

An unprecedented κ^2N,H bonding mode for a hydridotris(pyrazolyl)-borato ligand

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An unprecedented κ^2N,H bonding mode for a hydridotris(pyrazolyl)borato ($\text{Tp}^{\text{Me}_2,4\text{-Cl}}$) ligand is observed in $[\text{Rh}(\text{CO})(\text{PMePh}_2)_2(\text{Tp}^{\text{Me}_2,4\text{-Cl}})]$; the complex, which features two dangling pyrazole rings and a B-($\mu\text{-H}$)-Rh agostic bond, is highly fluxional in solution.

Hydridotris(pyrazolyl)borato ligands (Tp') have a strong preference for adopting a κ^3N,N',N'' bonding mode.¹ On some occasions, the electronic nature of the metal dictates a different coordination behaviour. A textbook example is the d^8 configuration in square-planar Rh complexes where κ^2N,N' coordination may also be observed, the two bonding modes interconverting in several cases.² The third pendant pyrazolyl arm may then fulfill subsequent electronic deficiency: oxidation of $[\text{Rh}(\text{CO})(\text{PPh}_3)(\kappa^2N,N'-\text{Tp}^{\text{Me}_2})]$ yields a pentacoordinated κ^3N,N',N'' rhodium(II) complex $[\text{Rh}(\text{CO})(\text{PPh}_3)(\kappa^3N,N',N''-\text{Tp}^{\text{Me}_2})]^+$.³ Also, stable species containing κ^2N,N' forms have been shown to be intermediates leading to κ^3N,N',N'' coordination as exemplified by the thermal loss of phosphine in octahedral $[\text{RuH}(\text{PPh}_3)_2(\kappa^2N,N'-\text{Tp})]$ which affords $[\text{RuH}(\text{PPh}_3)(\kappa^3N,N',N''-\text{Tp})]$.⁴ Isomerization from a κ^2N,N' to a κ^3N,N',H situation has been recently observed in $[\text{RuH}(\text{COD})\text{Tp}^{\text{H-Pr}_2}]$ (COD = cycloocta-1,5-diene).⁵ In this communication, we report yet another bonding mode for a hydridotris(pyrazolyl)borato ligand featuring two pendant pyrazolyl rings in the complex $[\text{Rh}(\text{CO})(\text{PMePh}_2)_2(\text{Tp}^{\text{Me}_2,4\text{-Cl}})]$. Only one pyrazolyl ring is N-bound to rhodium, and the B-bound hydrogen agostically interacts with rhodium leading to an unprecedented κ^2N,H bonding mode. A very recent example of a bridging ($\mu_3\text{-}1\kappa^1N:2\kappa^1N':3\kappa^1N''$) Tp' has been reported in a trinuclear silver complex.⁶

Treatment of $[\text{Rh}(\text{CO})_2(\text{Tp}^{\text{Me}_2,4\text{-Cl}})]$ **1a** with one equivalent of PMePh_2 leads to $[\text{Rh}(\text{CO})(\text{PMePh}_2)_2(\kappa^2N,N'-\text{Tp}^{\text{Me}_2,4\text{-Cl}})]$ **2a** [$\nu(\text{CO}) = 1996 \text{ cm}^{-1}$] in high yield. The κ^2 bonding mode is ascertained in the solid state by the result of an X-ray diffraction analysis[†] (Fig. 1). The square-planar arrangement around rhodium is similar to that observed in related $\kappa^2N,N'-\text{Tp}^{\text{Me}_2}$ $[\text{Rh}(\text{CO})(\text{L})(\text{Tp}^{\text{Me}_2})]$ (L = PMe_3 ,^{2c} PPh_3 ,³ PMePh_2 **2b**⁷).

A clean reaction converts **1a** and excess PMePh_2 into $[\text{Rh}(\text{CO})(\text{PMePh}_2)_2(\text{Tp}^{\text{Me}_2,4\text{-Cl}})]$ **3a** [$\nu(\text{CO}) = 1979 \text{ cm}^{-1}$] at 273 K. At 233 K, a single $^{31}\text{P}\{-^1\text{H}\}$ NMR doublet [δ 23.7 (d, $J_{\text{PRh}} = 125 \text{ Hz}$)] and a single $^{13}\text{C}\{-^1\text{H}\}$ NMR doublet of triplets (δ 190.6, $J_{\text{CRh}} = 69$, $J_{\text{CP}} = 16 \text{ Hz}$) indicate two equivalent *trans* phosphines and a *cis* carbonyl group bound to rhodium. This formulation is confirmed by the result of an X-ray structure determination[§] (Fig. 2). A single N-bound pyrazolyl ring, *trans* to the carbonyl, completes the coordination sphere of the rhodium in a slightly distorted square-planar geometry. Distances and angles within the square-plane are in the classical range. A potential axial site is occupied by the X-ray located B-bound hydrogen leading to a somewhat loose agostic B-($\mu\text{-H}$)-Rh system. The $\text{Rh}(1)\cdots\text{H}(1)$ distance of 2.35(3) Å seems long as compared to a typical $\text{Rh}(\text{I})\text{-H}$ bond length of ca. 1.55 Å.⁸ Also, the low frequency shift of $\nu(\text{BH})$ to 2350 cm^{-1}

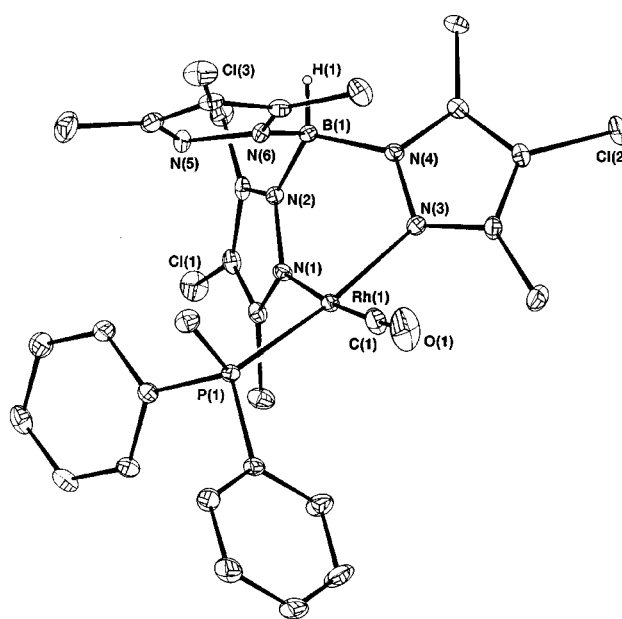


Fig. 1 Plot of the molecular structure of $[\text{Rh}(\text{CO})(\text{PMePh}_2)_2(\text{Tp}^{\text{Me}_2,4\text{-Cl}})]$ **2a** (30% probability ellipsoids). Relevant bond distances (Å) and angles ($^\circ$): $\text{Rh}(1)\text{-P}(2)$ 2.2529(5), $\text{Rh}(1)\text{-N}(1)$ 2.092(2), $\text{Rh}(1)\text{-N}(3)$ 2.092(2), $\text{Rh}(1)\cdots\text{N}(5)$ 3.800(2), $\text{Rh}(1)\text{-C}(1)$ 1.809(2); $\text{N}(1)\text{-Rh}(1)\text{-C}(1)$ 174.80(9), $\text{N}(3)\text{-Rh}(1)\text{-P}(2)$ 172.30(6), $\text{N}(1)\text{-Rh}(1)\text{-N}(3)$ 82.58(7).

(vbr, w) is modest as compared to a $\nu(\text{BH})$ of 2477 cm^{-1} (sharp, m) in **2a**. Thus the agostic interaction could be driven by steric interactions between the unbound pyrazolyl rings and the phenyl groups on phosphorus.⁹ Indeed, the most peculiar feature of the crystal structure is the presence of two unbound pyrazolyl rings. To our knowledge there is no example of such a bonding mode for a hydridotris(pyrazolyl)borato ligand. The κ^3N,N',H bonding mode (*i.e.* one pendant pyrazolyl ring) has been observed in $[\text{RuH}(\text{COD})\text{Tp}^{\text{i-Pr}_2}]$ ⁵ and $[\text{RuMe}(\text{Tp}^{\text{Me}_2})\text{-}(\text{COD})]$.¹⁰ Also the dihydridobis(3,5-trifluoromethylpyrazolyl)borato ($\text{Bp}^{\text{CF}_3\text{2}}$) is κ^3N,N',H in $[\text{RuH}(\text{COD})(\text{Bp}^{\text{CF}_3\text{2}})]$ ($\text{Ru}\text{-H}$ 1.43(3) Å, $\text{Ru}\cdots\text{H}$ 1.97 Å) and $[\text{RuH}(\text{PPh}_3)_2(\text{Bp}^{\text{CF}_3\text{2}})]$, a somewhat classical bonding situation in Bp' chemistry.¹¹ The bonding mode is κ^2N,H in $[\text{RuH}(\text{H}_2)(\text{Bp}^{\text{CF}_3\text{2}})(\text{PCy}_3)_2]$ [$\nu(\text{BH}) = 2514, 2149, 2007 \text{ cm}^{-1}$], the change being attributed to the different cone angle of the phosphines.¹¹

Inter- and intra-molecular dynamic processes are observed in solution. First, **3a** partially dissociates into **2a** and free phosphine (**3a/2a** \approx 4 at 293 K). ^{31}P NMR shows characteristic broadening of the signals of the three species above room temperature, and **2a** is converted into **3a** upon addition of excess PMe_2Ph . Complex **3a** is also highly fluxional. In $[\text{D}_8\text{-}]\text{toluene}$, the ^{31}P NMR doublet broadens below 233 K to ultimately give a doublet of doublets (193 K, δ 22.5, 33.2, $^1J_{\text{RhP}} = 125$, $^2J_{\text{PP}} = 320 \text{ Hz}$). In the ^1H NMR spectrum at 183 K, five

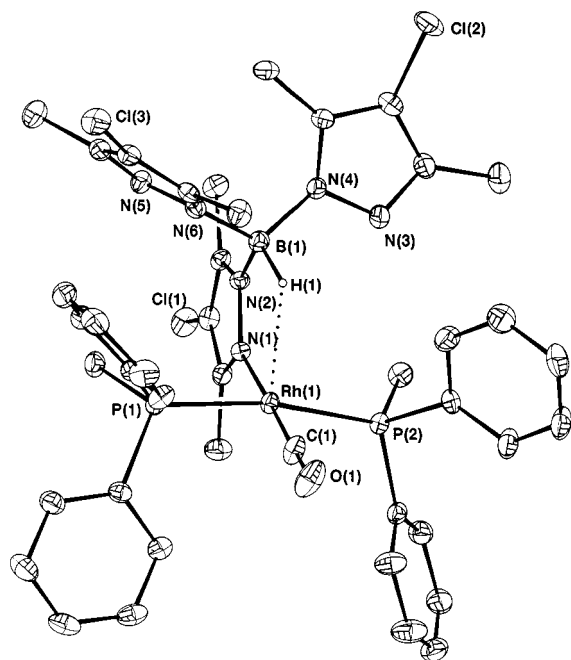


Fig. 2 Plot of the molecular structure of $[\text{Rh}(\text{CO})(\text{PMePh}_2)_2(\text{Tp}^{\text{Me}_2,4\text{-Cl}})]$ **3a** (30% probability ellipsoids). Relevant bond distances (Å) and angles ($^\circ$): Rh(1)–P(1) 2.3273(8), Rh(1)–P(2) 2.3317(8), Rh(1)–N(1) 2.105(3), Rh(1)–C(1) 1.802(2), Rh(1)···H(1) 2.35(3); N(1)–Rh(1)–C(1) 178.0(2), P(1)–Rh(1)–P(2) 167.54(3), P(1)–Rh(1)–N(1) 89.97(7), P(2)–Rh(1)–N(1) 90.21(7), Rh(1)–H(1)–B(1) 126(2).

pyrazole methyl signals out of six are well resolved. Between 213 and 273 K, four peaks in a 1:1:2:2 ratio for the pyrazolyl methyls together with an unresolved multiplet for the phosphine methyls are observed which now accounts for a symmetry plane on the NMR time scale. When the temperature is further raised, pyrazolyl methyl signals broaden and merge, first within each set of 1:2 peaks to give two very broad peaks, then altogether. The signal of the hydrogen bound to boron remains large in the δ 5 region, except below 233 K where it vanishes into the base line, questioning the presence of a strong agostic interaction in solution.^{5,10,11} These observations are consistent with a low temperature asymmetric structure akin to that observed in the solid state. In the intermediate temperature range, exchange of the unbound pyrazolyl rings occurs *via* rotation about the B–N bonds. This includes rotation about B(1)–N(2) and opening of the B–(μ -H)–Rh interaction. At higher temperatures, we cannot as yet differentiate unambiguously mechanisms in which the three pyrazolyl rings interconvert *intramolecularly* in **3a** or *intermolecularly* *via* the equilibrium with **2a** and free phosphine.

Finally the ease with which **3a** is formed from **1a** and PMePh_2 is striking. We have observed that, under comparable conditions, neither **1b** nor **2b** reacts with PMePh_2 to give putative $[\text{Rh}(\text{CO})(\text{PMePh}_2)_2(\text{Tp}^{\text{Me}_2})]$. Pyrazolylborates $\text{Tp}^{\text{Me}_2,4\text{-Cl}}$ and Tp^{Me_2} have similar steric requirements but markedly differ in their electron withdrawing properties.¹² Thus although steric effects are undoubtedly responsible for the observed structure of **3a**, the reduced electron density at the rhodium allows the reaction to occur in the case of **1a** only.

Notes and references

† Crystal data for **2a**: $\text{C}_{29}\text{H}_{32}\text{BCl}_3\text{N}_6\text{OPRh}$, $M = 731.7$, triclinic, $P\bar{1}$, $a = 9.026(1)$, $b = 10.434(2)$, $c = 17.290(2)$ Å, $\alpha = 88.91(2)$, $\beta = 85.96(2)$, $\gamma = 77.91(2)^\circ$, $U = 1556.8(3)$ Å³, $Z = 2$, $\mu = 8.657$ cm⁻¹, $T = 180(2)$ K, reflections collected/unique/used: 15694/5810 ($R_{\text{int}} = 0.0338$)/4794 [$I > 2\sigma(I)$], 384 parameters, R/R_w 0.0237/0.0273.

‡ Preparation of **3a**. Addition of PMePh_2 (0.335 ml, 1.82 mmol) to a cooled (273 K) pentane solution (30 ml) of $[\text{Rh}(\text{CO})_2(\kappa^3\text{-Tp}^{\text{Me}_2,4\text{-Cl}})]$ (0.505 g, 0.90 mmol) yielded an orange precipitate. Recrystallisation from pure pentane at 273 K afforded orange crystals of the product (0.55 g, 68 mmol, 76%) (Found: C, 53.9; H, 5.0; N, 8.9. $\text{C}_{42}\text{H}_{45}\text{BCl}_3\text{N}_6\text{OP}_2\text{Rh}$ requires C, 54.1; H, 4.9; N, 9.0%). IR (KBr): $\nu(\text{CO})$ 1979, $\nu(\text{BH})$ 2442–2405 (vbr) cm⁻¹. NMR (233 K, 400 MHz for ¹H, except phenyl resonances, all s unless specified). ¹H ($[\text{P}^2\text{H}]_8$ -toluene): δ 2.63 (6 H, $\text{C}_3\text{N}_2\text{ClMe}_2$), 2.55 (3 H, $\text{C}_3\text{N}_2\text{ClMe}_2$), 2.24 (3 H, $\text{C}_3\text{N}_2\text{ClMe}_2$), 2.13 (6 H, $\text{C}_3\text{N}_2\text{ClMe}_2$), 1.84 (6 H, PPh_2Me). ³¹P-¹H ($[\text{P}^2\text{H}]_8$ -toluene): δ 23.7 (d, J_{RhP} 125 Hz). ¹³C-¹H (CD_2Cl_2): δ 190.6 (dt, RhCO , J_{CRh} 69, J_{CP} 16 Hz), 144.4, 143.9, 143.0, 139.6 ($\text{CN}_2\text{ClCMe}_2$), 107.9, 106.4 ($\text{C}_3\text{N}_2\text{Me}_2\text{CCl}$), 11.3 (t, MeP , J_{PC} 14 Hz), 12.6, 11.0, 9.8, 8.5 ($\text{C}_3\text{N}_2\text{ClMe}_2$). ¹⁰³Rh-¹H (CD_2Cl_2): δ 344.3 (d, J_{RhP} 125 Hz).

§ Crystal data for **3a**: $\text{C}_{42}\text{H}_{45}\text{BCl}_3\text{N}_6\text{OP}_2\text{Rh}$, $M = 931.88$, triclinic, $P\bar{1}$, $a = 11.164(2)$, $b = 12.006(2)$, $c = 17.097(3)$ Å, $\alpha = 101.07(2)$, $\beta = 102.28(2)$, $\gamma = 92.46(2)^\circ$, $U = 2189.1(6)$ Å³, $Z = 2$, $\mu = 6.785$ cm⁻¹, $T = 180(2)$ K, reflections collected/unique/used: 17587/6532 ($R_{\text{int}} = 0.049$)/5120 [$I > 2\sigma(I)$], 510 parameters, R/R_w 0.0407/0.0425. CCDC reference number 186/1279. See <http://www.rsc.org/suppdata/dt/1999/271/> for crystallographic files in .cif format.

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