The Synthesis of Mixed-valence Dirhodium Carbonyl Complexes, and the *X*-Ray Crystal Structures of $[\{Rh(CO)(PPh_3)(\mu\text{-}RNNNR)\}_2]$ and $[\{Rh(CO)(PPh_3)(\mu\text{-}RNNNR)\}_2][PF_6]$ (R = *p*-Tolyl)

Neil G. Connelly, Crispin J. Finn, Mark J. Freeman, A. Guy Orpen, and Janet Stirling
Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

X-Ray structural studies on $[\{Rh(CO)(PPh_3)(\mu\text{-}RNNNR)\}_2]^{z+}$ (R = *p*-tolyl, $z = 0$ and 1) show that the mixed-valence cation is formed by electron-loss from a metal–metal anti-bonding orbital; the asymmetric compounds $[Rh_2(CO)_2L(PPh_3)\{\mu\text{-}PhNC(Me)NPh\}_2]^{z+}$ [L = $P(OPh)_3$, $AsPh_3$, *etc.*, $z = 0$ and 1] result from the oxidatively induced substitution of $[Rh_2(CO)_3(PPh_3)\{\mu\text{-}PhNC(Me)NPh\}_2]$.

The current intense interest in the reactions of ligand-bridged dirhodium complexes,[1] particularly those depending on metal–metal bond formation and cleavage, and in the chemistry of mixed-valence compounds,[2] prompts us to report on the one-electron oxidation of $[Rh_2(CO)_{4-n}(PPh_3)_n(\mu\text{-}RNXNR)_2]$ (X = CMe, R = Ph; X = N, R = *p*-tolyl, $n = 1$ or 2). Electron loss, to give the stable, paramagnetic monocations $[Rh_2(CO)_{4-n}(PPh_3)_n(\mu\text{-}RNXNR)_2]^+$, is accompanied by an increase in the rhodium–rhodium bond order and activation towards carbonyl substitution.

Cyclic voltammetry shows that $[\{Rh(CO)_2(\mu\text{-}RNNNR)\}_2]$ (**1**, R = *p*-tolyl) (Figure 1)[3] is oxidised in three, reversible,

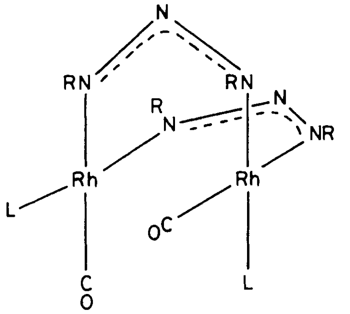

Figure 1. Complex (**2**), R = *p*-tolyl, L = PPh$_3$.

Table 1. Electrochemical and e.s.r. spectral data.

Complex[a]	$E°$/V[b]	$g_{av.}$[c]
$[\{Rh(CO)_2(X)\}_2]$ (**1**)	0.84	—
$[\{Rh(CO)(PPh_3)(X)\}_2]$ (**2**)	0.19	—
$[\{Rh(CO)(PPh_3)(X)\}_2][PF_6]$ (**3**)	0.20	2.135
$[Rh_2(CO)_3(PPh_3)(Y)_2]$ (**4**)	0.20	—
$[Rh_2(CO)_3(PPh_3)(Y)_2][PF_6]$ (**5**)	0.22	2.124
$[Rh_2(CO)_2(PPh_3)L(Y)_2][PF_6]$ (**6**)		
L = PPh$_3$	−0.06	2.133
L = AsPh$_3$	−0.10	2.132
L = P(OPh)$_3$	−0.04	2.124
$[Rh_2(CO)_2(PPh_3)L(Y)_2]$ (**7**)		
L = PPh$_3$	−0.07	—
L = AsPh$_3$	−0.10	—
L = P(OPh)$_3$	−0.04	—

[a] X = μ-*p*-MeC$_6$H$_4$NNNC$_6$H$_4$Me-*p*; Y = μ-PhNC(Me)NPh. [b] Potential for the first oxidation wave, *vs.* an aqueous, saturated calomel electrode (s.c.e.), at a platinum electrode, in CH$_2$Cl$_2$ containing 0.1 mol dm^{-3} [NBu$^n_4$][PF$_6$] as base electrolyte. Under these conditions, $E°$ for the oxidation of ferrocene was 0.48 V. [c] In CH$_2$Cl$_2$, at room temperature.

diffusion-controlled one-electron steps ($E°$ = 0.84, 1.43, and 1.78 V *vs.* s.c.e., in CH$_2$Cl$_2$, at a platinum bead electrode). Although the magnitudes of the oxidation potentials are such that stable cations will be difficult to prepare, carbonyl substitution of (**1**) renders the monocation chemically accessible. Thus, $[\{Rh(CO)(PPh_3)(\mu\text{-}RNNNR)\}_2]^3$ (**2**, R = *p*-tolyl) ($E°$ = 0.19, 1.29, and 1.58 V) reacts instantly with [N$_2$C$_6$H$_4$F-*p*][PF$_6$] in CH$_2$Cl$_2$ to give the air-stable, paramagnetic salt $[\{Rh(CO)(PPh_3)(\mu\text{-}RNNNR)\}_2][PF_6]$ (**3**, R = *p*-tolyl), orange-brown crystals, 69%, $\tilde{\nu}$(CO) (CH$_2$Cl$_2$) 2 047 and 2 027 cm^{-1}.

The e.s.r. spectrum of (**3**) (Table 1) shows no hyperfine coupling, but the isotropic *g*-value suggests the half-occupied orbital to be largely metal-based. *X*-Ray structural studies on (**2**) and (**3**) have served to delineate more fully the redox orbital.

Crystal Data: Complex (**2**) as its toluene solvate: $C_{66}H_{58}N_6O_2P_2Rh_2\cdot C_7H_8$, M = 1326, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, No. 14), a = 13.045(12), b = 25.478(2), c = 19.743(17) Å, β = 101.19(7)°, U = 6438(9) Å^3, temp. 220 K, Z = 4, D_c = 1.37 g cm^{-3}, $F(000)$ 2728 electrons, graphite-monochromated *X*-radiation, $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 5.99 cm^{-1}. Complex (**3**) as its dichloromethane solvate: $C_{66}H_{58}N_6O_2P_2Rh_2\cdot PF_6\cdot CH_2Cl_2$, M = 1464, triclinic, space group $P\bar{1}$ (No. 2), a = 12.961(3), b = 21.402(9), c = 13.768(5) Å, α = 84.25(4), β = 90.00(3), γ = 113.97(3)°, U = 3468(2) Å^3, temp. 295 K, Z = 4, D_c = 1.40 g cm^{-3}, $F(000)$ = 1482 electrons, graphite-monochromated *X*-radiation, $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 6.74 cm^{-1}. Data were collected for unique volumes of reciprocal space for (**2**) as its toluene solvate in the range $4 < 2\theta < 45°$, and for (**3**) as its dichloromethane solvate in the range $4 < 2\theta < 50°$, using a Nicolet P3m diffractometer. Least-squares refinement of 3693 unique, absorption-corrected, observed $[I > 2\sigma(I)]$ intensity data from (**2**)·C$_7$H$_8$ led to final residuals R = 0.076 (R' = 0.068); for (**3**)·CH$_2$Cl$_2$ R = 0.054 (R' = 0.058) for 10 617 data with $I > 1.5\sigma(I)$.

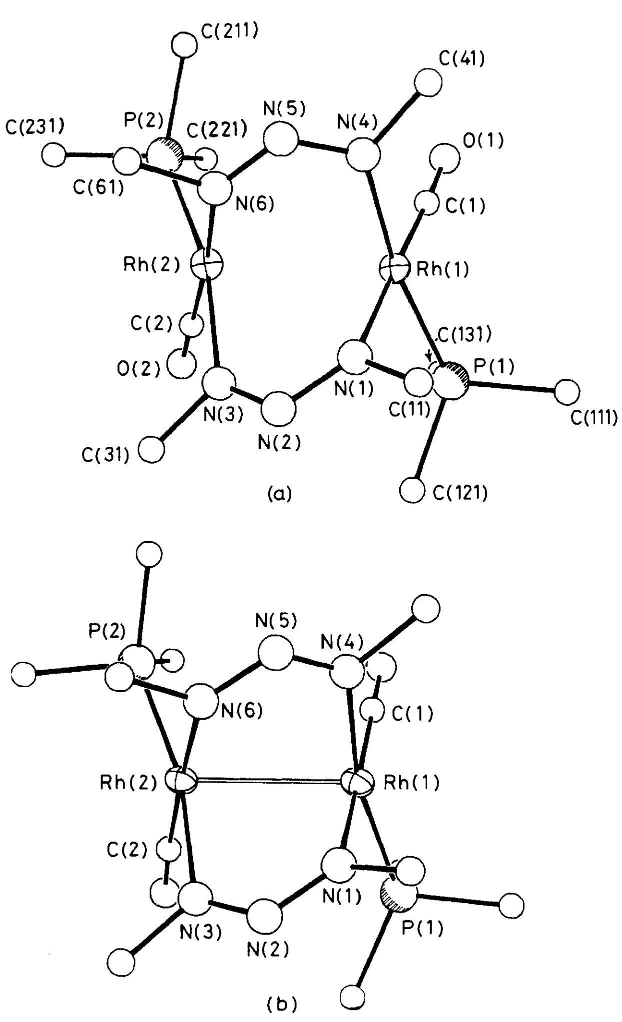

Figure 2. Molecular geometry of (a) (**2**); (b) the monocation of (**3**); only the contact carbon atoms of the PPh$_3$ and triazenido ligands have been included, for clarity. Important interatomic distances for (**2**) [with those for (**3**) in brackets] are: Rh(1)–Rh(2) 2.960(4) [2.698(1)], Rh(1)–P(1) 2.279(5) [2.333(1)], Rh(1)–N(1) 2.151(11) [2.091(3)], Rh(1)–N(4) 2.120(12) [2.098(3)], Rh(1)–C(1) 1.830(19) [1.856(5)], Rh(2)–P(2) 2.300(5) [2.336(1)], Rh(2)–N(3) 2.157(13) [2.093(4)], Rh(2)–N(6) 2.122(13) [2.103(3)], Rh(2)–C(2) 1.798(20) [1.861(4)] Å.

The molecular geometries† of (**2**) and the cation of (**3**) are shown in Figure 2. In each case the ligand arrangement around each rhodium atom approximates to square planar and the symmetry of the Rh$_2$N$_6$P$_2$(CO)$_2$ unit to C_2. The triazenido

---

† The atomic co-ordinates for the crystal structures of (**2**)·C$_7$H$_8$ and (**3**)·CH$_2$Cl$_2$ are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

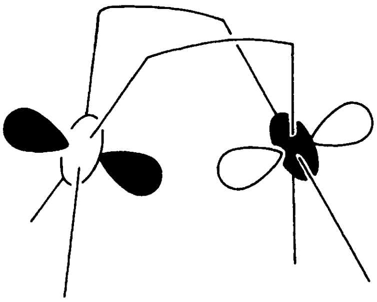

Figure 3

ligands bridge the dirhodium unit with terminal nitrogen atoms bonded *cis* to the nitrogen of a second triazenido ligand. The square planes of the rhodium atoms are somewhat staggered [hence P(1)–Rh(1) · · · Rh(2)–P(2) torsion angles are −115.0 for (**2**) and −111.5° for (**3**)], with the staggering maximising the separation of the PPh_3 ligands. The most marked effect of oxidation is on the Rh(1) · · · Rh(2) separation; in (**2**) this is 2.960(4) Å and in (**3**) 2.698(1) Å. The implication of this observation is that the h.o.m.o. of (**2**), which becomes half occupied in the cation of (**3**), is Rh–Rh antibonding. This orbital, which is schematically illustrated in Figure 3, is presumably the out-of-phase combination of the 'd_{z^2}' orbitals on the locally square-planar co-ordinated rhodium atoms. Clearly this orbital in the d^8–d^8 (**2**) and d^8–d^7 (**3**) systems is related to the σ* l.u.m.o. in the d^7–d^7 rhodium(II) dimers {*e.g.* $[Rh_2(mhp)_4]$,[4] Hmhp = 2-hydroxy-6-methylpyridine, and others} although in (**2**) and (**3**) the rhodium co-ordination planes are not parallel (interplanar angles are 40.8 and 31.3°). The Rh · · · Rh separations observed in (**2**) and (**3**) show a progression towards the values observed for bridged d^7–d^7 rhodium(II) dimers {*e.g.* 2.359 Å in $[Rh_2(mhp)_4]$[4]} which have formal bond orders of unity as compared with zero and one-half for (**2**) and (**3**) respectively.

Although (**3**) is a symmetrical mixed-valence complex (in that each metal atom is bonded to the same ligand set), the oxidation of the acetamidino-bridged compound $[Rh_2(CO)_3(PPh_3)\{\mu\text{-}PhNC(Me)NPh\}_2]$ (**4**) provides a route to asymmetric species.

The cyclic voltammogram of (**4**) shows a reversible one-electron oxidation wave ($E°$ = 0.20 V) and a second, irreversible process at *ca.* 1.2 V; reaction with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ gives the paramagnetic tricarbonyl $[Rh_2(CO)_3(PPh_3)\{\mu\text{-}PhNC(Me)NPh\}_2][PF_6]$ (**5**), orange-brown, 52%, $\tilde{\nu}$(CO) (CH_2Cl_2) 2099s, 2054s, and 2039sh cm^{-1}.

Cation (**5**) readily undergoes substitution with donor ligands, L, to give $[Rh_2(CO)_2(PPh_3)L\{\mu\text{-}PhNC(Me)NPh\}_2][PF_6]$ [**6**; L = PPh_3, $AsPh_3$, or $P(OPh)_3$] the $E°$ values of which (Table 1) suggest facile chemical reduction. Accordingly, reaction of (**6**) with $[NBu^n_4][BH_4]$ in CH_2Cl_2 gives the red to maroon neutral complexes $[Rh_2(CO)_2(PPh_3)L\{\mu\text{-}PhNC(Me)NPh\}_2]$ [**7**; L = PPh_3, $AsPh_3$, or $P(OPh)_3$] which *cannot* be prepared by the direct thermal substitution of (**4**).

The physical properties of the asymmetric cations (**5**) and [**6**; L = $AsPh_3$ or $P(OPh)_3$] are very similar to those of the symmetrical species (**3**) and (**6**, L = PPh_3), particularly their isotropic *g* values (Table 1). Although, therefore, all the mixed-valence complexes described appear to be of the same type, the available spectroscopic and structural data do not allow a distinction to be made between trapped-valence (Rh^IRh^{II}) or delocalised (each metal with oxidation state 1.5) species (Classes I, II, or III[5]).

The m.o. description given above allows an understanding of the observation that (**5**) is far more reactive towards carbonyl substitution than is (**4**), since depopulation of the rhodium d_{z^2} orbitals will facilitate an associative mechanism involving approach of an additional ligand along the perpendicular to one of the rhodium co-ordination planes.[6]

In summary, the work described here shows that a wide range of mixed-valence dirhodium complexes can be prepared. Variation of X, L, and *n* in $[Rh_2(CO)_{4-n}L_n(\mu\text{-}X)_2]^+$ allows the reduction potential of the cation to be varied by *ca.* 1.0 V (Table 1).

We thank Johnson Matthey for a generous loan of rhodium trichloride.

Received, 9th May 1984; Com. 641

References

1 See, for example, T. R. Felthouse, *Prog. Inorg. Chem.*, 1982, **29**, 73; I. S. Sigal, K. R. Mann, and H. B. Gray, *J. Am. Chem. Soc.*, 1980, **102**, 7252; W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20**, 159; F. E. Wood, J. Hvoslef, and A. L. Balch, *J. Am. Chem. Soc.*, 1983, **105**, 6986; M. Cowie and T. G. Southern, *Inorg. Chem.*, 1982, **21**, 246; C. P. Kubiak, C. Woodcock, and R. Eisenberg, *Inorg. Chem.*, 1982, **21**, 2116; A. R. Chakravarty, F. A. Cotton, and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, 1984, 501; T. P. Zhu, M. Q. Ahsan, T. Malinski, K. M. Kadish, and J. L. Bear, *Inorg. Chem.*, 1984, **23**, 2.

2 C. Creutz, *Prog. Inorg. Chem.*, 1983, **30**, 1; J. D. Buhr and H. Taube, *Inorg. Chem.*, 1980, **19**, 2425; 'Mixed-Valence Compounds', ed. D. M. Brown, Reidel, Dordrecht, Holland, 1980; G. C. Allen and N. S. Hush, *Prog. Inorg. Chem.*, 1967, **8**, 357.

3 N. G. Connelly, H. Daykin, and Z Demidowicz, *J. Chem. Soc., Dalton Trans.*, 1978, 1532.

4 W. Clegg, *Acta Crystallogr., Sect. B*, 1980, **36**, 2437.

5 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.

6 R. L. Harlow, R. J. McKinney, and J. F. Whitney, *Organometallics*, 1983, **2**, 1839.