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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 ($Tp^{Me2,4-Cl}$) ligand is observed in $[Rh(CO)(PMePh_2)_2(Tp^{Me2,4-Cl})]$; the complex, which features two dangling pyrazole rings and a B–(μ-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 $[Rh(CO)(PPh_3)(\kappa^2N,N'\text{-}Tp^{Me2})]$ yields a pentacoordinated κ^3N,N',N'' rhodium(II) complex $[Rh(CO)(PPh_3)(\kappa^3N,N',N''\text{-}Tp^{Me2})]^+$.[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 $[RuH(PPh_3)_2(\kappa^2N,N'\text{-}Tp)]$ which affords $[RuH(PPh_3)(\kappa^3N,N',N''\text{-}Tp)]$.[4] Isomerization from a κ^2N,N' to a κ^3N,N',H situation has been recently observed in $[RuH(COD)Tp^{i\text{-}Pr2}]$ (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 $[Rh(CO)(PMePh_2)_2(Tp^{Me2,4-Cl})]$. *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* (μ_3-$1\kappa^1N$:$2\kappa^1N'$:$3\kappa^1N''$) Tp′ has been reported in a trinuclear silver complex.[6]

Treatment of $[Rh(CO)_2(Tp^{Me2,4-Cl})]$ **1a** with one equivalent of $PMePh_2$ leads to $[Rh(CO)(PMePh_2)(\kappa^2N,N'\text{-}Tp^{Me2,4-Cl})]$ **2a** [ν(CO) = 1996 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 κ^2N,N'-Tp^{Me2} $[Rh(CO)(L)(Tp^{Me2})]$ (L = PMe_3,[2c] PPh_3,[3] $PMePh_2$ **2b**[7]).

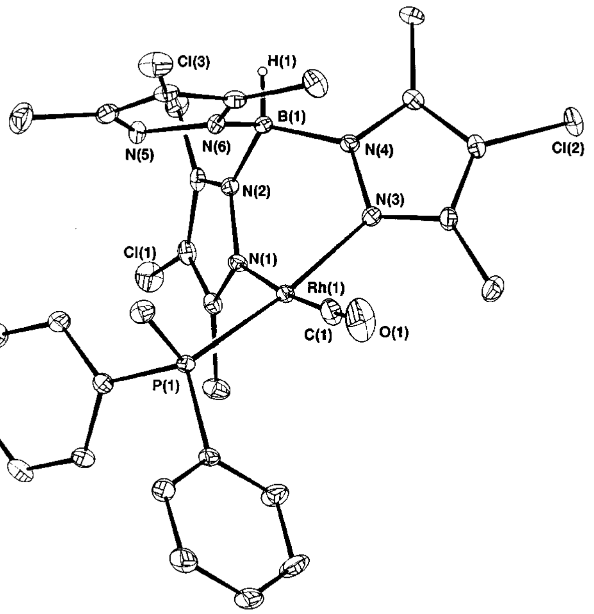

Fig. 1 Plot of the molecular structure of $[Rh(CO)(PMePh_2)(Tp^{Me2,4-Cl})]$ **2a** (30% probability ellipsoids). Relevant bond distances (Å) and angles (°): Rh(1)–P(2) 2.2529(5), Rh(1)–N(1) 2.092(2), Rh(1)–N(3) 2.092(2), Rh(1)···N(5) 3.800(2), Rh(1)–C(1) 1.809(2); N(1)–Rh(1)–C(1) 174.80(9), N(3)–Rh(1)–P(2) 172.30(6), N(1)–Rh(1)–N(3) 82.58(7).

A clean reaction converts **1a** and excess $PMePh_2$ into $[Rh(CO)(PMePh_2)_2(Tp^{Me2,4-Cl})]$ **3a**‡ [ν(CO) = 1979 cm^{-1}] at 273 K. At 233 K, a single ^{31}P-{^{1}H} NMR doublet [δ 23.7 (d, J_{PRh} = 125 Hz)] and a single ^{13}C-{^{1}H} NMR doublet of triplets (δ 190.6, J_{CRh} = 69, J_{CP} = 16 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–(μ-H)–Rh system. The Rh(1)···H(1) distance of 2.35(3) Å seems long as compared to a typical Rh(I)–H bond length of *ca.* 1.55 Å.[8] Also, the low frequency shift of ν(BH) to 2350 cm^{-1} (vbr, w) is modest as compared to a ν(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 $[RuH(COD)Tp^{i\text{-}Pr2}]$[5] and $[RuMe(Tp^{Me2})(COD)]$.[10] Also the dihydridobis(3,5-trifluoromethylpyrazolyl)borato ($Bp^{(CF3)2}$) is κ^3N,N',H in $[RuH(COD)(Bp^{(CF3)2})]$ (Ru–H 1.43(3) Å, Ru···H 1.97 Å) and $[RuH(PPh_3)_2(Bp^{(CF3)2})]$, a somewhat classical bonding situation in Bp′ chemistry.[11] The bonding mode is κ^2N,H in $[RuH(H_2)(Bp^{(CF3)2})(PCy_3)_2]$ [ν(BH) = 2514, 2149, 2007 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** ≈ 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 $[^2H]_8$-toluene, the ^{31}P NMR doublet broadens below 233 K to ultimately give a doublet of doublets (193 K, δ 22.5, 33.2, $^1J_{RhP}$ = 125, $^2J_{PP}$ = 320 Hz). In the ^{1}H NMR spectrum at 183 K, five

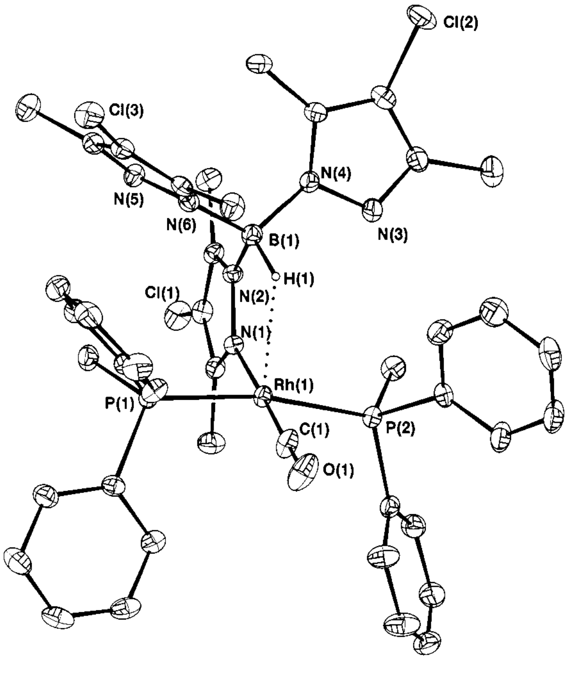

Fig. 2 Plot of the molecular structure of $[\mathrm{Rh(CO)(PMePh_2)_2(Tp^{Me2,4\text{-}Cl})}]$ **3a** (30% probability ellipsoids). Relevant bond distances (Å) and angles (°): Rh(1)–P(1) 2.3273(8), Rh(1)–P(2) 2.3317(8), Rh(1)–N(1) 2.105(3), Rh(1)–C(1) 1.802(2), Rh(1)···H(1) 2.35(3); N(1)–Rh(1)–C(1) 178.0(2), 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 *intra*molecularly in **3a** or *inter*molecularly *via* the equilibrium with **2a** and free phosphine.

Finally the ease with which **3a** is formed from **1a** and $\mathrm{PMePh_2}$ is striking. We have observed that, under comparable conditions, neither **1b** nor **2b** reacts with $\mathrm{PMePh_2}$ to give putative $[\mathrm{Rh(CO)(PMePh_2)_2(Tp^{Me2})}]$. Pyrazolylborates $\mathrm{Tp^{Me2,4\text{-}Cl}}$ and $\mathrm{Tp^{Me2}}$ 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**: $\mathrm{C_{29}H_{32}BCl_3N_6OPRh}$, $M = 731.7$, triclinic, $P\bar{1}$, $a = 9.026(1)$, $b = 10.434(2)$, $c = 17.290(2)$ Å, $\alpha = 88.91(2)$, $\beta = 85.96(2)$, $\gamma = 77.91(2)°$, $U = 1556.8(3)$ Å^3, $Z = 2$, $\mu = 8.657$ cm^{-1}, $T = 180(2)$ K, reflections collected/unique/used: 15694/5810 ($R_{\mathrm{int}} = 0.0338$)/4794 [$I > 2\sigma(I)$], 384 parameters, R/R_{w} 0.0237/0.0273.

‡ Preparation of **3a**. Addition of $\mathrm{PMePh_2}$ (0.335 ml, 1.82 mmol) to a cooled (273 K) pentane solution (30 ml) of $[\mathrm{Rh(CO)_2(\kappa^3\text{-}Tp^{Me2,4\text{-}Cl})}]$ (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. $\mathrm{C_{42}H_{45}BCl_3N_6OP_2Rh}$ requires C, 54.1; H, 4.9; N, 9.0%). IR (KBr): ν(CO) 1979, ν(BH) 2442–2405 (vbr) cm^{-1}. NMR (233 K, 400 MHz for ^{1}H, except phenyl resonances, all s unless specified). ^{1}H ([^{2}H]$_8$-toluene): δ 2.63 (6 H, $\mathrm{C_3N_2Cl}Me_2$), 2.55 (3 H, $\mathrm{C_3N_2Cl}Me_2$), 2.24 (3 H, $\mathrm{C_3N_2Cl}Me_2$), 2.13 (6 H, $\mathrm{C_3N_2Cl}Me_2$), 1.84 (6 H, $\mathrm{PPh_2}Me$). ^{31}P-{^{1}H} ([^{2}H]$_8$-toluene): δ 23.7 (d, J_{RhP} 125 Hz). ^{13}C-{^{1}H} ($\mathrm{CD_2Cl_2}$): δ 190.6 (dt, Rh*C*O, J_{CRh} 69, J_{CP} 16 Hz), 144.4, 143.9, 143.0, 139.6 ($\mathrm{CN_2Cl}C_2\mathrm{Me_2}$), 107.9, 106.4 ($\mathrm{C_2N_2Me_2}C\mathrm{Cl}$), 11.3 (t, *Me*P, J_{PC} 14 Hz), 12.6, 11.0, 9.8, 8.5 ($\mathrm{C_3N_2Cl}Me_2$). ^{103}Rh-{^{1}H} ($\mathrm{CD_2Cl_2}$): δ 344.3 (d, J_{RhP} 125 Hz).

§ Crystal data for **3a**: $\mathrm{C_{42}H_{45}BCl_3N_6OP_2Rh}$, $M = 931.88$, triclinic, $P\bar{1}$, $a = 11.164(2)$, $b = 12.006(2)$, $c = 17.097(3)$ Å, $\alpha = 101.07(2)$, $\beta = 102.28(2)$, $\gamma = 92.46(2)°$, $U = 2189.1(6)$ Å^3, $Z = 2$, $\mu = 6.785$ cm^{-1}, $T = 180(2)$ K, reflections collected/unique/used: 17587/6532 ($R_{\mathrm{int}} = 0.049$)/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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