Redox-catalysed Isomerisation of $[Rh_2(\mu\text{-}CO)(bipy)(Ph_2PCH_2CH_2PPh_2)(\mu\text{-}N^1,N^3\text{-}RNNNR)_2]^{2+}$ to $[Rh_2(\mu\text{-}CO)(bipy)(Ph_2PCH_2CH_2PPh_2)(\mu\text{-}N^{1,3},N^3\text{-}RNNNR)(\mu\text{-}N^1,N^3\text{-}RNNNR)]^{2+}$ (bipy = 2,2′-bipyridyl, R = *p*-tolyl); An Unprecedented Bonding Mode for the Bridging Triazenide Ligand

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Treatment of $[Rh_2(\mu\text{-}CO)(bipy)(dppe)(\mu\text{-}N^1,N^3\text{-}RNNNR)_2]^{2+}$ $\mathbf{1}^{2+}$ [bipy = 2,2′-bipyridyl, dppe = 1,2-bis(diphenylphosphino)ethane, R = *p*-tolyl] with a catalytic amount of $[NBu^n_4][BH_4]$ gave $[Rh_2(\mu\text{-}CO)(bipy)(dppe)(\mu\text{-}N^{1,3},N^3\text{-}RNNNR)(\mu\text{-}N^1,N^3\text{-}RNNNR)]^{2+}$ $\mathbf{3}^{2+}$ X-ray studies on which show one 'normal' bridging triazenide ligand and one in which one of the terminal N atoms binds one Rh atom while the second bonds to both metal atoms; the triazenide ligands of $\mathbf{3}^{2+}$ are *cis*-bound to one metal centre and *trans*-bound to the second.

We have recently shown[1] that the sequential treatment of $[\{Rh_2I(CO)(bipy)(\mu\text{-}RNNNR)_2\}_2][PF_6]_2$ (bipy = 2,2′-bipyridyl, R = *p*-tolyl) in CH_2Cl_2 with $AgPF_6$ and then bis(diphenylphosphino)methane (dppm) yields $[Rh_2(\mu\text{-}CO)(bipy)(dppm)(\mu\text{-}RNNNR)_2]^{2+}$, which may be formally described as a ketonic carbonyl-bridged $[Rh_2]^{6+}$ complex with an 'open-book' structure and no metal–metal bond, and which is in equilibrium with the 'normal', metal–metal bonded, $[Rh_2]^{4+}$ face-to-face isomer $[Rh_2(CO)(bipy)(dppm)(\mu\text{-}RNNNR)_2]^{2+}$. The analogous 1,2-bis(diphenylphosphino)ethane (dppe) complex, which only exists in the 'open-book' form $[Rh_2(\mu\text{-}CO)(bipy)(dppe)(\mu\text{-}RNNNR)_2]^{2+}$ $\mathbf{1}^{2+}$, undergoes one-electron reduction to $[Rh_2(CO)(bipy)(\sigma\text{-}dppe)(\mu\text{-}RNNNR)_2]^+$ $\mathbf{2}^+$ in which the face-to-face structure is regenerated. We now show that the first step in the reduction of $\mathbf{1}^{2+}$ to $\mathbf{2}^+$ involves the redox-catalysed formation of a third isomer, of formula $[Rh_2(CO)(bipy)(dppe)(\mu\text{-}N^{1,3},N^3\text{-}RNNNR)(\mu\text{-}N^1,N^3\text{-}RNNNR)]^{2+}$, in which one of the μ-triazenides is converted from a simple bridge into one in which one of the N atoms is simultaneously bound to both metal atoms.

The cyclic voltammogram of $\mathbf{1}^{2+}$ shows two apparently reversible reduction waves, at −0.20 and −0.53 V [Fig. 1(*a*)], implying the stepwise formation of $[Rh_2(\mu\text{-}CO)(bipy)(dppe)(\mu\text{-}RNNNR)_2]^+$ $\mathbf{1}^+$ and $[Rh_2(\mu\text{-}CO)(bipy)(dppe)(\mu\text{-}RNNNR)_2]$ $\mathbf{1}$. As noted previously,[1] the addition of one equivalent of $[BH_4]^-$ to $\mathbf{1}^{2+}$ gives the paramagnetic cation $[Rh_2(CO)(bipy)(\sigma\text{-}dppe)(\mu\text{-}RNNNR)_2]^+$ $\mathbf{2}^+$. However, treatment of $\mathbf{1}^{2+}$ with 5–10 mole per cent of the same reagent gave a red-brown solution from which *diamagnetic* red-orange crystals of $\mathbf{3}^{2+}$ were separable in 40–60% yield. The presence of one IR band at 1795 cm^{-1} confirmed the retention of the bridging carbonyl ligand but the ^{31}P NMR spectrum [−80 °C, acetone–$[^2H_6]$acetone (1:1)] δ 61.5 [dd, $J(^{31}P^{103}Rh)$ 132.7, $J(^{31}P^{31}P)$ 19.8] and 63.3 [dd, $J(^{31}P^{103}Rh)$ 174.4, $J(^{31}P^{31}P)$ 19.8 Hz] revealed the high asymmetry of $\mathbf{3}^{2+}$. In the absence of further useful spectroscopic information, the structure of the $[PF_6]^-$ salt of $\mathbf{3}^{2+}$ as a solvate was determined by single-crystal X-ray diffraction methods.*

The molecular structure of $\mathbf{3}^{2+}$ is illustrated in Fig. 2 which shows the dramatic changes in geometry that occur when $\mathbf{1}^{2+}$ rearranges to $\mathbf{3}^{2+}$. One triazenide ligand is bound to the Rh_2 unit in an unprecedented[2] mode in which it chelates one metal [Rh(2)] while bridging to the other *via* one nitrogen atom [N(4)]. In view of the asymmetry of the bridge [Rh(1)–N(4) 2.278(8), Rh(2)–N(4) 2.121(8) Å] it is probably best to describe the chelation of Rh(2) as the primary interaction. In addition it is notable that whereas in $\mathbf{1}^{2+}$ the two μ-triazenide ligands

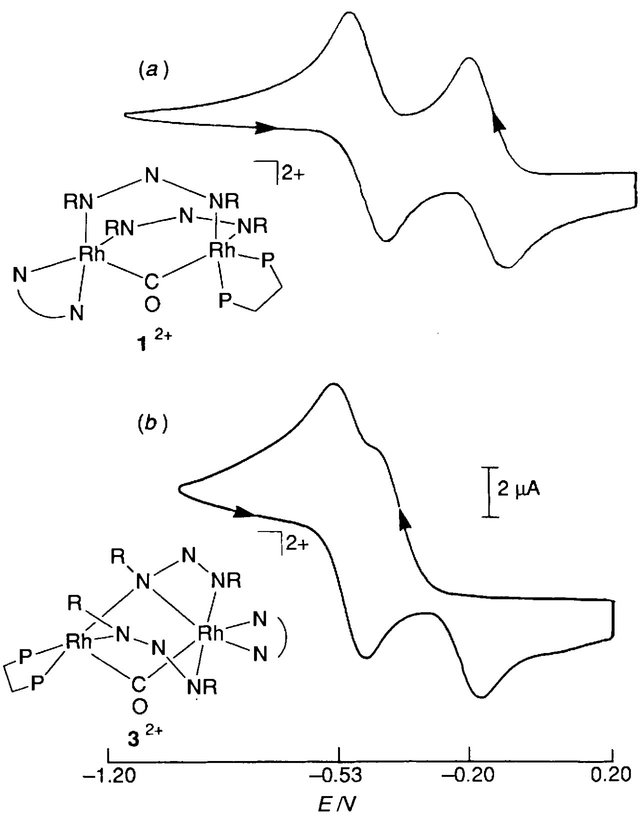

Fig. 1 The cyclic voltammogram at a platinum disc electrode in CH_2Cl_2 of (*a*) $\mathbf{3}^{2+}$ and (*b*) $\mathbf{1}^{2+}$. Potentials are *vs.* the saturated calomel electrode; under the experimental conditions used E° for the oxidation of ferrocene is 0.47 V (R = *p*-tolyl, P–P = $Ph_2PCH_2CH_2PPh_2$, N–N = 2,2′-bipyridyl)

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* See footnote on following page.

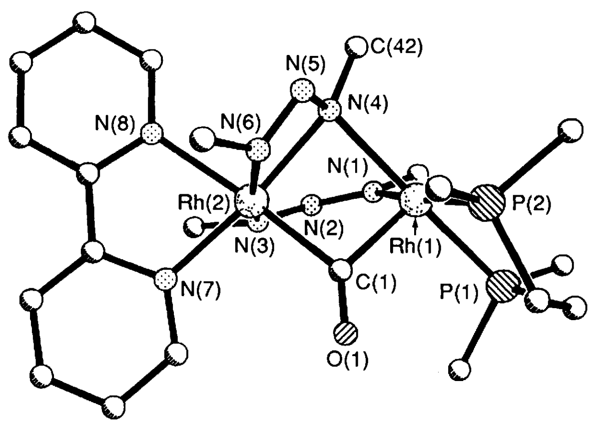
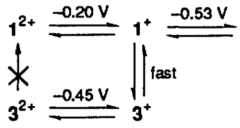


Fig. 2 Molecular geometry of the dication of 3^{2+}; phenyl and *p*-tolyl groups are represented by the *ipso* carbon atoms for clarity. Important molecular geometry parameters include: bond lengths (Å) Rh(1)–Rh(2) 2.908(1), Rh(1)–P(1) 2.315(3), Rh(1)–P(2) 2.299(3), Rh(1)–N(1) 2.149(8), Rh(1)–N(4) 2.278(8), Rh(1)–C(1) 1.963(10), Rh(2)–N(3) 2.042(8), Rh(2)–N(4) 2.121(8), Rh(2)–N(6) 2.035(9), Rh(2)–N(7) 2.053(8), Rh(2)–N(8) 2.151(8), Rh(2)–C(1) 2.005(10); bond angles (°) Rh(1)–C(1)–Rh(2) 94.2(4), Rh(1)–C(1)–O(1) 130.6(8), Rh(2)–C(1)–O(1) 135.1(8), Rh(1)–N(4)–Rh(2) 82.7(3), Rh(1)–N(4)–N(5) 125.0(6), Rh(2)–N(4)–N(5) 92.5(6), Rh(1)–N(4)–C(42) 104.8(6), Rh(2)–N(4)–C(42) 143.1(6), N(5)–N(4)–C(42) 110.6(8)

occupy *cis* sites on Rh(2), in 3^{2+} N(6) is *trans* to N(3). The co-ordination geometry at Rh(1) is, however, essentially unaffected remaining approximately square pyramidal with the bridging carbonyl occupying an axial site, much as in the structure of the dppm analogue of 1^{2+}. In contrast the co-ordination geometry of Rh(2) is much altered being distorted octahedral in 3^{2+} (ignoring the Rh ··· Rh interaction throughout this description).

One may envisage the rearrangement of 1^{2+} as taking place at square-pyramidal Rh(2) by a Berry pseudo-rotation which puts a bipyridyl nitrogen atom into the axial site [N(7)] and the carbonyl into an equatorial site while forcing N(3) and N(6) into *trans* sites. Finally the N(4)–Rh(2) bond is formed by folding the Rh_2N_3 unit to give the observed geometry of 3^{2+}.

The cyclic voltammogram of 3^{2+} [Fig. 1(*b*)] shows an irreversible reduction wave, with a peak potential of *ca.* −0.45 V, accompanied by two product waves at potentials identical to those of the reduction waves of 1^{2+}. The voltammetric behaviour, together with the catalytic conversion of 1^{2+} into 3^{2+}, can be rationalised simply in terms of a 'square scheme' (Scheme 1). The reduction of 1^{2+} (at −0.20 V) to 1^{+} is followed by isomerisation to 3^{+} which is then capable of reducing 1^{2+} *via* the 'cross reaction' in equation (1) (for which there is a driving force of *ca.* 0.2 V).



Scheme 1

$$3^{+} + 1^{2+} \rightleftharpoons 3^{2+} + 1^{+} \qquad (1)$$

The thermodynamic stability of 3^{2+}, which does not isomerise back to 1^{2+}, also favours the catalytic process. In order to account for the observation of the product waves at −0.20 and −0.53 V in the cyclic voltammogram of 3^{2+} the interconversion of 3^{+} and 1^{+} must be rapid.

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* Crystal data for $3^{2+}\cdot 2PF_6\cdot H_2O\cdot 0.67C_6H_{14}$. $C_{65}H_{60}F_{12}N_8OP_4Rh_2\cdot H_2O\cdot 0.67C_6H_{14}$, $M_r = 1602.4$, orthorhombic, space group *Pbcn* (no. 60), $a = 14.892(5)$, $b = 27.401(7)$, $c = 34.111(8)$ Å, $U = 13\,919(6)$ Å^3, $Z = 8$, $D_c = 1.53$ g, cm^{-3}, $\lambda = 0.710\,69$ Å, μ(Mo-Kα) = 6.5 cm^{-1}, $F(000) = 6528$, $T = 295$ K. Diffraction measurements were made on a single crystal (dimensions *ca.* 0.3 × 0.5 × 0.55 mm) and data were collected on a Nicolet P3m diffractometer for a unique portion of reciprocal space for $4 < 2\theta < 47°$. The structure was solved by heavy-atom methods and refined without positional constraints (except for the hexane solvate molecules for which C–C distances were held close to a common value, one $[PF_6]^-$ which was forced to have a near-octahedral geometry, and the C–H distances which were set to 0.96 Å) by least squares (679 parameters) to $R = 0.064$, $R' = 0.065$, $S = 1.30$ for 5820 unique, observed, absorption corrected $[I > 2\sigma(I)]$ intensity data $\{R = \Sigma|\Delta|\Sigma|F_o|$, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$, $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$, where $\Delta = F_o - F_c$ and N_o, N_v are the numbers of observations and variables$\}$. Weights, *w*, were set equal to $[\sigma_c^2(F_o) + 0.0007\ F_o^2]^{-1}$. The hexane solvate is disordered about two unique centres of inversion. The disorder and high mean-square displacement in the $[PF_6]^-$ anions led to relatively weak diffraction. All calculations were made with programs of the SHELXTL system.[3] Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.