Redox-induced κ^2–κ^3 isomerisation in rhodium hydrotris(3,5-dimethylpyrazolyl)borate chemistry: the stabilisation of square-pyramidal rhodium(II)

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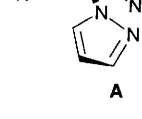
One-electron oxidation of the square-planar, 16-electron complex $[Rh(CO)(PPh_3)(\kappa^2\text{-}Tp')]$ with $[FeCp_2][PF_6]$ gives the square-pyramidal Rh^{II} complex $[Rh(CO)(PPh_3)(\kappa^3\text{-}Tp')][PF_6]$ in which the third pyrazolyl group of Tp′ is N-bound in the axial position by a three-electron two-centre bond ($Rh–N_{axial}$ 0.13 Å longer than $Rh–N_{basal}$).

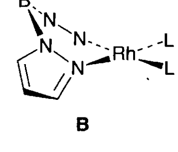
The analogy between cyclopentadienyl ($[\eta\text{-}C_5H_5]^-$, $[\eta\text{-}C_5Me_5]^-$, *etc.*) and hydrotris(pyrazolyl)borate ($[HBR_3]^-$; R = pyrazolyl, Tp; R = 3,5-dimethylpyrazolyl, Tp′, *etc.*) ligands has been widely drawn.[1] However, the differences in behaviour between the two types of ligand are often more interesting than the similarities. For example, in rhodium(I) chemistry, $[RhL_2(HBR_3)]$ [L = CO, L_2 = cod (cycloocta-1,5-diene) or nbd (norbornadiene)] can exist in one or more of three forms, namely two square-planar, 16-electron isomers $[RhL_2(\kappa^2\text{-}HBR_3)]$ and a five-coordinate, 18-electron isomer $[RhL_2(\kappa^3\text{-}HBR_3)]$ (structures **A**–**C**);[2–4] the relative abundance of the three forms depends on R and L and, in solution, the solvent. By contrast, $[Rh(CO)_2(\eta\text{-}C_5H_5)]$ shows no such variability of structure. The formation of $[Rh(CO)_2(\kappa^2\text{-}HBR_3)]$ from $[Rh(CO)_2(\kappa^3\text{-}HBR_3)]$ is particularly important because this step is implicated in the photoinduced C–H activation reactions of such species with both saturated and aromatic hydrocarbons {to give six-coordinate Rh^{III} hydrido alkyl or aryl complexes, for example $[RhHPh(CO)(\kappa^3\text{-}HBR_3)]$ with benzene}.[5]

Here we show that the electrochemistry and electronic structure of pyrazolylborate rhodium complexes is also significantly different from that of their cyclopentadienyl analogues. Whereas the short-lived 17-electron cation $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ dimerises to the fulvalene complex $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}\eta^5,\eta'^5\text{-}C_{10}H_8)]^{2+}$,[6] $[Rh(CO)(PPh_3)(\kappa^2\text{-}Tp')]$ undergoes an unprecedented, redox-induced isomerisation involving bidentate-to-tridentate transformation of a hydrotris(pyrazolyl)borate ligand on oxidation. The resulting cation, $[Rh(CO)(PPh_3)(\kappa^3\text{-}Tp')]^+$, not only is a rare example of a stable, paramagnetic, mononuclear rhodium(II) complex but also provides a potential model for the intermediate in the associative substitution reactions of square-planar Rh^{II}.

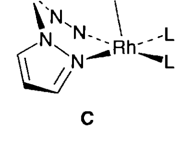
Heating $[Rh(CO)_2(Tp')]$ with PPh_3 under reflux in *n*-hexane gave yellow crystals of $[Rh(CO)(PPh_3)(Tp')]$ **1**,† the room-temperature ^1H NMR spectrum of which showed only three resonances for the pyrazolyl rings (two methyls and one ring proton) allowing no distinction to be made between structures **A**–**C**. However, an X-ray structure analysis‡ showed that in the solid state **1** adopts a structure of type **B**. The molecular structure of **1** (Fig. 1) shows a square-planar rhodium atom bound to CO, PPh_3 and to one N atom of each of two of the pyrazolyl rings; the third pyrazolyl ring is rotated away from the metal atom, resulting in an Rh···N(pyrazolyl) separation of 3.537(5) Å [Rh···B(1)–N(2)–N(1) torsion angle 89.9°, *cf.* Rh···B–N(5)–N(6) 6.0, Rh···B–N(3)–N(4) −1.0°]. IR spectroscopic studies suggest that $[Rh(CO)_2(Tp')]$ adopts[4] exclusively the κ^3 form (form **C**) in cyclohexane; substitution of CO by PPh_3 to give $[Rh(CO)(PPh_3)(Tp')]$ clearly results in increased steric interference and dissociation of one Rh–N bond.



A



B



C

The cyclic voltammogram (CV) of **1**, at a platinum electrode in either CH_2Cl_2 or thf, shows one oxidation wave {*e.g.* in thf, *ca.* 0.41 V *vs.* SCE; $E°'$ = −0.09 V for the couple $[Fe(\eta\text{-}C_5Me_5)_2]^{+1/0}$ as an internal standard}. The wave does not meet all of the criteria for a fully reversible system, showing a broadening of the forward, oxidation, peak (relative to the return reduction peak) in both solvents.§ Nevertheless, treatment of **1** with 1 equiv. of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ in CH_2Cl_2 gave green crystals of the stable, paramagnetic Rh^{II} salt $[Rh(CO)(PPh_3)(Tp')][PF_6]$, $\mathbf{1}^+[PF_6]^-$† (the CV of which is the same as that of **1** except that the wave observed corresponds to a reduction process).

An X-ray analysis‡ of $\mathbf{1}^+$, as the dichloromethane solvate of its $[PF_6]^-$ salt, revealed a marked change in the coordination about rhodium, from square planar (form **B**) to square pyramidal (form **C**), on one-electron oxidation. The molecular structure of $[Rh(CO)(PPh_3)(\kappa^3\text{-}Tp')]^+$ is shown in Fig. 2. The rhodium atom is bonded to the CO and PPh_3 ligands and to two (mutually *cis*) pyrazolyl nitrogen atoms in a plane; the fifth (apical) position is occupied by one nitrogen atom, N(1), of the

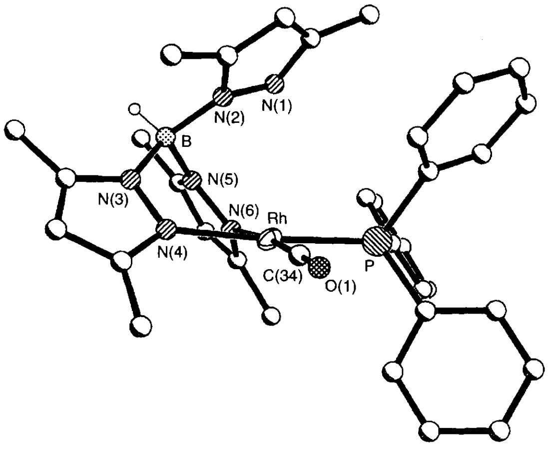


Fig. 1 Molecular structure of **1** with methyl, phenyl and pyrazolyl hydrogen atoms omitted for clarity. Important distances (Å) include: Rh–N(4) 2.108(4), Rh–N(6) 2.119(5), Rh···N(1) 3.537(5), Rh–P 2.272(2), Rh–C(34) 1.824(6).

third pyrazolyl ring. At 2.224(2) Å, this third Rh–N bond is longer than those in the square plane [2.093(2) and 2.091(2) Å] but it is considerably shorter than the Rh–N$_{apical}$ bond length in the square-pyramidal Rh^I complexes [Rh(CO)$_2$(κ^3-HBR$_3$)] [R = 3-trifluoromethyl-5-methylpyrazolyl, 2.623(8) Å;[2,4] R = 4,5-dihydro-2*H*-benz[g]indazol-2-yl 2.779(4) Å[7]]. Compared with **1**, the apical pyrazolyl group in **1$^+$** is rotated, as is required for its coordination [Rh···B–N(2)–N(1) torsion angle −7.5°, Rh···B–N(5)–N(6) 13.4, Rh···B–N(3)–N(4) 1.0°].

The redox-induced isomerisation [κ^2- to κ^3-coordination of the hydrotris(pyrazolyl)borate ligand] observed on oxidation of **1** to **1$^+$** is unprecedented, and is apparently brought about by electronic rather than steric factors. The structural changes, and the EPR spectrum¶ of **1$^+$**, are consistent with a SOMO of **1$^+$** [and HOMO for the hypothetical (type **C**) square-pyramidal form of **1**] which is based on the Rh–N σ* interaction between the 4d$_{z^2}$ orbital of the rhodium atom (the *z*-axis perpendicular to the square plane) and the apical nitrogen lone pair. The presence of only one electron in this orbital allows the formation of the (relatively long) two-centre three-electron Rh–N$_{apical}$ bond in **1$^+$**. The HOMO of **1** in form **C** would therefore contrast with the HOMO of [M(CO)$_2$(η-C$_5$H$_5$)] (M = Co or Rh) which involves[8] an antibonding interaction between the e$_1{}^+$ C$_5$H$_5$ ring orbital and the metal d$_{xz}$ orbital.

Cation **1$^+$** may be regarded as a model for the likely five-coordinate intermediate in the substitution reactions of square-planar Rh^{II}, reactions which a CV study suggests to be much faster than those for the analogous Rh^I complex [Rh(CO)$_2$(Tp′)]. Thus, in thf in the presence of PPh$_3$ the oxidation wave of [Rh(CO)$_2$(Tp′)] [(E_p)$_{ox}$ = 0.69 V] is accompanied by a product reduction wave [(E_p)$_{red}$ = 0.32 V] due to the rapid formation of **1$^+$** from [Rh(CO)$_2$(Tp′)]$^+$ and the phosphine ligand. Moreover, treatment of a 1 : 1 mixture of [Rh(CO)$_2$(Tp′)] and PPh$_3$ with [Fe(η-C$_5$H$_5$)$_2$][PF$_6$] in CH$_2$Cl$_2$ affords [Rh(CO)(PPh$_3$)(κ^3-Tp′)][PF$_6$] in minutes (*cf.* the slow thermal reaction between [Rh(CO)$_2$(Tp′)] and PPh$_3$†); similar oxidative substitution reactions may provide a route to other stabilised Rh^{II} complexes.

We thank the EPSRC for awards of a Research Studentship (to M. J. Q.) and a Research Assistantship (to B. M.).

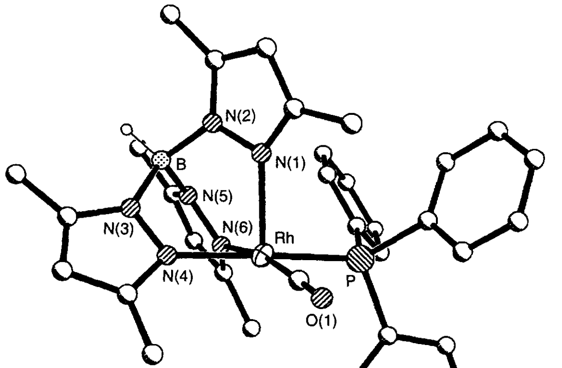


Fig. 2 Molecular structure of **1$^+$** with methyl, phenyl and pyrazolyl hydrogen atoms omitted for clarity. Important bond lengths (Å) include: Rh–N(4) 2.091(2), Rh–N(6) 2.093(2), Rh–N(1) 2.224(2), Rh–P 2.328(1), Rh–C(34) 1.879(3).

Footnotes

† Preparation of [Rh(CO)(PPh$_3$)(κ^2-Tp′)]. A solution of [Rh(CO)$_2$(Tp′)] (1.00 g, 2.19 mmol) and PPh$_3$ (0.575 g, 2.19 mmol) in *n*-hexane (250 cm^3) was heated under reflux for 2 h to give a yellow solution from which yellow crystals of **1** were isolated on cooling the solution to 0 °C. Recrystallisation from *n*-hexane gave the air-stable product, yield 1.01 g (67%). IR: ν(CO)(CH$_2$Cl$_2$) 1978 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): 5.65 (s, 1 H, C$_3$N$_2$*H*Me$_2$), 2.16 (s, 3 H, C$_3$N$_2$H*Me*$_2$), 1.82 (s, 3 H, C$_3$N$_2$H*Me*$_2$). ^{31}P NMR (C$_6$D$_6$; relative to H$_3$PO$_4$): 42.55 [d, J(^{103}Rh^{31}P) 162 Hz].

Preparation of [Rh(CO)(PPh$_3$)(κ^3-Tp′)][PF$_6$]. Addition of [Fe(η-C$_5$H$_5$)$_2$][PF$_6$] (0.182 g, 0.55 mmol) to **1** (0.40 g, 0.58 mmol) in CH$_2$Cl$_2$ (50 cm^3) gave a dark green solution from which **1$^+$** was isolated as the [PF$_6$]$^-$ salt after evaporation to dryness, washing the residue with hexane (4 × 20 cm^3) to remove [Fe(C$_5$H$_5$)$_2$] and recrystallisation from CH$_2$Cl$_2$–*n*-hexane, yield 0.34 g (71%). IR: ν(CO)(CH$_2$Cl$_2$) 2070 cm^{-1}.

Both new complexes gave satisfactory C, H and N analyses.

‡ *Crystal data* for [Rh(CO)(PPh$_3$)(κ^2-Tp′)] **1**: C$_{34}$H$_{37}$BN$_6$OPRh, M = 690.39, monoclinic, space group $P2_1/n$ (no. 14), a = 9.428(2), b = 16.510(5), c = 20.735(6) Å, β = 97.73(3)°, U = 3198(2) Å^3, Z = 4, D_c = 1.434 Mg m^{-3}, $\bar{\lambda}$ = 0.710 73 Å, μ = 0.62 mm^{-1}, F(000) = 1424, T = 173(2) K. Data were collected on a Siemens SMART diffractometer for 2.2 < θ < 25.2° on a crystal of poor singularity. The structure was solved by heavy-atom methods and refined by least-squares methods against F^2 to $R1$ = 0.069 ($wR2$ = 0.159) for 4668 unique observed [$I > 2\sigma(I)$] intensity data corrected for absorption.

Crystal data for [Rh(CO)(PPh$_3$)(κ^3-Tp′)][PF$_6$]·CH$_2$Cl$_2$ **1$^+$**[PF$_6$]$^-$·CH$_2$Cl$_2$: C$_{35}$H$_{39}$BCl$_2$F$_6$N$_6$OP$_2$Rh, M = 920.28, monoclinic, space group $P2_1/n$ (no. 14), a = 10.667(2), b = 15.090(3), c = 26.261(4) Å, β = 90.78(2)°, U = 4065.6(12) Å^3, Z = 4, D_c = 1.503 Mg m^{-3}, $\bar{\lambda}$ = 0.710 73 Å, μ = 0.694 mm^{-1}, F(000) = 1868, T = 173(2) K. Data were collected on a Siemens SMART diffractometer for 2.0 < θ < 25.0°. The structure was solved by heavy-atom methods and refined by least-squares methods against F^2 to $R1$ 0.0331 ($wR2$ = 0.0703) for 6042 unique observed [$I > 2\sigma(I)$] intensity data corrected for absorption. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/193.

§ The CV appears to be consistent with a solution process in which oxidation is accompanied by a structural change, as observed in the solid-state X-ray structural study. More detailed kinetic studies of this oxidative isomerisation process, and of the electrochemistry of related complexes, are in progress: W. E. Geiger and B. Yeomans, personal communication.

¶ The EPR spectrum of **1$^+$**, in CH$_2$Cl$_2$–thf (2 : 1), shows a broad singlet at room temperature (g_{iso} = 2.141) and three-fold anisotropy (g_x = 2.258, g_y = 2.163, g_z = 1.992; g_{av} = 2.138) in frozen solution (100 K). The high-field component of the anisotropic spectrum shows hyperfine coupling to 1 N (29 G), 1 P (32 G) and 1 Rh (7 G) atoms.

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Received, 28th May 1996; Com. 6/03674K