The First Bimetallic Metallaboratrane: $[Rh_2\{B(mt)_3\}_2\{\kappa^2\text{-}S,S'\text{-}HB(mt)_3\}]Cl$ and Its Synthesis from the Fluxional Rhodaboratrane Salt $[Rh\{B(mt)_3\}(\eta^4\text{-}C_8H_{12})]Cl$, ($Rh \rightarrow B$, mt = Methimazolyl)

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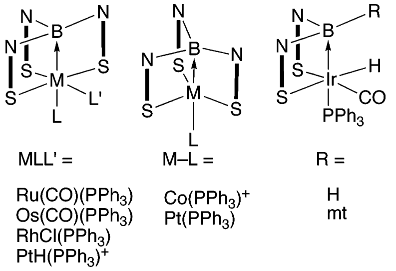
Received April 4, 2005

Summary: The prolonged reaction of $[Rh\{B(mt)_3\}(\eta^4\text{-}C_8H_{12})]Cl$*, prepared from* $[Rh(\eta^4\text{-}C_8H_{12})Cl]_2$ *and 2 equiv of* $Na[HB(mt)_3]$*, with a further excess of* $Na[HB(mt)_3]$ *leads to formation of the first binuclear metallaboratrane salt,* $[Rh_2[B(mt)_3]_2\{\kappa^2\text{-}S,S'\text{-}HB(mt)_3\}]Cl$*. This compound, which is also observed as a decomposition product of rhodium tris(methimazolyl)borane complexes, affords the first evidence for bridging of transition metals by the methimazolyl sulfur donors.*

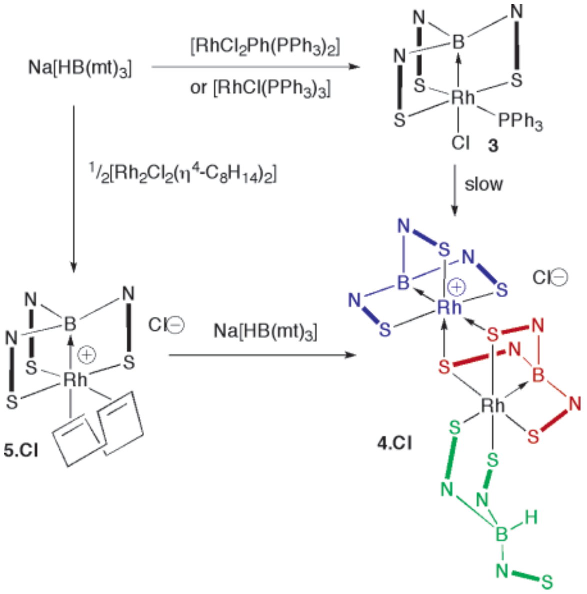
Introduction

The poly(methimazolyl)borate ligands,[1] often viewed as soft analogues of Trofimenko's ubiquitous poly(pyrazolyl)borates,[2] constitute unique tools in modern synthetic organometallic and coordination chemistry. The greater flexibility of the larger chelate rings has enabled the isolation of previously inaccessible structural motifs and bonding scenarios, alongside novel B−H activation processes. These were first illustrated by the isolation of metallaboratranes $[M(CO)(PPh_3)\{B(mt)_3\}]$ ($M \rightarrow B$) (Chart 1, mt = methimazolyl, M = Ru **1**,[3] Os **2**[4]); the first unambiguous examples of previously contentious metal→boron "dative" interactions.[5]

Chart 1. Metallaboratranes



Scheme 1. Synthesis of the Dirhodaboratrane Salt [4]Cl



Subsequent work has extended this to include examples from groups 9 (Co,[6] Rh,[7] Ir[8]) and 10 (Pt),[9] establishing a generality for the metallaboratrane geometry among metals with a minimum d^8 electron configuration. However, thus far the metallaboratrane geometry has been restricted to mononuclear systems, with no evidence for bridging by the methimazolyl buttresses. Indeed, the methimazolyl sulfur donor has been described as a "tame" thiolate,[10] with a reduced propensity for bridging, although a handful of examples exist among thallium[11] and zinc[12] complexes. Herein, we report the serendipitous isolation, and systematic pursuit, of the first bimetallic metalla-

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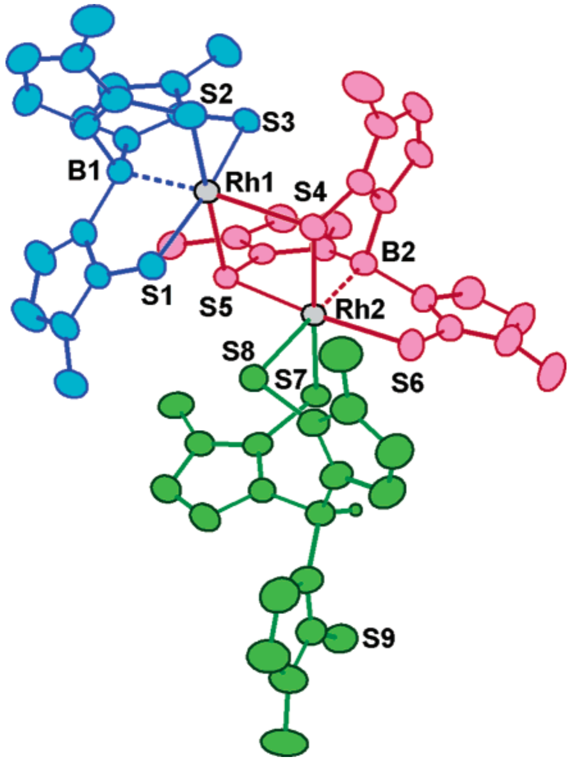

Figure 1. Molecular geometry of 4^+ in a crystal of **[4]Cl.6·CHCl$_3$H$_2$O**. Hydrogen atoms attached to carbon are omitted for clarity (50% thermal elipsoids). Selected bond lengths (Å): Rh(1)−B(1) 2.098(6), Rh(1)−S(1) 2.376(2), Rh(1)−S(2) 2.351(2), Rh(1)−S(3) 2.352(2), Rh(1)−S(4) 2.670(2), Rh(1)−S(5) 2.375(2), Rh(2)−B(2) 2.091(5), Rh(2)−S(4) 2.375(2), Rh(2)−S(5) 2.336(2), Rh(2)−S(6) 2.353(2), Rh(2)−S(7) 2.392(2), Rh(2)−S(8) 2.622(2).

boratrane, the remarkable dinuclear rhodium complex salt [Rh$_2${B(mt)$_3$}$_2${κ^2-S,S′-HB(mt)$_3$}]Cl (**4.Cl**) (Scheme 1, Figure 1).

Results and Discussion

We initially encountered salt **4.Cl** while investigating the mononuclear rhodaboratrane [RhCl(PPh$_3$){B(mt)$_3$}] (**3**), prepared from [RhCl$_2$(Ph)(PPh$_3$)$_2$] and one equivalent of Na[HB(mt)$_3$] as previously described.[7] Attempts to further optimize the yield of **3**, and indeed to explore its reactivity, were repeatedly confounded by the lability of the phosphine, which ^{31}P NMR spectroscopic studies reveal to be lost to afford an intractable phosphine-free species. When these CDCl$_3$ solutions of **3** are allowed to stand in air for several days, vivid orange, poorly soluble crystals are observed to form, which X-ray diffraction analysis revealed to be **4.Cl** as the hexachloroform monohydrate. The complex cation 4^+ comprises two mononuclear rhodaboratrane fragments, bridged by two methimazolyl buttresses, which are incumbent to the same rhodium atom, while the remaining two coordination sites at this center are occupied by a terminal [HB(mt)$_3$] ligand, which adopts a κ^2-*S,S′* chelation mode, unprecedented for transition metals.

The process by which this species forms remains unclear, although it can be postulated to involve nucleophilic displacement of chloride and triphenylphosphine from one molecule of **3**, by the attack of a second. This would seem remarkable on two counts: (i) that methimazolyl sulfur donors, each residing upon a Rh(I) center, are sufficiently nucleophilic to initiate this process and (ii) that the dative rhodium(I)→B interaction can be sustained at a cationic center. In this latter respect we have recently encountered several instances in which a cationic complex is favored by the metallaboratrane motif (e.g., [PtH(PPh$_3$){B(mt)$_3$}]Cl[9]); thus, one may surmise that it is this preference which predominates. Somewhat more surprising, however, is the presence of the terminal HB(mt)$_3$ ligand within 4^+, given the absence of free Na[HB(mt)$_3$] in the initial sample of **3**. This might imply that consumption of three equivalents of **3** is necessary to afford one molecule of 4^+, with the terminal proton presumably arising from ambient moisture. This fact would account for the apparently low yields of 4^+ obtained and correlates with our previous observations of transition metal methimazolylborate complexes behaving as an active source of the free HB(mt)$_3$ ligand over prolonged periods in solution.[13]

Mindful of these facts, and the isolation of further samples of **4.Cl** from the solution-phase decomposition of several other rhodaboratranes, and indeed tris(methimazolyl)borate complexes of rhodium, we sought a systematic synthesis for this intriguing binuclear compound. The reactions of [RhCl$_2$(Ph)(PPh$_3$)$_2$] and [RhCl(PPh$_3$){B(mt)$_3$}] with excess of the Na[HB(mt)$_3$] reagent were thus explored with limited success, both proving to be impracticable substrates due largely to unavoidable contamination of the products with PPh$_3$ (or OPPh$_3$ when samples were worked up aerobically). A precursor devoid of phosphines was thus required, to which end we prepared the new rhodaboratrane salt [Rh{B(mt)$_3$}(η^4-C$_8$H$_{12}$)]Cl (**5.Cl**), through the reaction of [Rh(η^4-C$_8$H$_{12}$)Cl]$_2$ and two equivalents of Na[HB(mt)$_3$] in chlorinated solvents. While anticipated to afford the neutral tris(methimazolyl)borate complex [Rh{κ^3-HB(mt)$_3$}(η^4-C$_8$H$_{12}$)], the formulation of **5.Cl** as a boratrane salt was initially inferred from, inter alia (i) the absence of a B−H stretching mode, (ii) its diamagnetism and (iii) microanalytical data. However, the ambient-temperature ^{1}H NMR spectrum of **5.Cl** exhibits only a single set of "mt" resonances for the B(mt)$_3$ chelate (δ_H 3.58 (9 H), 6.92, 6.98 (2 × 3 H)). Furthermore the η^4-C$_8$H$_{12}$ ligand gives rise to three resonances (δ_H 1.77, 2.48, 4.16 (3 × 4 H)), seemingly inconsistent with a conformationally locked hexacoordinate rhodaboratrane motif. This fact we attribute to rapid (^{1}H NMR timescale) equilibration of the three methimazolyl buttresses, which we presume to occur via a pentacoordinate intermediate (local C_3 symmetry at the boratrane bridgehead cf. [Pt(PPh$_3$){B(mt)$_3$}]^9), accessed through dissociation of one π-system of the C$_8$H$_{12}$ ligand (Scheme 2). While this mechanistic interpretation remains speculative, VT-NMR studies clearly confirm the operation of a thermally dependent equilibration process, all ^{1}H NMR resonances associated with both B(mt)$_3$ and C$_8$H$_{12}$ ligands exhibiting coalescence behavior during the temperature interval −30 to −50 °C. Thus, at −80 °C it is possible to fully resolve the two unique methimazolyl environments (2:1 ratio) characteristic of the metallaboratrane motif, together with six ^{1}H environ-

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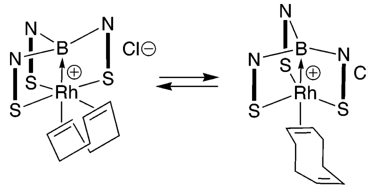
Scheme 2. Proposed Fluxionality of the Rhodaboratrane Salt [5]Cl



ments for the cyclooctadiene ligand. While these latter resonances remain broad, suggesting some continuing fluxionality, they are consistent with our formulation of an approximately octahedral rhodaboratrane cation with pseudo-plane-of-symmetry bisecting the C_8H_{12} ligand; an assertion that is further supported by ^{13}C and 2-D correlation (COSY, HMQC) NMR spectroscopic data.

It is additionally noteworthy, that temperature dependence is also observed in the $^{11}B\{^1H\}$ NMR spectrum, which at 25 °C consists of two (broad) resonances at δ 3.09 and 9.63 in a 9:1 ratio. Around −50 °C these two coalesce; thus, at −80 °C a single, heavily broadened, resonance can be resolved at $\delta_B = 4.11$. The implications of this remain unclear, since **5.**Cl should exhibit a single ^{11}B NMR resonance, given the absence of any data to suggest contaminants. One possible interpretation would be to ascribe the higher frequency resonance to a small amount of the elusive pentacoordinate intermediate, which would hold if there exists a significant disparity in the frequency separation of the ^{11}B resonances, compared with those of ^1H and ^{13}C; i.e. $\Delta\nu(^{11}B) \gg k_{\text{exchange}}$, $\Delta\nu(^1H \text{ or } ^{13}C) \approx k_{\text{exchange}}$. However, in the absence of confirmatory ^1H and ^{13}C NMR spectroscopic evidence this must remain conjecture.

The reaction between **5.Cl** and excess Na[HB(mt)$_3$] proceeds, in dichloromethane or chloroform solution, over the course of several days to afford a quantity (20% yield) of a poorly soluble orange precipitate, which can be isolated by centrifugation. The characterization of this material is difficult, due in part to its low solubility and the complexity inherent from its nine unique methimazolyl units. Indeed, the complexity and quality of the ^1H NMR spectrum (DMSO) have thus far precluded unequivocal assignment. However, the presence of 18 unique aromatic imidazolyl protons is apparent, observed as overlapping doublet resonances in the region 8.24−6.85 ppm, which integrate consistently against a similarly overlapping pattern of singlet resonances (27 H) in the characteristic methimazolyl NCH_3 region (δ_H 3.5−3.3). Moreover, while not apparent from the NMR data, the presence of a [HB(mt)$_3$] ligand is confirmed by the observation of an infrared band at 2457 cm^{-1}, characteristic of a terminal B−H stretching mode. These data are directly comparable to those obtained from the single crystals of **4.Cl**·6CHCl$_3$·H$_2$O, which have been studied on several occasions; thus, we are confident of the product identity. This is further supported by microanalytical data, which are largely consistent with the formulation [Rh$_2$\{B(mt)$_3$\}$_2$\{κ^2-*S,S′*-HB(mt)$_3$\}]Cl·CHCl$_3$, given that the single crystals are prone to loss of occluded chloroform.

The molecular geometry of **4**$^+$ depicted in Figure 1 reveals several notable features with regard to the geometry of the rhodaboratrane fragments. Foremost is the absence of any appreciable distortions of the boratrane cages to accommodate the bridging methimazolyl moieties. Moreover, the terminal and bridging Rh−S linkages [2.3915(13) − 2.3360(12) Å] are comparable, both internally to **4**$^+$ and to those observed for **3** [2.3693(17) − 2.2867(15) Å], thus confirming beyond doubt the bimetallic nature of **4**$^+$ and precluding the possibility of weakly associating mononuclear complexes. An exception lies with the two Rh−S linkages trans to the "dative" rhodium → boron interactions, both of which are appreciably longer than might be anticipated [Rh(1)−S(4) 2.670(2); Rh(2)−S(8) 2.622(2) Å]. This would seem counterintuitive, given that a dative Rh → B linkage might, classically, be expected to exert an inverse trans influence. Similarly, the Rh−B linkages [Rh(1)−B(1) 2.098(6); Rh(2)−B(2) 2.091(5)] while mutually comparable, are appreciably shorter than that observed of the neutral complex **3** [2.132(6) Å], despite the cationic character of **4**$^+$, which might have been anticipated to diminish the Rh−B bond-strength. However, it should be noted that the influence of the trans ligand upon the strength of the M → B interaction remains to be quantified, due to the still limited number of available examples. Furthermore, the effect of additional (π-dative) sulfur donors on each Rh^{I} center, relative to **3**, cannot be predicted, this being the first example of a metallaboratrane with only sulfur donors in the metal coordination sphere, and indeed the first example of a mixed borane−borate complex.

Our favored interpretation of M → B bonding within these molecules invokes one of several formalisms, which we deem most applicable on the grounds of electroneutrality arguments. An alternative model may describe the bridgehead boron not as a σ-Lewis acid but rather an internally base-stabilized σ-boryl,[14] acting as donor to a Rh^{III} center. Since σ-boryls are increasingly considered to be very strong σ-donors with a strong trans influence, this alternative stance may indeed account for the observed lengthening of the trans Rh−S linkages and the apparently contracted Rh−B separation relative to the neutral system. Caution is, however, warranted since these Rh−B distances are still appreciably longer than those seen in rhodium boryls. While zwitterionic canonical forms for bonding should not be discounted, we suspect that they constitute, at best, a modest contribution to the M−B bonding.

Conclusion

The reaction of [Rh(η^4-C$_8$H$_{12}$)Cl]$_2$ with two equivalents of Na[HB(mt)$_3$] affords preferentially the rhodaboratrane salt [Rh\{B(mt)$_3$\}(η^4-C$_8$H$_{12}$)]Cl (**4.Cl**), reflecting a growing trend for the formation of the metallaboratrane motif at cationic metal centers. This compound serves as a precursor to the enigmatic dinuclear boratrane [Rh$_2$\{B(mt)$_3$\}$_2$\{κ^2-S,S′-HB(mt)$_3$\}]Cl (**4.Cl**), which can thus be obtained in modest quantities. Most commonly encountered as a decomposition product of rhodium tris(methimazolyl)borate complexes, the counterintuitive nature of **4**$^+$ (both synthesis and structural features) suggests that a detailed understanding of the

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bonding scenario within metallaboratrane motifs requires substantial, further investigation.

Experimental Section

General Procedures. Unless otherwise stated, reactions were performed under anaerobic conditions, using standard Schlenk and vacuum-line techniques. The salt Na[HB(mt)$_3$][1,3] and metal complexes [RhCl$_2$(Ph)(PPh$_3$)$_2$][7] and [Rh(η^4-C$_8$H$_{12}$)Cl]$_2$[15] were prepared via published procedures. Microanalytical data were obtained from the ANU Analytical service. All NMR spectra were recorded on a Varian Inova 300 spectrometer, and infrared data, on a Perkin-Elmer Spectrum One instrument.

Preparation of [Rh{B(mt)$_3$}(η^4-C$_8$H$_{12}$)]Cl (5.Cl). A mixture of [Rh(η^4-C$_8$H$_{12}$)Cl]$_2$ (0.100 g, 0.202 mmol) and Na[HB(mt)$_3$] (0.157 g, 0.420 mmol) in dichloromethane (20 cm^3) was stirred anaerobically for 8 h. The reaction mixture was then filtered anaerobically and the solvent removed in vacuo to afford **5.Cl** as an orange-yellow solid. Yield 0.145 g, 60%. Mp 158−162 °C dec. NMR: (acetone-d_6, 25 °C) ^{1}H (299.945 MHz) δ_H 1.77, 2.48 (m br × 2, 4 H × 2, C$_8$H$_{12}$), 3.58 (s, 9 H, NCH$_3$), 4.16 (s br, 4 H, C$_8$H$_{12}$), 6.92, 6.98 (d × 2, J_{HH} 2 Hz, 3 H × 2, NCH=CH); ^{13}C{^{1}H}(75.428 MHz) δ_C 33.2 (s × 2, CH$_2$ × 2, C$_8$H$_{12}$), 35.8 (s, NCH$_3$), 80.4 (s, CH, C$_8$H$_{12}$), 122.1, 120.8 (s × 2, NCH=CH), 164.3 (s br, C=S); ^{11}B{^{1}H}(96.232 MHz) δ_B 3.09 (s, 9 B, hhw 110 Hz), 9.63 (s, 1 B, hhw 160 Hz). (acetone-d_6, −80 °C) δ_H 1.61 (H$_a$), 1.78 (H$_b$), 2.26 (H$_b$′), 2.60 (H$_a$′) (m br × 4, 2 H × 4, C$_8$H$_{12}$), 3.49 (s, 3 H, NCH$_3$), 5.53 (s, 6 H, NCH$_3$), 4.04 (H$_c$), 4.10 (H$_d$) (s br × 2, 2 H × 2, C$_8$H$_{12}$), 6.51 (s br, 1 H, NCH=CH), 6.81 (s br, 2 H, CH=CH), 7.10 (s br, 2 H, CH=CH), 7.14 (s br, 1 H, CH=CH). δ_C 31.8 (C$_a$), 33.2 (C$_b$) (*C*HH′ × 2, C$_8$H$_{12}$); 75.0 (C$_c$), 81.6 (C$_d$) (*C*H × 2, C$_8$H$_{12}$, CH=CH); 34.5, 35.0 (CH$_3$ × 2, NCH$_3$); 118.8, 120.2, 121.5, 120.8 (CH × 4, NCH=CH). δ_B 4.11 (br s hhw 2000 Hz). Anal. Found: C, 40.72; H, 4.75; N, 14.50; S, 16.19. Calcd for C$_{20}$H$_{27}$B$_1$N$_6$RhS$_3$Cl: C, 40.25; H, 4.56; N, 14.08; S, 16.12.

Synthesis of [Rh$_2${B(mt)$_3$}$_2${κ^2-S,S′-HB(mt)$_3$}]Cl (4.Cl). Under aerobic conditions **5.Cl** (0.100 g, 0.168 mmol) was stirred in chloroform (15 cm^3) with an excess (0.134 g, 0.358 mmol) of Na[HB(mt)$_3$] for 5 days. The resulting orange-red precipitate was collected by centrifugation and decantation of the supernatant liquor. The solid which exhibits limited solubility, thus precluding recrystallization, was then dried in vacuo. Yield 0.020 g, 22%. NMR (DMSO, 25 °C) ^{1}H (299.945 MHz) δ_H 3.46, 3.44, 3.43, 4.42, 3.41, 3.40 (br 27H), 8.24, 7.74, 7.59, 7.57, 7.28, 6.85 (6 × br d, 6H), 7.94, 7.34, 7.32, 7.25, 7.23, 7.15 (6 × br d,{overlapped}, 12 H), 8.32 (CHCl$_3$, 1 H). IR ν_{max} 2457 (B−H). Anal. Found: C, 33.19; H, 4.00; N, 17.89; S, 20.08; Cl, 11.99. Calcd for C$_{36}$H$_{46}$B$_3$N$_{18}$Rh$_2$S$_9$Cl.CHCl$_3$: C, 31.46; H, 3.45; N, 17.85; S, 20.43; Cl, 10.04. Crystals of **4.Cl·6CHCl$_3$·H$_2$O** suitable for crystallographic analysis were slowly deposited from a dilute solution in apparently moist CDCl$_3$. *Crystal data for* **4.Cl·6CHCl$_3$·H$_2$O**: [C$_{36}$H$_{46}$B$_3$N$_{18}$Rh$_2$S$_9$]-Cl.6CHCl$_3$·H$_2$O, $M = 2027.40$, triclinic, $P\bar{1}$ (No. 2), $a = 13.1713(2)$ Å, $b = 17.0169(2)$ Å, $c = 19.6245(3)$ Å, $\alpha = 70.1676(5)°$, $\beta = 72.3412(6)°$, $\gamma = 86.8232(9)°$, $V = 3937.14(10)$ Å^3, $Z = 2$, $D_c = 1.708$ Mg m^{-3}, μ(Mo Kα) = 1.350 mm^{-1}, $T = 200$ K, orange plates, 18008 independent measured reflections, F refinement, $R_1 = 0.0471$, w$R_2 = 0.0519$ for 10502 reflections [$I > 3\sigma(I)$; $2\theta_{max} = 55°$], 858 parameters. CCDC 250753.

Acknowledgment. We are grateful to one reviewer for guidance in relation to discussion of the ^{11}B NMR spectrum of compound **5.Cl**. We thank the Australian Research Council (ARC) for financial support (Grant No. DP034270).

Supporting Information Available: Full details of the crystal structure determination of **4.Cl·6CHCl$_3$·H$_2$O** (CCDC 250753) including positional and thermal parameters and an ORTEP representation. This material is available free of charge via the Internet at http://pubs.acs.org.

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