Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 26.[1] The Synthesis of Paramagnetic Triazenido- and Aryl(1-aryliminoethyl)amido-bridged Dirhodium Carbonyl Derivatives containing the $[Rh_2]^{3+}$ Core

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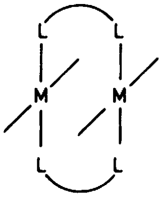
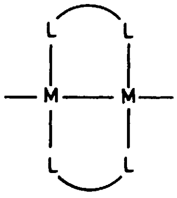
Cyclic voltammetry shows that $[Rh_2(CO)_4(\mu\text{-}L')_2]$ [**1**, L′ = RNNNR, R = *p*-tolyl; **2**, L′ = R′NC(Me)NR′, R′ = Ph], $[Rh_2(CO)_2L_2(\mu\text{-}RNNNR)_2]$ (**3**, L = PPh_3 or $CNBu^t$), $[Rh_2(CO)_2(PPh_3)L\{\mu\text{-}R'NC(Me)NR'\}_2]$ (**4**, L = CO), $[Rh_2(\eta^4\text{-diene})_2(\mu\text{-}RNNNR)_2]$ [**5**, diene = nbd (norborna-2,5-diene) or cod (cyclo-octa-1,5-diene)], and $[Rh_2(CO)_3(CNBu^t)(\mu\text{-}RNNNR)_2]$ (**6**) undergo at least two diffusion-controlled one-electron oxidations at a platinum bead electrode in CH_2Cl_2. The first process is reversible for all of the complexes and corresponds to the formation of a monocation with a $[Rh_2]^{3+}$ core. The second step is fully reversible only for (**1**), (**3**, L = PPh_3), and (**5**, diene = nbd), and for the first two of these complexes a third reversible oxidation wave is also observed. The paramagnetic monocations ($\mathbf{3}^+$, L = PPh_3 or $CNBu^t$), ($\mathbf{4}^+$, L = CO), and ($\mathbf{5}^+$, diene = nbd) have been isolated as stable hexafluorophosphate salts *via* the oxidation of the appropriate neutral complex with either $[N_2C_6H_4F\text{-}p][PF_6]$ or $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ in CH_2Cl_2. The related complex $[Rh_2(CO)_2(\mu\text{-dppm})(\mu\text{-}RNNNR)_2][PF_6]$ ($\mathbf{7}^+$, dppm = $Ph_2PCH_2PPh_2$) was also prepared, by the $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ oxidation of a mixture of (**1**) and dppm. The tricarbonyl ($\mathbf{4}^+$, L = CO) undergoes substitution with Lewis bases, L, to give the cationic dicarbonyls [$\mathbf{4}^+$, L = PPh_3, $AsPh_3$ or $P(OPh)_3$] which are readily reduced by $[NBu^n{}_4][BH_4]$ in CH_2Cl_2 to give the otherwise inaccessible neutral species [**4**, L = PPh_3, $AsPh_3$, or $P(OPh)_3$].

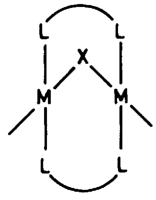
The chemistry of dirhodium complexes continues to attract considerable attention.[2,3] The three basic structural types, (A)—(C), can be extensively modified by varying the ligands, the number of bridges, the extent of metal–metal bonding, and the formal oxidation states of the metal atoms. Thus, there is an enormous range of compounds available with a diversity of chemical and physical properties. Most known compounds are diamagnetic and yet a rich and varied chemistry can be anticipated for paramagnetic species with radical-like properties. One route to such species would involve the one-electron oxidation or reduction of a diamagnetic precursor, and sufficient electrochemical studies have been carried out[4—11] to show that paramagnetic dirhodium complexes can be of importance both in the study of structure and bonding and as chemical reagents. For example, the tetra-bridged species $[Rh_2(\mu\text{-}Y)_4]^Z$ [Y = carboxylate,[5] HNC(Me)O,[6] PhNC(Me)O,[7] PhNC(Ph)NPh,[8] or anilinopyridine[9]] undergo sequential one-electron transfer reactions linking the monoanionic ($Z = -1$) and dicationic ($Z = +2$) species, and spectroscopic and theoretical studies[2,7,8,10] suggest delocalised bonding in mixed-valence complexes containing the $[Rh_2]^{3+}$ ($Z = -1$) and $[Rh_2]^{5+}$ ($Z = +1$) cores. In addition, redox-active isocyanide complexes such as $[Rh_2(dimen)_4]^{2+}$ (dimen = 1,8-di-isocyanomenthane)[11] and pyrazolyl-bridged dimers such as $[\{M(\eta^4\text{-cod})(\mu\text{-pz})\}_2]$ (M = Rh or Ir, cod = cyclo-octa-1,5-diene, pz = pyrazol-1-yl)[12] undergo photochemically initiated electron transfer leading respectively to the catalysed production of hydrogen from aqueous acid[13] and to the oxidative addition of alkyl halides to the dimetal centre.[14]



(A)
face-to-face



(B)
side-by-side



(C)
A-frame

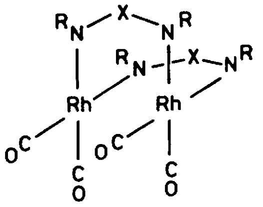


Figure 1. Face-to-face species; X = N or CMe, R = aryl

In this paper, we detail[15] our studies of the redox chemistry of face-to-face species of the type shown in Figure 1. The tetracarbonyls $[Rh_2(CO)_4(\mu\text{-}L')_2]$ [L′ = RNNNR or R′NC(Me)NR′ *] and certain of their Group 5 donor, isocyanide, and η^4-diene ligand derivatives undergo up to three successive, one-electron oxidations in which the $[Rh_2]^{Z+}$ unit remains intact for Z = 2—5. In most cases the paramagnetic monocations have been fully characterised, and the carbonyl substitution reactions of $[Rh_2(CO)_3(PPh_3)\{\mu\text{-}R'NC(Me)NR'\}_2]^+$ have been shown to provide a route to otherwise inaccessible complexes containing the $[Rh_2]^{2+}$ core.

The results of spectroscopic and *X*-ray structural studies, and of molecular orbital calculations, which relate to the bonding in these species will be presented elsewhere.[16]

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* Throughout this paper RNNNR = $p\text{-}MeC_6H_4NNNC_6H_4Me\text{-}p$ and R′NC(Me)NR′ = PhNC(Me)NPh.

Table 1. Analytical and i.r. and e.s.r. spectroscopic data for dirhodium complexes

Complex[a]	Yield (%)	Analysis (%)[b] C	H	N	$\tilde{\nu}(CO)^c/cm^{-1}$	g_{av}
$[Rh_2(CO)_3(CNBu^t)(\mu\text{-}RNNNR)_2]$	20	52.9 (52.6)	4.7 (4.5)	11.9 (11.9)	2 164ms,[d] 2 062, 2 010, 1 998m[e]	—
$[Rh_2(CO)_3(PPh_3)\{\mu\text{-}R'NC(Me)NR'\}_2]$	—	—	—	—	2 053, 1 987, 1 968 (sh)[f]	—
$[Rh_2(CO)_3(PPh_3)\{\mu\text{-}R'NC(Me)NR'\}_2][PF_6]$	72	52.5 (52.7)	3.9 (3.7)	4.6 (5.0)	2 099, 2 054, 2 039 (sh)	2.124
$[Rh_2(CO)_2(CNBu^t)_2(\mu\text{-}RNNNR)_2]$	80	54.5 (54.8)	5.3 (5.3)	12.5 (12.8)	2 161br,[d] 1 987br	—
$[Rh_2(CO)_2(CNBu^t)_2(\mu\text{-}RNNNR)_2][PF_6]$	70	46.7 (47.0)	4.6 (4.5)	10.9 (11.0)	2 205br,[d] 2 070, 2 058	2.117
$[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}RNNNR)_2]$	—	—	—	—	1 977, 1 963[f]	—
$[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}RNNNR)_2][PF_6]$	69	54.4 (54.9)[g]	3.9 (4.1)	5.5 (5.7)	2 047, 2 027	2.135
$[Rh_2(CO)_2(dppm)(\mu\text{-}RNNNR)_2]$	—	—	—	—	1 990, 1 958m	—
$[Rh_2(CO)_2(dppm)(\mu\text{-}RNNNR)_2][PF_6]$	75	53.0 (53.3)	4.0 (4.1)	6.2 (6.8)	2 063, 2 032m	2.119
$[Rh_2(CO)_2(PPh_3)_2\{\mu\text{-}R'NC(Me)NR'\}_2]$	31	65.8 (65.8)	5.0 (4.7)	4.4 (4.7)	1 964, 1 958	—
$[Rh_2(CO)_2(PPh_3)_2\{\mu\text{-}R'NC(Me)NR'\}_2][PF_6]$	66	58.2 (58.7)	3.9 (4.2)	3.9 (4.2)	2 035, 2 014	2.133
$[Rh_2(CO)_2(PPh_3)(AsPh_3)\{\mu\text{-}R'NC(Me)NR'\}_2]$	50	63.9 (63.5)	5.2 (4.5)	4.7 (4.5)	1 962, 1 950	—
$[Rh_2(CO)_2(PPh_3)(AsPh_3)\{\mu\text{-}R'NC(Me)NR'\}_2][PF_6]$	52	56.2 (56.9)	3.7 (4.0)	3.4 (4.0)	2 033, 2 012	2.132
$[Rh_2(CO)_2(PPh_3)\{P(OPh)_3\}\{\mu\text{-}R'NC(Me)NR'\}_2]$	40	63.4 (63.3)	5.0 (4.5)	4.5 (4.5)	1 985, 1 964	—
$[Rh_2(CO)_2(PPh_3)\{P(OPh)_3\}\{\mu\text{-}R'NC(Me)NR'\}_2][PF_6]$	56	56.5 (56.7)	3.8 (4.0)	4.3 (4.0)	2 051, 2 027	2.124

[a] R = C_6H_4Me-*p*, R′ = Ph. [b] Calculated values in parentheses. [c] Strong bands in CH_2Cl_2 unless stated otherwise; m = medium, br = broad, s = strong, sh = shoulder. [d] $\tilde{\nu}$(CN). [e] In n-hexane. [f] Data taken from ref. 17. Analysed as a 1.0 CH_2Cl_2 solvate.

Results and Discussion

The syntheses of $[Rh_2(CO)_4(\mu\text{-}RNNNR)_2]$ (**1**), $[Rh_2(CO)_4\{\mu\text{-}R'NC(Me)NR'\}_2]$ (**2**), $[Rh_2(CO)_2L_2(\mu\text{-}RNNNR)_2]$ (**3**, L = PPh_3), $[Rh_2(CO)_2(PPh_3)L\{\mu\text{-}R'NC(Me)NR'\}_2]$ (**4**, L = CO), and $[Rh_2(\eta^4\text{-diene})_2(\mu\text{-}RNNNR)_2]$ [**5**, diene = nbd (norborna-2,5-diene, bicyclo[2.2.1]hepta-2,5-diene) or cod] have been described previously[17] although we have now found a more convenient and efficient method for the preparation of (**1**). Thus, the addition of NEt_3 to a solution of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ and the triazene, RNNNHR, in CH_2Cl_2 immediately yielded a deep red solution from which (**1**) was readily isolated in near quantitative yield.

The isocyanide derivatives $[Rh_2(CO)_3(CNBu^t)(\mu\text{-}RNNNR)_2]$ (**6**) and (**3**, L = $CNBu^t$) are also simply prepared, from (**1**) and $CNBu^t$ in n-hexane. Good yields of (**3**, L = $CNBu^t$) are precipitated directly from the reaction at room temperature whereas (**6**) can be isolated *via* column chromatography of the mixture formed at −78 °C; the yield of the tricarbonyl, although only poor, was optimised by carefully monitoring the substitution reaction by i.r. spectroscopy. Both of the new complexes were characterised by elemental analysis and i.r. (Table 1) and ^1H n.m.r. spectroscopy (see Experimental section).

Cyclic Voltammetry of Complexes (**1**)—(**6**).—Complexes (**1**)—(**6**) have been studied by cyclic voltammetry at a platinum bead electrode in CH_2Cl_2. In general these species, and others described below, undergo at least two diffusion-controlled* one-electron oxidations in the potential range −0.20 to 1.80 V (Table 2) (no other processes were found between −0.20 and −1.80 V). Without exception, the first oxidation is reversible but in most cases the second is chemically irreversible. Where the second wave does correspond to the formation of a stable dication a third wave may also be apparent although this is close to the potential limit imposed by the base electrolyte.

Complex (**1**) shows three oxidation waves corresponding to the sequential formation of $[Rh_2(CO)_4(\mu\text{-}RNNNR)_2]^{Z+}$ (Z = 1—3). Taken together with studies on the complexes $[Rh_2(\mu\text{-}Y)_4]^Z$ (see above), one may conclude that the face-to-face dirhodium structure can remain intact in at least five different redox states, *i.e.* as the $[Rh_2]^{2+}$ nucleus is oxidised stepwise to $[Rh_2]^{6+}$.†

The phenyl(1-phenyliminoethyl)amino-bridged complex (**2**) is more restricted in its redox chemistry than (**1**), showing only one irreversible wave in addition to that for the formation of ($\mathbf{2}^+$). Although the dication ($\mathbf{2}^{2+}$) is therefore less stable than ($\mathbf{1}^{2+}$), the more important difference between (**1**) and (**2**) relates to the E values for monocation formation. The relative ease with which (**2**) is oxidised to ($\mathbf{2}^+$) [the E° value is *ca.* 360 mV more negative than that for the couple (**1**)–($\mathbf{1}^+$)] implies that $[RNNNR]^-$ is a worse σ donor or better π acceptor than $[R'NC(Me)NR']^-$; this implication is also mirrored in the higher i.r. carbonyl stretching frequencies observed[17] for (**1**) and its derivatives (Table 1).

As expected, carbonyl substitution in (**1**) and (**2**) results in a shift of all of the oxidation waves to more negative potentials. The data in Table 2 show that for the series (**1**), (**6**), and (**3**, L = $CNBu^t$), the replacement of each CO by $CNBu^t$ renders the complex more easily oxidised to the monocation by *ca.* 0.35 V. The second oxidation wave of (**6**) is incompletely reversible ($i_{red}/i_{ox} < 1.0$; $v = 200$ mV s^{-1}) and that of (**3**, L = $CNBu^t$) is irreversible at all scan rates used. Nevertheless, on carbonyl substitution the oxidation peak potentials, E_{pk}, show a similar shift to lower values, albeit to a lesser extent (140—220 mV).

At this stage it may also be noted that the potential for the oxidation of $[Rh_2(CO)_{4-n}L_n(\mu\text{-}L')_2]$ not only depends on n and L′ but also on L. Thus, complex (**3**, L = PPh_3), which shows three reversible waves in the cyclic voltammogram (Figure 2), is oxidised to the monocation less readily than (**3**, L = $CNBu^t$) by *ca.* 70 mV. Although the effect of L is small relative to that of n and L′, it does provide an additional means by which the redox potential can be altered. Effectively, the first oxidation potential

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* Throughout this paper, diffusion-controlled waves show $i/v^{\frac{1}{2}}$ constant for scan rates $50 < v < 500$ mV s^{-1}; reversibility is characterised by $i_{ox}/i_{red} = 1$ (over the same range of scan rates). Numerical data are given only when necessary.

† Formally, this corresponds to the conversion of a Rh^IRh^I binuclear complex to one containing two Rh^{III} atoms. However, the assignment of individual oxidation states, particularly to the metal atoms of mixed-valence species with $[Rh_2]^{3+}$ and $[Rh_2]^{5+}$ cores, is not justified in the absence of definitive bonding studies.

Table 2. Cyclic voltammetric data for dirhodium complexes

Complex	Process[a]	$E^{\ominus}$/V[b]	Process[a]	$E^{\ominus}$ or E_{pk}/V[b]	Process	$E^{\ominus}$/V
$[Rh_2(CO)_4(\mu\text{-RNNNR})_2]$	$0 \longrightarrow +1$	0.83	$+1 \longrightarrow +2$	1.42(R)	$+2 \longrightarrow +3$	1.70
$[Rh_2(CO)_4\{\mu\text{-R}'\text{NC(Me)NR}'\}_2]$	$0 \longrightarrow +1$	0.47	$+1 \longrightarrow +2$	1.37(I)	—	—
$[Rh_2(CO)_3(CNBu^t)(\mu\text{-RNNNR})_2]$	$0 \longrightarrow +1$	0.45	$+1 \longrightarrow +2$	1.28(I)	—	—
$[Rh_2(CO)_2(CNBu^t)_2(\mu\text{-RNNNR})_2]$	$0 \longrightarrow +1$	0.11	$+1 \longrightarrow +2$	1.06(I)[c]	—	—
$[Rh_2(CO)_2(CNBu^t)_2(\mu\text{-RNNNR})_2][PF_6]$	$+1 \longrightarrow 0$	0.11	$+1 \longrightarrow +2$	1.09(I)	—	—
$[Rh_2(CO)_2(PPh_3)_2(\mu\text{-RNNNR})_2]$	$0 \longrightarrow +1$	0.18	$+1 \longrightarrow +2$	1.28(R)	$+2 \longrightarrow +3$	1.57
$[Rh_2(CO)_2(PPh_3)_2(\mu\text{-RNNNR})_2][PF_6]$	$+1 \longrightarrow 0$	0.19	$+1 \longrightarrow +2$	1.29(R)	$+2 \longrightarrow +3$	1.58
$[Rh_2(CO)_2(dppm)(\mu\text{-RNNNR})_2][PF_6]$	$+1 \longrightarrow 0$	0.07	$+1 \longrightarrow +2$	1.17(R)	—	—
$[Rh_2(\eta^4\text{-nbd})_2(\mu\text{-RNNNR})_2]$	$0 \longrightarrow +1$	0.36	$+1 \longrightarrow +2$	1.09(R)	—	—
$[Rh_2(\eta^4\text{-nbd})_2(\mu\text{-RNNNR})_2][PF_6]$	$+1 \longrightarrow 0$	0.36	$+1 \longrightarrow +2$	1.09(R)	—	—
$[Rh_2(\eta^4\text{-cod})_2(\mu\text{-RNNNR})_2]$	$0 \longrightarrow +1$	0.53	$+1 \longrightarrow +2$	1.28(I)	—	—
$[Rh_2(CO)_3(PPh_3)\{\mu\text{-R}'\text{NC(Me)NR}'\}_2]$	$0 \longrightarrow +1$	0.18	$+1 \longrightarrow +2$	1.28(I)	—	—
$[Rh_2(CO)_3(PPh_3)\{\mu\text{-R}'\text{NC(Me)NR}'\}_2][PF_6]$	$+1 \longrightarrow 0$	0.20	$+1 \longrightarrow +2$	1.24(I)	—	—
$[Rh_2(CO)_2(PPh_3)_2\{\mu\text{-R}'\text{NC(Me)NR}'\}_2]$	$0 \longrightarrow +1$	−0.08	$+1 \longrightarrow +2$	1.26(I)	—	—
$[Rh_2(CO)_2(PPh_3)_2\{\mu\text{-R}'\text{NC(Me)NR}'\}_2][PF_6]$	$+1 \longrightarrow 0$	−0.08	$+1 \longrightarrow +2$	1.24(I)	—	—
$[Rh_2(CO)_2(PPh_3)(AsPh_3)\{\mu\text{-R}'\text{NC(Me)NR}'\}_2]$	$0 \longrightarrow +1$	−0.11	$+1 \longrightarrow +2$	1.21(I)	—	—
$[Rh_2(CO)_2(PPh_3)(AsPh_3)\{\mu\text{-R}'\text{NC(Me)NR}'\}_2][PF_6]$	$+1 \longrightarrow 0$	−0.11	$+1 \longrightarrow +2$	1.21(I)	—	—
$[Rh_2(CO)_2(PPh_3)\{P(OPh)_3\}\{\mu\text{-R}'\text{NC(Me)NR}'\}_2]$	$0 \longrightarrow +1$	−0.05	$+1 \longrightarrow +2$	1.22(I)	—	—
$[Rh_2(CO)_2(PPh_3)\{P(OPh)_3\}\{\mu\text{-R}'\text{NC(Me)NR}'\}_2][PF_6]$	$+1 \longrightarrow 0$	−0.05	$+1 \longrightarrow +2$	1.22(I)	—	—

[a] All processes are diffusion-controlled and one-electron, obeying the criterion $i/v^{\frac{1}{2}}$ = constant for scan rates, v, in the range 50—500 mV s^{-1}. [b] $E^{\ominus}$ values are reported for reversible (R) processes, calculated as the average of the cathodic and anodic peak potenitals. Peak potentials, E_{pk}, are reported for irreversible (I) processes, at v = 200 mV s^{-1} unless stated otherwise. All potentials are *versus* the aqueous saturated calomel electrode, 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 $E^{\ominus}$ values for the couples $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ and $[Fe(\eta\text{-}C_5Me_5)_2]^+$–$[Fe(\eta\text{-}C_5Me_5)_2]$ are 0.47 and −0.07 V respectively. [c] At a scan rate of 100 mV s^{-1}.

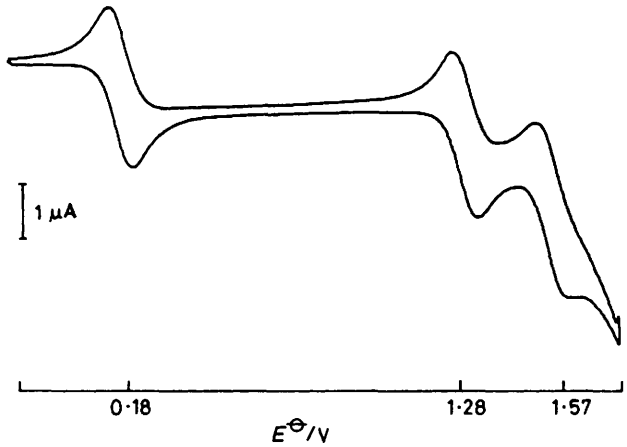


Figure 2. The cyclic voltammogram of $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-RNNNR})_2]$ (3, L = PPh_3) in CH_2Cl_2 at a platinum bead electrode

of $[Rh_2(CO)_{4-n}L_n(\mu\text{-L}')_2]$ can be systematically varied over a range of *ca.* 1.0 V (Table 2).

Both of the complexes $[Rh_2(\eta^4\text{-diene})_2(\mu\text{-RNNNR})_2]$ (**5**, diene = nbd or cod) show two oxidation waves but differ in that the second step is reversible for the nbd derivative but chemically irreversible for the cod analogue. In addition, (**5**, diene = cod) slowly decomposed during the electrochemical measurement to give an unidentified product with an irreversible oxidation wave (E_{pk} = 0.82 V, v = 200 mV s^{-1}).

X-Ray structural studies on (**3**, L = PPh_3) and (**3**$^+$, L = PPh_3) have shown that a substantial decrease (from 2.96 to 2.70 Å) in the Rh–Rh distance occurs on oxidation, and a further contraction is to be expected as a second electron is removed.[15] Clearly, a decrease in the metal–metal bond length will result in an increase in the non-bonding repulsions between the ligands on adjacent rhodium atoms. Thus, in the case of (**5**$^+$, diene = cod) further oxidation may well lead to insupportable interactions between the bulky cod ligands; norborna-2,5-diene is sterically less demanding so that (**5**$^{2+}$, diene = nbd) remains intact (at least on the cyclic voltammetric time-scale).

It is also interesting to note that the oxidation of (**5**, diene = nbd) to (**5**$^+$, diene = nbd) occurs at a more positive potential than that of the couple (**3**)–(**3**$^+$), whereas further oxidation to (**5**$^{2+}$) takes place at a more negative potential than that of the couple (**3**$^+$)–(**3**$^{2+}$). The factors which influence ΔE, the difference between the potentials for the first and second oxidations of the complexes described (Table 2), are not clear. However, the steric factors which appear to influence the reversibility of the second wave (see above) will also affect the potential of that wave. In addition, ΔE will be influenced by the extent to which the bonding in these complexes is delocalised. These points will be discussed further in the light of molecular orbital calculations currently in progress.[16]

Synthesis of Paramagnetic Triazenido Complexes containing the $[Rh_2]^{3+}$ *Core.*—The electrochemical studies described above show that in all cases the dications $[Rh_2(CO)_{4-n}L_n(\mu\text{-L}')_2]^{2+}$ are formed at potentials more positive than 1.0 V. Thus, their synthesis has not been attempted. However, with the exception of the tetracarbonyls (**1**) and (**2**) and of the tricarbonyl (**6**), for which the E° values are relatively high, the data in Table 2 suggest that monocation formation should be readily effected with mild chemical oxidants. Accordingly, a wide range of paramagnetic complexes with the $[Rh_2]^{3+}$ core has been prepared and fully characterised.

The reactions in CH_2Cl_2 of solid $[N_2C_6H_4F\text{-}p][PF_6]$ with (**3**, L = PPh_3), or of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ with (**3**, L = $CNBu^t$), rapidly gave dark brown solutions from which the brown crystalline salts $[Rh_2(CO)_2L_2(\mu\text{-RNNNR})_2][PF_6]$ (**3**$^+$, L = PPh_3 or $CNBu^t$) were readily isolated in good yield (Tables 1 and 2).

The i.r. carbonyl spectra of (**3**$^+$, L = PPh_3 or $CNBu^t$) show two closely spaced bands of equal intensity, shifted as expected to higher wavenumbers (by *ca.* 70 cm^{-1}) compared with those of

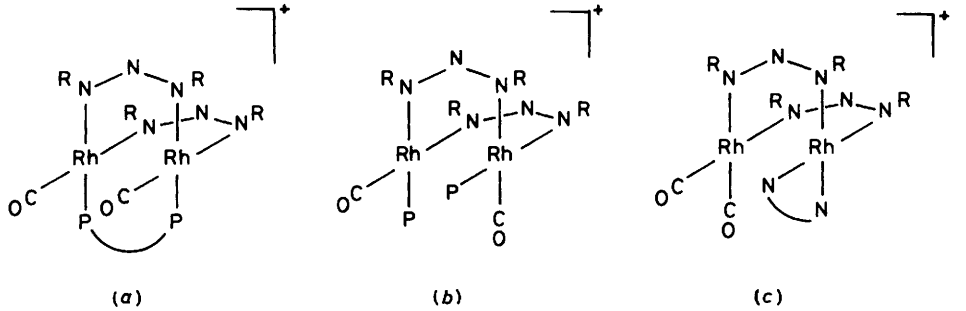


Figure 3. Structures of (*a*) $[Rh_2(CO)_2(\mu\text{-dppm})(\mu\text{-RNNNR})_2]^+$ (7^+), (*b*) $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-RNNNR})_2]^+$ (3^+), P = PPh_3, and (*c*) $[Rh_2(CO)_2(bipy)(\mu\text{-RNNNR})_2]^+$; R = *p*-tolyl

(3, L = PPh_3 or $CNBu^t$); the $\tilde{\nu}$(CN) bands of (3^+, $CNBu^t$) are similarly shifted, by *ca.* 45 cm^{-1}.

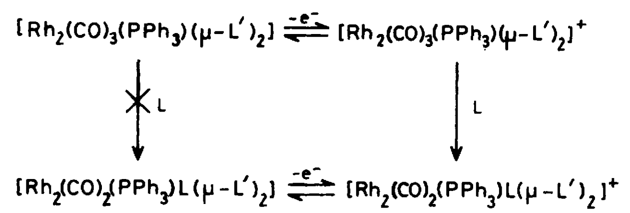
The room-temperature e.s.r. spectra of the cations appear as broad, featureless single lines with g_{av} = 2.12—2.14 (Table 1). Although otherwise uninformative, they do serve to confirm that the complexes are paramagnetic. By contrast, the frozen solution spectra are well resolved and show evidence for hyperfine coupling to both rhodium atoms. When fully analysed these spectra, and those of the other paramagnetic dirhodium complexes described below, will be discussed further elsewhere.[16] At this stage it is sufficient to note that they provide evidence for delocalised bonding in the mixed-valence $[Rh_2]^{3+}$ complexes.

Electrochemical studies conclusively prove that (3) and (3^+) differ only by one electron. Thus the cyclic voltammograms of the monocations are virtually superimposable on those of the neutral species except that the wave with the most negative potential corresponds to a reduction process for (3^+).

One other dicarbonyl cation related to (3^+, L = PPh_3 or $CNBu^t$) can be prepared, namely $[Rh_2(CO)_2(\mu\text{-dppm})(\mu\text{-RNNNR})_2][PF_6]$ (7^+, dppm = $Ph_2PCH_2PPh_2$). The rapid addition of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ to a mixture of (**1**) and dppm in CH_2Cl_2 gave an orange-brown solution from which a high yield of the brown crystalline product was obtained (Table 1). The i.r. carbonyl spectrum suggests that (7^+) has a tri-bridged structure [Figure 3(*a*)] in which the Rh_2P_2 unit is isomeric with that observed[15] for [3^+, L = PPh_3, Figure 3(*b*)]. Thus, the two carbonyl bands of (7^+) are of very different intensity implying a small dihedral angle OC–Rh–Rh–CO; the analogous dihedral angle for (3^+, L = PPh_3), which has a very different carbonyl spectrum (see above), is *ca.* 90°. The third possible structure for (7^+), in which the dppm would chelate one metal atom, can be ruled out. Such a structure is adopted[18] by $[Rh_2(CO)_2(bipy)(\mu\text{-RNNNR})_2]^+$ [bipy = 2,2′-bipyridyl, Figure 3(*c*)] which shows two i.r. carbonyl bands of equal intensity but with very different energies [$\tilde{\nu}$(CO)(CH_2Cl_2) = 2 095 and 2 051 cm^{-1}].

The cation (7^+) is both oxidised and reduced in reversible one-electron steps at a platinum electrode (Table 2). The E° value associated with the reduction is such that the ready formation of (7) was expected. Accordingly, (7^+) was reacted with $[NBu^n{}_4][BH_4]$ in CH_2Cl_2 to give a red solution similar in colour to those formed by (3). Surprisingly, however, all attempts to isolate (7) failed despite its stability on the cyclic voltammetric time-scale.

The preparative route to (7^+) (see above) would seem to suggest that (7) is formed from (**1**) and dppm prior to one-electron oxidation, but the neutral complex could not be isolated in the absence of oxidant. Small quantities of a red precipitate were formed from (**1**) and dppm in n-hexane, and the i.r. spectrum, run rapidly in CH_2Cl_2, showed bands at 1 990 (strong) and 1 958 (medium) cm^{-1} as expected for (7). However, the compound rapidly decomposed in polar solvents and could not be further characterised.



Scheme. L = PhNC(Me)NPh

The stability of (7^+), relative to that of (7), may once again relate to the structural changes associated with electron transfer. If a lengthening of the Rh–Rh bond in (7^+) occurs on reduction [as observed[15] for (3^+)] strain induced in the Rh_2P_2 core of the rigid tri-bridged structure may lead to decomposition.

The reaction of (5, diene = nbd) with $[N_2C_6H_4F\text{-}p][PF_6]$ in CH_2Cl_2 also gave a dark brown crystalline product in excellent yield. In spite of repeated recrystallisations, no satisfactory elemental analysis could be obtained for (5^+, diene = nbd). Nevertheless, the cyclic voltammogram of the salt (Table 2) was identical to that of (5, diene = nbd), showing two reversible waves corresponding to the formation of (5, diene = nbd) and (5^{2+}, diene = nbd). In addition, the isotropic e.s.r. spectrum (*g* = 2.143) of the product was similar to those of (3^+, L = PPh_3 or $CNBu^t$).

Oxidatively-induced Substitution Reactions of (4, L = CO).—The tricarbonyl (4, L = CO) reacts with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ to give good yields of the brown, crystalline $[PF_6]^-$ salt of (4^+, L = CO) (Tables 1 and 2). Unlike the neutral precursor (4, L = CO), the cation readily undergoes substitution with Lewis bases to give dicarbonyl derivatives. Thus, CH_2Cl_2 solutions of (4^+, L = CO) evolve CO in the presence of PPh_3 or $P(OPh)_3$ at room temperature, or with $AsPh_3$ when heated under reflux, to give moderate to good yields of [4^+, L = PPh_3, $AsPh_3$, or $P(OPh)_3$]. In the cyclic voltammogram, each of the complexes shows one reversible reduction wave and an oxidation wave [which shows some evidence of reversibility for L = $P(OPh)_3$]. As noted above, the variation of E° with L for the reduction process is small. More important, however, the magnitude of the potentials is such that [4^+, L = PPh_3, $AsPh_3$, or $P(OPh)_3$] are rapidly reduced by $[NBu^n{}_4][BH_4]$ in CH_2Cl_2, and the red to purple complexes [4, L = PPh_3, $AsPh_3$, or $P(OPh)_3$] (Tables 1 and 2) could be isolated as crystalline solids after column chromatography.

The isolation of the neutral dicarbonyls completes the sequence of reactions shown in the Scheme; the conversion of the substitutionally inert tricarbonyl (4, L = CO) to [4, L = PPh_3, $AsPh_3$, or $P(OPh)_3$] provides another example where one-electron transfer leads to otherwise inaccessible complexes.

Conclusions

When considered with other electrochemical studies$^{5-10}$ on tetra-bridged species such as $[Rh_2(\mu\text{-}Y)_4]$ (Y = carboxylate), the work described herein shows that the face-to-face dirhodium structure can remain intact in an electron-transfer series of complexes containing the $[Rh_2]^{2+}$ to $[Rh_2]^{6+}$ cores. We have also shown that varying *n*, L, and L′ in $[Rh_2(CO)_{4-n}L_n(\mu\text{-}L')_2]$ can allow E°, the potential for the couple $[Rh_2]^{2+}$–$[Rh_2]^{3+}$, to be systematically varied over a range of *ca.* 1.0 V (from −0.11 to 0.83 V).

The synthesis of ($\mathbf{4}^+$, L = CO), and of [$\mathbf{4}^+$, L = $AsPh_3$ or $P(OPh)_3$] by oxidatively-induced carbonyl substitution, demonstrates that species with asymmetric *geometric* structures can be generated within the series $[Rh_2(CO)_{4-n}L_n(\mu\text{-}L')_2]^+$. The influence of geometric structure on *electronic* structure, and attempts to synthesise both localised and delocalised mixed-valence compounds with the $[Rh_2]^{3+}$ core, will be described in subsequent papers in this series.

Experimental

The preparation, purification, and reactions of the complexes were carried out under an atmosphere of dry nitrogen; i.r. spectroscopy was generally used to monitor the course of the reactions. Unless otherwise stated, products (*i*) were purified by dissolution 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, dissolving in polar solvents such as CH_2Cl_2 or tetrahydrofuran (thf) to give solutions which slowly decompose in air. The compounds $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$,[19] $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}RNNNR)_2]$,[17] $[Rh_2(CO)_3L\{\mu\text{-}R'NC(Me)NR'\}_2]$ (L = CO or PPh_3),[17] $[Rh_2(\eta^4\text{-diene})_2(\mu\text{-}RNNNR)_2]$ (diene = nbd or cod),[17] $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$,[20] $[N_2C_6H_4F\text{-}p][PF_6]$,[21] and Bu^{t}NC[22] were prepared by published methods; $[NBu^n{}_4][BH_4]$ was purchased from the Aldrich Chemical Co., Inc.

Infrared spectra were recorded on a Nicolet MX-5 FT spectrometer, or a Perkin-Elmer PE257 spectrometer with calibration against the absorption band of polystyrene at 1 601 cm^{-1}. Hydrogen-1 n.m.r. spectra were recorded on a JEOL PMX60 instrument and calibrated against $SiMe_4$ as internal reference. *X*-Band e.s.r. spectra were recorded on a Varian Associates 4502/15 instrument and were calibrated against a solid sample of the diphenylpicrylhydrazyl radical. Electrochemical studies were carried out using an AMEL Electrochemolab instrument in conjunction with a three-electrode cell. For cyclic voltammetry the working electrode was a platinum bead, the auxiliary electrode a platinum wire, and the reference an aqueous saturated calomel electrode (s.c.e.) separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. Voltammetry used a platinum bead electrode rotated at 600 revolutions min^{-1}. Solutions were 0.5×10^{-3} mol dm^{-3} in complex and 0.1 mol dm^{-3} in $[NBu^n{}_4][PF_6]$ as supporting electrolyte. After cyclic voltammetric measurements were carried out on each complex, either $[Fe(\eta\text{-}C_5H_5)_2]$ or $[Fe(\eta\text{-}C_5Me_5)_2]$ was added to the test solution as an internal calibrant.[23] Under the conditions described above, 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. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

*Di-*μ*-(di-*p*-tolyltriazenido-*N^{1}N^3*)-bis(dicarbonylrhodium)*, $[Rh_2(CO)_4(\mu\text{-}RNNNR)_2]$.—To a stirred mixture of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ (0.50 g, 1.3 mmol) and RNNNHR (0.58 g, 2.6 mmol) in CH_2Cl_2 (80 cm^3) was added NEt_3 (0.40 cm^3, 3.0 mmol). After 5 min, the resulting deep red solution was evaporated to dryness, and the residue extracted with n-hexane (80 cm^3). Evaporation of the extract to low volume (*ca.* 15 cm^3) and cooling to 0 °C gave the complex as dark red crystals, yield 0.88 g (90%).

*Tricarbonyl-di-*μ*-(di-*p*-tolyltriazenido-*N^{1}N^3*)-(t-butyl isocyanide)dirhodium*, $[Rh_2(CO)_3(CNBu^t)(\mu\text{-}RNNNR)_2]$.—To a stirred, cooled (−78 °C) solution of $[Rh_2(CO)_4(\mu\text{-}RNNNR)_2]$ (0.10 g, 0.13 mmol) in n-hexane (20 cm^3) was added dropwise a solution of Bu^{t}NC (6.5 mg, 0.08 mmol) in the same solvent (10 cm^3). After warming to room temperature the mixture was concentrated *in vacuo* and then added to an alumina–n-hexane chromatography column. Elution with n-hexane–diethyl ether (5:1) gave an orange band, containing unreacted $[Rh_2(CO)_4(\mu\text{-}RNNNR)_2]$; elution with diethyl ether gave a pink band which was removed, reduced to low volume *in vacuo*, and cooled to 0 °C to give dark red crystals of the product, yield 0.021 g (20%) [^{1}H n.m.r. ($CDCl_3$): δ 7.30 (16 H, m, C_6H_4), 2.29 (12 H, s, $C_6H_4Me\text{-}p$), 1.27 (9 H, s, CNBu^t)].

The complex is soluble in all common organic solvents to give red solutions.

*Dicarbonyl-di-*μ*-(di-*p*-tolyltriazenido-*N^{1}N^3*)-bis(t-butyl isocyanide)dirhodium*, $[Rh_2(CO)_2(CNBu^t)_2(\mu\text{-}RNNNR)_2]$.—To a stirred solution of $[Rh_2(CO)_4(\mu\text{-}RNNNR)_2]$ (0.10 g, 0.13 mmol) in n-hexane (30 cm^3) was added Bu^{t}NC (0.022 g, 0.26 mmol). After 4 h the pink precipitate was removed by filtration, washed with n-hexane, and dried *in vacuo*, yield 0.09 g (80%) [^{1}H n.m.r. ($CDCl_3$): δ 7.32 (16 H, m, C_6H_4), 2.27 (12 H, s, $C_6H_4Me\text{-}p$), 1.26 (18 H, s, CNBu^t)].

*Dicarbonyl-di-*μ*-(di-*p*-tolyltriazenido-*N^{1}N^3*)-bis(triphenylphosphine)dirhodium Hexafluorophosphate*, $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}RNNNR)_2][PF_6]$.—To a deep red, stirred solution of $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}RNNNR)_2]$ (0.30 g, 0.24 mmol) in CH_2Cl_2 (20 cm^3) was added $[N_2C_6H_4F\text{-}p][PF_6]$ (0.08 g, 0.30 mmol). After 10 min, n-hexane (*ca.* 100 cm^3) was added to the filtered dark brown solution to give a brown precipitate. Purification from CH_2Cl_2–n-hexane gave dark brown crystals, yield 0.23 g (69%).

The complexes $[Rh_2(CO)_2(CNBu^t)_2(\mu\text{-}RNNNR)_2][PF_6]$ and $[Rh_2(\eta^4\text{-nbd})_2(\mu\text{-}RNNNR)_2][PF_6]$ were prepared similarly, as dark brown microcrystals in 70 and 86% yields respectively. In the case of the isocyanide derivative, however, $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ was used as the oxidant.

μ*-Bis(diphenylphosphino)methane-dicarbonyl-di-*μ*-(di-*p*-tolyltriazenido-*N^{1}N^3*)-dirhodium Hexafluorophosphate*, $[Rh_2(CO)_2(\mu\text{-}dppm)(\mu\text{-}RNNNR)_2][PF_6]$.—To a solution of $[Rh_2(CO)_4(\mu\text{-}RNNNR)_2]$ (0.15 g, 0.20 mmol) in CH_2Cl_2 (25 cm^3) was added dppm (0.075 g, 0.20 mmol). After stirring for 3 min, $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (0.065 g, 0.20 mmol) was added and the maroon solution became dark orange. Filtration, addition of n-hexane (25 cm^3), and partial evaporation of the solvent *in vacuo* gave a brown precipitate. Purification from CH_2Cl_2–n-hexane gave the product as brown microcrystals, yield 0.18 g (75%).

*Tricarbonyl-di-*μ*-[phenyl(1-phenyliminoethyl)amido-*NN′*]-triphenylphosphinedirhodium Hexafluorophosphate*, $[Rh_2(CO)_3(PPh_3)\{\mu\text{-}R'NC(Me)NR'\}_2][PF_6]$.—To a stirred, dark red solution of $[Rh_2(CO)_3(PPh_3)\{\mu\text{-}R'NC(Me)NR'\}_2]$ (1.0 g, 1.03 mmol) in CH_2Cl_2 (50 cm^3) was added $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (0.36 g, 1.09 mmol). The solution became dark brown immediately and after filtration n-hexane (*ca.* 200 cm^3) was added to give a brown precipitate. Purification from thf–n-hexane gave the product as brown crystals, yield 0.83 g (72%).

*Dicarbonyl-di-μ-[phenyl(1-phenyliminoethyl)amido-*NN′*]-bis(triphenylphosphine)dirhodium Hexafluorophosphate*, $[Rh_2(CO)_2(PPh_3)_2\{\mu\text{-}R'NC(Me)NR'\}_2][PF_6]$.—To a solution of $[Rh_2(CO)_3(PPh_3)\{\mu\text{-}R'NC(Me)NR'\}_2][PF_6]$ (0.10 g, 0.09 mmol) in CH_2Cl_2 (20 cm^3) was added PPh_3 (0.03 g, 0.10 mmol). The solution was then filtered, and n-hexane added to give the product as a brown solid, yield 0.08 g (66%).

The complexes $[Rh_2(CO)_2(PPh_3)L\{\mu\text{-}R'NC(Me)NR'\}]$-$[PF_6]$ [L = $AsPh_3$ or $P(OPh)_3$] were prepared similarly, but the reaction with $AsPh_3$ required heating the mixture under reflux for 4 h.

*Dicarbonyl-di-μ-[phenyl(1-phenyliminoethyl)amido-*NN′*]-bis(triphenylphosphine)dirhodium*, $[Rh_2(CO)_2(PPh_3)_2\{\mu\text{-}R'NC(Me)NR'\}_2]$.—To a solution of $[Rh_2(CO)_2(PPh_3)_2\{\mu\text{-}R'NC(Me)NR'\}_2][PF_6]$ (0.25 g, 0.19 mmol) in CH_2Cl_2) (50 cm^3) was added $[NBu^n{}_4][BH_4]$ (0.06 g, 0.23 mmol). The intense red solution was then evaporated to dryness, and the residue dissolved in a minimum volume of CH_2Cl_2 and chromatographed on an alumina–n-hexane column. Elution of the dark red band with CH_2Cl_2–n-hexane (1:1) gave a red solution which was evaporated to low volume *in vacuo* to yield the product as a bright red solid, yield 0.07 g (31%).

The complexes $[Rh_2(CO)_2(PPh_3)L\{\mu\text{-}R'NC(Me)NR'\}_2]$ [L = $AsPh_3$ or $P(OPh)_3$] were prepared similarly.

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