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Retention of $Pt\rightarrow B$ Bonding in Oxidative Addition Reactions of the Platinaboratrane $[Pt(PPh_3)\{B(mt)_3\}](Pt\rightarrow B)^{10}$ (mt = Methimazolyl)

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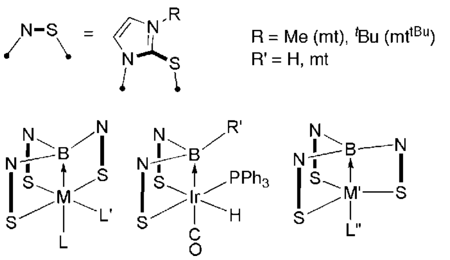
Summary: The platinaboratrane $[Pt(PPh_3)\{B(mt)_3\}](Pt\rightarrow B)^{10}$ *(mt = methimazolyl) is prone to oxidative addition reactions with a range of substrates* (Cl_2, Br_2, I_2, HCl, CH_3I) *without disrupting the platinum−boron dative bond, as illustrated by the first structurally characterized platinaboratranes* $[PtH(PPh_3)\{B(mt)_3\}]Cl(Pt\rightarrow B)^8$ *and* $[PtI_2\{B(mt)_3\}](Pt\rightarrow B)^8$.

The field of metallaboratrane chemistry[1] has grown rapidly in recent years, such that examples have now been isolated for all the metals of groups 8–10 (Chart 1).[2–8]

The unique feature of a metallaboratrane is the inclusion of a metal−boron dative bond[9–11] within a cage structure. Examples of such compounds have been structurally authenticated for each of these metals, with the exception of platinum, although spectroscopic data (^{195}Pt and ^{11}B NMR) reliably attest to the presence of a direct $Pt\rightarrow B$ interaction.[2i] With this wealth of examples, it is noteworthy that very little is actually known about the reactivity of the $M\rightarrow B$ bond. Coligand substitutions have been reported for the rhodaboratrane $[RhCl(PPh_3)\{B(mt)_3\}]$,[2h] while the putative thiocarbonyl derivative $[RhH(CS)(PPh_3)\{BH(mt)_2\}]$ evolves spontaneously into the unusual CS-insertion product $[RhH(PPh_3)\{SC(PPh_3)BH(mt)_2\}]$.[2j] Parkin's ferraboratrane $[Fe(CO)_2\{B(mt^{tBu})_3\}]$ reacts with chlorinated solvents to cleave the $Fe\rightarrow B$ bond with formation of the complex $[FeCl\{ClB(mt^{tBu})_3\}]$, while $[Fe(O_2CPh)\{PhCO_2B(mt^{tBu})_3\}]$ is similarly obtained with benzoyl peroxide,[5b] both reactions presumably proceeding via radical pathways.

Chart 1. Metallaboratranes and Related Compounds[1–8 a]



[a] MLL′ = Ru(CO)(PPh_3), Ru(CO)(CNR), Ru(CS)(PPh_3), Os(CO)(PPh_3), $Fe(CO)_2$, RhCl(PPh_3), $Rh(cod)^+$, $Rh(PMe_3)_2{}^+$, $Rh(S_2CNEt_2)$, RhH(PPh_3), Rh(PPh_3)(CNR), $PtH(PR'_3)^+$; M′L″ = Pt(PPh_3), NiCl, Pd(PMe_3), $Co(PPh_3)^+$ (R = ᵗBu, $C_6H_3Me_2$-2-6, $C_6H_2Me_3$-2,4,6; R′ = Ph, Me, Et).

The platinaboratrane $[Pt(PPh_3)\{B(mt)_3\}](Pt\rightarrow B)^{10}$ (**1**)[2i] has the metal *formally* in the zero oxidation state,[12] and accordingly, the electron-rich metal center might be expected to undergo oxidative addition reactions, assuming it is not deactivated by the presence of the $Pt\rightarrow B$ bond. We report herein (i) a range of

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(1) We have coined the term metallaboratrane to refer to a cage structure in which there is a transannular metal−boron dative bond. The majority of such compounds involve three supporting heterocyclic bridges; however, for those in which the $M\rightarrow B$ bond is only supported by two bridges, the "atrane" terminology is perhaps less appropriate: Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J *Angew. Chem., Int. Ed.* **1999**, *38*, 2759.

(2) (a) Hill, A. F. *Organometallics* **2006**, *25*, 4741. (b) Foreman, M. R. St.-J.; Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 4446. (c) Foreman, M. R. St.-J.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Organometallics* **2004**, *23*, 913. (d) Crossley, I. R.; Foreman, M. R. St.-J.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2005**, 221. (e) Crossley, I. R.; Hill, A. F.; Humphrey, E. R.; Willis, A. C. *Organometallics* **2005**, *24*, 4083. (f) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2006**, *25*, 289. (g) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2005**, *24*, 1062. (h) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2006**, *25*, 289. (i) Crossley, I. R.; Hill, A. F. *Organometallics* **2004**, *23*, 5656. (j) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2007**, *26*, 3891.

(3) Mihalcik, D. J.; White, J. L.; Tanski, J. M.; Zakharov, L. N.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L.; Rabinovich, D. *Dalton Trans.* **2004**, 1626.

(4) Senda, S.; Ohki, Y.; Yasuhiro, H.; Tomoko, T.; Toda, D.; Chen, J.-L.; Matsumoto, T.; Kawaguchi, H.; Tatsumi, K. *Inorg. Chem.* **2006**, *45*, 9914.

(5) (a) Landry, V.; Melnick, J. G.; Buccella, D.; Pang, K.; Ulichny, J. C.; Parkin, G. *Inorg. Chem.* **2006**, *45*, 2588. (b) Figueroa, J. S.; Melnick, J. G.; Parkin, G. *Inorg. Chem.* **2006**, *45*, 7056. (c) Pang, K.; Quan, S. M.; Parkin, G. *Chem. Commun.* **2006**, 5015.

(6) Blagg, R. J.; Charmant, J. P. H.; Connelly, N. G.; Haddow, M. F.; Orpen, A. G. *Chem. Commun.* **2006**, 2350.

(7) (a) Bontemps, S.; Gornitzka, H.; Bouhadir, G.; Miqueu, K.; Bourissou, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1611. (b) Bontemps, S.; Bouhadir, G.; Miqueu, K.; Bourissou, D. J. *Am. Chem. Soc.* **2006**, *128*, 12056. (c) Bebbington, M. W. P.; Bouhadir, G.; Bourissou, D. *Eur. J. Org. Chem.* **2007**, 4483. (d) Vergnaud, J.; Ayed, T.; Hussein, K.; Vendier, L.; Grellier, M.; Bouhadir, G.; Barthelat, J.-C.; Sabo-Etienne, S.; Bourissou, D. *Dalton Trans.* **2007**, 2370.

(8) (a) Bontemps, S.; Sircoglou, M.; Bouhadir, G.; Puschmann, H.; Howard, J. A. K.; Dyer, P. W.; Miqueu, K.; Bourissou, D. *Chem. Eur. J.* doi: 10.1002/chem.200701027. (b) Sircoglou, M.; Bontemps, S.; Mercy, M.; Saffon, N.; Takahashi, M.; Bouhadir, G.; Maron, L.; Bourissou, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 8583.

(9) Many early examples of compounds formulated as having metal−boron dative bonds[10] have subsequently been called into question.[11] In any event, the only structurally characterized examples of $M\rightarrow B$ dative bonding remain within the metallaboratrane class of complexes and those involving chelated β-phosphinoboranes developed by Bourissou.[7,8]

(10) Gilbert, K. B.; Boocock, S. K.; Shore, S. G. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 6, pp 880–886.

(11) (a) Braunschweig, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1786. (b) Braunschweig, H.; Kollann, C.; Rais, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 5254.

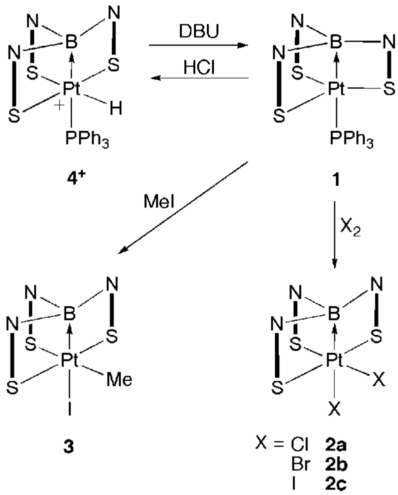
(12) Boron is more electropositive than the six platinum group metals. Accordingly, in deriving *hypothetical* oxidation states the bonding pair of electrons is *axiomatically* assigned to the more electronegative element (the metal). The *valency* of platinum in **1** has been variously defined as zero[2i] or two,[5a,c] depending on one's perspective as to the extent of electron pair transfer from platinum to boron. Because five M−L bonds are required and only four electron pairs are provided by the ligands, it may be argued that the metal center is depleted by two electrons and is hence divalent. We recommend that in discussing such matters the notation $(M\rightarrow B)^n$ follow line formulae wherein "*n*" refers to the total number of d electrons including the pair involved in dative bonding to boron.[2a] See also: Parkin, G. *Organometallics* **2006**, *25*, 4744 and ref 8.

10.1021/om700835h CCC: $40.75

such reactions that leave the Pt→B bond intact despite oxidation of the metal center and (ii) the first structural data for platinaboratranes.

Treating **1** with Cl_2, Br_2, or I_2 results in clean formation of phosphine-free products formulated as the platinaboratranes $[PtX_2\{B(mt)_3\}](Pt{\rightarrow}B)^{8}$ (X = Cl (**2a**), Br (**2b**), I (**2c**); Scheme 1) on the basis of spectroscopic data[13] and, in the case of **2c**, a crystallographic study,[13d] the results of which are summarized in Figure 1.

Scheme 1. Oxidative Addition Reactions of the Platinaboratrane [Pt(PPh$_3$){B(mt)$_3$}] (1)



Spectroscopic data for **2** conform to precedent for other metallaboratranes[1,2] and are generally unremarkable, with the exception of NMR data that specifically reflect the Pt→B dative bonding. Thus, the ^{11}B NMR spectra for the series (**2a**, 0.44 ppm; **2b**, 2.07 ppm; **2c**, 5.05 ppm) show a gradual shift in δ_B to higher frequency, while the values of $^{1}J_{PtB}$ (**2a**, 359 Hz; **2b**, 364 Hz; **2c**, 362 Hz) are essentially invariant. In each case the ^{195}Pt resonance appears as a 1:1:1:1 quartet due to coupling to boron, the chemical shifts reflecting a progressively more shielded platinum center (**2a**, –2815 ppm; **2b**, –3183 ppm; **2c**, –3860 ppm; cf. $\delta_{Pt}(K_2PtCl_6)$ 0). Despite the geometric constraints of the cage structure, angles at platinum are close to octahedral, with cis-interligand angles spanning the range 86.42(13)−96.22(3)° and with all those involving boron being slightly acute. Suitable structural data against which to compare the Pt1−B1 bond (2.119(4) Å) are rare. Those for bonds between platinum and four-coordinate boron are limited to the plethora of data for metallapolyborane and metallacarbaborane clusters with delocalized multicenter bonding, such that direct

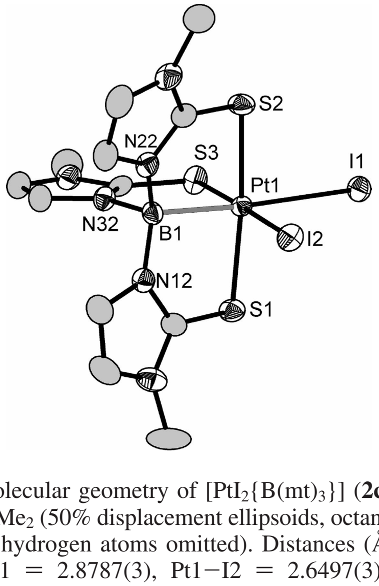


Figure 1. Molecular geometry of [PtI$_2${B(mt)$_3$}] (**2c**) in a crystal of **2c**·0.5OCMe$_2$ (50% displacement ellipsoids, octant hatching for heteroatoms, hydrogen atoms omitted). Distances (Å) and angles (deg): Pt1−I1 = 2.8787(3), Pt1−I2 = 2.6497(3), Pt1−S1 = 2.344(1), Pt1−S2 = 2.343(1), Pt1−S3 = 2.358(1), Pt1−B1 = 2.119(4); I1−Pt1−I2 = 93.89(1), I1−Pt1−S1 = 96.22(3), I2−Pt1−S1 = 88.50(3), I1−Pt1−S2 = 91.08(3), I2−Pt1−S2 = 87.84(3), I1−Pt1−S3 = 87.80(3), S1−Pt1−S3 = 90.40(4), S2−Pt1−S3 = 93.05(4), I2−Pt1−B1 = 89.69(13), S1−Pt1−B1 = 86.42(13), S2−Pt1−B1 = 86.50(13), S3−Pt1−B1 = 88.66(13), N32−B1−N12 = 107.8(3), N32−B1−N22 = 109.1(3), N12−B1−N22 = 115.9(3), N32−B1−Pt1 = 108.4(3), N12−B1−Pt1 = 107.4(3), N22−B1−Pt1 = 108.0(3).

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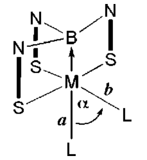
(13) (a) **2a**: [Pt(PPh$_3$){B(mt)$_3$}] (**1**; 0.100 g, 0.124 mmol) in CH_2Cl_2 (20 mL) was treated with gaseous chlorine (11 mL in three doses, ca. 5 mmol) and stirred for 1 h, after which time the orange supernatant was cannulated from the pale yellow precipitate, which was dried in vacuo. Yield: 0.040 g (53%). A further crop was obtained by concentrating and cooling the cannulate. NMR (d_6-DMSO, 25°C): ^{1}H, 3.47 (s, 9H, NCH_3), 7.14 (1H), 7.48 (1H), 7.51 (2H), 7.77 (2H) (d × 4, NCHCHN, $^{3}J_{HH} \approx 1.9$ Hz); ^{13}C (HMQC), 33.5 (NCH_3), 116.4 (1C), 117.2 (2C), 125.0 (2C), 126.8 (1C) (NCHCHN), 158.1 (1C), 160.8 (2C) (CS); $^{11}B\{^{1}H\}$, δ_B 0.44 ($^{1}J_{PtB} = 359$ Hz); ^{195}Pt, δ_{Pt}–2815. MS-ESI$^+$: *m/z* 580.3 $[M - Cl]^+$. HR-MS: *m/z* found (calcd) 614.9553 (614.9639) $[M]^+$. Anal. Found: C, 26.07; H, 2.74; N, 11.82; S, 13.50. Calcd for $C_{12}H_{15}BCl_2N_6PtS_3 \cdot CH_2Cl_2$: C, 22.27; H, 2.44; N, 11.98; S, 13.72. The CH_2Cl_2 monosolvate was confirmed by ^{1}H NMR integration. (b) **2b**: [Pt(PPh$_3$){B(mt)$_3$}] (**1**; 0.100 g, 0.124 mmol) in CH_2Cl_2 (20 mL) was treated with a solution of Br_2 in $CHCl_3$ (1.30 mL, 0.098 M) and stirred for 1 h, after which time the orange supernatant was cannulated from the pale yellow precipitate, which was dried in vacuo. Yield: 0.058 g (67%). NMR (d_6-DMSO, 25°C): ^{1}H, 3.46 (3H), 3.47 (9H) (NCH_3), 7.13 (1H), 7.49 (1H), 7.51 (2H), 7.78 (2H) (d × 4, NCHCHN, $^{3}J_{HH} \approx 1.9$ Hz); ^{13}C (HMQC), 33.5 (NCH_3), 116.3 (1C), 117.2 (2C), 125.0 (2C), 127.0 (1C) (NCHCHN), 159.3 (1C), 162.1 (2C) (CS); $^{11}B\{^{1}H\}$, δ_B 2.07 ($^{1}J_{PtB} = 364$ Hz); ^{195}Pt, δ_{Pt}–3813. Anal. Found: C, 20.94; H, 2.40; N, 10.58; S, 12.09. Calcd for $C_{12}H_{15}BBr_2N_6PtS_3 \cdot CH_2Cl_2$: C, 19.76; H, 2.17; N, 10.64; S, 12.18. The CH_2Cl_2 monosolvate was confirmed by ^{1}H NMR integration. (c) **2c**: [Pt(PPh$_3$){B(mt)$_3$}] (**1**; 0.100 g, 0.124 mmol) in CH_2Cl_2 (10 mL) was treated with iodine (0.031 g, 0.122 mmol) and stirred for 3 h, after which time the supernatant was cannulated from the deep orange precipitate, which was dried in vacuo. Yield: 0.080 g (82%). A crystallographic sample was recrystallized from a mixture of DMSO and acetone. NMR (d_6-DMSO, 25°C): ^{1}H, 3.47, 3.48 (9H, NCH_3), 7.10 (1H), 7.50 (1H), 7.58 (2H), 7.81 (2H) (s br × 4, NCHCHN); ^{13}C (HMQC), 33.5 (NCH_3), 115.2 (1C), 116.9 (2C), 125.3 (2C), 127.2 (1C) (NCHCHN), 154.4 (1C), 162.2 (2C) (CS); $^{11}B\{^{1}H\}$, δ_B 5.05 ($^{1}J_{PtB} = 362$ Hz); ^{195}Pt, δ_{Pt}–3860. MS-ESI$^+$: *m/z* 1471 $[M_2 - I]^+$, 821 $[NaM]^+$, 672 $[M - I]^+$. HR-MS: *m/z* found (calcd) 821.8289 (821.8248) $[NaM]^+$, 671.9339 (671.9306) $[M - I]^+$. Anal. Found: C, 19.21; H, 2.16; N, 10.23; S, 11.54. Calcd for $C_{12}H_{15}BI_2N_6PtS_3$: C, 17.66; H, 1.94; N, 10.52; S, 12.03. N.B.: in each case the measured % C was inexplicably but consistently found to be ca. 2% higher than expected, while H, N, and S values were close to those calculated. (d) *Crystal data for* **2c**·0.5OCMe$_2$: $C_{12}H_{15}BI_2N_6PtS_3 \cdot 0.5C_3H_6O$, $M_w = 828.24$, monoclinic, $P2_1/n$, $a = 9.8899(2)$ Å, $b = 20.0454(4)$ Å, $c = 11.3937(2)$ Å, $\beta = 99.562(1)°$, $V = 2227.38(7)$ Å^3, $Z = 4$, $D_{calcd} = 2.470$ Mg m^{-3}, μ(Mo Kα) = 9.368 mm^{-1}, $T = 200(2)$ K, orange needle, 5090 independent reflections, *F* refinement, $R = 0.017$, $R_w = 0.016$ for 3625 reflections ($I > 3\sigma(I)$, $2\theta_{max} = 55°$), 262 parameters, CCDC 657147.

(14) (a) *Conquest, Version 1.7*; Cambridge Crystallographic Data Centre: Cambridge, U.K., November 2006. (b) Curtis, D.; Lesley, M. J. G.; Norman, N. C.; Orpen, A. G.; Starbuck, J. *J. Chem. Soc., Dalton Trans.* **1999**, 1687. (c) Habereder, T.; Noth, H. *Appl. Organomet. Chem.* **2003**, *17*, 525. (d) Kerr, A.; Marder, T. B.; Norman, N. C.; Orpen, A. G.; Quayle, M. J.; Rice, C. R.; Timms, P. L.; Whittell, G. R. *Chem. Commun.* **1998**, 319. (e) Clegg, W.; Johann, T. R. F.; Marder, T. B.; Norman, N. C.; Orpen, A. G.; Peakman, T. M.; Quayle, M. J.; Rice, C. R.; Scott A. J. *J. Chem. Soc., Dalton Trans.* **1998**, 1431. (f) Braunschweig, H.; Lutz, M.; Radacki, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 5647. (g) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F. *Angew. Chem., Int. Ed.* **2006**, *45*, 1066. (h) Lesley, G.; Nguyen, P.; Taylor, N. J.; Marder, T. B.; Scott, A. J.; Clegg, W.; Norman, N. C. *Organometallics* **1996**, *15*, 5137. (i) Clegg, W.; Lawlor, F. J.; Lesley, G.; Marder, T. B.; Norman, N. C.; Orpen, A. G.; Quayle, M. J.; Rice, C. R.; Scott, A. J.; Souza, F. E. S. *J. Organomet. Chem.* **1998**, *550*, 183. (j) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F. *Organometallics* **2004**, *23*, 5545. (k) Lu, N.; Norman, N. C.; Orpen, A. G.; Quayle, M. J.; Timms, P. L.; Whittell, G. R. *Dalton Trans.* **2000**, 4032. (l) Iverson, C. N.; Smith, M. R., III *J. Am. Chem. Soc.* **1995**, *117*, 4403. (m) Ishiyama, T.; Matsuda, N.; Murata, M.; Ozawa, F.; Suzuki, A.; Miyaura, N. *Organometallics* **1996**, *15*, 713. (n) Braunschweig, H.; Lutz, M.; Radacki, K.; Schaumloffel, A.; Seeler, F.; Unkelbach, C. *Organometallics* **2006**, *25*, 4433. N.B.: The semibridging boryl ligands reported in ref 14b might be described as including a significant, albeit weak, Pt→B component to the bonding.

Table 1. Selected Structural Data for Metallaboratranes $[ML_2\{B(mt)_3\}]$



ML_2	α (deg)	*a* (Å)	*b* (Å)	*a/b*
$Fe(CO)_2$[5b]	95.3	1.803	1.717	1.050
$[Rh(PMe_3)_2]^{+}$[2h]	94.6	2.459	2.293	1.072
	94.3	2.471	2.292	1.078
PtI_2	93.9	2.879	2.650	1.086

comparisons are not meaningful. Platinum σ-boryl bonds, i.e. those to three-coordinate boron, span the range 1.964–2.108 Å and, taking into account the decreased coordination number at boron (sp^2 vs sp^3), the Pt→B bond in **2c** would appear to be comparatively short. With both coligands being the same (σ- and π-donor iodides) the structure of **2c** affords an opportunity to assess the trans influence of the M→B dative bond alongside data for the two other metallaboratranes which also have a pair of identical coligands,: viz. the ferraboratrane $[Fe(CO)_2\{B(mt^{tBu})_3\}]$[5b] (CO being a classical π-acid) and the rhodaboratrane $[Rh(PMe_3)_2\{B(mt)_3\}]^+$ (PMe_3 being an essentially pure σ-donor). Table 1 collates selected structural data for these, from which it can be seen that, despite the disparate types of coligands, a substantial trans influence operates in every case. This is greatest for the diiodide **2c** and least for the dicarbonylferraboratrane. It would, however, be overly simplistic to ascribe this entirely to the Pt→B bond. For the ligand trans to boron, the collar of three cis π-basic sulfur donors will exert attractive (CO, π-acidic), negligible (PMe_3, no significant π-interactions), or repulsive (I, π-donor) secondary interligand interactions, thereby clouding the issue.

The reaction of **1** with iodomethane provides the first σ-alkyl metallaboratrane, $[Pt(CH_3)I\{B(mt)_3\}]$ (**3**).[15] The regiochemistry of oxidative addition (Scheme 1) is assumed to result in the cis disposition of Pt→B and Pt−C bonds, given that the $Pt-CH_3$ group gives rise to a sharp singlet resonance in both the ^1H and ^{13}C NMR spectra (δ_H 1.49; HMQC with δ_C 4.4), each resonance being straddled by ^{195}Pt satellites ($^2J_{PtH} = 63.8$ Hz, $^1J_{PtC} = 517$ Hz) with no significant quadrupolar broadening. This is further supported by the regioselective protonation of **1** by ethanolic HCl, which leads to the formation of $[PtH(PPh_3)\{B(mt)_3\}]Cl$ (**4**Cl). It should be recalled that this salt previously provided the initial entry point for platinaboratrane chemistry from the reaction of $[PtCl_2(PPh_3)_2]$ with $Na[HB(mt)_3]$, its formulation being based on spectroscopic data alone.[2i] Given that via this route the hydrido ligand arises from transfer between boron and platinum, it should by necessity occupy a site cis to the boron, a supposition that we have now verified crystallographically[16] for the solvate $\mathbf{4}Cl\cdot 2CH_2Cl_2$ (Figure 2). Spectroscopic data for samples of **4**Cl obtained by either route, B−H activation or protonation of **1**, are identical.

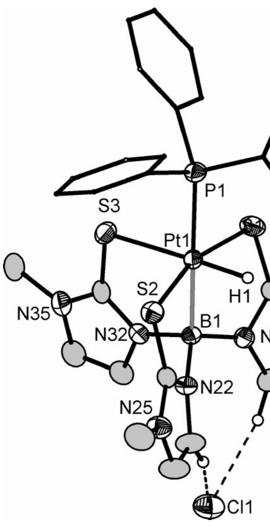


Figure 2. Molecular geometry of $[PtH(PPh_3)\{B(mt)_3\}]Cl$ (**4**Cl) in a crystal of $\mathbf{4}Cl\cdot 2CH_2Cl_2$ (50% displacement ellipsoids, octant hatching for heteroatoms, hydrogen atoms omitted, phenyl groups simplified). Distances (Å) and angles (deg): Pt1−S1 = 2.3481(10), Pt1−S2 = 2.3550(9), Pt1−S3 = 2.4594(9), Pt1−P1 = 2.4626(9), Pt1−B1 = 2.157(4), Pt1−H1 = 1.53(2), S1−C11 = 1.718(4), S2−C21 = 1.728(4), S3−C31 = 1.710(4), N12−B1 = 1.545(5), N32−B1 = 1.560(5), N32−B1 = 1.560(5); S1−Pt1−S3 = 96.25(4), S2−Pt1−S3 = 96.51(3), S1−Pt1−P1 = 94.27(3), S2−Pt1−P1 = 94.94(3), S3−Pt1−P1 = 91.95(3), S1−Pt1−B1 = 85.08(11), S2−Pt1−B1 = 85.73(11), S3−Pt1−B1 = 87.92(10), S1−Pt1−H1 = 83.3(6), S2−Pt1−H1 = 83.6(6), P1−Pt1−H1 = 90.1(6), B1−Pt1−H1 = 90.0(6), Pt1−S1−C11 = 96.62(12), Pt1−S2−C21 = 96.77(12), Pt1−S3−C31 = 94.83(12), N32−B1−N12 = 109.2(3), N32−B1−N22 = 108.4(3), N12−B1−N22 = 113.1(3), N32−B1−Pt1 = 108.0(2), N12−B1−Pt1 = 108.8(2), N22−B1−Pt1 = 109.2(2).

The crystal structure determination confirms the molecular geometry and, in particular, the regiochemistry previously inferred from spectroscopic data.[2i] The platinum adopts pseudo-octahedral geometry, the most significant departures being associated with the (located and positionally refined) hydrido ligand, wherein in contrast to **2c**, the two methimazolyl groups bend toward the sterically unassuming hydride. The unique methimazolyl group in octahedral metallaboratranes typically shows an elongation of the metal−sulfur bond relative to the trans pair,[1,2] and in the case of $\mathbf{4}^+$, this is further enhanced by the typically high trans influence of the hydrido ligand. The Pt1−B1 bond length (2.157(4) Å) is elongated relative to that in **2c**, presumably reflecting the effect of positive charge and the absence of π-donor coligands upon the dative bond. A similar lengthening of the Rh−B bond in $[Rh(PMe_3)_2\{B(mt)_3\}]^+$ vs $[RhCl(PPh_3)\{B(mt)_3\}]$ has been noted.[2h] The chloride counterion is associated weakly with the complex via hydrogen-bonding interactions (C−H···Cl1 = 2.508, 2.618 Å) with two of the methimazolyl groups.

To conclude, in contrast to the facile oxidative cleavage of the Fe→B bond in $[Fe(CO)_2\{B(mt^{tBu})_3\}]$, oxidative addition reactions involving **1** occur without cleavage of the Pt→B bond, as do the protonation of **1** and deprotonation of

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(15) **3**: $[Pt(PPh_3)\{B(mt)_3\}]$ (**1**; 0.100 g, 0.124 mmol) in CH_2Cl_2 (20 mL) was treated with CH_3I (0.020 g, 0.14 mmol) and stirred for 1 h, after which time the solvent was cannulated from the yellow precipitate, which was dried in vacuo. Yield: 0.048 g (56%). NMR (d_6-DMSO, 25 °C): ^1H, δ_H 1.47 (s + d, 3 H, $^2J_{PtH} = 64$ Hz), 3.41 (3H), 3.45 (6H) (s × 2, NCH_3), 6.97 (1H), 7.30 (1H), 7.54 (2H), 7.77 (2 H) (s br × 4, NCHCHN); $^{11}B\{^1H\}$, δ_B 4.28 (s br, hhw = 88 Hz, $^1J_{PtB} = 472$ Hz); ^{195}Pt, δ_{Pt}–3627 (cf. $\delta_{Pt}(K_2PtCl_6)$ 0), $^1J_{PtB} = 470$ Hz). Anal. Found: C, 23.82; H, 2.95; N, 10.65; S, 12.05. Calcd for $C_{13}H_{18}BIN_6S_3Pt\cdot CH_2Cl_2$: C, 21.77; H, 2.61; N, 10.88; S, 12.46. The CH_2Cl_2 monosolvate was confirmed by ^1H NMR integration.

(16) **4**Cl: see ref 2h for spectroscopic data. *Crystal data for* $\mathbf{4}Cl\cdot 2CH_2Cl_2$: $C_{30}H_{31}BClN_6PPtS_3\cdot 2CH_2Cl_2$, $M_w = 1014.01$, triclinic, $P\bar{1}$ (No. 2), $a = 9.7438(2)$ Å, $b = 12.9979(2)$ Å, $c = 17.1896(3)$ Å, $\alpha = 109.9647(9)°$, $\beta = 101.3046(13)°$, $\gamma = 93.5646(11)°$, $V = 1986.73(6)$ Å^3, $Z = 2$, $D_{calcd} = 1.695$ Mg m^{-3}, μ(Mo Kα) = 4.098 mm^{-1}, $T = 200(2)$, yellow block, 9123 independent reflections, *F* refinement, $R = 0.026$, $R_w = 0.028$ for 7119 reflections ($I > 3\sigma(I)$, $\theta_{max} = 55°$), 455 parameters, CCDC 657148.

4$^+$. The electron-rich (relative to the ferraboratrane) platinum center presumably enhances the Pt→B interaction. It should be noted that calculations by Parkin for the complex [Pd(PMe$_3$){B(mt^{tBu})$_3$}] suggest that the HOMO is not the orbital primarily associated with the Pd→B bond but, rather, the degenerate d_{xy}, $d_{x^2-y^2}$ pair, to which it is orthogonal, perhaps explaining why the Pt→B bond in **1** is not compromised by oxidation.

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Supporting Information Available: CIF files giving full details of the crystal structure determinations of **2c**·0.5OCMe$_2$ (CCDC 657147) and **4**Cl·2CH$_2$Cl$_2$ (CCDC 657148). This material is available free of charge via the Internet at http://pubs.acs.org.

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