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A Less Carbocentric View of Agostic Interactions: The Complexes $[Rh(\eta^4\text{-cod})\{H_2A(mt)_2\}]$ ($A = B, C^+$; mt = Methimazolyl)

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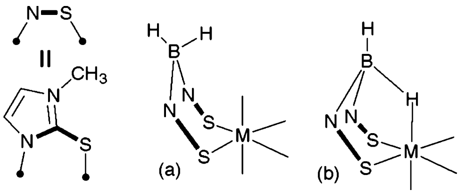
The reaction of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ (cod = 1,5-cyclooctadiene) with $Na[H_2B(mt)_2]$ (mt = methimazolyl) provides the complex $[Rh(cod)\{H_2B(mt)_2\}]$ (**1**), which in turn reacts with CO or $CNC_6H_3Me_2\text{-}2,6$ to provide the derivatives $[RhL_2\{H_2B(mt)_2\}]$ (L = CO (**2**), $CNC_6H_3Me_2\text{-}2,6$ (**3**)). In a similar manner $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ reacts with $H_2C(mt)_2$ to provide the cationic complex $[Rh(cod)\{H_2C(mt)_2\}]^+$ (**4**$^+$), which was isolated after counteranion metathesis as either **4**$\cdot BF_4$ or **4**$\cdot PF_6$. Carbonylation of **4**$\cdot PF_6$ provides $[Rh(CO)_2\{H_2C(mt)_2\}]PF_6$ (**5**$\cdot PF_6$); however, the reaction is reversible in the presence of cod, regenerating **4**$\cdot PF_6$ under reduced pressure. The reactions of **4**$\cdot PF_6$ with $CNC_6H_3Me_2\text{-}2,6$ or $CNCMe_3$ provide respectively the salts $[Rh(CNC_6H_3Me_2\text{-}2,6)_2\{H_2C(mt)_2\}]PF_6$ (**6**$\cdot PF_6$) and $[Rh(CNCMe_3)_4]PF_6$. The crystal structures of **1**, **4**$\cdot BF_4$, **4**$\cdot PF_6$, and **6**$\cdot BF_4$ reveal long B−H···Rh or C−H···Rh interactions; however, such an interaction is effectively absent for **5**$\cdot PF_6\cdot CHCl_3$, while solution spectroscopy (^1H NMR and IR) indicates that none of these interactions persist in solution. The complexes **1** and **4**$^+$ represent the first structurally characterized isoelectronic pair involving, albeit weak, three-center−two-electron B−H−metal or C−H−metal interactions.

Introduction

Strictly speaking, the term *agostic*, as introduced by Brookhart and Green,[1] should only refer to "*covalent interactions between carbon−hydrogen groups and transition metals in organometallic compounds.*"[1a] This view might be considered somewhat carbocentric, given the variety of element−hydrogen σ-bonds that have been found to associate with transition-metal centers in a three-center−two-electron (3c−2e) manner.[2] Furthermore, this would appear to exclude organolanthanoid, actinoid, and group 1 and 2 derivatives, for which C−H···M interactions are also featured, though they are generally less covalent in nature. While the coordination of H−H and C−H bonds especially captures the attention of organometallic chemists, the study of interactions of Si−H and B−H bonds with metal centers is a well-developed and in some respects more mature field. To establish whether carbon actually warrants special consideration, e.g. compared to boron, it would be worthwhile to consider a pair of isoelectronic complexes that varies only in the replacement of carbon by boron. To the best of our knowledge, structural data for such a hypothetical couple are not available, precluding any comparison, with all other factors being equal.

We have recently become concerned with the activation of B−H bonds by metal centers while attempting to unravel the mechanistic details of metallaboratrane formation (Chart 1),[3] for which both 3c−2e B−H···M interactions and B−H addition products B−M−H play a role. Metallaboratrane formation has arisen tangentially from our investigations of the organometallic chemistry of Reglinski's hydrotris(methimazolyl)borate[4] and Parkin's dihydrobis(methimazolyl)borate ligands[5] ($H_xB(mt)_{4-x}$; mt = methimazolyl; $x = 1, 2$) with heavier metals from groups 8−10. Notably, these are all metals with a proven track record in the activation of H−H, C−H, B−H, and Si−H bonds. In part, we attribute the ease of metallaboratrane formation to the specific geometric features of methimazolyl-based chelates, the topology of which appears to predispose the bridgehead B−H functionality toward 3c−2e interactions with metals.[3,5−9] If indeed the apparently favorable adoption of this type of B−H···M interaction is driven by the geometry of the $H_xB(mt)_{4-x}$ ligands, then in principle other element−hydrogen bonds might be similarly activated, were the bridgehead boron to be replaced by the element of interest. Herein we address this question with

Chart 1. Bis(methimazolyl)borate Coordination[a]



[a] Legend: (a) κ^2S,S'; (b) κ^3H,S,S'.

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respect to a bridgehead carbon group which has led us to contrive and structurally characterize the first pair of isoelectronic complexes[10,11] in which a 3c−2e electron interaction involves either B−H···M or C−H···M interactions, all other things being equal. If, as indeed transpires, similar interactions can be mooted, then perhaps the carbocentricity of the term "agostic" might be dispensed with, in favor of wider application to ligands with any pendant element−H···M 3c−2e interactions.

Results and Discussion

Bis(methimazolyl)borate Complexes. We have recently described the reaction of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ (cod = 1,5-cyclooctadiene) with $Na[HB(mt)_3]$, which provides the unusual rhodaboratrane salt $[Rh(cod)\{B(mt)_3\}]Cl(Rh\rightarrow B)$ rather than the anticipated complex $[Rh(cod)\{HB(mt)_3\}]$.[3e,h] In a similar manner, the reaction of $Na[H_2B(mt)_2]$ with Vaska's complex provides the iridaboratrane $[IrH(CO)(PPh_3)\{HB(mt)_2\}](Ir\rightarrow B)$[3f] rather than the complex $[Ir(CO)(PPh_3)\{H_2B(mt)_2\}]$, which might have been anticipated by simple analogy with $[Rh(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ (bta = benzotriazolyl),[12] $[M(CO)(PPh_3)\{H_2B(pz)_2\}]$ (M = Rh, Ir; pz = pyrazolyl),[13] and $[Rh(CO)(PPh_3)\{H_2B(pzMe_2\text{-}3,5)_2\}]$.[14] In contrast, the reaction of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ with $Na[H_2B(mt)_2]$ proceeds in a straightforward manner to provide a neutral complex which is formulated as $[Rh(cod)\{H_2B(mt)_2\}]$ (**1**) on the basis of spectroscopic and crystallographic data. Given the characteristic stability of the d^8 square-planar geometry, the existence of a 3c−2e B−H···Rh linkage is by no means essential; indeed, structural data for κ^3H,N,N′ coordination of polypyrazolylborates to rhodium have yet to emerge.[15] While the solid-state IR spectrum of **1** reveals signatures for both terminal ν_{BH} (2370) and 3c−2e ν_{BHRh} vibrations (2192 cm^{-1}), in solution (CH_2Cl_2) both B−H bonds appear to be terminal (ν_{BH} 2344, 2303 cm^{-1}). A broad resonance is observed at δ_H −0.5 in the ^1H NMR spectrum, while the ^{11}B NMR consists of an apparent triplet (δ_B −5.5, $^1J_{BH} \approx 90$ Hz); however, the breadth of the resonance does not allow us to confidently distinguish between a triplet or double-doublet structure with similar couplings. The appearance of these two resonances changes over the temperature range −80 to +25 °C, due presumably to thermal decoupling of the ^{11}B quadrupole; however, the chemical shifts are invariant, thus providing no definitive information about potential fluxional processes. We have generally observed $(mt)_2B{-}H{-}$metal interactions to give rise to resonances in the region δ_H −3 to −6 ppm, while the terminal B−H group of poly(methimazolyl)borates generally give rise to extremely broad resonances in the region 4−5 ppm. Thus, interpretations based on the position of the upfield resonance for **1**, midway between these two regions, remain equivocal.

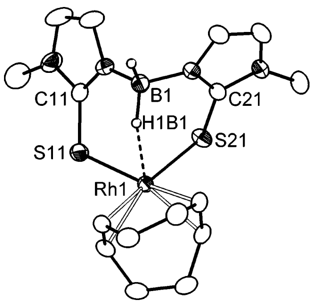

Figure 1. Molecular geometry of **1** (50% displacement ellipsoids, octants indicate heteroatoms, cod and methimazolyl hydrogen atoms omitted). Selected bond distances (Å) and angles (deg): Rh1−S11 = 2.3799(8), Rh1−S21 = 2.4425(13), S11−Rh1−S21 = 92.31(2), Rh1···H1B1 = 2.13(3), Rh1···B1 = 3.033(6), Rh1−C(cod) = 2.124(2)−2.163(2), N21−B1−N11 = 110.03(16), C11−S11−Rh1 = 106.60(7), C21−S21−Rh1 = 104.75(7), B1−H1B1···Rh1 = 134(2).

Given that the spectroscopic data failed to conclusively discriminate between a free or coordinated BH_2 group (or fluxionality), complex **1** was structurally characterized. The results of this study are summarized in Figure 1, which reveals that, consistent with the solid-state IR data, there is indeed a 3c−2e B−H···Rh interaction with Rh···H1B1 and Rh···B separations of 2.13(3) and 3.033(6) Å, respectively. A wide continuum of geometric data exists for B−H−Rh interactions, the majority arising from metallaboranes,[15a] and those for **1** are somewhat long, though within the range for 3c−2e interactions. While metal−boron distances provide more precise geometric parameters than the positions of hydrogen atoms proximal to a heavy metal, it should be noted that, in contrast to κ^3H,N,N′ coordination of poly(pyrazolyl)borates, the extra atom present in each "mt" arm of methimazolyl derived borates, by necessity, results in wider M−H−B angles and greater M···B separations. There is an apparent lengthening of the B−H bond associated with the rhodium center; however, this is not statistically significant (2σ). While bond lengths and strengths do not necessarily correlate, the long B···Rh and H1B1···Rh separations would account for the apparently facile dissociation (hemilability) inferred in solution. Other geometric features for **1** essentially conform to expectations for square-planar rhodium(I) and for complexes of the $H_2B(mt)_2$ ligand.[5−9,15]

As is usually observed for Rh(I) cod complexes, the cod ligand in **1** is readily replaced by carbon monoxide (1 atm), with the formation of the orange complex $[Rh(CO)_2\{H_2B(mt)_2\}]$ (**2**) (Scheme 1). As in the case of **1**, it appears that in the solid

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[10] A rare, though exceedingly elegant, example of a complex featuring *both* C−H−M and B−H−M interactions is provided by $[Ca(HBEt_3)(thf)_2(\eta\text{-}C_5H_2(SiMe_3)_3]$,[20] with Ca−H(B) = 2.209 Å, Ca−B(H) = 2.782 Å, Ca−H(C) = 2.412 Å, and Ca−C(H) = 3.233 Å. Thus, all things being equal, (B)H−M and (H)B−M separations might be expected to be approximately 10 and 15% shorter than the corresponding (C)H−M and (H)C−M interactions, respectively.

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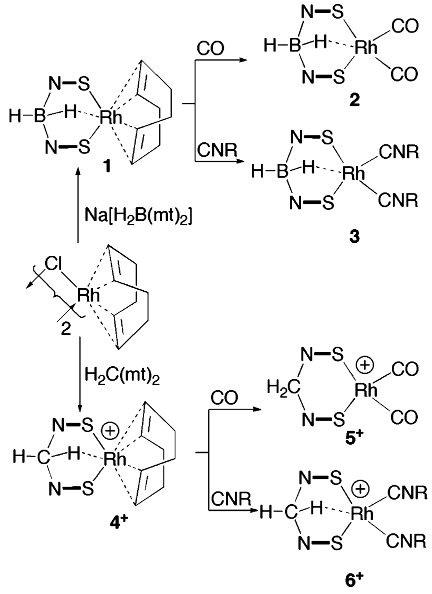
Scheme 1. Synthesis and Reactions of Bis(methimazolyl)borate and Bis(methimazolyl)methane Complexes of Rhodium[a]



[a] R = $C_6H_3Me_2$-2,6.

state a 3c−2e B−H···Rh interaction occurs, as indicated by both terminal ν_{BH} (2385) and 3c−2e ν_{BHRh} (2191 cm^{-1}) IR absorptions. However, in solution these are replaced by two more closely spaced absorptions (2346, 2304 cm^{-1}), both in a region typical of terminal B−H absorptions. Resonances attributable to the BH_2 group were not reliably identified in the ^1H NMR spectrum (25 °C); however, a triplet resonance is observed in the ^{11}B NMR spectrum with a chemical shift and coupling (δ_B −6.5, $^1J_{BH}$ = 96 Hz) similar to those observed for **1**. In a similar manner, the reaction of **1** with $CNC_6H_3Me_2$-2,6 (2 equiv) proceeds smoothly with replacement of the cod ligand and formation of the complex $[Rh(CNC_6H_3Me_2\text{-}2,6)_2\{H_2B(mt)_2\}]$ (**3**). The use of $CNCMe_3$, however, results in the formation of mixtures, the infrared spectra of which indicate the formation of significant amounts of $[Rh(CNCMe_3)_4]^+$, presumably with $[H_2B(mt)_2]^-$ as counteranion.

Bis(methimazolyl)methane Complexes. The ligand $H_2C(mt)_2$ has been previously reported[16] but has not yet been employed in transition-metal coordination chemistry, other than the vague claim that precipitates form with a range of metal salts.[16e] Treating a suspension of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ in methanol with $H_2C(mt)_2$ results in the formation of a yellow solution presumed to contain the salt $[Rh(cod)\{H_2C(mt)_2\}]Cl$ (**4**·Cl), which was converted to the more readily crystallized salts **4**·PF_6 and **4**·BF_4. Spectroscopic data arising from the cations of **4**·Cl, **4**·PF_6 and **4**·BF_4 were comparable. Neither the NMR nor IR data obtained for 4^+ at room temperature include anything untoward that might suggest a 3c−2e C−H−Rh interaction ($CDCl_3$: $\delta_H(CH_2)$ 7.33 br; $\delta_C(CH_2)$ = 58.2). However, cooling a solution of **4**·PF_6 in d_6-acetone results in changes in the ^1H NMR spectrum consistent with the arrested inversion of the C(mt)$_2$Rh boat conformation. Thus, the singlet resonance at δ_H 7.17 broadens progressively from 0 to −60 °C and disappears at ca. −75 °C, to be replaced by the emergence of two signals at 6.58 and 8.06 ppm. These begin to reveal doublet structure approaching the practical temperature limit of −92 °C; however, the AB system is not entirely resolved at this temperature. The separation of the two resonances for the exo and endo protons of 1.48 ppm is substantial; however, that observed to higher field would not appear to be shifted sufficiently to invoke any significant agostic interaction with the rhodium center.

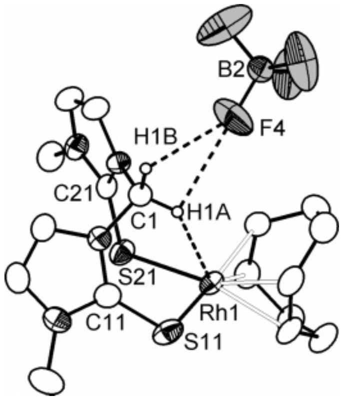


Figure 2. Molecular geometry of **4**·BF_4 (50% displacement ellipsoids, octants indicate heteroatoms, cod and methimazolyl hydrogen atoms omitted). Selected bond distances (Å) and angles (deg): Rh1−S11 = 2.3735(11), Rh1−S21 = 2.4097(12), S11−C11 = 1.708(3), S21−C21 = 1.698(3), Rh1−C(cod) = 2.135(3)−2.156(3), Rh1···H1A = 2.577(6), S11−Rh1−S21 = 93.31(4), C11−S11−Rh1 = 107.72(10), C21−S21−Rh1 = 109.12(10), Rh1···H1A−C1 = 134.4(2). The BF_4 anion is held in close proximity to the cation by two hydrogen bonds (H···F = 2.541, 2.587 Å) between one fluoride and the two methylene protons.

Given that 4^+ is isoelectronic with **1**, the crystal structures of both **4**·BF_4 and **4**·PF_6 were investigated in order to compare the effect upon the geometry of replacing "B" with "C^+", all else being equal. In practice, all else is not equal; the requisite counteranion was found to play a role in the solid-state geometry of the complexes, due to the possibility of hydrogen bonding to various sites on the ligands. However, the solid-state structures of both **4**·BF_4 (Figure 2) and **4**·PF_6 (Figure 3) indicate a C−H−Rh interaction, albeit lengthy (**4**·BF_4, Rh−H1A = 2.577(6) Å, Rh−C1 = 3.346(8) Å; **4**·PF_6, Rh1···H1B = 2.685(6), Rh1−C1 = 3.424(8) Å). Table S1 (Supporting Information) collates structural data for complexes claimed to possess C−H−Rh interactions with Rh···HC and Rh···C(H) separations spanning the ranges 1.884−2.422 and 2.273−3.144 Å, respectively. Thus, the extent of C−H···Rh interaction in 4^+ is equivocal; however, a more convincing example is discussed below. A point of distinction between the isoelectronic complexes **1** and 4^+ is that C−$H^{\delta+}$ and B−$H^{\delta-}$ bonds have reversed polarities. It is therefore perhaps not surprising that, in both salts of 4^+, the counteranion enters into bifurcated hydrogen bonding with protons of the bridgehead methylene. This is also a feature of the crystal structures of **5**·PF_6 and **6**·PF_6 discussed below, and it is difficult to assess the extent to which this perturbs incipient C−H···Rh interactions.

The reactions of **4**·PF_6 with CO and isonitriles mimic those of **1**, with one distinction. Although carbonylation of **4**·PF_6 is achieved quantitatively (1 atm, ^1H NMR), attempts to isolate the product by concentration under reduced pressure results in the isolation of mixtures of **4**·PF_6 and $[Rh(CO)_2\{H_2C(mt)_2\}]PF_6$ (**5**·PF_6), the implication being that the CO coordination is labile such that in the absence of excess CO (evacuation), the

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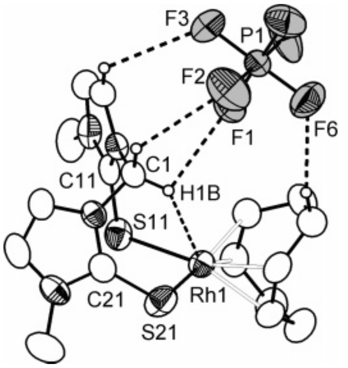

Figure 3. Molecular geometry of **4**·PF$_6$ (50% displacement ellipsoids, octants indicate heteroatoms, cod and methimazolyl hydrogen atoms omitted). Selected bond distances (Å) and angles (deg): Rh1−S21 = 2.3563(12), Rh1−S11 = 2.4122(14), S11−C11 = 1.703(4), S21−C21 = 1.710(4), Rh1−C(cod) = 2.128(3)−2.157(4), Rh1···H1B = 2.685(6), S21−Rh1−S11 = 93.47(5), C11−S11−Rh1 = 108.19(11), C21−S21−Rh1 = 108.39(12), Rh1···H1B−C1 = 131.7(2). The PF$_6$ anion is held in close proximity to the cation by four hydrogen bonds (H···F = 2.466−2.816 Å) between four fluorides and two methylene protons, one methimazolyl proton, and one cyclooctadiene proton.

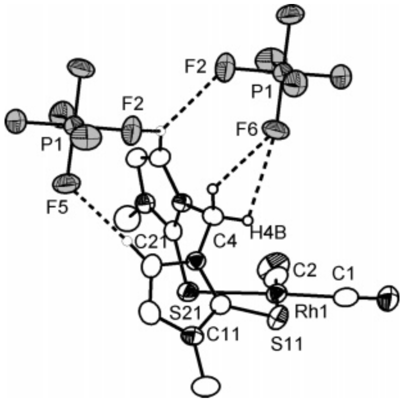

Figure 4. Molecular geometry of **5**·PF$_6$ (50% displacement ellipsoids, octants indicate heteroatoms, cod and methimazolyl hydrogen atoms omitted, two symmetry-related PF$_6$ anions depicted). Selected bond distances (Å) and angles (deg): Rh1−C2 = 1.866(4), Rh1−C1 = 1.866(4), Rh1−S11 = 2.3751(10), Rh1−S21 = 2.3950(10), Rh1···H4B = 2.92(3), Rh1···C4 = 3.560(15), C2−Rh1−C1 = 92.41(15), C1−Rh1−S11 = 87.33(11), C2−Rh1−S21 = 85.05(11), S11−Rh1−S21 = 95.11(3), C11−S11−Rh1 = 107.75(11), C21−S21−Rh1 = 104.18(10), Rh1···H4B−C4 = 123.7(2). The PF$_6$ counteranion is held in close proximity to two cations by five hydrogen bonds (H···F = 2.299−2.590 Å) connecting four fluoride atoms to two methylene protons and one proton of each methimazolyl ring.

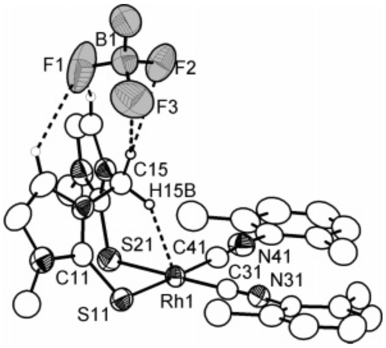

Figure 5. Molecular geometry of **6**·BF$_4$ (50% displacement ellipsoids, octants indicate heteroatoms, cod and methimazolyl hydrogen atoms omitted). Selected bond distances (Å) and angles (deg): Rh1−C31 = 1.906(4), Rh1−C41 = 1.902(4), Rh1−S11 = 2.3996(18), Rh1−S21 = 2.4026(11), Rh1···H15B = 2.346(3), Rh1···C15 = 3.190(6), C31−Rh1−C41 = 92.16(14), C31−Rh1−S11 = 88.44(10), C41−Rh1−S21 = 87.99(11), S11−Rh1−S21 = 91.41(4), C11−S11−Rh1 = 109.64(12), C21−S21−Rh1 = 106.65(12), S11−Rh1−C41 = 179.13(13), S21−Rh1−C31 = 179.44(14), Rh1···H15B−C15 = 142.7(2). The BF$_4$ counteranion is held in close proximity to the cation by a network of four hydrogen bonds (H···F = 2.387−2.719 Å) connecting three fluoride atoms to one methylene proton and one methimazolyl proton of each mt ring.

involatile cod recoordinates. An analytically and spectroscopically pure sample of **5**·PF$_6$ could be obtained by precipitation under an atmosphere of CO. The chelate ligand of **4**$^+$ can be displaced by excess isonitrile more readily than in the case of **1**. Thus, the reaction of **4**·PF$_6$ with CNCMe$_3$ provided primarily [Rh(CNCMe$_3$)$_4$]PF$_6$; however, by employing a less nucleophilic, less volatile, and more accurately and easily dispensed isonitrile (CNC$_6$H$_3$Me$_2$-2,6) it was possible to control the stoichiometry and reaction progress, allowing the isolation of the salt [Rh(CNC$_6$H$_3$Me$_2$-2,6)$_2${H$_2$C(mt)$_2$}]PF$_6$ (**6**·BF$_4$). Both of the salts **5**·PF$_6$ and **6**·BF$_4$ were structurally characterized, and the results of these studies are summarized in Figures 4 and 5, respectively. Notably, the geometry adopted by the H$_2$C(mt)$_2$ ligand in both structures positions one C−H bond proximal to rhodium; however, the extent of the interaction with rhodium is significantly different for the two complexes, despite CO and isonitriles being isoelectronic. Thus, while the methylene bridgehead in **5**$^+$ is essentially beyond bonding distance (**5**$^+$, Rh···H4B = 2.92(3) Å), one proton of the methylene group in **6**$^+$ approaches the rhodium to within the range previously observed for agostic C−H···Rh interactions (Rh···H15B = 2.346(3) Å). This agostic interaction does not, however, lead to any significant pyramidalization of the rhodium center in **6**$^+$, with angles between the remaining ligands summing to 360.0(5)° (359.9(4)° for **5**$^+$). In contrast, the cod ligand in **1** is displaced away from the B−H−Rh group such that C35, C32, S11, and S21 adopt an essentially square-planar arrangement (angle sum 359.5(2)°.

Concluding Remarks

The first transition-metal complexes of the H$_2$C(mt)$_2$ ligand have been isolated and structurally characterized, alongside the first rhodium complexes of the H$_2$B(mt)$_2$ ligand. In all cases, the geometry imposed by the H$_2$A(mt)$_2$Rh (A = B, C$^+$) metallacycle positions one A−H bond proximal to the rhodium center. While the A−H···Rh interactions are not particularly short and are clearly labile in solution, compound **1** and salts of **4**$^+$ represent the first pair of isoelectronic complexes with 3c−2e A−H···M (A = B, C$^+$) interactions. Replacement of the cod ligand in **4**$^+$ with CO results in a greater C−H···Rh separation, while substitution by a less π-acidic isonitrile provides a complex in which the C−H···Rh separation falls indisputably within accepted norms for agostic C−H···Rh bonding. The comparative value of the structural data provided is, however, compromised to some extent by the presence of counteranions, which in all cases enter into hydrogen bonding with the complex cations. Figure 6 presents the metallacyclic cores of **1**, **4**$^+$, **6**$^+$ and that of [Rh(cod){H$_2$B(pzCN-4)$_2$}],[17] the last species exemplifying κ^2N,N′ coordination of a bis(pyrazolyl)borate ligand to rhodium. Taken together, these illustrate that a continuum of concavity may be expected for bis(pyrazolyl)- and bis(methimazolyl)-derived chelates but that the

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(17) Rheingold, A. L.; Incarvito, C. D.; Trofimenko, S. *Inorg. Chem.* **2000**, *39*, 5569.

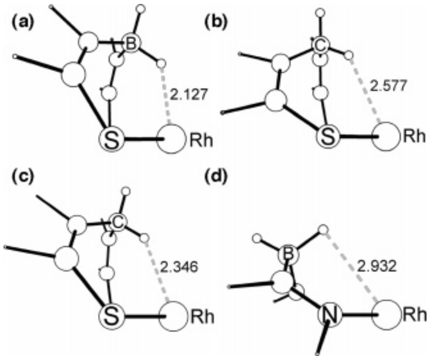

Figure 6. Comparison of the metallacyclic cores of (a) **1**, (b) **4**$^+$, (c) **6**$^+$, and (d) [Rh(cod){H_2B(pzCN-4)$_2$}],[17] as viewed along S,S′ or N,N′ vectors (dimensions in Å).

latter favor deeper "boat" geometries that bring bridgehead groups into closer proximity with metal centers.

Experimental Section

General Methods. Conventional Schlenk and vacuum-line techniques were routinely employed throughout for the exclusion of air. Isolated products generally exhibited moderate air stability as solids. Solvents were distilled under prepurified nitrogen from appropriate drying agents. The compounds [Rh_2(μ-Cl)$_2$(cod)]$_2$,[18] H_2C(mt)$_2$,[16b] and Na[H_2B(mt)$_2$][6a] were prepared according to published procedures. All other materials were obtained from commercial sources and used as supplied after spectroscopic and analytical verification of purity. All NMR spectra were recorded on a Varian Inova 300 instrument (^{1}H at 299.945 MHz and ^{13}C at 75.428 MHz, referenced to external $SiMe_4$; ^{31}P at 121.420 MHz, referenced to external 85% H_3PO_4; ^{11}B at 96.232 MHz, referenced to external $BF_3{\cdot}OEt_2$). Carbon-13 NMR assignments were confirmed, when required, with recourse to 2-D correlation (HMQC and HMBC) spectra. Elemental microanalytical and mass spectrometric data and raw crystallographic data sets for **1** and **4**·BF_4 were provided by the ANU analytical services.

Synthesis of [Rh(cod){H_2B(mt)$_2$}] (1). A mixture of [Rh_2(μ-Cl)$_2$(cod)]$_2$ (100 mg, 0.40 mmol) and Na[H_2B(mt)$_2$] (227 mg, 0.80 mmol) in dichloromethane (30 mL) was stirred anaerobically for 15 h and then freed of resulting NaCl by cannula filtration. The filtrate was freed of volatiles and the residue crystallized from a mixture of dichloromethane and diethyl ether to provide a yellow microcrystalline solid that was isolated and dried in vacuo. Yield: 260 mg (72%). Data for **1** are as follows. IR: CH_2Cl_2, 2344, 2303 ν_{BH} cm^{-1}; KBr, 2370 ν_{BH}, 2192 ν_{BHRh} cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ_H 1.85, 2.45, 4.10 (m × 3 unresolved, 4H × 3, C_8H_{12}), 3.50 (s, 6H, NCH_3), 6.58, 6.75 (s br × 2, 2H × 2, NCHCHN); ^{11}B{^{1}H}, δ_B −5.5 (s, hhw = 110 Hz); ^{11}B, δ_B −5.5 (t, $^1J_{BH}$ = 90 Hz); ^{13}C{^{1}H}, δ_C 31.9, 34.9 (cod CH_2), 78.2 (d, $^1J_{RhC}$ = 11.7 Hz, cod CH═CH), 119.1, 122.4 (NCH═CHN), quaternary CS not identified. NMR (d_6-acetone, 25 °C): ^{1}H, δ_H =1.85, 2.38, 3.97 (m × 3, 4H × 3, C_8H_{12}), 3.46 (s, 6H, NCH_3), 6.92, 6.95 (d × 2, 2H × 2, $^3J_{HH}$ = 2 Hz); ^{11}B, δ_B −1.4 (dd, $^1J_{BH}$ = 90, 103 Hz). FAB-MS (nba matrix): *m/z* 450 [M]$^+$, 340 [M − cod]$^+$. Anal. Found: C, 42.53; H, 5.27; 12.24. Calcd For $C_{16}H_{24}BN_4RhS_2$: C, 42.68; H, 5.37; N, 12.44. Crystal data for **1**: $C_{16}H_{24}BN_4RhS_2$, M_r = 450.23, monoclinic, $P2_1/a$, a = 14.975(5) Å, b = 8.088(5) Å, c = 16.133(5) Å, β = 106.651(5)°, V = 1872.1(14) Å^3, Z = 4, ρ_{calcd} = 1.597 Mg m^{-3}, μ(Mo Kα) = 1.141 mm^{-1}, T = 200(2) K, orange prism, 5481 independent measured reflections, R1 = 0.027, wR2 = 0.064 for 4599 independent observed absorption-corrected reflections ($I > 2\sigma(I)$, $2\theta \le 60°$), 226 parameters. CCDC 287998.

Synthesis of [Rh(CO)$_2${H_2B(mt)$_2$}] (2). In a Schlenk flask, [Rh(cod){H_2B(mt)$_2$}] (**1**; 150 mg, 0.33 mmol) was dissolved in dichloromethane (25 mL) under an atmosphere of nitrogen. Carbon monoxide was then bubbled through the solution for 30 min with continued stirring, after which the solvent volume was reduced under reduced pressure and hexane added to effect precipitation of an orange-brown solid. The remaining solvent was filtered off and the solid dried in vacuo. The crude compound was recrystallized from a mixture of dichloromethane and hexane. Yield: 90 mg (75%). Data for **2** are as follows. IR: CH_2Cl_2, 2346, 2304 ν_{BH}, 2062, 1995 ν_{CO} cm^{-1}; KBr, 2385 ν_{BH}, 2191 ν_{BHRh}, 2054, 1986 ν_{CO} cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ_H 3.63 (s, 6H, NCH_3), 6.69, 6.86 (d × 2, 2H × 2, $^3J_{HH}$ = 2 Hz); ^{11}B, δ_B −6.5 (dd, $^1J_{BH}$ = 95, 99, hhw = 65 Hz); ^{13}C{^{1}H}, δ_C 35.1 (NCH_3), 120.0, 123.1 (NCHCHN), 159.2 (CS), 185.3 (d, $^1J_{RhC}$ = 69 Hz, CO). FAB-MS (nba matrix): *m/z* 396 [M]$^+$, 341 [M − 2CO]$^+$. Anal. Found: C, 29.42; H, 3.13; N, 13.54. Calcd for $C_{10}H_{12}BN_4O_2RhS_2$: C, 30.17; H, 3.04; N, 13.54.

Synthesis of [Rh(CNC$_6$H$_3$Me$_2$-2,6)$_2${H_2B(mt)$_2$}] (3). [Rh(cod){H_2B(mt)$_2$}] (**1**; 200 mg, 0.44 mmol) was suspended in diethyl ether (80 mL), to which was then added 2,6-dimethylphenyl isocyanide (120 mg, 0.92 mmol). The mixture was stirred anaerobically for 12 h and the resulting brick red precipitate isolated by filtration, washed with pentane, and dried in vacuo. The complex could be recrystallized from a mixture of dichloromethane and hexane. Yield: 85 mg (32%). Data for **3** are as follows. IR: THF, 2362, 2276 ν_{BH}, 2118, 2053 $\nu_{C\equiv N}$ cm^{-1}; KBr, 2396, 2277, 2251 ν_{BH}, 2132, 2096 $\nu_{C\equiv N}$ cm^{-1}. NMR (d_6-acetone): ^{1}H, δ_H 2.35 (s, 12 H, CCH_3), 3.56 (s, 6H, NCH_3), 6.94, 7.11 (m × 2, 10H, NCHCHN and C_6H_3). FAB-MS: *m/z* 680 [M + Et_2O]$^+$, 472 [M − CNR]$^+$, 341 [M − 2CNR]$^+$. Anal. Found: C, 50.82; H, 4.72; N, 13.38. Calcd for $C_{26}H_{30}BN_6RhS_2{\cdot}0.5H_2O$: C, 50.91; H, 5.09; N, 13.70 (H_2O confirmed by ^{1}H NMR integration).

Synthesis of [Rh(cod){H_2C(mt)$_2$}]PF$_6$ (4·PF$_6$). [Rh_2(μ-Cl)$_2$(cod)]$_2$ (100 mg, 0.40 mmol) (300 mg, 0.60 mmol) was suspended in methanol (90 mL). To this suspension was added bis(methimazolyl)methane (H_2C(mt)$_2$, 300 mg, 1.25 mmol), resulting in the formation of a yellow solution, which was stirred anaerobically for 90 min. $NaPF_6$ (220 mg, 1.30 mmol) was added and the mixture stirred for a further 30 min, during which time a yellow solid began to form. Slow concentration of the mixture under reduced pressure resulted in the deposition of a yellow solid, which was collected by filtration and dried in vacuo. Yield: 475 mg (63%). The salt could be recrystallized from a mixture of dichloromethane and hexane. A similar procedure, employing $NaBF_4$ in place of $NaPF_6$, provided **4**·BF_4. Data for **4**·PF_6 are as follows. NMR ($CDCl_3$, 25 °C): ^{1}H, δ_H 2.02, 2.46 (m × 2, 4H × 2, cod CH_2), 3.64 (s, 6H, NCH_3), 4.43 (s br., 4H, cod CH═CH), 6.90, 7.46 (m × 2, 2H × 2, NCHCHN), 7.17 (s br, 2H, NCH_2); ^{31}P{^{1}H}, δ_P −142.9 (h, $^1J_{PF}$ = 213 Hz); ^{13}C{^{1}H}, δ_C 31.3 (cod CH_2), 35.8 (NCH_3), 58.2 (NCH_2), 86.4 (d, $^1J_{RhC}$ = 11 Hz, cod CH═CH), 119.7, 120.7 (NCHCHN), 157.7 (CS); ^{31}P{^{1}H}, δ_P −142.9 (h, $^1J_{PF}$ = 213 Hz). ESI$^+$-MS: *m/z* 451.1 [M]$^+$, 343.1 [M − cod]$^+$, 211.2 [M − H_2C(mt)$_2$]$^+$. Anal. Found: C, 33.98; H, 4.11; N, 9.30. Calcd for $C_{17}H_{24}BN_4F_6PRhS_2$: C, 33.63; H, 3.98; N, 9.23. Further data for **4**·BF_4 are as follows. APCI$^+$-MS: *m/z* 451 [M − 2H]$^+$. Anal. Found: C, 37.65; H, 4.55; N, 10.53. Calcd for $C_{17}H_{24}BN_4F_4RhS_2$: C, 37.94; H, 4.49; N, 10.41. Crystal data for **4**·BF_4: $C_{17}H_{24}BF_4N_4RhS_2$, M_r = 538.24, triclinic, $P\bar{1}$ (No. 2), a = 10.121(5) Å, b = 10.293(5) Å, c = 10.705(5) Å, α = 91.279(5)°, β = 93.935(5)°, γ = 112.567(5)°, V = 1025.9(9) Å^3, Z = 2, ρ_{calcd} = 1.738 Mg m^{-3}, μ(Mo Kα) = 1.082 mm^{-1}, T = 200(2) K, yellow prism, 4686 independent measured reflections, R1 = 0.037, wR2 = 0.098 for 4218 independent observed absorption-corrected reflections ($I > 2\sigma(I)$, $2\theta \le 55°$), 265 parameters, CCDC 287997. Crystal data for **4**·PF_6: $C_{17}H_{24}F_6N_4PRhS_2$, M_r = 596.40, triclinic, $P\bar{1}$ (No. 2), a = 10.188(5) Å, b = 10.712(5) Å, c = 11.050(5) Å, α = 87.467(5)°, β = 87.690(5)°, γ

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[18] Komiya, S.; Fukuoka, A. In *Synthesis of Organometallic Compounds: A Practical Guide*; Koyima, S., Ed.; Wiley: New York, 1996; p 238.

= 65.582(5)°, $V = 1113.3(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.779$ Mg m^{-3}, μ(Mo Kα) = 1.089 mm^{-1}, $T = 200(2)$ K, orange prism, 5114 independent measured reflections, R1 = 0.038, wR2 = 0.088 for 3925 independent observed absorption-corrected reflections ($I > 2\sigma(I)$, $2\theta \leq 55°$), 283 parameters, CCDC 287994.

Synthesis of [Rh(CO)$_2${H$_2$C(mt)$_2$}]PF$_6$ (5·PF$_6$). In a Schlenk flask, [Rh(cod){H$_2$B(mt)$_2$}]PF$_6$ (**4**·PF$_6$; 100 mg, 0.17 mmol) was dissolved in dichloromethane (10 mL) under an atmosphere of nitrogen. Carbon monoxide was then bubbled through the solution for 30 min with continued stirring, after which hexane (20 mL) was added to effect precipitation of an orange solid. The remaining solvent was filtered off and the solid washed with petroleum ether (40−60 °C). Data for **5**·PF$_6$ are as follows. IR: CH$_2$Cl$_2$, 2085, 2024 ν_{CO} cm^{-1}; KBr, 2080, 2010 ν_{CO} cm^{-1}. NMR (d_6-acetone, 25 °C): ^{1}H, δ_H 3.87 (s, 6H, NCH$_3$), 6.92 (s br, 2H, N$_2$CH$_2$, no decoalescence behavior above −90 °C), 7.60, 7.76 (s br × 2, 2H × 2, NCH═CHN); ^{13}C{^{1}H}, δ_C 37.3 (NCH$_3$), 61.2 (N$_2$CH$_2$), 122.6, 124.4 (NCH═CHN), 155.4 (CS), 183 (br, unresolved, CO); ^{31}P{^{1}H}, δ_P 143 (h, $^1J_{PF}$ = 213 Hz). ESI$^+$-MS: m/z 399 [M]$^+$, 371 [M − CO]$^+$, 343 [M − 2CO]$^+$. Anal. Found: C, 24.51; H, 2.53; N, 9.74. Calcd for $C_{11}H_{12}F_6N_4PRhS_2O_2$: C, 24.28; H, 2.22; N, 10.29. Crystal data for **5**·PF$_6$·CHCl$_3$: $C_{11}H_{12}F_6N_4O_2PRhS_2$·CHCl$_3$, M_r = 538.24, triclinic, $P\bar{1}$ (No. 2), $a = 10.121(5)$ Å, $b = 10.293(5)$ Å, $c = 10.705(5)$ Å, $\alpha = 91.279(5)°$, $\beta = 93.935(5)°$, $\gamma = 112.567(5)°$, $V = 1025.9(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.738$ Mg m^{-3}, μ(Mo Kα) = 1.082 mm^{-1}, $T = 200(2)$ K, yellow prism, 4686 independent measured reflections, R1 = 0.038, wR2 = 0.098 for 4218 independent observed absorption-corrected reflections ($I > 2\sigma(I)$, $2\theta \leq 55°$), 265 parameters. CCDC 287997.

Synthesis of [Rh(CNC$_6$H$_3$Me$_2$-2,6)$_2${H$_2$C(mt)$_2$}]PF$_6$ (6·PF$_6$). [Rh(cod){H$_2$C(mt)$_2$}]PF$_6$ (**4**·PF$_6$; 50 mg, 0.08 mmol) was dissolved in dichloromethane (20 mL). To this was added 2,6-dimethylphenyl isocyanide (22 mg, 1.7 mmol), after which the yellow solution was stirred for 5 h. Solvent removed at reduced pressure afforded the title compound as a burgundy solid, which was washed with hexane. Yield: 40 mg (67%). Data for **6**·PF$_6$ are as follows. IR: CH$_2$Cl$_2$, 2147, 2100 $\nu_{C\equiv N}$ cm^{-1}; KBr, 2140, 2090 $\nu_{C\equiv N}$ cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H, δ_H 2.40 (s, 12H, CCH$_3$), 3.71 (s, 6H, NCH$_3$), 6.98, 7.44 (s br × 2, 2H × 2, NCH═CHN), 7.07 (s br, 1H, H^4(C$_6$H$_3$)), 7.09 (s br, 2H, H^{3,5}(C$_6$H$_3$)), 7.31 (s br, 2H, N$_2$CH$_2$); ^{13}C{^{1}H}, δ_C 18.9 (C*C*H$_3$), 35.8 (NCH$_3$), 58.5 (N$_2$CH$_2$), 119.4, 120.9 (NCH═CHN), 128.1 (C^4(C$_6$H$_3$)), 128.9 (C^{3,5}(C$_6$H$_3$)), 151.7 (d, $^1J_{RhC}$ = 68 Hz, C≡N), 158.1 (CS); ^{31}P{^{1}H}, δ_P −143 (h, $^1J_{PF}$ = 213 Hz). ESI$^+$-MS: m/z 605 [M]$^+$, 365 [M − H$_2$C(mt)$_2$]$^+$, 234.1 [M − H$_2$C(mt)$_2$ − CNR]$^+$, (also 627 [Rh(CNR)$_4$]$^+$ due to fragmentation in matrix). Anal. Found: C, 41.58; H, 4.02; N, 9.98. Calcd for $C_{27}H_{30}F_6N_6PRhS_2$·0.5CH$_2$Cl$_2$: C, 41.65; H, 3.94; N, 10.60. Similar treatment of **4**·BF$_4$ provided the salt **6**·BF$_4$, which yielded crystals suitable for diffractometry. Crystal data for **6**·BF$_4$·0.5CH$_2$Cl$_2$: $C_{27}H_{30}F_4N_4RhS_2$·0.5CH$_2$Cl$_2$, M_r = 726.01, monoclinic, $C2/c$, $a = 17.146(5)$ Å, $b = 22.332(5)$ Å, $c = 17.492(5)$ Å, $\beta = 106.448(5)°$, $V = 6424(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.501$ Mg m^{-3}, μ(Mo Kα) = 0.776 mm^{-1}, $T = 200(2)$ K, yellow prism, 7379 independent measured reflections, R1 = 0.046, wR2 = 0.120 for 5523 independent observed absorption-corrected reflections ($I > 2\sigma(I)$, $2\theta \leq 55°$), 410 parameters. CCDC 287996.

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Supporting Information Available: Full details of the crystal structure determinations of **1** (CCDC 287998), **4**·BF$_4$ (CCDC 287997), **4**·PF$_6$ (CCDC 287994), **5**·PF$_6$·CHCl$_3$ (CCDC 287997), and **6**·BF$_4$·0.5CH$_2$Cl$_2$ (CCDC 287996) as CIF files and Table S1, collating representative structural data for 3c−2e C−H−Rh interactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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