Di- and Zerovalent Platinaboratranes: The First Pentacoordinate d^{10} Platinum(0) Complex

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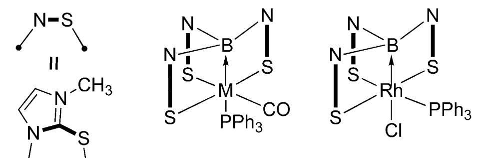
Summary: The reaction of [PtCl$_2$(PPh$_3$)$_2$] with Na[HB(mt)$_3$] (mt = methimazolyl) affords the platinaboratrane salt [PtH(PPh$_3$){B(mt)$_3$}]Cl($Pt^{II}\rightarrow B$), the first example of a metallaboratrane with the metal center in the +2 oxidation state. Base-induced dehydrochlorination affords the first d^{10} metallaboratrane, [Pt(PPh$_3$){B(mt)$_3$}]($Pt^0\rightarrow B$), based on an unprecedented pentacoordinate platinum(0) geometry.

Chart 1. Metallaboratranes



M = Ru (**1**), Os (**2**)

(**3**)

The hydrotris(methimazolyl)borate ligand[1] may be viewed as a softer analogue of Tofimenko's ubiquitous poly(pyrazolyl)borates.[2] However, the greater flexibility of the larger chelate rings has provided opportunities for identifying previously inaccessible structural motifs, a number of these arising in an organometallic context. A case in point in the isolation of the novel metallaboratranes [M(CO)(PPh$_3$){B(mt)$_3$}]($M^0\rightarrow B$) (Chart 1; mt = methimazolyl, M = Ru (**1**),[3] Os (**2**)[4]), which provided the first unambiguous authentication of the long-mooted metal−boron dative interactions.[5] In these tricyclo[3.3.3.0] cage compounds the transannular bond between the formally zerovalent d^8 metal and boron(III) is supported by three methimazolyl buttresses. These constrain the metal ML$_5$ fragment to assume a monovacant octahedral geometry, such that relaxation to either a trigonal-bipyramidal or d^8-ML$_4$ square-planar geometry (i.e., ligand dissociation) is precluded. The implication, or at least our interpretation,[6] is that one pair of electrons is housed in a metal→boron dative bond.

Geometric constraints notwithstanding, metal σ basicity should remain a dominant factor in attaining an effective dative metal−boron interaction; however, such a working hypothesis requires validation. Specifically, the propensity for boratrane formation needs to be tested as a function of the metal, oxidation state, charge, and ancillary ligands. In seeking to explore the inherent limitations of these factors, we have recently succeeded in synthesizing the first rhodaboratrane, [RhCl(PPh$_3$){B(mt)$_3$}]($Rh\rightarrow B$) (**3**),[6] in which the metal adopts the +1 oxidation state, rendering it isoelectronic with **1** and **2**.[7] In a progression of our study we have now turned our attention to the metals of group 10. Given that in isoelectronic terms an octahedral metallaboratrane based on a divalent metal would seem plausible, the issue of the σ basicity of a divalent metal might be expected to become a question. Herein we report the synthesis and isolation of the first group 10 metallaboratranes with examples based on both octahedral d^8-Pt(II) and trigonal-bipyramidal d^{10}-Pt(0).

The reaction of *cis*-[PtCl$_2$(PPh$_3$)$_2$] with Na[HB(mt)$_3$] in dichloromethane proceeds rapidly, to immediately afford a vivid yellow solution of an "intermediate" complex (**4**). The isolation and unequivocal identification of **4** have proven problematic,[8] due to its propensity for further reaction in solution, to afford a second species, which we formulate as the platinaboratrane salt [PtH(PPh$_3$){B(mt)$_3$}]Cl($Pt^{II}\rightarrow B$) (**5·Cl**) on the basis of a range of spectroscopic data (Scheme 1).[9] Although we have not been successful in structurally characterizing the salt

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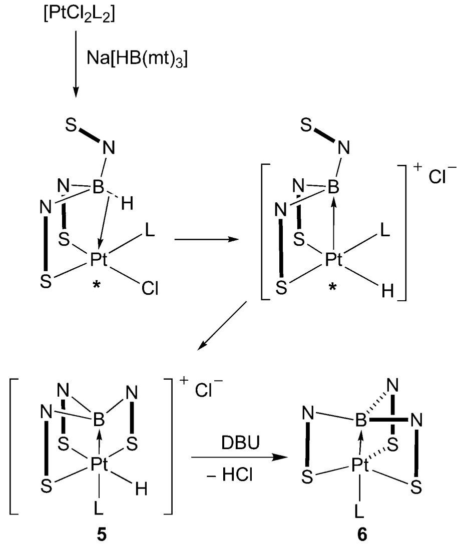
(7) A cobaltaboratrane has very recently been crystallographically identified in the salt [Co(PPh$_3$){B(mt^{tBu})$_3$}]BPh$_4$, which appears to arise as an adventitious decomposition product of the salt [Co(PPh$_3$){HB(mt^{tBu})$_3$}]BPh$_4$ and for which spectroscopic data are not yet available. This curious trigonal-bipyramidal complex has two less valence electrons than the octahedral examples **1**−**3** and therefore falls outside our bonding scheme: 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* **2004**, 1626.

(8) Preliminary spectroscopic studies suggest the presence of a coordinated HB(mt)$_3$ ligand, possibly with the κ^3S,S′,H chelation mode which we have previously identified in the complex [RuH(CO)(PPh$_3$){HB(mt)$_3$}].[3b] Several other intermediates in the formation of **5** are also observed transiently.

(9) Data for **5·Cl** are as follows. Yield: 65%. IR (KBr): ν_{PtH} 2193 cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H (299.945 MHz), δ_H −13.8 (d, 1 H, $^2J_{HP}$ = 4, $^1J_{PtH}$ = 980 Hz), 3.40 (s, 6 H, NCH$_3$), 3.48 (s, 3H, N CH$_3$), 6.90, 7.91 (br s × 2, 1 H × 2, NCH=CH), 7.10, 8.93 (d, $^3J_{HH}$ = 2 Hz, NCH=CH × 2), 7.50−7.40 (m, 15 H, PPh$_3$); ^{13}C{^{1}H} (75.428 MHz) δ_C 33.8, 34.3 (NCH$_3$ × 2), 119.8, 124.9 (NCH=CH), 121.0, 125.3 (NCH=CH), 128.7 (d, J_{PC} = 9.8 Hz, C^{3,5}(C$_6$H$_5$)), 130.7 (s, C^4(C$_6$H$_5$)), 131.2 (d, J_{PC} = 36.0 Hz, C^1(C$_6$H$_5$)), 133.6 (d, J_{PC} = 12.8 Hz, C^{2,6}(C$_6$H$_5$)), 160.9 (d, J_{PC} = 19.5 Hz, C × 2, C=S), 161.0 (d, J_{PC} = 18.7 Hz, C, C=S); ^{31}P{^{1}H} (121.420 MHz) δ_P 4.0 (br m, $^1J_{PtP}$ = 1020 Hz); ^{11}B{^{1}H} (96.232 MHz), δ_B 1.59 (br d, $^2J_{PB}$ = 100 Hz, $^1J_{PtB}$ 300 Hz); ^{195}Pt (64.222 MHz) δ_{Pt} −3899 (m, see Figure 1). Anal. Found: C, 42.65; H, 4.01; N, 10.61; S, 11.63. Calcd for C$_{30}$H$_{31}$BClN$_6$PPtS$_3$: C, 42.69; H, 3.70; N, 9.96; S, 11.39.

10.1021/om040114+ CCC: $27.50

Scheme 1. Formation of Platinaboratranes[a]



[a] The asterisks denote suggested intermediates (**4**); L = PPh$_3$.

5·Cl, the formulation follows unequivocally from multinuclear NMR spectroscopic studies, drawing on our growing library of data for the metallaboratrane motif.[3,4,6] In addition to confirming the presence of two conformationally locked methimazolyl environments (ratio 1:2) and one phosphane ligand, the ^{1}H NMR data include a low-frequency resonance (δ_H −13.8, J_{PH} = 4 Hz, J_{PtH} = 980 Hz) which is attributable to a platinum hydride ligand coordinated cis to the single phosphane. Notably, the spectrum is devoid of resonances in regions typical of either terminal B−H or agostic B−H−Pt groups; the infrared spectrum is similarly lacking in signatures for these functional groups. The ^{31}P{^{1}H} NMR spectrum comprises a single but particularly broadened resonance (δ_P 4.0, $^{1}J_{PtP}$ = 1020 Hz, half-height width 180 Hz). This is consistent with the ^{31}P NMR resonances we have observed for other metallaboratranes, in which the phosphane adopts a transoid disposition relative to the dative M→B linkage. This inference is supported by the observation of a broad doublet resonance (δ_B 1.56, $^{2}J_{PB}$ = 100 Hz, hhw = 180 Hz) in the ^{11}B{^{1}H} NMR spectrum, with attendant ^{195}Pt satellites (J_{PtB} = 300 Hz). The coupling of the boron nucleus to both platinum and phosphorus would seem indicative of a direct metal−boron interaction.

Verification of a single platinum environment is afforded by the ^{195}Pt NMR spectrum, which exhibits a complex multiplet resonance centered at −3899 ppm (with respect to K$_2$PtCl$_6$) in the region characteristic of Pt(II) nuclei. Resolution of individual spin−spin coupling constants is precluded by the complexity of the overlapping 16-line pattern arising from coupling to two $I = {}^{1}/_{2}$ nuclei (^{1}H, ^{31}P) and one $I = {}^{3}/_{2}$ (^{11}B) center, a difficulty compounded by the inherently wide line widths imposed by the quadrupolar boron nucleus. The situation is somewhat simplified in the ^{195}Pt{^{1}H} NMR spectrum (8 lines), although the resonance remains broad. Both observed patterns are, however, in good agreement with simulated spectra (Figure 1), which affords confidence in our assignments.

The platinaboratrane **5·Cl** represents the first example of the boratrane geometry being adopted by a metal center in the +2 oxidation state. Given that the complex is also cationic, this would appear to suggest that the efficacy of M→B dative interactions is less dependent upon metal basicity than we had presumed and might therefore be deemed a general phenomenon for d^{8} centers of suitable geometry. Cationic platinum hydride complexes are typically prone to deprotonation, and accordingly **5·Cl** presented itself as a possible candidate for reductive dehydrohalogenation. Indeed, treatment of a methanolic solution of **5·Cl** with DBU (1,8-diaza[5.4.0]bicycloundec-7-ene), under ambient conditions, results in the immediate precipitation of a yellow solid, which is formulated as the platinaboratrane [Pt(PPh$_3$){B(mt)$_3$}]($Pt^0 \rightarrow B$) (**6**) on the basis of elemental microanalytical and spectroscopic data.[10]

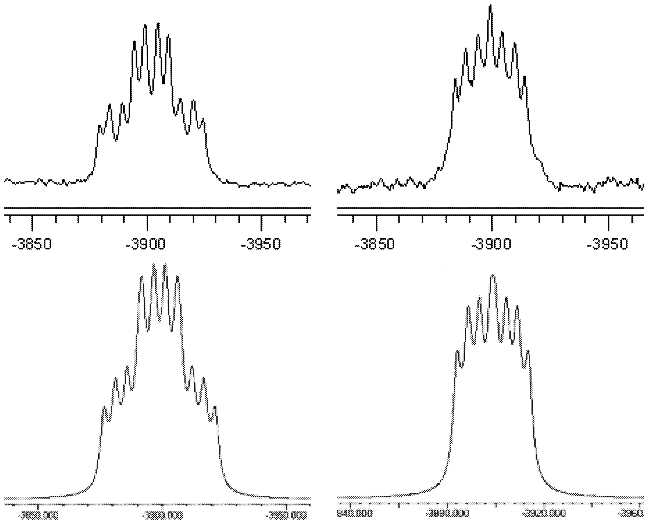


Figure 1. Observed (top) and simulated (bottom) ^{195}Pt NMR resonances for **5**$^{+}$ with (right) and without (left) proton decoupling. The simulations used imposed line widths of 200 Hz.

The ^{1}H NMR spectrum of **6** indicates loss of the hydride ligand and is consistent with an increase in molecular symmetry over that of **5**$^{+}$, resulting in chemical equivalence of the three methimazolyl buttresses, a feature that is also reflected in the ^{13}C and correlation (HMQC) NMR spectra. Retention of the single PPh$_3$ ligand is also apparent in the ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra, most informatively in the last, which comprises a single broad resonance (δ_P 26.5, hhw = 250 Hz) with attendant platinum satellites (J_{PtP} = 1370 Hz). The significant downfield shift of this resonance, relative to that in **5**$^{+}$ (δ_P 4.0) possibly reflects enhanced communication between the phosphorus and electrophilic boron center arising from increased s character in the metal−ligand σ-bonding orbitals upon adoption of five-coordinate geometry. Indeed, this is also consistent with notable increases in the magnitude of the ^{195}Pt−^{31}P coupling constant and the ^{195}Pt−^{11}B (J_{PtB} = 490 Hz) and ^{31}P−^{11}B (J_{PB} = 110 Hz) interactions, both of which are

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(10) Data for **6** are as follows. Yield: 60%. NMR (CDCl$_3$, 25 °C): ^{1}H (299.945 MHz) δ_H 3.37 (s, 9 H, NCH$_3$), 6.65, 8.30 (br s, 3 H × 2, NCH=CH), 7.60−7.52 (m, 6 H, PPh$_3$), 7.41−7.35 (m, 9 H, PPh$_3$); ^{13}C (75.428 MHz) δ_C 33.7 (NCH$_3$), 118.7, 124.4 (NCH=CH), 165.0 (d, J_{PC} = 18.9 Hz, C, C=S), 128.1 (d, J_{PC} = 9.0 Hz, C^{3,5}(C$_6$H$_5$)), 129.5 (s, C^{4}(C$_6$H$_5$)), 133.9 (d, J_{PC} = 13.2 Hz, C^{2,6}(C$_6$H$_5$)); ^{31}P{^{1}H} (121.420 MHz) δ_P 26.5 (br m, $^{1}J_{PtP}$ = 1370 Hz); ^{11}B{^{1}H} (96.232 MHz) δ_B 1.47 (d, $^{2}J_{PB}$ = 110 Hz, $^{1}J_{PtB}$ 490 Hz); ^{195}Pt (64.222 MHz) δ_{Pt} −4396 (m, see Figure 2). Anal. Found: C, 45.06; H, 3.98; N, 10.13; S, 11.13. Calcd for C$_{30}$H$_{30}$BN$_6$PPtS$_3$: C, 44.61; H, 3.74; N, 10.41; S, 11.91.

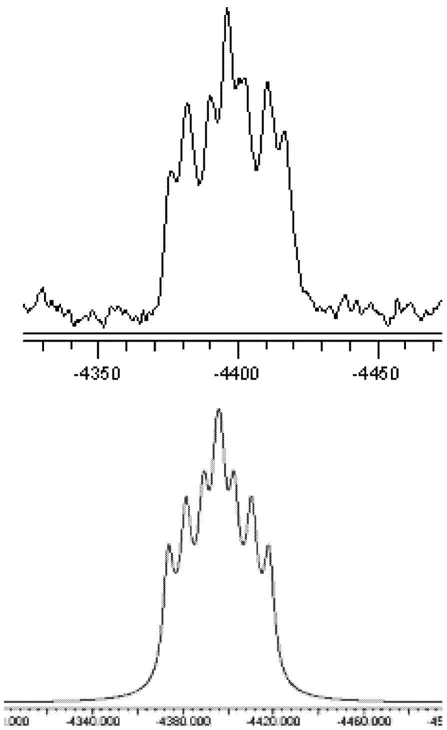

Figure 2. Observed (top) and simulated (bottom) ^{195}Pt NMR resonances for **6**. The simulated spectrum imposed a line width of 200 Hz.

clearly observed in the ^{11}B NMR spectrum. This spectrum is significantly better resolved (hhw = 35 Hz) than is the case for $\mathbf{5}^+$, presumably a result of the increased local symmetry of **6** (relative to $\mathbf{5}^+$) reducing the electric field gradient (EFG) and, accordingly, the extent of quadrupolar relaxation. This would seem to support a five-coordinate geometry and mitigate against fluxional equilibration of the methimazolyl buttresses (vide supra).

The character of the platinum center was again probed by ^{195}Pt NMR spectroscopy, which revealed the presence of a single platinum environment, observed as an overlapping eight-line multiplet resonance (Figure 2) centered at −4396 ppm (with respect to K_2PtCl_6). The shift to lower frequency (−407 ppm) relative to $\mathbf{5}^+$ would suggest appreciably greater shielding of the platinum nucleus in **6**, consistent with a reduction in the oxidation state, although this alone does not conclusively identify a Pt(0) center. The chemical shift falls in an ambiguous region of the spectrum, perhaps not surprisingly, given the unique nature of **6** and the yet to be quantified influence of the Lewis acidic B(III) ligand. Moreover, to our knowledge, complex **6** represents the first example of a five-coordinate Pt(0) complex; thus, no suitable data exist for comparison. At best, an albeit loose analogy with borallyl complexes of platinum(II), e.g., $[(Ph_2P(CH_2)_nPPh_3)PtB_3H_7]$ (n = 2−4),[11] might be entertained and while no ^{195}Pt NMR data are available, the magnitudes of the ^{11}B−^{195}Pt coupling constants (ca. 500 ± 25 Hz) are at least comparable to those observed in **6**.

In conclusion, we have reported the systematic preparation of the first group 10 metallaboratrane complexes, viz. $[PtH(PPh_3)\{B(mt)_3\}]Cl$ (**5·Cl**) and $[Pt(PPh_3)\{B(mt)_3\}]$ (**6**). These constitute the first examples of the metallaboratrane geometry being adopted by the same metal in different oxidation states and suggest the generality of this motif for metals with a minimum d^8 electron count. Moreover, **6** is the first example of a five-coordinate complex of Pt(0); indeed, adherence to the effective atomic number (18-electron) rule requires that such a geometry would only be available were one of the substituents a σ Lewis acid.

Acknowledgment. One reviewer has suggested that the "B(mt)$_3$" ligand might be viewed as a dianion coordinated to di- and tetravalent platinum in the complexes **6** and $\mathbf{5}^+$, respectively. While we do not dispute the possible contribution of extreme zwitterdianionic canonical forms in a valence bond description, this would require coordination of monovalent boron to a cationic tetravalent platinum center in the case of $\mathbf{5}^+$. Given that the ^{195}Pt chemical shift for $\mathbf{5}^+$ falls within the region typical for divalent platinum, and in deference to the principles of covalency and electroneutrality, we feel that any contribution of these higher oxidation state canonical forms would be, at best, modest. We thank the Australian Research Council (ARC) for financial support (Grant No. DP034270).

OM040114+

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