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Poly(methimazolyl)borate Complexes of Platinum

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Summary: The reaction of iodotrimethylplatinum(IV) with 1 equiv of Na[$HB(mt)_3$] or Na[$H_2B(mt)_2$] (mt = methimazolyl) affords respectively the octahedral organometallic complexes [$PtMe_3\{HB(mt)_3\}$] and [$PtMe_3\{H_2B(mt)_2\}$], the first isolated examples of poly(methimazolyl)borate complexes of platinum, which prove remarkably stable toward the reductive elimination of methane. The latter reacts further with [$PtMe_3I$]$_4$ to afford the novel, sulfur-bridged dinuclear complex [$Me_3Pt\{\mu\text{-}H_2B(mt)_2\}PtMe_3I$].

Since their independent development by Reglinski[1] and Parkin,[2] interest in the coordination chemistry of the poly(methimazolyl)borate ligands $HB(mt)_3$ and $H_2B(mt)_2$ (mt = methimazolyl) has grown apace, such that numerous complexes are now known for metals in low oxidation states (0−2) from groups 6−10.[3] With the exception of the complexes [$MCl_3(\eta\text{-}C_5Me_5)\{\kappa^2\text{-}ClHB(mt)_2\}$] (M = Nb^{V}, Ta^{V}) and [$MCl_2(NC_6H_3iPr_2\text{-}2,6)\{HB(mt)_3\}$],[4] work has exclusively focused on later transition metals in low oxidation states, a situation we suggest may have arisen from a presumed incompatibility of the "soft" methimazolyl donors with metals in higher oxidation states. The consequent dearth of higher-valent complexes has potentially profound implications for the organometallic chemistry of the poly(methimazolyl)borates, in particular the novel B−H activation processes implicated en route to metallaboratranes, the original examples of which, [$M(CO)(PPh_3)\{B(mt)_3\}$] ($M^0\!\rightarrow\!B$, M = Ru **1**,[5] Os **2**,[6] Chart 1), were obtained by reductive elimination of RH from organometallic precursors.

Chart 1. Metallaboratranes

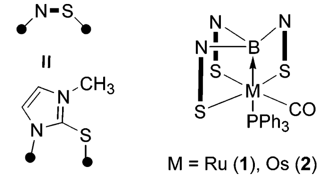
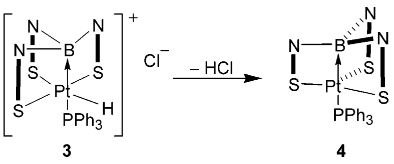


Chart 2. Platinaboratranes



We have subsequently shown that these novel cage compounds are accessible for metal centers in positive oxidation states (i.e., Rh(I),[7] Ir(I),[8] Pt(II)[9]) directly from coordinately unsaturated precursors and that, for platinum, the dehydrochlorination of [$Pt^{II}H\{B(mt)_3\}(PPh_3)$]Cl ($M^{II}\!\rightarrow\!B$) (**3**) by exogenous base allows access to the zerovalent d^{10} complex [$Pt^0\{B(mt)_3\}(PPh_3)$] ($M^0\!\rightarrow\!B$) (**4**) (Chart 2). While exploring the chemistry of this molecule we have observed a susceptibility toward oxidative substitution by electrophilic species of the type RX or X_2 (R = alkyl; X = Cl, Br, I), to afford the platinum(II) metallaboratrane complexes [$Pt^{II}(R)X\{B(mt)_3\}$] (**5**) and [$Pt^{II}X_2\{B(mt)_3\}$] (**6**) ($M^{II}\!\rightarrow\!B$).[10] Given the stability of these species, it seemed likely that a dialkylmetallaboratrane, e.g., [$Pt^{II}(Me)_2\{B(mt)_3\}$], would be a viable proposition; a premise we have sought to verify.

Both **5** and **6** are effectively insoluble in solvents that are sufficiently inert for organotransmetalation, and accordingly this avenue was not explored. Rather, an alternative synthetic approach was considered. The reductive elimination of RH from an organoplatinum(IV) complex of $HB(mt)_3$ presented an obvious possibility. We reasoned that Pope's archetypal platinum(IV) organyl [$PtMe_3I$]$_4$[11] should be ideally suited to this role, since the discrete $HB(mt)_3$ complex [$PtMe_3\{HB(mt)_3\}$] (**7**) might be expected to readily undergo elimination of methane or, alternatively, ethane.

However, the reaction between [$PtMe_3I$]$_4$ and Na[$HB(mt)_3$] (Scheme 1) in dichloromethane solution, which proceeds slowly over the course of 12 h, surprisingly

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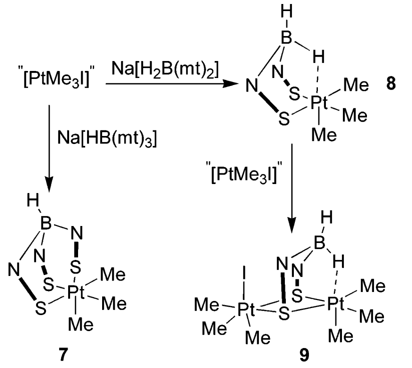
Scheme 1. Formation of Platinum(IV) Poly(methimazolyl)borates



affords exclusively the platinum(IV) hydrotris(methimazolyl)borate complex $[PtMe_3\{HB(mt)_3\}]$ (**7**), which was unequivocally identified on the basis of spectroscopic and analytical data.[12] The ^1H NMR spectrum reveals the presence of a single methimazolyl environment, i.e., one NCH_3 resonance (δ 3.70, 9 H) and two imidazole CH resonances (δ 6.78, 3 H; 6.82, 3 H), which integrate consistently with the single Pt-methyl resonance (δ 0.94, 9 H, $^3J_{PtH}$ 70 Hz), suggesting facially tridentate κ^3-*S,S′,S″* coordination of the $HB(mt)_3$ ligand. This is supported by the ^{195}Pt NMR spectrum, which exhibits a dectet resonance (δ −2780.9), thus confirming a mononuclear species comprising three equivalent methyl groups. Finally, the retention of the terminal B−H functionality is confirmed by the observation of a characteristic stretching mode at 2391 cm^{-1} in the infrared spectrum and the presence of a broad ^1H NMR signal (δ_H 4.63, 1 H, hhw 160 Hz) associated with the boron hydride. This formulation was subsequently confirmed by a single-crystal X-ray diffraction study (vide infra), the results of which are illustrated in Figure 1.[13]

Complex **7** exhibits remarkable stability and is reluctant to undergo isomerization to the κ^3-*S,S′,H* chelation mode, a prerequisite of B−H activation. Indeed, **7** is quantitatively recovered, unaltered, after prolonged (>24 h) reflux in toluene, conditions under which one might anticipate the onset of decomposition. Moreover, attempts to bypass the formation of **7**, by conducting the reaction of $[PtMe_3I]_4$ and $Na[HB(mt)_3]$ under prolonged reflux, have thus far proven similarly ineffectual.

While we continue to pursue the thermal and chemical activation of **7**, the analogous complex of the dihydrobis(methimazolyl)borate ligand, $H_2B(mt)_2$, presented a possible alternative target, since it should necessarily exhibit the κ^3-*S,S′,H* chelation mode and thus be more prone to B−H activation. The complex $[PtMe_3\{\kappa^3$-*S,S′,H*-$H_2B(mt)_2\}]$ (**8**) was thus prepared in an analogous manner to **7**, and its identity established on the basis of spectroscopic and analytical data.[14] Once again, the ^1H NMR spectrum indicates the presence of a single methimazolyl environment, but now exhibits two unique Pt-methyl resonances [δ_H12 (6 H, $^3J_{PtH}$ 67.7); 1.23 (3 H, $^3J_{PtH}$ 76.6 Hz)]. The 3c-2e B−H−Pt function is apparent from a broad (hhw 120 Hz) multiplet resonance (δ_H −3.2, $^1J_{PtH}$ 330 Hz) and exhibits a characteristic stretching mode in the infrared spectrum (ν = 2229 cm^{-1}), as does the terminal B−H function (ν = 2448 cm^{-1}), the hydride of which resonates at ca. 4 ppm in the ^1H NMR spectrum. The $^{195}Pt\{^1H\}$ NMR spectrum exhibits a single resonance (δ −3037) that is appreciably broadened (hhw 225 Hz) due to the ^2J interaction with the boron quadrupole, an effect that precludes resolution of the theoretical 42-line (A_3B_6X) pattern in the fully coupled spectrum. Selective decoupling of the 3c-2e B−H−Pt proton fails to diminish this broadening effect; thus the 21 lines attributable to coupling with the methyl groups alone (A_3B_6) are also unresolved. However, decoupling of the methyl protons does allow for resolution of the doublet coupling due to the B−H−Pt proton. A similar approach allows the assignment of two couplings observed in the ^{11}B NMR spectrum to the terminal ($^1J_{BH}$ 100 Hz) and B−H−Pt ($^1J_{BH}$ 70 Hz) interactions. It should be noted that this is the first compound for which these data have been unequivocally assigned.

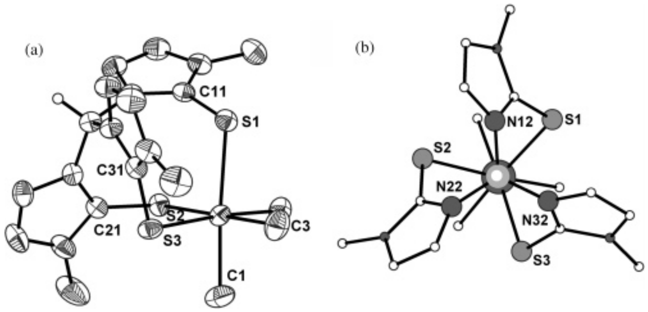


Figure 1. Molecular geometry of $[PtMe)_3\{HB(mt)_3\}]$ (**7**) (a) with carbon-bound hydrogen atoms omitted for clarity (50% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Pt−C(1) = 2.087(3), Pt−C(2) = 2.069(3), Pt−C(3) = 2.081(3), Pt−S(1) = 2.4739(7), Pt−S(2) = 2.4671(7), Pt−S(3) = 2.4644(7), C(1)−Pt−C(2) = 88.1 (2), C(1)−Pt−C(3) = 88.7(2), C(2)−Pt−C(3) = 87.2(2), S(1)−Pt−S(2) = 94.05(2), S(1)−Pt−S(3) = 93.92(2), S(2)−Pt−S(3) = 94.63(2). (b) Projection along the B⋯Pt vector.

While it has not yet proven possible to obtain X-ray quality single crystals of **8** itself, relevant structural data have been fortuitously obtained. It has been found that if the synthesis of either **7** or **8** is halted in advance of 12 h, small, inseparable, quantities of $[PtMe_3I]_4$ remain. While otherwise innocuous to the characteriza-

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(12) Data for **7**. Yield: 70%. IR (KBr): ν_{BH} 2391 cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H (299.945 MHz): δ_H 0.94 (s, J_{PtH} 70.1 Hz, 9 H, Pt−CH_3), 3.70 (s, 9 H, NCH_3), 4.63 (br m, hhw 160 Hz, 1 H, BH), 6.78, 6.82 (d × 2, $^3J_{HH}$ 2.0 Hz, 3 H × 2, NCH═CH). $^{13}C\{^1H\}$ (75.428 MHz): δ_C 0.75 (s, J_{PtC} 656 Hz, CH_3), 35.2 (s, NCH_3), 119.1, 122.7 (s, NCH═CH), 159.2 (s, J_{PtC} 16.7 Hz, CS). $^{11}B\{^1H\}$ (96.232 MHz). δ_B −1.27 (s br, hhw 139 Hz). ^{195}Pt (64.222 MHz): δ_{Pt} −2780.9 (dectet, J_{PtH} 70.1 Hz). Anal. Found: C, 30.09; H, 4.46; N, 12.78. Calcd for $C_{15}H_{25}BN_6PtS_3$: C, 30.46; H, 4.26; N, 14.21.

(13) *Crystal data for* **7**: $[C_{15}H_{25}BN_6PtS_3]$, $M = 591.50$, triclinic, $P\bar{1}$ (No. 2), $a = 9.1188(2)$ Å, $b = 10.0153(1)$ Å, $c = 12.3565(2)$ Å, $\alpha = 84.0944(11)°$, $\beta = 85.3737(9)°$, $\gamma = 82.6657(11)°$, $V = 1110.70(3)$ Å^3, $Z = 2$, $D_c = 1.769$ g cm^{-3}, μ(Mo Kα) = 6.610 mm^{-1}, $T = 200(2)$ K, yellow block, 5075 independent reflections, F refinement, $R_1 = 0.0227$, $wR_2 = 0.0263$ for 4613 independent absorption-corrected reflections [$I > 3\sigma(I)$; $2\theta_{max} = 55°$], 311 parameters, CCDC 271217.

(14) Data for **8**. Yield: 70%. IR (KBr): ν_{BH} 2448, ν_{BHPt} 2229 cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H (299.945 MHz): δ_H −3.2 (br m, J_{PtH} 330 Hz, 1 H, B−H−Pt), 1.12 (s, J_{PtH} 67.7 Hz, 6 H, Pt−$CH_{3(eq)}$), 1.23 (s, J_{PtH} 76.6 Hz, 3 H, Pt−$Me_{3(ax)}$), 3.53 (s, 6 H, NCH_3), 4.07 (br m, hhw 100 Hz, 1 H, BH), 6.64, 6.84 (d × 2, $^3J_{HH}$ 2.0 Hz, 2 H × 2, NCH═CH). $^{13}C\{^1H\}$ (75.428 MHz): δ_C −2.4 (s, J_{PtC} 680 Hz, $CH_{3(ax)}$), 1.3 (s, J_{PtC} 605 Hz, $CH_{3(eq)}$) 34.6 (s, NCH_3), 121.5, 121.8 (s × 2, NCH═CH), 163.1 (s, J_{PtC} 14.0 Hz, CS). ^{11}B (96.232 MHz): δ_B −5.80 (dd, $J_{BH(terminal)}$ 100 Hz, $J_{BH(agostic)}$ 70 Hz). $^{195}Pt\{^1H\}$ (64.222 MHz): δ_{Pt} −3037 (s). Anal. Found: C, 26.90; H, 4.36; N, 10.68. Calcd for $C_{11}H_{21}BN_4PtS_2$: C, 27.56; H, 4.42; N, 11.69.

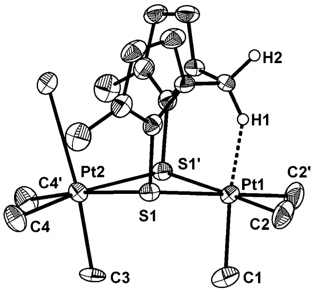

Figure 2. Molecular geometry of [$Me_3Pt\{\mu\text{-}H_2B(mt)_2\}PtMe_3I$] (**9**) with carbon-bound hydrogen atoms omitted for clarity (50% displacement ellipsoids). The molecule possesses a crystallographic mirror plane. Selected bond lengths (Å) and angles (deg): Pt(1)−C(1) = 2.047(8), Pt(1)−C(2) = 2.059(5), Pt(1)−S(1) = 2.468(1), Pt(2)−C(3) = 2.068(6), Pt(2)−C(4) = 2.068(5), Pt(2)−S(1) = 2.539(2), Pt(2)−I(1) = 2.7833(5), S(1)−Pt(1)−S(1′) = 83.41(5), S(1)−Pt(1)−C(1) = 94.5(2), S(1)−Pt(1)−C(2) = 93.7(2), C(2)−Pt(1)−C(2′) = 89.2(4), S(1)−Pt(2)−S(1′) = 80.60(5), S(1)−Pt(2)−C(3) = 89.1(2), S(1)−Pt(2)−C(4) = 94.8(2), C(4)−Pt(2)−C(4′) = 89.1(3).

tion of these materials, when contaminated samples of **8** are stood for prolonged periods, X-ray quality crystals of the dinuclear complex [$Me_3Pt\{\mu\text{-}H_2B(mt)_2\}PtMe_3I$] (**9**) are observed to form (Figure 2).[15] The absence of a comparable dimer derived from **7** is attributable to the chiral twist inherent to $HB(mt)_3$ complexes (Figure 1), which disfavors the μ-*S,S′* bridging mode. We have previously quantified this twist in terms of the parameter θ_n, defined as the N_n−B−[M]−S_n torsion and its mean θ^m.[16] For complex **7**, θ_1 = 46.7°, θ_2 = 46.7°, θ_3 = 46.6°, and θ^m = 46.7°, each falling within recognized norms.

The Pt−S distances within the [$PtMe_3\{H_2B(mt)_2\}$] fragment of **9** are comparable to those within **7**, which are in turn typical of complexes comprising the $PtMe_3$ fragment and monoanionic sulfur donors, e.g., [$Me_3Pt(\mu\text{-}SMe)]_4$ [Pt−S 2.465−2.481 Å],[17a] while slightly longer than those observed for the only true facially tridentate analogue [$Me_3Pt([9]aneS_3)$]Cl ([9]aneS_3 = 1,4,7-trithiacyclononane, Pt−S 2.405−2.410 Å).[17b] A similar situation is observed, within the bounds of standard uncertainty, for the Pt−C linkages within both molecules. While the interligand angles within **7** are close to the ideal octahedral value, lying in the range 86.7−91.7°, those of **9** exhibit greater distortion, inherent from accommodating the μ-*S,S′* bridging mode. Thus, the S−Pt(1)−S angle is appreciably diminished [83.41(5)°], and ∠S−Pt(1)−C widened [93.7(2)°]. A similar, more extreme, scenario exists within the "$PtMe_3I$" fragment, which can presumably be attributed to the accommodation of the axial iodide ligand, which necessitates a 22° displacement of that fragment from the C2−C2′−S1′−S1 plane, and can presumably be implicated in the greater length of the bridging Pt−S interactions.

The X-ray crystallographic study of **9** is supported by spectroscopic and microanalytical data obtained for the crystals.[18] The ^1H NMR spectrum reveals again a single methimazolyl environment, which is magnetically distinct from that of the mononuclear complex **8**, with two resonances associated with the equatorially disposed Pt-methyl groups (δ 1.50, 6 H, $^3J_{PtH}$ 77.1 Hz, [$PtMe_3(\kappa^3$-*S,S′,H*)]; 1.03, 6 H, $^3J_{PtH}$ 69.2 Hz, [$PtMe_3(\kappa^2$-*S,S′*)I]). A third methyl resonance (δ 1.52, 6 H, J_{PtH} 74.6 Hz) is presumably attributable to the two axial disposed groups, the greater breadth of this signal (hhw, 7 Hz) implying two overlapped resonances. The resonance associated with the B−H−Pt functionality exhibits a shift to higher frequency (δ −2.3) relative to that in **8**, though is not fully resolved. We have subsequently undertaken to establish a systematic synthetic route to complex **9**, which we have found can be prepared quantitatively, either by the reaction of Na[$H_2B(mt)_2$] with 2 equiv of "[$PtMe_3I$]" or from preformed samples of **8** and 1 equiv of the 14-electron fragment. The isolation of **9** in exclusion of either **8** or [$PtMe_3I]_4$ has, however, thus far proven problematic and is the subject of ongoing work.

In conclusion, we have reported the synthesis of the first poly(methimazolyl)borate complexes of platinum, viz., [$PtMe_3\{HB(mt)_3\}$] (**7**) and [$PtMe_3\{H_2B(mt)_2\}$] (**8**), the first examples based around high-valent, late transition metals. Both of these compounds exhibit a remarkable level of stability and resistance to the thermally induced reductive elimination of either CH_4 or C_2H_6, which has thus far rendered them inviable as precursors to the sought-after dialkyl-platinaboratranes. The remarkable ease with which complex **8** forms a sulfur-bridged adduct with the 14-electron fragment "-[$PtMe_3I$]" highlights once more[19] an important caveat for the use of these supposed "tame-thiolates"[20] as biological mimics.

The development of $HB(mt)_3$ coordination chemistry has been inspired in part by anticipated parallels with other facially tridentate ligands, and in this respect compound **7** joins the series [$PtMe_3L$] (L = η-C_5H_5,[21] η-C_5Me_5,[22] $HB(pz)_3$ (pz = pyrazol-1-yl), $B(pz)_4$,[23] $HB(pzMe_2\text{-}3,5)_3$,[24] $(C_2H_4S)_{3,4}$[25]). Among these, poly(pyrazolyl)borates and crown thioethers provide perhaps the closest analogy, and it is therefore noteworthy that in the complex [$PtMe_3\{B(pz)_4\}$] rapid exchange of pyrazolyl

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[15] *Crystal data for* **9**: [$C_{14}H_{30}BIN_4Pt_2S_2$], *M* = 846.45, orhorhombic, *Pnma* (No. 62), *a* = 16.6470(4) Å, *b* = 12.6685(3) Å, *c* = 10.4921(2) Å, *V* = 2212.71(9) Å^3, *Z* = 4, D_c = 2.541 g cm^{-3}, μ(Mo Kα) = 14.219 mm^{-1}, *T* = 200(2) K, yellow block, 2649 independent measured reflections, *F* refinement, R_1 = 0.0230, wR_2 = 0.0266 for 2037 independent absorption-corrected reflections [$I > 3\sigma(I)$; $2\theta_{max}$ = 55°], 166 parameters, CCDC 271218.

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[18] Selected data for crystals of **9**. NMR ($CDCl_3$, 25 °C) ^1H (299.945 MHz): δ_H −2.3 (br m, hhw 100 Hz, 1 H, B−H−Pt), 1.03 (s, J_{PtH} 69.2 Hz, 6 H, Pt−Me_{eq}), 1.50 (s, J_{PtH} 77.1 Hz, 6 H, Pt−Me_{eq}), 1.52 (br s, J_{PtH} 74.6 Hz, 6 H, Pt−Me_{ax}), 3.69 (s, 6 H, NCH_3), 6.89, 7.03 (d × 2, $^3J_{HH}$ 1.9 Hz, 2 H × 2, NCH=CH). Anal. Found: C, 20.14; H, 3.63; N, 6.53; S, 7.29. Calcd for $C_{14}H_{30}BIN_4Pt_2S_2$: C, 19.87; H, 3.57; N, 6.62; S, 7.58.

[19] We have observed several examples of this behavior, for example: Crossley, I. R.; Hill, A. F.; Humphrey, E. R.; Willis, A. C. *Organometallics* **2005**, *24*, 4083. Hill, A. F.; Tshabang, N.; Willis, A. C. Manuscript in preparation.

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groups is observed as low as −60 °C,[23] while for the cation $[PtMe_3\{(C_2H_4S)_4\}]^+$, metallatropism between three of the four sulfur donors was found to be facile.[25] Each of these fluxional processes requires dissociation of one donor of the tripodal ligand, as would the conversion of **7** to a platinaboratrane via either B−H/C−H addition−elimination or σ-metathesis pathways. The failure of such a process to operate might therefore suggest that the $HB(mt)_3$ ligand *in this system* lacks the geometric flexibility offered by these other ligands.

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Supporting Information Available: Figures and tables giving full details of crystal structure determinations of **7** (CCDC 271217) and **9** (CCDC 271218), including positional and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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