

The Synthesis of Mixed-valence Dirhodium Carbonyl Complexes, and the X-Ray Crystal Structures of $[\{\text{Rh}(\text{CO})(\text{PPh}_3)(\mu\text{-RNNNR})\}_2]$ and $[\{\text{Rh}(\text{CO})(\text{PPh}_3)(\mu\text{-RNNNR})\}_2][\text{PF}_6]$ ($\text{R} = p\text{-Tolyl}$)

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

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 $[\text{Rh}_2(\text{CO})_{4-n}(\text{PPh}_3)_n(\mu\text{-RNXNR})_2]$ ($\text{X} = \text{CMe}$, $\text{R} = \text{Ph}$; $\text{X} = \text{N}$, $\text{R} = p\text{-tolyl}$, $n = 1$ or

2). Electron loss, to give the stable, paramagnetic monocations $[\text{Rh}_2(\text{CO})_{4-n}(\text{PPh}_3)_n(\mu\text{-RNXNR})_2]^+$, is accompanied by an increase in the rhodium-rhodium bond order and activation towards carbonyl substitution.

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

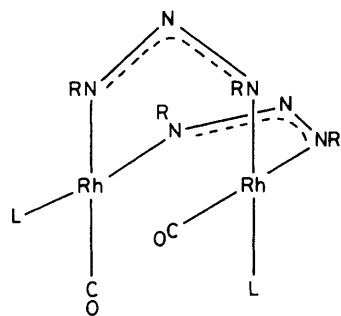


Figure 1. Complex (2), R = *p*-tolyl, L = PPh₃.

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*-MeC₆H₄NNNC₆H₄Me-*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 CH₂Cl₂ containing 0.1 mol dm⁻³ [NBu₄][PF₆] as base electrolyte. Under these conditions, E° for the oxidation of ferrocene was 0.48 V. ^c In CH₂Cl₂, at room temperature.

diffusion-controlled one-electron steps (E° = 0.84, 1.43, and 1.78 V vs. s.c.e., in CH₂Cl₂, 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)(PPh₃)(μ -RNNNR)}₂]³ (2, R = *p*-tolyl) (E° = 0.19, 1.29, and 1.58 V) reacts instantly with [N₂C₆H₄-F-*p*][PF₆] in CH₂Cl₂ to give the air-stable, paramagnetic salt [{Rh(CO)(PPh₃)(μ -RNNNR)}₂][PF₆] (3, R = *p*-tolyl), orange-brown crystals, 69%, ν (CO) (CH₂Cl₂) 2047 and 2027 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: C₆₆H₅₈N₆O₂P₂Rh₂·C₇H₈, 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) Å³, temp. 220 K, Z = 4, D_c = 1.37 g cm⁻³, $F(000)$ 2728 electrons, graphite-monochromated X-radiation, λ = 0.710 69 Å, μ (Mo-K α) = 5.99 cm⁻¹. Complex (3) as its dichloromethane solvate: C₆₆H₅₈N₆O₂P₂Rh₂·PF₆·CH₂Cl₂, 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) Å³, temp. 295 K, Z = 4, D_c = 1.40 g cm⁻³, $F(000)$ = 1482 electrons, graphite-monochromated X-radiation, λ = 0.710 69 Å, μ (Mo-K α) = 6.74 cm⁻¹. Data were collected for

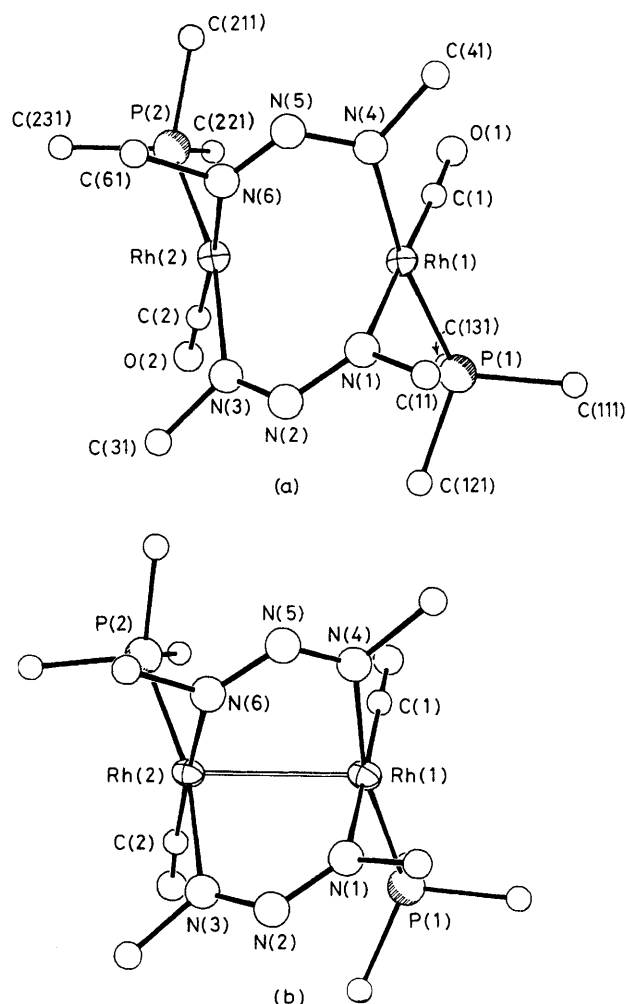


Figure 2. Molecular geometry of (a) (2); (b) the monocation of (3); only the contact carbon atoms of the PPh₃ and triazenido ligands have been included, for clarity. Important interatomic distances for (2) [with those for (3) in brackets] are: Rh(1)–Rh(2) 2.960(4) [2.698(1)], Rh(1)–P(1) 2.279(5) [2.333(1)], 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.

unique volumes of reciprocal space for (2) as its toluene solvate in the range $4 < 2\theta < 45^\circ$, and for (3) as its dichloromethane solvate in the range $4 < 2\theta < 50^\circ$, using a Nicolet P3m diffractometer. Least-squares refinement of 3693 unique, absorption-corrected, observed [$I > 2\sigma(I)$] intensity data from (2)·C₇H₈ led to final residuals R = 0.076 (R' = 0.068); for (3)·CH₂Cl₂ R = 0.054 (R' = 0.058) for 10 617 data with $I > 1.5\sigma(I)$.

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 Rh₂N₆P₂(CO)₂ unit to C₂. The triazenido

† The atomic co-ordinates for the crystal structures of (2)·C₇H₈ and (3)·CH₂Cl₂ 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.

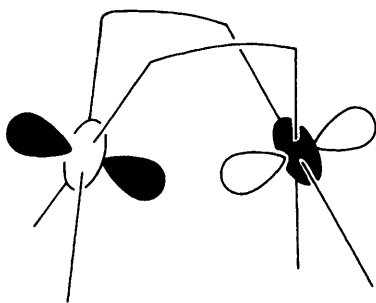


Figure 3

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) \cdots Rh(2)–P(2) torsion angles are -115.0° for (2) and -111.5° for (3)], with the staggering maximising the separation of the PPh₃ ligands. The most marked effect of oxidation is on the Rh(1) \cdots 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_z²' orbitals on the locally square-planar co-ordinated rhodium atoms. Clearly this orbital in the d⁸–d⁸ (2) and d⁸–d⁷ (3) systems is related to the σ^* l.u.m.o. in the d⁷–d⁷ rhodium(II) dimers {e.g. [Rh₂(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 \cdots Rh separations observed in (2) and (3) show a progression towards the values observed for bridged d⁷–d⁷ rhodium(II) dimers {e.g. 2.359 Å in [Rh₂(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 [Rh₂(CO)₃(PPh₃){ μ -PhNC(Me)NPh}₂] (4) provides a route to asymmetric species.

The cyclic voltammogram of (4) shows a reversible one-electron oxidation wave ($E^\circ = 0.20$ V) and a second, irreversible process at ca. 1.2 V; reaction with [Fe(η -C₅H₅)₂][PF₆] gives the paramagnetic tricarbonyl [Rh₂(CO)₃(PPh₃){ μ -PhNC(Me)NPh}₂][PF₆] (5), orange-brown, 52%, $\nu(\text{CO})$ (CH₂Cl₂) 2099s, 2054s, and 2039sh cm⁻¹.

Cation (5) readily undergoes substitution with donor ligands, L, to give [Rh₂(CO)₂(PPh₃)L{ μ -PhNC(Me)NPh}₂][PF₆] [6; L = PPh₃, AsPh₃, or P(OPh)₃] the E° values of which (Table 1) suggest facile chemical reduction. Accord-

ingly, reaction of (6) with [NBu₄][BH₄] in CH₂Cl₂ gives the red to maroon neutral complexes [Rh₂(CO)₂(PPh₃)L{ μ -PhNC(Me)NPh}₂] [7; L = PPh₃, AsPh₃, 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 = AsPh₃ or P(OPh)₃] are very similar to those of the symmetrical species (3) and (6, L = PPh₃), 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 III⁵).

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_{z₂} 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 [Rh₂(CO)_{4-n}L_{*n*}(μ -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

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