PF_6]$ which loses the axially bound nitrosyl ligand on one-electron reduction.

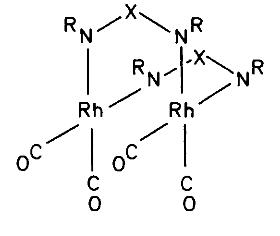
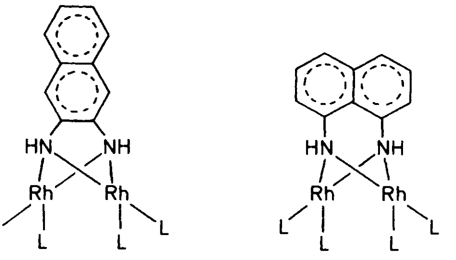


Figure 1. The structure of $[\{Rh(CO)_2(\mu\text{-RNXNR})\}_2]$ (X = CMe, R = Ph; X = N, R = *p*-tolyl)

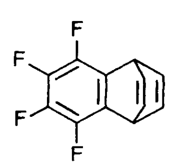


(1) (2)

Figure 2. The structures of compounds (1) and (2); L_2 = (CO)(PPh_3) or η^4-diene

Results and Discussion

The new complexes $[Rh_2(\eta^4\text{-diene})_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}]$ {η^4-diene = bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, nbd) or tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene (tetrafluorobenzobarrelene, tfbb)} were prepared by the method previously used[8] for the synthesis of the known cyclo-octa-1,5-diene (cod) analogue, namely the addition of 1,8-diaminonaphthalene to $[\{Rh(\mu\text{-OMe})(\eta^4\text{-diene})\}_2]$ (diene = nbd or tfbb). The red nbd and tfbb complexes are less stable than the cod compound, decomposing in air, so that electrochemical studies were carried out on freshly prepared samples.



tfbb

Electrochemical Studies.—Cyclic voltammetry shows that each of the complexes $[Rh_2L_4\{\mu\text{-}2,3\text{-}(NH)_2C_{10}H_6\}]$ [**1**; L_2 = (CO)(PPh_3) or η^4-cod] and $[Rh_2L_4\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}]$ [**2**; L_2 = (CO)(PPh_3), η^4-cod, η^4-nbd, or η^4-tfbb] undergoes two sequential one-electron oxidations at a platinum bead electrode. All of the complexes have been studied in CH_2Cl_2, and two, namely $[Rh_2(\eta^4\text{-cod})_2(\mu\text{-}L^1)]$ [L^1 = 2,3- or 1,8-$(NH)_2C_{10}H_6$], have been studied in tetrahydrofuran (thf).

Table 1. Cyclic voltammetric data[a] for μ-diamidonaphthalene complexes

Complex	E_1[b]/V	i_{red}/i_{ox}[c]	ν[d]/mV s^{-1}	E_2[e]/V
$[Rh_2(CO)_2(PPh_3)_2\{\mu\text{-}2,3\text{-}(NH)_2C_{10}H_6\}]$	0.33	0.65	—[f]	0.72
$[Rh_2(CO)_2(PPh_3)_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}]$	0.38	0.77	—[g]	0.95
$[Rh_2(\eta^4\text{-cod})_2\{\mu\text{-}2,3\text{-}(NH)_2C_{10}H_6\}]$	0.10	1.00	50	0.63[i]
	0.18[h]	1.00	50	0.49[h,i]
$[Rh_2(\eta^4\text{-cod})_2\{\mu\text{-}2,3\text{-}(NH)_2C_{10}H_6\}][BF_4]$[j]	0.10	1.00	50	0.60
$[Rh_2(\eta^4\text{-cod})_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}]$	0.20	0.80	200	0.91
	0.25[h]	0.97	100	0.62[h]
$[Rh_2(\eta^4\text{-cod})_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}][BF_4]$[j]	0.20	0.95	200	0.85
$[Rh_2(\eta^4\text{-nbd})_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}]$	0.09	0.88	200	0.70
$[Rh_2(\eta^4\text{-tfbb})_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}]$	0.29	0.83	200	—[k]

[a] Potentials are *versus* the saturated calomel electrode, measured at a platinum bead in CH_2Cl_2, unless stated otherwise, 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. [b] Oxidation potential for the first wave, taken as $[(E_p)_{ox} + (E_p)_{red}]/2$. [c] Ratio of the peak currents of the first wave, at a scan rate of 50 mV s^{-1}. [d] Scan rate at which i_{red}/i_{ox} for the first wave becomes unity. [e] Unless stated otherwise, E_2 is the oxidation peak potential at a scan rate of 200 mV s^{-1}. [f] At 500 mV s^{-1}, $i_{red}/i_{ox} = 0.91$. [g] At 500 mV s^{-1}, $i_{red}/i_{ox} = 0.92$. [h] In thf; E° for the couple $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ is 0.56 V. [i] Reversible wave, $E_2 = [(E_p)_{ox} + (E_p)_{red}]/2$. [j] At 0 °C. [k] Not measured.

At room temperature in CH_2Cl_2 the first wave of each complex is diffusion-controlled [$(i_p)_{ox}/v^{\frac{1}{2}}$ is constant for scan rates $50 \leqslant v \leqslant 500$ mV s^{-1}]. However, it is only fully chemically reversible at all the scan rates used for complex (**1**; $L_2 = \eta^4$-cod). For the other η^4-diene derivatives the wave is fully reversible only at the scan rates given in Table 1; the carbonylphosphine complexes show incompletely reversible oxidations even at 500 mV s^{-1}.

In most cases, the second oxidation waves are chemically irreversible so that Table 1 lists only the peak potentials, $(E_p)_{ox}$, at a scan rate of 200 mV s^{-1}. However, the cyclic voltammograms of $[Rh_2(\eta^4\text{-cod})_2(\mu\text{-}L^1)]$ [L^1 = 2,3- or 1,8-$(NH)_2C_{10}H_6$] show better defined reduction peaks on the return sweeps allowing the second oxidation potentials, E_2 {equal to $[(E_p)_{ox} + (E_p)_{red}]/2$}, to be estimated.

The cyclic voltammograms of the η^4-cod complexes in thf differ from those in CH_2Cl_2 in two ways. First, the initial oxidation wave is fully reversible in both cases, implying that the monocations ($\mathbf{1}^+$; $L_2 = \eta^4$-cod) and ($\mathbf{2}^+$; $L_2 = \eta^4$-cod) are more stable in thf than in CH_2Cl_2. Secondly, the separation, Δ, between the two oxidation waves for each complex is less (0.3—0.4 V) in thf than in CH_2Cl_2 (0.5—0.7 V).

Noting that the E° values for the oxidation of ferrocene $[Fe(\eta\text{-}C_5H_5)_2]$ in CH_2Cl_2 and thf are 0.47 and 0.56 V respectively, it is clear that the potential for the first oxidation of the η^4-cod complexes is essentially solvent-independent (Table 1). Thus, the decrease in Δ in thf is due to the shift of E_2 to a more negative value. The observed shifts most likely result from the addition of thf to one or both of the axial sites of the monocations; mono-co-ordination is certainly apparent from the e.s.r. spectroscopic studies described below. However, similar solvent-dependent cyclic voltammetric data have been obtained for the oxidation of $[\{Ir(\eta\text{-cod})(\mu\text{-pz})\}_2]$ (pz = pyrazolyl) in CH_2Cl_2 and MeCN mixtures, and interpreted[9] in terms of acetonitrile co-ordination to the dication $[\{Ir(\eta\text{-cod})(\mu\text{-pz})\}_2]^{2+}$. Clearly, more detailed studies are required, particularly with respect to the way in which the cyclic voltammetric waves, apparently fully reversible for the complexes described here, are affected by the equilibria between the solvent-co-ordinated and unco-ordinated cations. It is noteworthy, however, that in thf Δ for (**1**; $L_2 = \eta^4$-cod) decreases less than that of (**2**; $L_2 = \eta^4$-cod) suggesting that axial co-ordination is less favoured for the 2,3-diamidonaphthalene complex.

Apart from the effects of the solvent on the oxidation processes, the potential data given in Table 1 reveal several other trends. There is little dependence of E_1 on the nature of the bridging diamidonaphthalene ligand ($\leqslant$0.1 V). However, the η^4-diene complexes are significantly more easy to oxidise than the (carbonyl)triphenylphosphine analogues, and E_1 depends on the diene itself, in (**2**), in the order nbd < cod < tfbb.

A similar dependence of E^0 on the diene was also found[1] for the face-to-face complexes $[\{Rh(\eta^4\text{-diene})(\mu\text{-RNNNR})\}_2]$ (diene = nbd or cod; R = *p*-tolyl). However, for these triazenido-bridged species, the (carbonyl)triphenylphosphine analogue is more easily oxidised. Assuming that the oxidation of (**1**) or (**2**) is accompanied by a shortening of the Rh ··· Rh distance, as in the triazenido-complexes (*e.g.* $[\{Rh(CO)(PPh_3)(\mu\text{-RNNNR})\}_2]^Z$; $Z = 0$, Rh ··· Rh 2.96 Å; $Z = 1$, Rh ··· Rh 2.69 Å),[4] then the two series may differ because of differences in the steric interactions between the terminal ligands on the separate metal atoms. Repulsions between the two η^4-dienes will be greater in the face-to-face triazenido-complexes than in the A-frames.

For synthetic purposes the most important point to emerge from the cyclic voltammetric studies is that all of the complexes (**1**) and (**2**) are oxidised at potentials low enough (E_1 = 0.09—0.38 V) for the chemical generation of the monocations to require the use of only mild one-electron oxidants.

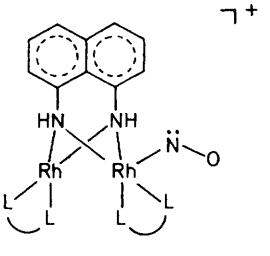
Chemical Studies.—The (carbonyl)triphenylphosphine complexes [(**1**) or (**2**); $L_2 = (CO)(PPh_3)$] react with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ in CH_2Cl_2, but as anticipated on the basis of the cyclic voltammetric studies described above, the monocations [($\mathbf{1}^+$) or ($\mathbf{2}^+$); $L_2 = (CO)(PPh_3)$] were too unstable even to detect spectroscopically. Similar reactions with the η^4-cod derivatives gave dark brown solids which showed e.s.r. spectra (see below) consistent with the formation of [($\mathbf{1}^+$) or ($\mathbf{2}^+$); $L_2 = \eta^4$-cod)]. However, analytically pure samples were not obtained, and the cyclic voltammograms of the isolated solids showed waves assignable not only to the $[Rh_2]^{3+}$ cations but also to $[Fe(\eta\text{-}C_5H_5)_2]^+$ as contaminant.

The increased reversibility of the oxidation waves for compounds [(**1**) or (**2**); $L_2 = \eta^4$-cod] in thf suggested that the monocations would be more stable in this solvent. Accordingly, [(**1**) or (**2**); $L_2 = \eta^4$-cod] in thf cooled to −78 °C was treated with a concentrated solution of $[CPh_3][BF_4]$ in CH_2Cl_2. Under these conditions, the analytically pure, dark brown salts $[Rh_2(\eta^4\text{-cod})_2(\mu\text{-}L^1)][BF_4]$ [($\mathbf{1}^+$); L^1 = 2,3-$(NH)_2C_{10}H_6$; ($\mathbf{2}^+$); L^1 = 1,8-$(NH)_2C_{10}H_6$] were deposited directly from the reaction mixture. The 1,8-diamidonaphthalene complex cation is more stable than the 2,3-diamidonaphthalene analogue, the latter slowly decomposing to unidentified products if left in contact with the mother-liquors of the reaction mixture.

Table 2. E.s.r. spectroscopic data for $[Rh_2(\eta^4\text{-diene})_2(\mu\text{-}L^1)]^+$

Diene	L^1	g_1	g_2	$g_{av.}$	Solvent	Temperature/°C
cod	$2,3\text{-}(NH)_2C_{10}H_6$	—	—	2.157	CH_2Cl_2	20
		2.061	1.995	2.017[a]	thf–CH_2Cl_2 (2:1)	−196
cod	$1,8\text{-}(NH)_2C_{10}H_6$	—	—	2.149	CH_2Cl_2	20
		2.164	2.102	2.143[b]	CH_2Cl_2	−196
		2.049	1.996	2.014[a]	thf–CH_2Cl_2 (2:1)	−196
nbd	$1,8\text{-}(NH)_2C_{10}H_6$	—	—	2.143	CH_2Cl_2	20
tfbb	$1,8\text{-}(NH)_2C_{10}H_6$	—	—	2.141	CH_2Cl_2	20

[a] $g_{av.} = \frac{1}{3}(g_1 + 2g_2)$. [b] $g_{av.} = \frac{1}{3}(2g_1 + g_2)$.



(3)

Figure 3. The proposed structure of $[Rh_2(NO)(\eta^4\text{-cod})_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}]^+$ (3)

The $[Rh_2]^{3+}$-containing cations were readily identified by cyclic and rotating platinum-electrode voltammetry (r.p.e.v.). Due to their poor solubility, the salts could not be studied in thf. However, satisfactory voltammetric data were obtained in CH_2Cl_2 by carrying out the experiments rapidly at 0 °C. Under these conditions, the cyclic voltammograms of (1^+) and (2^+) ($L_2 = \eta^4$-cod) were identical to those of the neutral precursors except that in each case the wave at lower potential was due to a reduction (as confirmed by r.p.e.v.).

Although $[NO]^+$ salts are stronger oxidants than the ferrocenium or $[CPh_3]^+$ cations, they do not react with compound (**1**) or (**2**) to give (1^+) or (2^+). Rather, they act as electrophiles giving nitrosyl complexes. The synthesis of the adducts $[Rh_2(CO)_2(NO)(PPh_3)_2(\mu\text{-}L^1)]^+$ [L^1 = 1,8- or 2,3-$(NH)_2C_{10}H_6$] will be described elsewhere[10] but the analogous η^4-cod derivatives are discussed here because of their relevance to the axial co-ordination of ligands to the $[Rh_2]^{3+}$-containing species (1^+; $L_2 = \eta^4$-cod) and (2^+; $L_2 = \eta^4$-cod).

The addition of $[NO][PF_6]$ to compound (**2**; $L_2 = \eta^4$-cod) in CH_2Cl_2 gave a deep purple solution from which the air-stable, purple solid $[Rh_2(NO)(\eta^4\text{-cod})_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}][PF_6]$ (**3**) was readily isolated. By contrast, the reaction with (**1**; $L_2 = \eta^4$-cod) did not give a nitrosyl adduct, again perhaps reflecting the lesser tendency of the 2,3-diamidonaphthalene derivative to undergo axial co-ordination (*cf.* the solvent-dependent cyclic voltammograms described above).

The structure proposed for compound (**3**) is shown in Figure 3, and is based on the ^1H n.m.r. spectrum, which shows inequivalent η^4-cod ligands {in $(CD_3)_2CO$, δ 2.29 [8 H, m, CH_2(cod)], 2.46 [4 H, m, CH_2(cod)], 2.58 [4 H, m, CH_2(cod)], 4.37 [2 H, br s, CH(cod)], 4.81 [4 H, m, CH(cod)], 5.75 [2 H, m, CH(cod)], 6.64 (2 H, br s, NH), 7.25 (4 H, m, $C_{10}H_6$), and 7.68 (2 H, dd, $C_{10}H_6$)}, and the i.r. spectrum, which shows one terminal nitrosyl stretching absorption, at 1 715 cm^{-1}. The application of Ibers' rules[11] for the prediction of the nitrosyl co-ordination mode gives a 'corrected' value of $\tilde{\nu}$(NO) = 1 605 cm^{-1}, implying a bent rather than linear Rh–N–O linkage. In agreement with this, the *X*-ray structure of the analogous complex $[Ir_2(NO)(\eta^4\text{-cod})_2(\mu\text{-pz})_2]^+$ [$\tilde{\nu}$(NO) = 1 715 cm^{-1}],[12] formed[13] from $[\{Ir(\eta^4\text{-cod})(\mu\text{-pz})\}_2]$ and $[NO]^+$, showed an Ir–N–O bond angle of 111°.

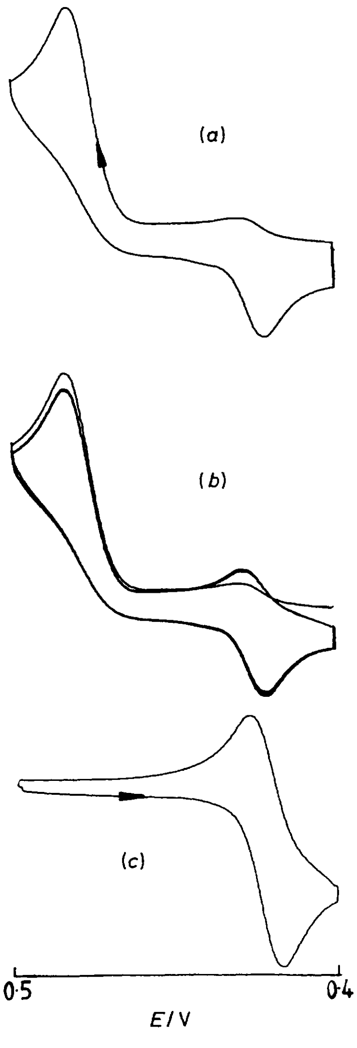


Figure 4. The cyclic voltammogram of $[Rh_2(NO)(\eta^4\text{-cod})_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}]^+$ in CH_2Cl_2: (*a*) single scan from 0.4 to −0.5 V; (*b*) multiple scan from 0.4 to −0.5 V; and (*c*) single scan from −0.5 to 0.4 V after the addition of $[Co(\eta\text{-}C_5H_5)_2]$

The electrochemistry of compound (**3**) is also of interest, showing that nitrosyl co-ordination is readily reversed on reduction. The cyclic voltammogram of (**3**), from 0.4 to −0.5 V, shows an irreversible reduction wave [$(E_p)_{red} = -0.37$ V; v = 100 mV s^{-1}] on the first sweep [Figure 4(*a*)] accompanied by a product wave which subsequent sweeps [Figure 4(*b*)] show to

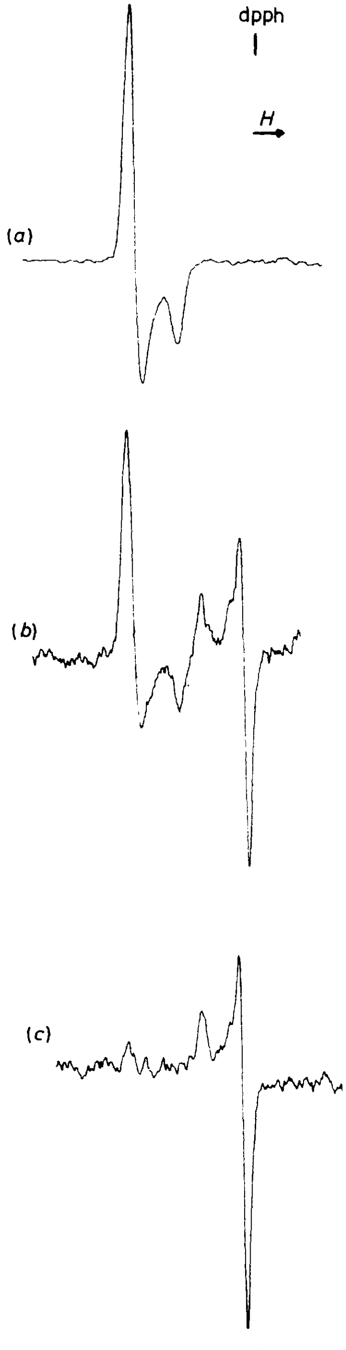


Figure 5. The e.s.r. spectrum of ($\mathbf{2}^+$; L_2 = η^4-cod) at −196 °C; (*a*) in pure CH_2Cl_2; (*b*) in thf–CH_2Cl_2 (2:1) at 5×10^{-3} mol dm^{-3}; and (*c*) as in (*b*) but at 2.5×10^{-3} mol dm^{-3}

be reversible and centred at 0.20 V. On addition of [Co(η-C_5H_5)$_2$] to the cell, the reduction wave of (**3**) is lost, and the chemical formation of the species responsible for the reversible product wave is observed [Figure 4(*c*)] (*i.e.* the product wave is enhanced). The potential of the product wave corresponds exactly to that of the first oxidation wave of compound (**2**; L_2 = η^4-cod) showing that reduction of (**3**) leads to loss of the nitrosyl ligand, most likely as NO.

E.S.R. Spectral Studies.—The e.s.r. spectra of the $[Rh_2]^{3+}$-containing η^4-diene complexes were recorded using either isolated samples (*i.e.* of the η^4-cod complexes described above) or solutions generated by *in situ* ferrocenium ion oxidation [*i.e.* of (**2**; L_2 = nbd or tfbb)].

At room temperature, in CH_2Cl_2 solution or in the solid state, ($\mathbf{2}^+$; L_2 = η^4-cod) shows one broad line with g = 2.149; the remaining complexes show similar CH_2Cl_2 solution spectra (Table 2). The low temperature (−196 °C) spectra, however, show a dependence on solvent which again suggests that the axial sites are activated towards co-ordination on oxidation. Figure 5(*a*)—(*c*) show the e.s.r. spectra of ($\mathbf{2}^+$; L_2 = η^4-cod) in CH_2Cl_2–thf mixtures at −196 °C. In pure CH_2Cl_2, the sole species present gives rise to an anisotropic spectrum (Table 2) with an average g value (2.143) close to that observed at room temperature. As the concentration of thf in CH_2Cl_2 is increased, a second species increases in relative abundance, showing a spectrum with a very different g value ($g_{av.}$ = 2.014). Similar changes are observed for ($\mathbf{1}^+$; L_2 = η^4-cod) although the spectra are less well defined due to the greater reactivity of the cation in CH_2Cl_2, and its poorer solubility in thf–CH_2Cl_2 mixtures.

The e.s.r. spectral changes may be explained if axial co-ordination of thf at one rhodium-centred square plane leads to trapped valency at the second. Clearly, nitrosonium ion addition to compound (**2**; L_2 = η^4-cod) to give (**3**), and the solvent dependence of the cyclic voltammograms of (**1**; L_2 = η^4-cod) and (**2**; L_2 = η^4-cod), show that axial co-ordination can occur. However, further spectroscopic characterisation of the adducts of ($\mathbf{1}^+$) and ($\mathbf{2}^+$) at low temperature is required. In this context, u.v.–visible spectroscopy will be important; it is noteworthy that the brown solutions of ($\mathbf{1}^+$; L_2 = η^4-cod) and ($\mathbf{2}^+$; L_2 = η^4-cod), prepared in thf–CH_2Cl_2 mixtures for e.s.r. spectroscopic measurements, become turquoise on cooling to −196 °C.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. The compounds [Rh_2(μ-Cl)$_2$(η^4-nbd)$_2$],[14] [Rh_2(η^4-tfbb)$_2$(μ-OMe)$_2$],[15] [Rh_2L_4(μ-L^1)] [L_2 = (CO)(PPh$_3$) or η^4-cod, L^1 = 2,3-$(NH)_2C_{10}H_6$ or 1,8-$(NH)_2C_{10}H_6$],[8] [CPh_3][BF_4],[16] and [Fe(η-C_5H_5)$_2$][PF_6][17] were prepared by published methods.

Infrared spectra were recorded on a Perkin-Elmer 1 710 IFTS instrument, hydrogen-1 n.m.r. spectra on a Bruker CW-80 SY or JEOL JNM GX-270 spectrometer and calibrated against $SiMe_4$ as internal reference. *X*-Band e.s.r. spectra were recorded on a Varian Associates 4502/15 instrument and were calibrated against a solid sample of the diphenylpicrylhydrazyl (dpph) radical.

Electrochemical studies were carried out as described previously.[18] Solutions were 0.5×10^{-3} mol dm^{-3} in the complex and 0.1 mol dm^{-3} in [NBu^n_4][PF_6] as supporting electrolyte, either in CH_2Cl_2 or thf. Under these conditions, the $E^{\circ\prime}$ values 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)$_2$] in CH_2Cl_2 are 0.47 and −0.07 V respectively; in thf, $E^{\circ\prime}$ for the couple [Fe(η-C_5H_5)$_2$]$^+$–[Fe(η-C_5H_5)$_2$] is 0.56 V. Microanalyses were carried out by the staffs of the Microanalytical Services of the School of Chemistry, University of Bristol, or the Department of Chemistry, University of Zaragoza.

Di-μ-methoxo-bis(η^4-norbornadiene)dirhodium, [{Rh(μ-OMe)(η^4-nbd)}$_2$].—To a stirred suspension of an excess of anhydrous sodium carbonate in methanol (20 cm^3) was added [{Rh(μ-Cl)(η^4-nbd)}$_2$] (225 mg, 0.49 mmol). After 24 h the yellow suspension was evaporated to dryness, washed with water and a small amount of methanol, and then dried *in vacuo*. The solid was then dissolved in CH_2Cl_2, the solution was filtered, methanol was added, and the mixture reduced in volume *in vacuo*. Cooling to −20 °C gave, after 12 h, yellow crystals of the product, yield 110 mg (50%) (Found: C, 42.2; H, 4.7. $C_{16}H_{22}O_2Rh_2$ requires C, 42.5; H, 4.9%). I.r. (Nujol) ν(C–O) 1 075 cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 0.96 [4 H, br, CH_2 (nbd)], 2.55 (6 H, s, OMe), 3.25 [8 H, br, =CH(nbd)], and 3.75 [4 H, br, CH (nbd)].

The complex is air-stable in the solid state. It is soluble in CH_2Cl_2 and thf, and partially so in diethyl ether and methanol; the yellow solutions slowly decompose in air.

μ-1,8-*Diamidonaphthalene-bis*(η^4-*norbornadiene*)*dirhodium*, [Rh_2(η^4-nbd)$_2${μ-1,8-$(NH)_2C_{10}H_6$}].—Solid 1,8-$(NH_2)_2C_{10}H_6$ (140 mg, 0.88 mmol) was added to a suspension of [{Rh(μ-OMe)(nbd)}$_2$] (400 mg, 0.88 mmol) in diethyl ether (20 cm^3). After 30 min, the red precipitate was removed by filtration, washed with diethyl ether, and dried *in vacuo*, yield 428 mg (89%) (Found: C, 53.3; H, 4.6; N, 4.8. $C_{24}H_{24}N_2Rh_2$ requires C, 52.8; H, 4.4; N, 5.1%). I.r. (Nujol): ν(N–H) 3 330 cm^{-1}.

The complex is air-sensitive in the solid state, and dissolves in CH_2Cl_2 and thf to give red, air-sensitive solutions.

μ-1,8-*Diamidonaphthalene-bis*(η^4-*tetrafluorobenzobarrelene*)-*dirhodium*, [Rh_2(η^4-tfbb)$_2${μ-1,8-$(NH)_2C_{10}H_6$}].—A mixture of 1,8-$(NH_2)_2C_{10}H_6$ (22 mg, 0.14 mmol) and [{Rh(μ-OMe)(η^4-tfbb)}$_2$] (100 mg, 0.14 mmol) in CH_2Cl_2 (20 cm^3) was stirred for 2 h. The red solution was then filtered through Celite and concentrated under reduced pressure. Addition of diethyl ether (20 cm^3) gave a red precipitate which was removed by filtration, washed with diethyl ether, and dried *in vacuo*, yield 63 mg (56%) (Found: C, 49.8; H, 3.2; N, 3.3. $C_{34}H_{20}F_8N_2Rh_2$ requires C, 50.1; H, 2.5; N, 3.4%). I.r. (Nujol): ν(N–H) 3 310 cm^{-1}.

The physical properties of this complex are similar to those of the nbd analogue described above.

Bis(η^4-*cyclo-octa*-1,5-*diene*)-μ-1,8-*diamidonaphthalene-dirhodium Tetrafluoroborate*, [Rh_2(η^4-cod)$_2${μ-1,8-$(NH)_2C_{10}H_6$}][BF_4].—To a stirred solution of [Rh_2(η^4-cod)$_2${μ-1,8-$(NH)_2C_{10}H_6$}] (80 mg, 0.14 mmol) in thf (10 cm^3) at −78 °C was added [CPh_3][BF_4] (50 mg, 0.15 mmol) in CH_2Cl_2 (2 cm^3). After 10 min the dark brown precipitate was removed by filtration and dried *in vacuo*, yield 56 mg (61%) (Found: C, 47.5; H, 5.2; N, 3.7. $C_{26}H_{32}BF_4N_2Rh_2$ requires C, 47.1; H, 4.8; N, 4.2%).

The complex [Rh_2(η^4-cod)$_2${μ-2,3-$(NH)_2C_{10}H_6$}][BF_4] was prepared similarly, in 50% yield (Found: C, 47.7; H, 5.1; N, 3.8. $C_{26}H_{32}BF_4N_2Rh_2$ requires C, 47.1; H, 4.8; N, 4.2%).

Both salts are soluble in CH_2Cl_2 to give brown solutions which decompose in air at room temperature.

Bis(η^4-*cyclo-octa*-1,5-*diene*)-μ-1,8-*diamidonaphthalene-nitrosyldirhodium Hexafluorophosphate*, [Rh_2(NO)(η^4-cod)$_2$-{μ-1,8-$(NH)_2C_{10}H_6$}][PF_6].—To a stirred solution of [Rh_2(η^4-cod)$_2${μ-1,8-$(NH)_2C_{10}H_6$}] (0.18 g, 0.31 mmol) in CH_2Cl_2 (40 cm^3) was added [NO][PF_6] (0.054 g, 0.31 mmol). After 15 min the deep purple solution was filtered, n-hexane (30 cm^3) was added, and the mixture reduced in volume *in vacuo*. The resulting purple precipitate was purified by dissolving in CH_2Cl_2, filtration, addition of n-hexane, and partial evaporation of the solvent *in vacuo* to induce precipitation, yield 0.174 g (74%) (Found: C, 40.8; H, 4.3; N, 5.8. $C_{26}H_{32}F_6N_3OPRh_2$ requires C, 41.4; H, 4.3; N, 5.6%).

The complex is soluble in polar solvents such as CH_2Cl_2, thf, or acetone to give purple solutions which slowly decompose in air.

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