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Formation of Metallaboratranes: The Missing Link. The First Iridaboratranes, $[IrH(CO)(PPh_3)\{\kappa^3\text{-}B,S,S'\text{-}B(mt)_2R\}](Ir\rightarrow B)$ (mt = Methimazolyl, R = mt, H)

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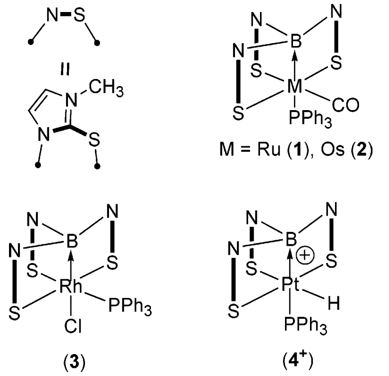
Summary: The reaction of Vaska's complex with 1 equiv of $Na[HB(mt)_3]$ or $Na[H_2B(mt)_2]$ (mt = methimazolyl) affords the iridaboratranes $[IrH(CO)(PPh_3)\{\kappa^3\text{-}B,S,S'\text{-}B(mt)_2R\}](Ir^I\rightarrow B)$ (R = mt, H), the first examples of metallaboratranes in which the transannular metal→boron bond is supported by only two methimazolyl buttresses.

The elucidation of the metallaboratrane structural motif, in the compounds $[M(CO)(PPh_3)\{B(mt)_3\}](M\rightarrow B)$ (M = Ru (**1**),[1] Os (**2**),[2] mt = methimazolyl; Chart 1), afforded the first unequivocal evidence for long mooted dative metal→boron interactions.[3] Within these tricyclo[3.3.3.0] cage structures, the transannular M→B interaction is supported and sterically shielded by three methimazolyl buttresses, which constrain the d^8 ML_5 fragment to adopt a monovacant octahedral geometry. The pair of metal valence electrons in such a constrained geometry are housed in a metal-based orbital of σ symmetry, oriented toward the Lewis acidic B^{III} center. The driving force for assembly of the metallaboratrane motif, and hence the dative interaction, may thus be considered a function of several factors, including d occupancy, geometric constraints, and metal σ basicity. In seeking to explore the inherent limitations of these factors, we have subsequently reported the preparation of metallaboratranes from groups 9 (Rh)[4,5] and 10 (Pt)[6] and have thus established this geometry to be a general motif for metals with d^8 and d^{10} electron configurations.

The first examples of the metallaboratrane geometry were obtained by the reaction of the hydrotris(methimazolyl)borate salt $Na[HB(mt)_3]$[7] with d^6 transition-metal organyls of the type $[M(R)Cl(L)(PPh_3)_3]$ (ML = RuCO, OsCO, RhCl; R = aryl, vinyl) to afford the d^8 metallaboratranes **1**, **2**, and $[RhCl(PPh_3)\{B(mt)_3\}]$ (**3**), respectively. Implicit in their formation is a process which involves activation of an agostic B−H−M linkage (vide infra) and subsequent reductive elimination of R−H: hence, the role of the σ-organyl as a hydrogen acceptor. However, with our recent report of the platinaboratrane salt $[PtH(PPh_3)\{B(mt)_3\}]Cl(Pt\rightarrow B)$ (**4·Cl**)[6] we have illustrated the capacity to obtain stable examples of the metallaboratrane motif directly from low-valent, nonorganometallic precursors, **4·Cl** being prepared from $Na[HB(mt)_3]$ and *cis*-$[PtCl_2(PPh_3)_2]$. We have thus begun to further examine the elements of group 9, reasoning that isoelectronic precursors may be similarly amenable to metallaboratrane formation. Moreover, pursuant to our goal of elucidating mechanisms that might operate, we envisaged that the incorporation of strongly π-acidic ancillary ligands might reduce the lability of key intermediate species and thus facilitate their isolation. For this purpose Vaska's complex, $[IrCl(CO)(PPh_3)_2]$, was chosen. Herein, we report the synthesis of the first iridaboratranes, $[IrH(CO)(PPh_3)\{\kappa^3\text{-}B,S,S'\text{-}B(mt)_2R\}](Ir\rightarrow B)$ (R = mt, H), which exhibit an unprecedented κ^3-*B,S,S′* chelation mode.

Chart 1. Metallaboratranes



The reaction of $Na[HB(mt)_3]$ with $[IrCl(CO)(PPh_3)_2]$ in dichloromethane solution results in the formation of a single product, which we formulate as the iridaboratrane $[IrH(CO)(PPh_3)\{\kappa^3\text{-}B,S,S'\text{-}B(mt)_3\}]$ (**5**) on the basis of spectroscopic and analytical data (Scheme 1).[8] While crystallographic grade crystals of **5** have thus far proven elusive, the formulation follows unequivocally from multinuclear NMR spectroscopic studies. Thus, the ^1H NMR spectrum reveals the presence of three unique methimazolyl environments, a single triphenylphosphine moiety, and a discrete metal hydride (δ_H −11.8),

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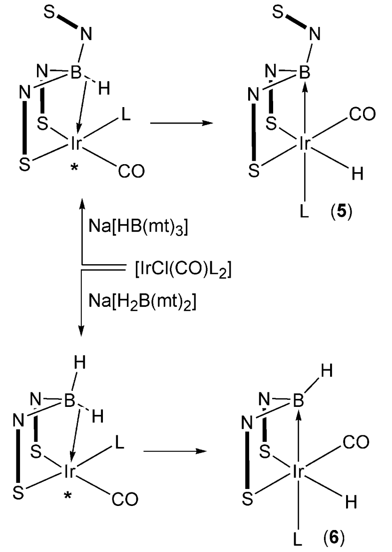
10.1021/om040128f CCC: \$30.25

Scheme 1. Formation of Iridaboratranes[a]



[a] Legend: L = PPh_3, mt = methimazolyl, * = proposed intermediate.

which is believed to lie cis to the phosphine, though $^{31}P-{}^{1}H$ coupling is not resolved. Notable by their absence are resonances associated with either agostic B−H−Ir or terminal B−H groups, their signatures being similarly absent from the infrared spectrum, which does, however, verify the retention of the carbonyl ligand (ν_{CO} 1990 cm^{-1}). The existence of an iridium−boron bond is inferred from the observation of a single, significantly broadened resonance in the $^{31}P\{^{1}H\}$ NMR spectrum (δ_P 4.52, half-height width 136 Hz), due to the triphenylphosphine ligand. This is consistent with those we have observed for other metallaboratranes in which a phosphine lies *transoid* to a dative metal−boron interaction. Having accounted for four coordination sites (CO, B, H, P), this leaves only two remaining for mt chelation; i.e., we must assume a pendant mt group.

Complex **5** is the first example of an iridaboratrane, and its isolation reinforces the emerging generality of this structural motif. Moreover, this is the first instance in which the $B(mt)_3$ fragment has been observed to adopt a bicyclo[3.3.0] cage structure at a metal center. This is significant, since our proposed mechanism for the formation of the platinaboratrane salt **4·Cl**, derived by analogy to those for compounds **1**−**3**, invokes such a species as the penultimate product, arising from (i) κ^2-*S*,*S′* chelation of the $HB(mt)_3$ ligand, (ii) dissociation of a phosphine ligand with formation of an agostic B−H−M interaction,[1b] and (iii) insertion of a metal into the B−H bond.[9] Formation of **4·Cl** is then believed to ensue by dissociation of the remaining chloride ligand and chelation of the pendant mt group. Complex **5** possesses no such labile ligand to allow coordination of the third mt group.

Complex **5** thus represents a "missing link" in the evolution of the metallaboratrane geometry and offers the first qualitative evidence for the stability of, and predilection for attaining, the dative metal−boron interaction. Indeed, of the previously isolated tricyclo[3.3.3.0]metallaboratranes, it might have been argued that it is the constrained cage geometry, inherent from the three buttressing methimazolyl donors, which dictates the spatial proximity of the boron(III) center and metal lone pair, rather than any predisposition toward M→B dative bonding. In contrast, the dibuttressed cage of **5** affords greater flexibility and does not preclude relaxation of the metal geometry to a potentially preferable square-planar arrangement, with dissociation of PPh_3. That such relaxation is not observed is presumably attributable to the presence of the Ir→B linkage. This would seem to confirm that the dative metal−boron interaction is a fundamental component of the bonding scenario within the metallaboratrane motif and is not merely a consequence of geometry.

Encouraged by our successful synthesis of compound **5**, we sought to establish whether the pendant mt group is influential in the B−H addition step and attempted an analogous reaction with the salt $Na[H_2B(mt)_2]$. We note that while several examples of the anionic $H_2B(mt)_2$ ligand adopting a κ^3-*S*,*S′*,*H* chelation mode in transition-metal complexes have been reported,[10] no evidence for insertion of a metal into the agostic B−H function has been previously observed. However, the reaction of $Na[H_2B(mt)_2]$ with $[IrCl(CO)(PPh_3)_2]$ affords a single product, in a manner analogous to that for **5**, which we have unequivocally established to be $[IrH(CO)(PPh_3)\{\kappa^3\text{-}B,S,S'\text{-}B(mt)_2H\}]$ (**6**) by both spectroscopic and crystallographic analysis.[11] Spectroscopically, compound **6** reflects the characteristic traits observed

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(8) Data for **5** are as follows. Yield: 66%. IR (KBr): $\nu_{C\equiv O}$ 1990 ν_{IrH} 2130 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H (299.945 MHz), δ_H −11.8 (s. br., 1 H, IrH), 3.39, 3.54, 3.58 (s × 3, 3 H × 3, NCH_3), 6.54, 6.64 (d × 2, $^{3}J_{HH}$ = 2.3 Hz, 1 H × 2, NCH=CH), 6.59, 6.61 (d × 2, $^{3}J_{HH}$ = 2.0 Hz, 1 H × 2, NCH=CH), 6.77, 6.92 (m br × 2, 1 H × 2, NCH=CH), 7.57−7.48 (m, 6 H, PPh_3), 7.41−7.32 (m, 9 H, PPh_3); $^{13}C\{^{1}H\}$ (75.428 MHz), δ_C 33.9, 34.4, 34.5 (CH_3 × 3), 117.3, 118.9 (NCH=CH), 118.0 (br, NCH=CH × 2) 122.4, 122.8 (NCH=CH), 128.1 (d, $^{3}J_{PC}$ = 9.5 Hz, $C^{3,5}(C_6H_5)$), 129.6 (d, $^{4}J_{PC}$ = 2.0 Hz, $C^{4}(C_6H_5)$), 133.8 (d, $^{2}J_{PC}$ = 12.5 Hz, $C^{2,6}(C_6H_5)$), 134.7 (d, $^{1}J_{PC}$ = 36.3 Hz, $C^{1}(C_6H_5)$), 163.6, 163.9, 166.3, 173.7 (C=S × 3, C≡O); $^{31}P\{^{1}H\}$ (121.420 MHz), δ_P 4.52 (m br, hhw 162 Hz); $^{11}B\{^{1}H\}$ (96.232 MHz) δ_B 3.19 (s br, hhw 149 Hz). Anal. Found: C, 44.36; H, 3.80; N, 9.84; S, 11.13. Calcd for $C_{31}H_{31}BIrN_6OPS_3$: C, 44.66; H, 3.75; N, 10.08; S, 11.54. N.B.: multiple recrystallizations from dichoromethane and light petroleum were necessary to obtain satisfactory elemental microanalytical data, which nevertheless indicate residual dichloromethane (Cl, 0.57).

(9) The term "oxidative addition" is not applicable in this instance, since the metal oxidation state is preserved.

(10) See for example: (a) Garcia, R.; Paulo, A.; Domingos, A.; Santos, I.; Ortner, K.; Alberto, R. *J. Am. Chem. Soc.* **2000**, *122*, 11240. (b) Garcia, R.; Paulo, A.; Domingos, A.; Santos, I. *J. Organomet. Chem.* **2001**, *632*, 41. (c) Garcia, R.; Xing, Y.-H.; Paulo, A.; Domingos, A.; Santos, I. *Dalton* **2002**, 4236. (d) Foreman, M. R. St.-J.; Hill, A. F.; Tshabang, N.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 5593. (e) Abernethy, R.; Hill, A. F.; Neumann, H.; Willis, A. C. *Inorg. Chim. Acta*, in press.

(11) Data for **6** are as follows. Yield: 83%. NMR ($CDCl_3$, 25 °C): ^{1}H (299.945 MHz), δ_H −13.4 (s br, 1 H, IrH), 3.35, 3.47 (s × 2, 3 H × 2, NCH_3 × 2), 6.69, 6.72 (d × 2, $^{3}J_{HH}$ = 2.0 Hz, 1 H × 2, NCH=CH), 6.74, 6.81 (d × 2, $^{3}J_{HH}$ = 1.9 Hz, 1 H × 2, NCH=CH), 7.60−7.52 (m, 6 H, PPh_3), 7.43−7.35 (m, 9 H, PPh_3); $^{13}C\{^{1}H\}$ (75.428 MHz), δ_C 33.8, 34.4 (NCH_3 × 2), 120.0, 120.3 (NCH=CH), 122.3, 122.7 (NCH=CH), 128.1 (d, $^{3}J_{PC}$ = 9.6 Hz, $C^{3,5}(C_6H_5)$), 129.8 (d, $^{4}J_{PC}$ = 1.5, $C^{4}(C_6H_5)$), 133.8 (d, $^{2}J_{PC}$ = 13.0, $C^{2,6}(C_6H_5)$), 135.5 (d, $^{1}J_{PC}$ = 35.0 Hz, $C^{1}(C_6H_5)$), 164.6, 164.9 (C=S), 175.6 (C≡O); $^{31}P\{^{1}H\}$ (121.420 MHz), δ_P 6.2 (m br, hhw 95 Hz); $^{11}B\{^{1}H\}$ (96.232 MHz), δ_B −4.5 (s br, hhw 300 Hz). Anal. Found: C, 42.96; H, 3.62; N, 7.23; S, 8.00. Calcd for $C_{27}H_{27}BIrN_4OPS_2 \cdot 0.5CH_2Cl_2$: C, 43.23; H, 3.69; N, 7.33; S, 8.39. N.B.: multiple recrystallizations were required to completely remove residual PPh_3 and provide an analytically pure sample of the dichloromethane hemisolvate (^{1}H NMR). Crystal data for **6·CHCl₃**: $[C_{27}H_{27}BIrN_4OPS_2] \cdot CHCl_3$, M_r = 841.05, triclinic, $P\bar{1}$ (No. 2), a = 9.3509(2) Å, b = 9.7847(2) Å, c = 19.1038(5) Å, α = 92.759(2)°, β = 99.661(1)°, γ = 110.926(1)°, V = 1598.35(7) Å³, Z = 2, D_c = 1.747 g cm^{-3}, μ(Mo Kα) = 46.4 cm^{-1}, T = 200(2) K, yellow plates, 7345 independent measured reflections, F refinement, R1 = 0.030, wR2 = 0.035 for 6032 independent absorption corrected reflections ($I > 3\sigma(I)$; $2\theta_{max}$ = 48°), 373 parameters, CCDC252699.

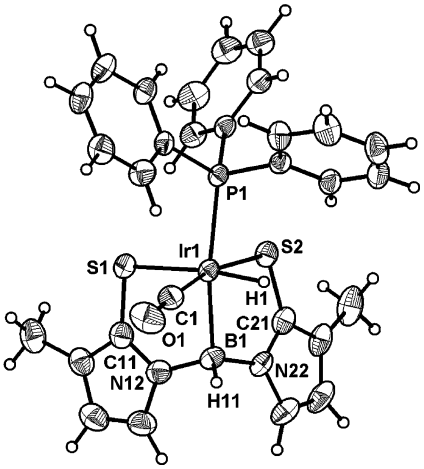

Figure 1. Molecular geometry of [IrH(CO)(PPh$_3$){κ^3-*B,S,S'*-B(mt)$_2$H}] (**6**) in **6·CHCl$_3$** with carbon-bound hydrogen atoms omitted for clarity (50% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Ir−B = 2.210(5), Ir−C = 1.826(5), Ir−P = 2.411(1), Ir−S(1) = 2.485(1), Ir−S(2) = 2.417(1), S(1)−C(11) = 1.717(5), S(2)−C(21) = 1.703(5), B−N(12) = 1.557(6), B−N(22) = 1.581(6); Ir−B−N(12) = 107.8(3), Ir−B−N(22) = 106.5(3), N(12)−B−N(22) = 107.4(3).

for **5**, viz. (i) unique environments for each mt group, (ii) a discrete Ir−H function (δ_H −13.4, d, J_{PH} = 7.6 Hz), (iii) retention of the carbonyl ligand ($\nu_{C\equiv O}$ 1988 cm^{-1}), (iv) absence of an agostic B−H−Ir group, and (v) *transoid* disposition of a single PPh$_3$ moiety and dative Ir→B interaction. Additionally, while it is not resolved in the ^{1}H NMR spectrum, the presence of a terminal B−H function is verified by a weak infrared stretching mode at 2384 cm^{-1}.

The molecular geometry of **6**, in a crystal of the monochloroform solvate, is illustrated in Figure 1, which confirms an octahedral arrangement about iridium, with a direct Ir−B bond (2.210(5) Å) buttressed by two methimazolyl bridges. The proposed arrangement of ancillary ligands is also confirmed, and a peak attributable to the iridium hydride is also observed in the electron density difference map, though this was refined under restraints to an idealized position. While meaningful discussion of the geometric parameters is largely precluded, due to the absence of any suitably comparable structures in the Cambridge Structural Database (CCDC), several features are noteworthy. The iridium−boron linkage may be compared to those observed in σ-boryl complexes, the most closely aligned examples of which are perhaps the 9-BBN complex [IrH$_2$(PMe$_3$)$_3$-(9-BBN)] (2.093 Å)[12] and the catecholborane derivative [IrHCl(CO)(PPh$_3$)$_2$(Bcat)] (2.044 Å),[13] though neither is directly comparable, each being three-coordinate at boron—a feature which would be expected to shorten the Ir−B separation. Perhaps more applicable are σ-carboranyl complexes, wherein the chelated B(III) vertex might be considered to act as a Lewis acid, engaged in dative metal→boron bonding. The few such examples which exist typically exhibit Ir−B linkages in the range 2.09−2.13 Å, though it is noteworthy that in each case the molecular geometry is also constrained by chelating sulfur donors,[14] with less inherent flexibility than those of **6**. Overall, however, the Ir−B separation in **6** is consistent with the formulation of a dative interaction, as compared with these examples and on the basis of covalent radii considerations ($\sum_r$(IrB) = 2.15 Å). The Ir−S distances are largely unremarkable, a strong inverse trans influence being observed for Ir−S2 (2.4173(10) Å; cf. Ir−S1 = 2.4847(11) Å) due to the carbonyl ligand. More unusual is the somewhat long Ir−P linkage (2.4113(10) Å), which exceeds over 96% of those recorded by the CCDC and is notably greater than the sum of covalent radii ($\sum_r$(IrP) = 2.37 Å). This would seem counterintuitive, since a dative Ir→B interaction might be anticipated to exert an inverse trans influence. However, a similar situation has been observed in the dirhodaboratrane salt [Rh$_2${B(mt)$_3$}$_2${κ-*S,S'*-HB(mt)$_3$}]Cl,[4] where lengthening of the bridging Rh−S linkages trans to boron was apparent. For the rhodium example, this effect is arguably consistent with an alternative bonding description, in which the bridgehead boron is described not as a Lewis acid but as an internally base-stabilized σ-boryl, acting as a donor to a Rh(III) center and thus exerting a strong trans influence. A similar argument may be applied to **6**, and indeed a marginal (5σ) discrepancy between the two B−N (1.557(6), 1.581(6) Å) linkages together with the relatively high carbonyl stretching frequency (1988 cm^{-1}) may well afford this credence. However, it remains our belief that while such contributions cannot be discounted, electroneutrality dictates that these be minor components of the overall bonding scenario. Nonetheless, we continue to explore the possibilities and implications in this respect.

In conclusion, we have reported the synthesis of the first iridaboratrane complexes, viz. [IrH(CO)(PPh$_3$)-{κ^3-*B,S,S'*-B(mt)$_3$}] (**5**) and [IrH(CO)(PPh$_3$){κ^3-*B,S,S'*-B(mt)$_2$H}] (**6**). These represent the first examples of the metallaboratrane motif in which the dative metal→boron bond is buttressed by only two methimazolyl groups, affording the complexes greater flexibility and thus potentially allowing relaxation to square-planar geometries. The isolation of these compounds thus implies the acquisition of the dative metal→boron interaction to be inherently favorable—not merely a consequence of a constrained monovacant octahedral geometry—and furthermore supports our proposed mechanism for the formation of such species. Moreover, complex **6** is the first metallaboratrane to possess a sterically unimpeded M→B linkage; thus, there exists now viable scope for derivatization at the metal−boron interface, a scenario which we are currently exploring.

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Supporting Information Available: Figures and tables giving full details of the crystal structure determination of **6·CHCl$_3$** (CCDC 252699), including positional and thermal parameters, and text giving synthetic procedures for **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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