

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

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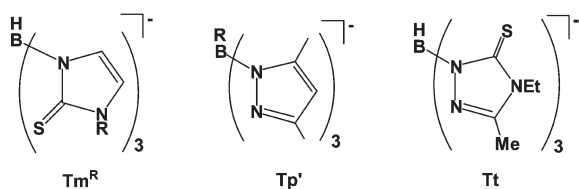
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Oxidative activation of a B–H bond of a coordinated scorpionate ligand provides an unprecedented route to rhodaboratranes.

The chemistry of hydrotris(pyrazolyl)borate rhodium complexes such as $[\text{Rh}(\text{CO})\text{LTp}]$ $\{\text{L} = \text{CO}$ or P -donor ligand; $\text{Tp} = \text{HB}(\text{pyrazolyl})_3$, 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 $\{\text{HB}(\text{mim}^R)_3$ 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.* $[\text{RhCl}(\text{PPh}_3)\{\text{B}(\text{mim}^R)_3\}]$ ($R = \text{Me}^{3,4}$ or Bu^t ⁵). (Other metallaboratranes include $[\text{Ru}(\text{CO})(\text{PPh}_3)\{\text{B}(\text{mim}^{\text{Me}})_3\}]$,⁶ $[\text{Co}(\text{PPh}_3)\{\text{B}(\text{mim}^{\text{Bu}^t})_3\}][\text{BPh}_4]$ ⁷ and $[\text{Ir}(\text{CO})(\text{PPh}_3)\{\text{B}(\text{mim}^{\text{Me}})_3\}]$.⁸)

Our interest in rhodium scorpionates has centred on the preparation of stable Rh(II) species by the one-electron oxidation of, for example, $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Tp}']$ $\{\text{Tp}' = \text{hydrotris}(3,5\text{-dimethylpyrazolyl})\text{borate}$, acting as a bidentate N_2 -donor $\}$ to $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Tp}']^+$ (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 $\{\text{HB}(\text{taz})_3$ 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 $[\{\text{RhCl}(\eta^4\text{-cod})\}_2]$ ($\text{cod} = \text{cycloocta-1,5-diene}$) with NaTt gives $[\text{Rh}(\eta^4\text{-cod})\text{Tt}]$ which reacts sequentially with CO and PPh_3 to give $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Tt}]$ (**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 $[\text{Rh}(\text{H}(1))\cdots\text{H}(1) 2.41 \text{ \AA}]$, and substantial angular distortion of the Rh(I) centre from square planar coordination (Fig. 1). This type of bonding mode, previously



Scheme 1

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observed, for example, in $[\text{Ba}(\text{H}_2\text{O})_2\text{Tm}]^{11}$ and contrasting markedly with N_2 -bonded Tp' in $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Tp}']$, has been described as S_2H -coordination. More recently, however, the $\text{Rh}\cdots\text{H}-\text{B}$ linkage in $[\text{Rh}(\eta^4\text{-cod})\{\text{H}_2\text{B}(\text{mt})_2\}]^{12}$ has been described as a three-centre–two-electron ($3c-2e$) agostic interaction. Cotton *et al.*¹³ noted an analogous $\text{B}-\text{H}\cdots\text{Mo}$ interaction in $[\text{Mo}(\text{CO})_2\{\text{H}_2\text{B}(3,5\text{-dimethylpyrazolyl})_2\}(\eta^3\text{-C}_7\text{H}_7)]$ which leads to an 18-electron count for molybdenum. We note that an axial $\text{BH}\cdots\text{Rh}$ or $\text{CH}\cdots\text{Rh}$ interaction in a square planar rhodium(I) complex might be better described as a $3c-4e$ interaction given the presence of the filled $\text{Rh } d_z^2$ orbital (see below).

As for the Tp' analogue, cyclic voltammetry at a glassy carbon electrode in CH_2Cl_2 shows that $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Tt}]$ **1** is irreversibly oxidised, with a peak potential of *ca.* 0.4 V. Treatment of **1** with two equivalents of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2][\text{PF}_6]$ in the presence of NEt_3 gives, after 30 min, a moderate yield of the red-orange rhodaboratrane complex $[\text{Rh}(\text{CO})(\text{PPh}_3)\{\text{B}(\text{taz})_3\}][\text{PF}_6]$ ($2^+[\text{PF}_6]^-$).[†] The ^{11}B NMR spectrum of cation 2^+ shows a well-defined doublet, $\{J(^{11}\text{B}^{103}\text{Rh}) 80 \text{ Hz}\}$, contrasting with the very

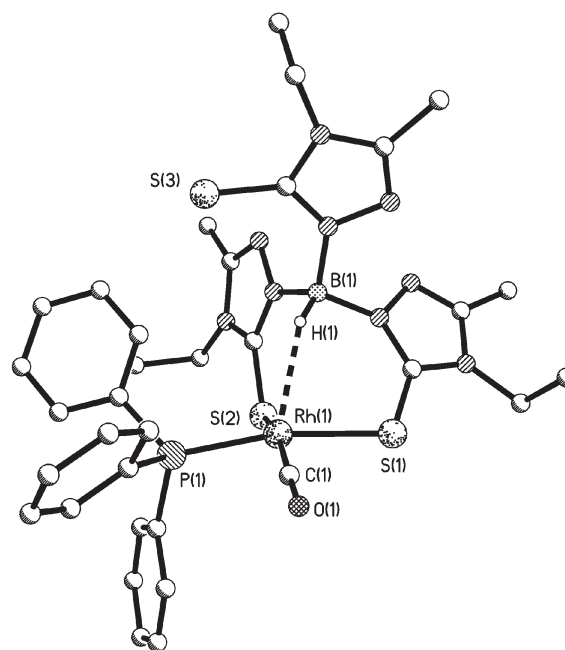


Fig. 1 The molecular structure of $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Tt}]$ **1**. (All hydrogen atoms except that attached to boron are omitted for clarity). Important bond distances and angles: $\text{Rh}(\text{H}(1))\cdots\text{H}(1) 2.41$, $\text{Rh}(\text{H}(1))\cdots\text{B}(1) 3.239$, $\text{Rh}(\text{H}(1))-\text{S}(1)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

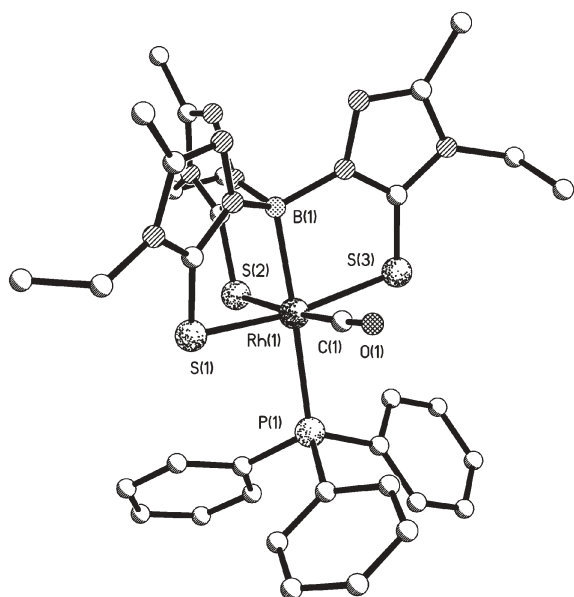
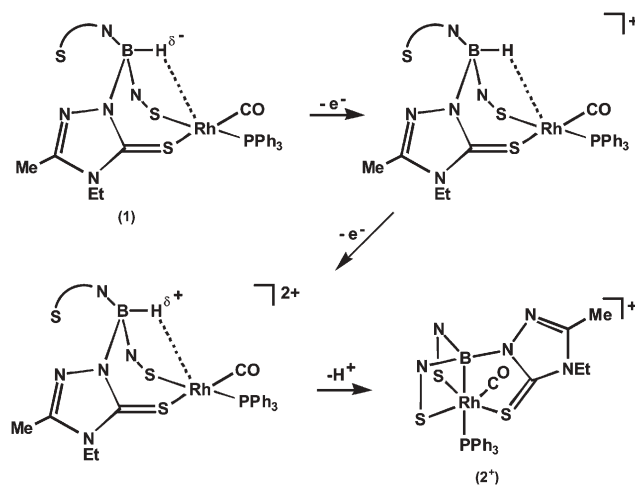


Fig. 2 Structure of the cation $[\text{Rh}(\text{CO})(\text{PPh}_3)\{\text{B}(\text{taz})_3\}]^{2+}$. (Hydrogen atoms are omitted for clarity). Important bond distances: Rh(1)–B(1) 2.155(5), Rh(1)–S(1) 2.397(1), Rh(1)–S(2) 2.387(1), Rh(1)–S(3) 2.386(1), Rh(1)–P(1) 2.495(1), Rh(1)–C(1) 1.856(5), C(1)–O(1)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

broad singlet previously observed for rhodaboratranes derived from Tm.^{3,4}

The X-ray structure[‡] of **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 $[\text{RhCl}(\text{PPh}_3)\{\text{B}(\text{mim}^{\text{Me}})_3\}]^{2+}$ {2.122(7) and 2.132(6) Å, for two independent molecules in the unit cell},³ $[\text{Rh}(\text{PMe}_3)_2\{\text{B}(\text{mim}^{\text{Me}})_3\}]^{2+}$ {2.153(11) and 2.148(10) Å}⁴ and $[\text{RhCl}(\text{PPh}_3)\{\text{B}(\text{mim}^{\text{Bu}})_3\}]^{2+}$ {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 $[\text{Rh}(\text{PMe}_3)_2\{\text{B}(\text{mim}^{\text{Me}})_3\}]^{2+}$ [2.459(3) and 2.471(3) Å for two independent molecules in the unit cell]. In this complex, the much shorter Rh–PMe₃ distance *cis* to the Rh–B bond [2.293(3) and 2.292(3) Å]⁴ suggests the lengthening in **2⁺** relative to **1** is a result of the strong *trans* influence of the boron donor, as might be expected for the dianion BR₃²⁻ (*cf.* the strong *trans* influence of the isoelectronic anion $[\text{SiR}_3]^{-14}$) rather than neutral BR₃ (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, $[\text{Ru}_2(\mu\text{-CH}_2)(\mu\text{-CO})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\eta\text{-C}_5\text{H}_5)_2]^{15}$ and $[\text{Mo}_2(\mu\text{-C}_8\text{Me}_8)(\eta\text{-C}_5\text{H}_5)_2]^{16}$ (which give $[\text{Ru}_2(\mu\text{-CH})(\mu\text{-CO})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\eta\text{-C}_5\text{H}_5)_2]^+$ and $[\text{Mo}_2(\mu\text{-C}_8\text{Me}_7\text{CH}_2)(\eta\text{-C}_5\text{H}_5)_2]^+$ respectively), *i.e.* by a double oxidation–deprotonation mechanism. A similar mechanism for the conversion of **1** to **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_{z²} 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 $[\text{Rh}(\text{CO})(\text{PPh}_3)(\text{Tp}'\text{-}\kappa^2)]$ where the formally 2c–4e Rh–N σ* interaction, involving the rhodium d_{z²} orbital and the



Scheme 2 S–N = thioxotriazolyl ring.

nitrogen atom of the third, unbound pyrazolyl ring, is converted to a 2c–3e bond in $[\text{Rh}(\text{CO})(\text{PPh}_3)(\text{Tp}'\text{-}\kappa^2)]^{2+}$.⁹) At the same time, the boron-bound hydrogen atom would be polarised from B–H^{δ-} to B–H^{δ+}, facilitating proton loss and formation of the B–Rh bond.

The route to **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 BR₃. However, the need for two equivalents of a one-electron oxidant to synthesise **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 **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 BR₃²⁻ (isoelectronic with CR₃⁻ and NR₃), acts as a donor to a rhodium(III) atom. Such a bonding description has been noted previously⁵ as a possibility for $[\text{MCl}(\text{PH}_3)_3\{\text{B}(\text{mim}^{\text{H}})_3\}]$ (M = Rh or Ir) but was discounted on the basis that BR₃²⁻ dianions are unknown (even though DFT calculations had suggested a d⁶ 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 $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Ti}]$ **1**; orange crystals; yield 75%; ν(CO) (CH₂Cl₂): 1977 cm⁻¹; ¹H NMR (CD₂Cl₂): 7.3–7.8, m, 15H, PPh₃; 3.88, q (br), *J* 5.9, 6H, C₂N₃S(CH₂CH₃)Me; 2.31, s, 9H, C₂N₃SEtMe; 1.21, t, *J* 7.2, 9H, C₂N₃S(CH₂CH₃)Me; ³¹P NMR (CD₂Cl₂): 40.8, d, *J*(³¹P¹⁰³Rh) 158; ¹¹B NMR (CD₂Cl₂): -4.95, s. Complex $[\text{Rh}(\text{CO})(\text{PPh}_3)\{\text{B}(\text{taz})_3\}][\text{PF}_6]^{2+}$ **2⁺**[PF₆]⁻; orange-red crystals, yield 26%; ν(CO) (CH₂Cl₂): 2064 cm⁻¹; ¹H NMR (CD₂Cl₂): 7.2–7.5, m, 15H, PPh₃; 3.80, q, *J* 7.3, 4H, C₂N₃S(CH₂CH₃)Me; 3.79, q, *J* 7.0, 2H, C₂N₃S(CH₂CH₃)Me; 2.37, s, 6H, C₂N₃SEtMe; 2.24, s, 3H, C₂N₃SEtMe; 1.24, t, *J* 7.3, 9H, C₂N₃S(CH₂CH₃)Me; ³¹P NMR (CD₂Cl₂): 8.0, v.br. PPh₃; -143.9, (heptet), *J*(³¹P¹⁹F) 710, PF₆⁻; ¹¹B NMR (CD₂Cl₂): -7.52, d, *J*(¹¹B¹⁰³Rh) 80.0.

[‡] X-ray data were collected on a Bruker SMART diffractometer at 100 K (for **1**) or 173 K (for **2⁺**[PF₆]⁻) for θ < 25° with λ = 0.71073 Å. The structures were solved by direct methods and refined by least-squares against all F₂ values.

Crystal data: $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Ti}]\text{-CH}_2\text{Cl}_2$ **1-CH}_2\text{Cl}_2 (from CH₂Cl₂-*n*-hexane); C₃₅H₄₅BCl₂N₉OPRhS₃, *M* = 916.55, triclinic, space group *P*-1 (No. 2), *a* = 13.122(3), *b* = 13.342(3), *c* = 13.744(3) Å, α = 76.38(3),**

$\beta = 79.99(3)$, $\gamma = 62.36(3)^\circ$, $V = 2065.9(10) \text{ \AA}^3$, $Z = 2$, $\mu = 0.774 \text{ mm}^{-1}$, $R_1 = 0.0503$. $[\text{Rh}(\text{CO})(\text{PPh}_3)\{\text{B}(\text{taz})_3\}][\text{PF}_6] \cdot 2\text{CH}_2\text{Cl}_2 \cdot 2^+[\text{PF}_6]^- \cdot 2\text{CH}_2\text{Cl}_2$ (from CH_2Cl_2 -*n*-hexane): $\text{C}_{36}\text{H}_{43}\text{BCl}_4\text{F}_6\text{N}_9\text{OP}_2\text{RhS}_3$, $M = 1145.43$, triclinic, space group *P*-1 (No. 2), $a = 12.899(2)$, $b = 14.035(2)$, $c = 14.286(2) \text{ \AA}$, $\alpha = 68.38(1)$, $\beta = 88.30(1)$, $\gamma = 87.74(1)^\circ$, $V = 2402.1(6) \text{ \AA}^3$, $Z = 2$, $\mu = 0.840 \text{ mm}^{-1}$, $R_1 = 0.0552$. CCDC 603867 and 603868. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604954k

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