Redox activation of a B–H bond: a new route to metallaboratrane complexes

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Oxidative activation of a B–H bond of a coordinated scorpionate ligand provides an unprecedented route to rhodaboratranes.

The chemistry of hydrotris(pyrazolyl)borate rhodium complexes such as [Rh(CO)LTp] {L = CO or *P*-donor ligand; Tp = HB(pyrazolyl)$_3$, the archetypal scorpionate ligand},[1] especially the photochemical activation of hydrocarbons by the dicarbonyls,[2] is well established. However, attempts to synthesise *S*-donor scorpionate analogues, using hydrotris(2-thio-1-R-imidazolyl)borate {HB(mim^R)$_3$ or Tm^R, Scheme 1}, have instead usually led to cleavage of the B–H bond and formation of well-defined rhodaboratranes with direct rhodium–boron bonds, *e.g.* [RhCl(PPh$_3$){B(mim^R)$_3$}] (R = Me[3,4] or Bu^t [5]). (Other metallaboratranes include [Ru(CO)(PPh$_3$){B(mim^{Me})$_3$}],[6] [Co(PPh$_3$){B(mim$^{Bu^t}$)$_3$}][BPh$_4$][7] and [Ir(CO)(PPh$_3$){B(mim^{Me})$_3$}].[8])

Our interest in rhodium scorpionates has centred on the preparation of stable Rh(II) species by the one-electron oxidation of, for example, [Rh(CO)(PPh$_3$)Tp′] {Tp′ = hydrotris(3,5-dimethylpyrazolyl)borate, acting as a bidentate N_2-donor} to [Rh(CO)(PPh$_3$)Tp′]$^+$ (where Tp′ is a tridentate N_3-donor).[9] In seeking to extend this redox chemistry by using hydrotris(4-ethyl-3-methyl-5-thioxo-1,2,4-triazolyl)borate {HB(taz)$_3$ or Tt, Scheme 1} (a potential *N*-, *S*- or mixed donor),[10] we have discovered an unprecedented route to rhodaboratranes involving the oxidative activation of the B–H bond of a coordinated scorpionate ligand.

The reaction of [{RhCl(η^4-cod)}$_2$] (cod = cycloocta-1,5-diene) with NaTt gives [Rh(η^4-cod)Tt] which reacts sequentially with CO and PPh$_3$ to give [Rh(CO)(PPh$_3$)Tt] (**1**).† The X-ray structure‡ of **1** shows a rhodium centre coordinated to two S atoms of the Tt ligand and the H atom of a B–H group positioned approximately axially above the Rh centre [Rh(1)···H(1) 2.41 Å], and substantial angular distortion of the Rh(I) centre from square planar coordination (Fig. 1). This type of bonding mode, previously observed, for example, in [Ba(H$_2$O)$_2$Tm][11] and contrasting markedly with N_2-bonded Tp′ in [Rh(CO)(PPh$_3$)Tp′], has been described as S_2H-coordination. More recently, however, the Rh···H–B linkage in [Rh(η^4-cod){H$_2$B(mt)$_2$}][12] has been described as a three-centre–two-electron (3c–2e) agostic interaction. Cotton *et al.*[13] noted an analogous B–H···Mo interaction in [Mo(CO)$_2${H$_2$B(3,5-dimethylpyrazolyl)$_2$}(η^3-C$_7$H$_7$)] which leads to an 18-electron count for molybdenum. We note that an axial BH···Rh or CH···Rh interaction in a square planar rhodium(I) complex might be better described as a 3c–4e interaction given the presence of the filled Rh d_z^2 orbital (see below).

As for the Tp′ analogue, cyclic voltammetry at a glassy carbon electrode in CH_2Cl_2 shows that [Rh(CO)(PPh$_3$)Tt] **1** is irreversibly oxidised, with a peak potential of *ca.* 0.4 V. Treatment of **1** with *two* equivalents of [Fe(η-C$_5$H$_5$)$_2$][PF$_6$] in the presence of NEt$_3$ gives, after 30 min, a moderate yield of the red-orange rhodaboratrane complex [Rh(CO)(PPh$_3$){B(taz)$_3$}][PF$_6$] (**2**$^+$[PF$_6$]$^-$).† The ^{11}B NMR spectrum of cation **2**$^+$ shows a well-defined doublet, {J(^{11}B^{103}Rh) 80 Hz}, contrasting with the very

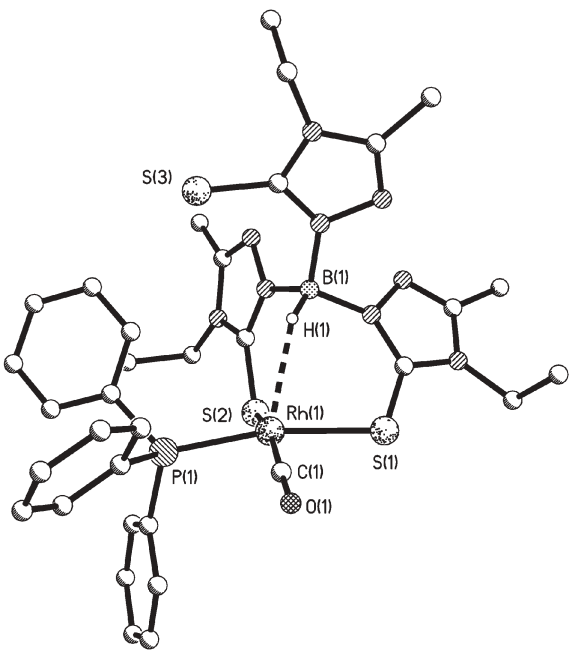
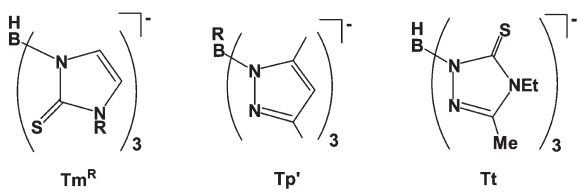


Fig. 1 The molecular structure of [Rh(CO)(PPh$_3$)Tt] **1**. (All hydrogen atoms except that attached to boron are omitted for clarity). Important bond distances and angles: Rh(1)···H(1) 2.41, Rh(1)···B(1) 3.239, Rh(1)–S(1) 2.414(1), Rh(1)–S(2) 2.431(1), Rh(1)–P(1) 2.264(1), Rh(1)–C(1) 1.817(3), C(1)–O(1) 1.152(4) Å; B(1)–H(1)···Rh(1) 139, S(1)–Rh(1)–P(1) 168.86(3), S(2)–Rh(1)–C(1) 162.59(12)°.



Scheme 1

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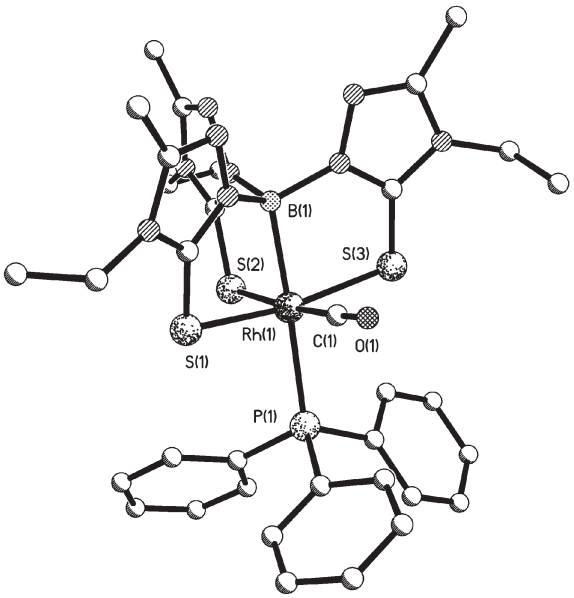
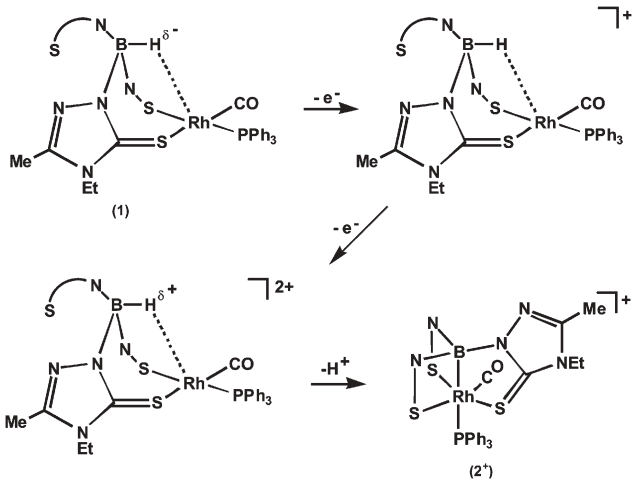


Fig. 2 Structure of the cation $[Rh(CO)(PPh_3)\{B(taz)_3\}]^+$ $\mathbf{2}^+$. (Hydrogen atoms are omitted for clarity). Important bond distances: Rh(1)–B(1) 2.155(5), Rh(1)–S(1) 2.397(1), Rh(1)–S(2) 2.387(1), Rh(1)–S(3) 2.386(1), Rh(1)–P(1) 2.495(1), Rh(1)–C(1) 1.856(5), C(1)–O(1) 1.147(6) Å.

broad singlet previously observed for rhodaboratranes derived from Tm.[3,4]

The X-ray structure‡ of $\mathbf{2}^+$ (Fig. 2) shows an octahedral rhodium centre coordinated to the three S atoms and the B atom of the $B(taz)_3$ ligand, with a Rh–B distance of 2.155(5) Å, comparable to those of Tm-derived rhodaboratranes such as $[RhCl(PPh_3)\{B(mim^{Me})_3\}]$ {2.122(7) and 2.132(6) Å, for two independent molecules in the unit cell},[3] $[Rh(PMe_3)_2\{B(mim^{Me})_3\}]^+$ {2.153(11) and 2.148(10) Å}[4] and $[RhCl(PPh_3)\{B(mim^{But})_3\}]$ {2.095(3) Å}.[5] The phosphine ligand is coordinated *trans* to the rhodium–boron bond with the Rh–P bond distance [2.495(1) Å] much longer than in **1** [2.264(1) Å]. A similarly long distance has been observed for (B)Rh–P_{trans} in $[Rh(PMe_3)_2\{B(mim^{Me})_3\}]^+$ [2.459(3) and 2.471(3) Å for two independent molecules in the unit cell]. In this complex, the much shorter Rh–PMe_3 distance *cis* to the Rh–B bond [2.293(3) and 2.292(3) Å][4] suggests the lengthening in $\mathbf{2}^+$ relative to **1** is a result of the strong *trans* influence of the boron donor, as might be expected for the dianion BR_3^{2-} (*cf.* the strong *trans* influence of the isoelectronic anion $[SiR_3]^-$ [14]) rather than neutral BR_3 (see below).

The activation of a B–H bond by a redox reaction is unprecedented but may occur as in the C–H activation reactions of, for example, $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)(\eta\text{-}C_5H_5)_2]$[15] and $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]$[16] (which give $[Ru_2(\mu\text{-}CH)(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)(\eta\text{-}C_5H_5)_2]^+$ and $[Mo_2(\mu\text{-}C_8Me_7CH_2)(\eta\text{-}C_5H_5)_2]^+$ respectively), *i.e.* by a double oxidation–deprotonation mechanism. A similar mechanism for the conversion of **1** to $\mathbf{2}^+$ (Scheme 2) is supported by the need for two equivalents of a one-electron oxidant in the presence of a base. Moreover, if the Rh···H–B bond involves a 3c–4e interaction (between a filled Rh d_{z^2} orbital and the B–H bond) stepwise oxidation of **1** would convert this into 3c–3e and 3c–2e bonds. (Similar behaviour occurs on one-electron oxidation of $[Rh(CO)(PPh_3)(Tp'\text{-}\kappa^2)]$ where the formally 2c–4e Rh–N σ* interaction, involving the rhodium d_{z^2} orbital and the nitrogen atom of the third, unbound pyrazolyl ring, is converted to a 2c–3e bond in $[Rh(CO)(PPh_3)(Tp'\text{-}\kappa^2)]^+$.[9]) At the same time, the boron-bound hydrogen atom would be polarised from $B\text{–}H^{\delta-}$ to $B\text{–}H^{\delta+}$, facilitating proton loss and formation of the B–Rh bond.



Scheme 2 S–N = thioxotriazolyl ring.

The route to $\mathbf{2}^+$ also has implications for the formal depiction of the Rh–B bond in rhodaboratranes. It has become conventional to draw this as a dative bond from Lewis basic Rh(I) to Lewis acidic BR_3. However, the need for two equivalents of a one-electron oxidant to synthesise $\mathbf{2}^+$ from **1**, the accompanying large increase in energy of ν(CO) of *ca.* 90 cm^{-1} (from 1977 cm^{-1} in **1** to 2064 cm^{-1} in $\mathbf{2}^+$, consistent with an increased formal metal oxidation state), and the octahedral geometry of **2**, unexpected for a Rh(I) complex, suggest an alternative formal description for the Rh–B bond, *i.e.* one in which the B atom of the dianion BR_3^{2-} (isoelectronic with CR_3^- and NR_3), acts as a donor to a rhodium(III) atom. Such a bonding description has been noted previously[5] as a possibility for $[MCl(PH_3)\{B(mim^H)_3\}]$ (M = Rh or Ir) but was discounted on the basis that BR_3^{2-} dianions are unknown (even though DFT calculations had suggested a d^6 configuration for the metal centre). One of the beauties of organometallic chemistry is the stabilisation of otherwise unstable ligands.

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Notes and references

† All new complexes had satisfactory elemental analyses (C, H and N). Complex [Rh(CO)(PPh_3)Tt] **1**; orange crystals; yield 75%; ν(CO) (CH_2Cl_2): 1977 cm^{-1}; ^1H NMR (CD_2Cl_2): 7.3–7.8, m, 15H, P*Ph*$_3$; 3.88, q (br), *J* 5.9, 6H, $C_2N_3S(CH_2CH_3)Me$; 2.31, s, 9H, C_2N_3SEtMe; 1.21, t, *J* 7.2, 9H, $C_2N_3S(CH_2CH_3)Me$; ^{31}P NMR (CD_2Cl_2): 40.8, d, $J(^{31}P^{103}Rh)$ 158; ^{11}B NMR (CD_2Cl_2): −4.95, s. Complex $[Rh(CO)(PPh_3)\{B(taz)_3\}][PF_6]$ $\mathbf{2}^+[PF_6]^-$; orange-red crystals, yield 26%; ν(CO) (CH_2Cl_2): 2064 cm^{-1}; ^1H NMR (CD_2Cl_2): 7.2–7.5, m, 15H, P*Ph*$_3$; 3.80, q, *J* 7.3, 4H, $C_2N_3S(CH_2CH_3)Me$; 3.79, q, *J* 7.0, 2H, $C_2N_3S(CH_2CH_3)Me$; 2.37, s, 6H, C_2N_3SEtMe; 2.24, s, 3H, C_2N_3SEtMe; 1.24, t, *J* 7.3, 9H, $C_2N_3S(CH_2CH_3)Me$; ^{31}P NMR (CD_2Cl_2): 8.0, v.br, P*Ph*$_3$; −143.9, (heptet), $J(^{31}P^{19}F)$ 710, PF_6^-; ^{11}B NMR (CD_2Cl_2): −7.52, d, $J(^{11}B^{103}Rh)$ 80.0.

‡ X-ray data were collected on a Bruker SMART diffractometer at 100 K (for **1**) or 173 K (for $\mathbf{2}^+[PF_6]^-$) for $\theta < 25°$ with $\lambda = 0.71073$ Å. The structures were solved by direct methods and refined by least-squares against all F_2 values.

Crystal data: $[Rh(CO)(PPh_3)Tt]\cdot CH_2Cl_2$ $\mathbf{1}\cdot CH_2Cl_2$ (from CH_2Cl_2–*n*-hexane): $C_{35}H_{42}BCl_2N_9OPRhS_3$, $M = 916.55$, triclinic, space group *P*-1 (No. 2), $a = 13.122(3)$, $b = 13.342(3)$, $c = 13.744(3)$ Å, $\alpha = 76.38(3)$,

β = 79.99(3), γ = 62.36(3)°, V = 2065.9(10) Å^3, Z = 2, μ = 0.774 mm^{-1}, R_1 = 0.0503. [Rh(CO)(PPh$_3$){B(taz)$_3$}][PF$_6$]·2CH$_2$Cl$_2$ **2**$^+$[PF$_6$]$^-$·2CH$_2$Cl$_2$ (from CH$_2$Cl$_2$–*n*-hexane): C$_{36}$H$_{43}$BCl$_4$F$_6$N$_9$OP$_2$RhS$_3$, M = 1145.43, triclinic, space group *P*-1 (No. 2), a = 12.899(2), b = 14.035(2), c = 14.286(2) Å, α = 68.38(1), β = 88.30(1), γ = 87.74(1)°, V = 2402.1(6) Å^3, Z = 2, μ = 0.840 mm^{-1}, R_1 = 0.0552. CCDC 603867 and 603868. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604954k

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