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Novel dicarbonyl and carbonylnitrosyl tris(μ-triazenide) dirhodium complexes

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The first neutral, tribridged $[Rh_2]^{3+}$ triazenide complex, $[(OC)Rh(\mu\text{-}RNNNR)_3Rh(CO)]$ ($R = C_6H_4Me\text{-}p$), reacts with NO gas to give the novel nitrosyl $[(OC)Rh(\mu\text{-}RNNNR)_3Rh(NO)]$ with an $[Rh_2]^{4+}$ core linked to NO^-.

Both tetrabridged $[Rh_2(\mu\text{-}L)_4]$ (L = carboxylate, amidinate, *etc.*), containing the $[Rh_2]^{4+}$ core in a face-to-face structure,[1] and the less rigid dibridged $[Rh_2]^{2+}$ triazenide complex $[(OC)_2Rh(\mu\text{-}RNNNR)_2Rh(CO)_2]$ ($R = C_6H_4Me\text{-}p$ throughout this paper)[2] are well established species with extensive redox-based chemistry linking the $[Rh_2]^{z+}$ (*z* = 2–6) cores by a series of sequential one-electron transfer reactions. We now report the synthesis and reactions of an unprecedented *tri*bridged $[Rh_2]^{3+}$ complex, namely $[(OC)Rh(\mu\text{-}RNNNR)_3Rh(CO)]$, and its reaction with NO to give the first triazenide-bridged nitrosyl complex $[(OC)Rh(\mu\text{-}RNNNR)_3Rh(NO)]$. The combination of the redox-active Rh_2 core with the NO ligand, a potential 'electron sink', leads to a novel structure best described as containing NO^- bound to $[Rh_2]^{4+}$.

Mixing CH_2Cl_2 solutions of the neutral triazene complexes $[RhCl(CO)_2\{N(H)RNNR\}]$ and $[RhCl(\eta^2\text{-coe})_2\{N(H)RNNR\}]$ {formed from the triazene RNNNHR and $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ or $[\{Rh(\mu\text{-}Cl)(\eta^2\text{-coe})_2\}_2]$ (coe = cyclooctene) respectively} for 25 min, adding one further equivalent of triazene and then treating the mixture with the base NEt_3 gave a red–brown mixture. Column chromatography on alumina gave a red band {a mixture of $[(OC)_2Rh(\mu\text{-}RNNNR)_2Rh(CO)_2]$ and a second compound, possibly $[(OC)(\eta^2\text{-coe})Rh(\mu\text{-}RNNNR)_2Rh(CO)_2]$} and a green band from which $[(OC)Rh(\mu\text{-}RNNNR)_3Rh(CO)]$ **1** was isolated as dark green crystals.†

The molecular structure of **1**‡ has three triazenide bridges symmetrically disposed about the (OC)Rh–Rh(CO) unit; the eclipsed arrangement of the two carbonyls is consistent with the observation of one strong and one medium weak IR carbonyl band, separated by 37 cm^{-1} (Table 1). For each metal atom, the mutually *trans* triazenides show an average Rh–N distance of 2.063 Å; the Rh–N distances for the third triazenide are longer [Rh(1)–N(4) = Rh(2)–N(6) = 2.087 Å] as a result of the greater *trans* influence of CO. Compared with the structures of *di*bridged $[Rh_2]^{3+}$ complexes {*e.g.* $[(OC)(Ph_3P)Rh(\mu\text{-}RNNNR)_2Rh(CO)(PPh_3)]^+$, Rh–Rh = 2.698 Å[3]}, the Rh–Rh distance of **1** (2.542 Å) is much shorter, presumably as a result of the constraints of the tribridged framework.

The cyclic voltammogram (CV) of **1** in CH_2Cl_2 at a platinum electrode shows two reversible oxidation waves (0.65 and 1.43 V *vs.* SCE) and one reversible reduction wave (at −0.72 V) corresponding to the formation of the $[Rh_2]^{4+}$ monocation, the $[Rh_2]^{5+}$ dication and the $[Rh_2]^{2+}$ anion $[(OC)Rh(\mu\text{-}RNNNR)_3Rh(CO)]^-$ respectively. A comparison with the CV data for dibridged $[Rh_2]^z$ triazenide complexes shows the higher oxidation levels to be stabilised by the lower overall charge of the tribridged complexes {compare the $[Rh_2]^{3+/4+}$ couples for **1** (0.65 V) and $[(OC)_2Rh(\mu\text{-}RNNNR)_2Rh(CO)_2]$ (1.42 V[4])}.

The room temperature ESR spectrum of paramagnetic **1** in toluene consists of a broad line (g_{iso} *ca.* 2.11) but the anisotropic spectrum (at 160 K) shows three well separated features ($g_1 = 2.215$, $g_2 = 2.117$, $g_3 = 2.016$, $g_{ave} = 2.116$) with that at high field a particularly well defined 1 : 2 : 1 triplet due to hyperfine coupling to two equivalent Rh nuclei [$A_1(^{103}Rh) = 6$, $A_2(^{103}Rh) = 6$, $A_3(^{103}Rh) = 17.3 \times 10^{-4}$ cm^{-1}]. The anisotropic spectrum is qualitatively similar to those of other $[Rh_2]^{3+}$ complexes for which a correlation between $\Delta g_3/\Delta\langle g\rangle$ (Δg is the difference between the appropriate *g*-value and that of the free electron) and β (half the angle between the two coordination planes of the $[Rh_2]^{3+}$ unit) is observed.[3] Applying this correlation to the ESR spectroscopic data for **1** gives a predicted value of β (5–10°) in good agreement with that determined by X-ray crystallography (6°).

Unlike cationic $[Rh_2]^{3+}$ complexes such as $[(OC)(Ph_3P)Rh(\mu\text{-}RNNNR)_2Rh(CO)(PPh_3)]^+$, the neutral paramagnetic complex **1** undergoes a 'radical coupling' reaction with NO (and subsequent CO loss). Thus, the dropwise addition of a dilute CH_2Cl_2 solution of NO gas to **1** in the same solvent gave a brown–green solution from which dark brown crystals of $[(CO)Rh(\mu\text{-}RNNNR)_3Rh(NO)]$ **2** were isolated in good yield.

The X-ray structure of $[(OC)Rh(\mu\text{-}RNNNR)_3Rh(NO)]$ **2** (Fig. 1)‡ is very similar to that of **1**, with three triazenide bridges, one CO ligand on one Rh atom and one NO ligand on the other. The mutually *trans* triazenide Rh–N bonds (average 2.053 Å) are slightly shorter than those of **1**. The Rh–N bond distances for the third bridging ligand are different; Rh(1)–N(4), *trans* to CO (2.086 Å), is similar to that of **1** whereas Rh(2)–N(6), *trans* to NO (2.123 Å), is significantly longer, consistent with the *trans* labilising effect of the nitrosyl ligand.[5]

The Rh–Rh distance of **2** (2.518 Å) is slightly shorter than that of **1**. Thus, a formal description of **2** as containing a 'bent'

Table 1 IR and electrochemical data for tribridged dirhodiumtriazenide complexes

Complex	Yield (%)	Colour	$\nu(CO)^a$/cm^{-1}	$E^{\circ\prime\, b}$/V $[Rh_2]^{2+/3+}$	$[Rh_2]^{3+/4+}$	$[Rh_2]^{4+/5+}$
$[(OC)Rh(\mu\text{-}RNNNR)_3Rh(CO)]$ **1**	24	Green	2048, 2011mw	−0.72	0.65	1.43
$[(OC)Rh(\mu\text{-}RNNNR)_3Rh(NO)]$ **2**	64	Brown	2041, 1705m,br^c	—	−0.82	0.99(I)
$[(OC)Rh(\mu\text{-}RNNNR)_3Rh(CO)I]$ **4**	75	Green	2077, 2049m	—	−0.42(I)	1.25(I)
$[(OC)Rh(\mu\text{-}RNNNR)_3Rh(CO)Br]$ **5**	70	Green	2086, 2052m	—	—	—

^{a} In CH_2Cl_2, strong absorptions unless otherwise stated, m = medium, w = weak, br = broad. ^{b} In CH_2Cl_2, at a platinum electrode, with 0.1 mol dm^{-3} $[NBu_4][PF_6]$ as supporting electrolyte. For an irreversible (I) process, the peak potential, $(E_p)_{ox}$ or $(E_p)_{red}$, is given at a scan rate of 200 mV s^{-1}. All potentials are relative to the saturated calomel electrode, SCE. Under the experimental conditions, $E^{\circ\prime}$ for the one-electron oxidations of $[Fe(\eta\text{-}C_5Me_5)_2]$ (calibrant for **1**) and $[Fe(\eta\text{-}C_5H_5)_2]$ (calibrant for **2**, **4** and **5**) is −0.08 and 0.47 V respectively. ^{c} ν(NO).

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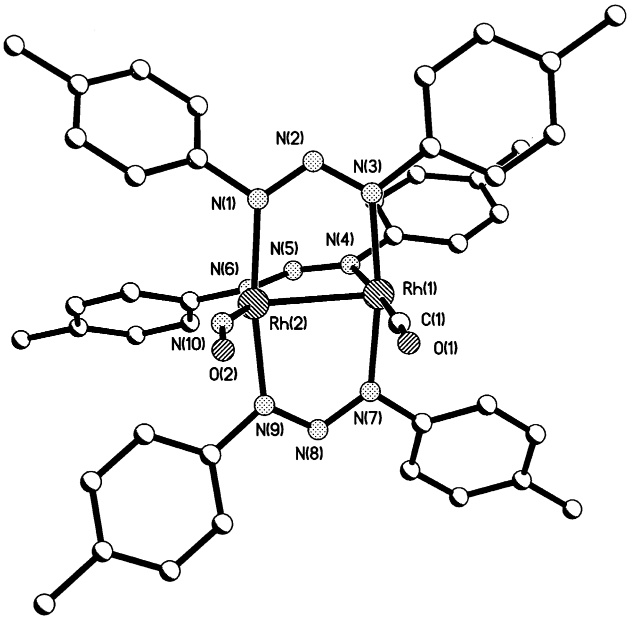

Fig. 1 Structure of [(OC)Rh(μ-RNNNR)$_3$Rh(NO)] **2** (hydrogen atoms omitted for clarity). Important bond lengths and angles: Rh(1)–Rh(2) = 2.518(1), Rh(1)–N(3) = 2.053(4), Rh(1)–N(4) = 2.086(4), Rh(1)–N(7) = 2.051(4), Rh(2)–N(1) = 2.045(4), Rh(2)–N(6) = 2.123(4), Rh(2)–N(9) = 2.064(4), Rh(1)–C(1) = 1.843(6), Rh(2)–N(10) = 1.803(4), N(10)–O(2) = 1.166(5) Å; Rh(1)–C(1)–O(1) = 175.8(5), Rh(2)–N(10)–O(2) = 156.7(4)°. The structure of [(OC)Rh(μ-RNNNR)$_3$Rh(CO)] **1** is similar to that of **2**. Important bond lengths and angles: Rh(1)–Rh(2) = 2.542(1), Rh(1)–N(3) = 2.068(2), Rh(1)–N(4) = 2.087(2), Rh(1)–N(7) = 2.057(2), Rh(2)–N(1) = 2.057(2), Rh(2)–N(6) = 2.087(2), Rh(2)–N(9) = 2.068(2), Rh(1)–C(1) = 1.857(2), Rh(2)–C(2) = 1.857(2) Å; Rh(1)–C(1)–O(1) = 176.8(2), Rh(2)–C(2)–O(2) = 176.8(2)°.

NO^- group attached to a $[Rh_2]^{4+}$ core seems more appropriate than linear 'NO^+' attached to $[Rh_2]^{2+}$ (where a longer Rh–Rh distance might be expected). However, the Rh–N–O angle of **2** (156.7°) is intermediate between the values usually associated with bent (120–140) and linear (160–180°) nitrosyls.[6]

The observation of ν(NO) at 1705 cm^{-1} is also ambiguous given that $\nu(NO^+)$ usually occurs in the range 1950–1600 cm^{-1} and $\nu(NO^-)$ in the range 1720–1520 cm^{-1}.[6] However, other spectrochemical and electrochemical evidence supports the $NO^-/[Rh_2]^{4+}$ description. First, the FAB mass spectrum of **2** shows the loss of NO before CO from the parent ion; the nitrosyl ligand, when acting as a strong π-acceptor (*i.e.* formally as NO^+), is usually lost after CO. Second, compound **2** is formed *via* an intermediate, **3**, with an IR spectrum [ν(CO) = 2078 and 2041 cm^{-1}, ν(NO) = 1711 cm^{-1}] very similar to that of [(OC)Rh(μ-RNNNR)$_3$Rh(CO)I] **4** (see below). Assuming, by analogy with I^- in **4**, an NO^- ligand in [(OC)Rh(μ-RNNNR)$_3$Rh(CO)(NO)] **3**, the small change in ν(NO) when **3** loses CO leads to the same assignment for **2**. Finally, the CV of **2** shows an irreversible oxidation wave at 0.99 V and a reversible reduction wave at −0.82 V. If the nitrosyl group is regarded as NO^+, complex **2** would contain an $[Rh_2]^{2+}$ core and the waves at 0.99 and −0.82 V would be due to the $[Rh_2]^{2+/3+}$ and $[Rh_2]^{+/2+}$ couples respectively. As there are no examples known of the $[Rh_2]^+$ core, voltammetry also suggests that **2** is a $[Rh_2]^{4+}$ complex of NO^-.

Complexes with the $[Rh_2]^{4+}$ core result when **1** couples with halogens (X_2, as a source of $X^\bullet$). Thus, addition of solid I_2 to **1** in CH_2Cl_2 gave a dark green solution from which fine green needles of [(OC)Rh(μ-RNNNR)$_3$Rh(CO)I] **4** were isolated; a similar reaction with Br_2 in CH_2Cl_2 gave dark green microcrystals of [(OC)Rh(μ-RNNNR)$_3$Rh(CO)Br] **5**.

The CV of **4** shows an irreversible oxidation wave at 1.25 V, and an irreversible reduction wave at *ca.* −0.42 V accompanied by a reversible product wave centred at −0.74 V. The similarity in potential of the product wave to that for the formation of $[(OC)Rh(\mu\text{-RNNNR})_3Rh(CO)]^-$ **1**$^-$ from **1** ($E^{\circ\prime}$ = −0.72 V) suggests that one-electron reduction of **4** to $[(OC)Rh(\mu\text{-RNNNR})_3Rh(CO)I]^-$ **4**$^-$ (at −0.42 V) is followed by iodide loss to give **1** (which is then reversibly reduced to **1**$^-$).

Complex **5** can also be prepared by adding [Fe(η-C_5H_5)(η-C_5H_4COMe)][BF_4] ($E^{\circ\prime}$ = 0.74 V) to **1** in the presence of [PPh_4]Br in CH_2Cl_2 *i.e.* by a reaction involving one-electron oxidation. The CV of **1** in the presence of PPh_3 also provides evidence for oxidative activation *via* **1**$^+$. Thus, the first oxidation wave of **1** becomes irreversible and reversible product waves appear at 0.38 (oxidation) and −1.12 (reduction) V, consistent with the formation of $[(OC)Rh(\mu\text{-RNNNR})_3Rh(PPh_3)]^+$.

Axial coordination to the dibridged $[Rh_2]^{z+}$ core of triazenide complexes is enhanced as z is increased.[7] The stabilisation of the higher core oxidation levels $[Rh_2]^{z+}$ in the novel tribridged complexes described above should therefore provide access to further species suitable for exploitation in the systematic construction of dirhodium-based supramolecular assemblies.[8]

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Notes and references

† All new complexes had satisfactory elemental analyses (C, H and N).

‡ Crystal data: [(OC)Rh(μ-RNNNR)$_3$Rh(CO)] **1** (from CH_2Cl_2–*n*-heptane): $C_{44}H_{42}N_9O_2Rh_2$, M = 934.69, monoclinic, space group *C*2/*c* (no. 15), a = 12.225(2), b = 23.801(4), c = 14.292(3) Å, β = 91.34(2)°, V = 4157.4(13) Å^3, Z = 4, T = 173(2) K, μ = 0.842 mm^{-1}, $R1$ = 0.024. Molecules of **1** lie at sites of C_2 symmetry.

[(OC)Rh(μ-RNNNR)$_3$Rh(NO)]·CH_2Cl_2 **2**·CH_2Cl_2 (from CH_2Cl_2–propan-2-ol): $C_{44}H_{44}N_{10}O_2Cl_2Rh_2$, M = 1021.61, monoclinic, space group *C*2/*c* (no. 15), a = 19.293(3), b = 18.266(4), c = 26.178(3) Å, β = 102.56(1)°, V = 9004(3) Å^3, Z = 8, T = 173(2) K, μ = 0.900 mm $^{-1}$, $R1$ = 0.0398. CCDC reference numbers 173464 and 173465. See http://www.rsc.org/suppdata/dt/b1/b109972h/ for crystallographic data in CIF or other electronic format.

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