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Synthesis and Characterization of a Cationic Ruthenium Complex Featuring an Unusual Bis(η^2-BH) Monoborane Ligand

Kevin D. Hesp,[†] Matthew A. Rankin,[†] Robert McDonald,[‡] and Mark Stradiotto*,[†]

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3, and the X-Ray Crystallography Laboratory, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

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The reaction of $\mathrm{Cp^*Ru(P^iPr_3)Cl}$ with $\mathrm{MesBH_2}$ (Mes = 2,4,6-trimethylphenyl), followed by chloride abstraction with $\mathrm{LiB(C_6F_5)_4 \cdot 2.5OEt_2}$ ($\mathrm{LiBF_{20}}$), afforded the crystallographically characterized complex $\mathrm{[Cp^*Ru(P^iPr_3)(BH_2Mes)]^+B(C_6F_5)_4^-}$; notably, this represents the first reported cationic complex to feature an η^2-BH monoborane ligand, as well as a rare example of bis(η^2-BH) ligation.

There is widespread interest in documenting the stoichiometric reactivity of transition-metal complexes with B−H-containing substrates, both in the quest to uncover unusual metal−ligand bonding motifs and as a means of advancing our understanding of prominent metal-catalyzed transformations such as the hydroboration of unsaturated molecules, the dehydrogenative borylation of hydrocarbons, and the dehydrogenation of Lewis adducts including ammonia borane.[1] In this regard, η^2-BH complexes of simple monoboranes represent appealing synthetic targets because such species are commonly implicated in B−H oxidative addition/reductive elimination cycles[1] and can serve as models of reactive σ-CH intermediates in hydrocarbon activation chemistry.[2] However, isolable examples of such η^2-BH complexes remain quite rare,[3−6] especially in comparison to related complexes featuring η^2-HH[7] and η^2-SiH[8] ligands.[1a] Furthermore, despite the potential utility of cationic, coordinatively unsaturated platinum group metal complexes in mediating B−H bond activation chemistry,[1] only neutral complexes supported by η^2-BH monoborane ligands have appeared thus far in the literature.[3,4]

Coordinatively unsaturated species of the type $\mathrm{[Cp^*RuP_n]^+X^-}$ ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$) exhibit rich and diverse reactivity,[9] including reactions with organosilanes leading to isolable η^2-SiH adducts,[1a,8] as well as to catalytically active $\mathrm{[Cp^*(PR_3)(H)_2Ru{=}SiHR]^+X^-}$ species generated via double geminal Si−H bond activation.[10] Given the diagonal relationship between silicon and boron, we became interested in exploring the B−H activation chemistry of simple borane substrates within the coordination sphere of $\mathrm{[Cp^*RuP_n]^+X^-}$ complexes. Herein we report on the reaction of Cp*Ru-

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* To whom correspondence should be addressed. E-mail: mark.stradiotto@dal.ca.

[†] Dalhousie University.

[‡] University of Alberta.

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(5) Conversely, a number of borane adducts of the type $(\eta^1\text{-}\mathrm{BH_3 \cdot L})\mathrm{ML}_n$ have been prepared. For $\mathrm{ML}_n = \mathrm{Cp'RuP_2}^+$ see: Kawano, Y.; Hashiva, M.; Shimoi, M. *Organometallics* **2006**, *25*, 4420, and references cited therein.

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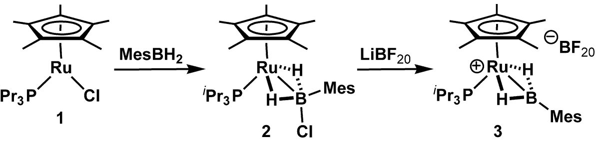
10.1021/ic801300m CCC: $40.75

Scheme 1. Synthesis of **2** and **3**a



^{a} LiBF$_{20}$ = LiB(C$_6$F$_5$)$_4$·2.5OEt$_2$; Mes = 2,4,6-trimethylphenyl.

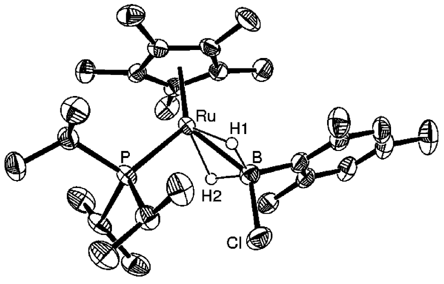


Figure 1. ORTEP diagram of **2** shown with 50% ellipsoids. Selected H atoms have been omitted. Selected interatomic distances (Å) and angles (deg): Ru−P 2.3589(6); Ru···B 2.162(3); Ru−H1 1.63(3); Ru−H2 1.71(3); B−H1 1.29(2); B−H2 1.30(3); B−Cl 1.887(3); B−C 1.586(3); Ru−B−C 123.13(16); P−Ru−B 98.63(7); H1−Ru−H2 71.5(12); H1−B−H2 98.2(16).

(P^{i}Pr$_3$)Cl (**1**)[11] with MesBH$_2$ (Mes = 2,4,6-trimethylphenyl)[12] to give Cp*Ru(P^{i}Pr$_3$)(BH$_2$MesCl) (**2**), which serves as a precursor to [Cp*Ru(P^{i}Pr$_3$)(BH$_2$Mes)]$^+$B(C$_6$F$_5$)$_4^-$ (**3**). Notably, **3** represents the first reported cationic complex to feature an η^2-BH monoborane ligand, as well as a rare example of bis(η^2-BH) ligation.

Treatment of a dark-blue hexanes solution of **1** with 1 equiv of MesBH$_2$ resulted in an immediate color change to orange; ^{31}P NMR analysis of the reaction mixture after 0.5 h revealed the quantitative formation of **2** (Scheme 1),[13] which was isolated as a crystalline solid in 68% yield. The assignment of **2** as a C_S-symmetric chloroborate complex arising from chlorine transfer from ruthenium to boron is supported by NMR spectroscopic data [e.g., $\delta(^1\mathrm{H}) = -11.8$, Ru($H$)$_2$B; $\delta(^{31}\mathrm{P}) = 66.6$; $\delta(^{11}\mathrm{B}) = 46.5$], as well as X-ray diffraction data (Figure 1).[13b,c] The structural features of **2** are in agreement with those of the only other closely related borate complex Cp*Ru(PMe$_3$)(BH$_3$Cl),[14] and the Ru···B distance in **2** [2.162(3) Å] is in keeping with other crystallographically characterized bidentate borohydride complexes.[6,14]

In viewing **2** as a potential precursor to an unusual cationic ruthenium complex of MesBH$_2$, a solution of **2** in hexanes was treated with a solution of LiB(C$_6$F$_5$)$_4$·2.5OEt$_2$ in fluorobenzene (Scheme 1). The addition caused an immediate color change from orange to orange-yellow, and monitoring of the progress of the reaction by use of NMR methods revealed the consumption of **2**, along with the formation of a single new product **3** [$\delta(^{31}\mathrm{P}) = 72.0$].[15] Integration of the ^{1}H NMR spectral data for isolated analytically pure **3** (54%) confirmed the presence of Cp*, P^{i}Pr$_3$, Mes, and two hydrides in this complex. As well, the broad doublet observed in the hydride region of the ^{1}H NMR spectrum (−10.3 ppm, $^2J_{\mathrm{PH}}$ = 15.0 Hz) was observed as a considerably more sharp doublet in the corresponding ^{1}H{^{11}B} NMR spectrum, thereby suggesting the presence of B−H linkages in **3**. The solid-state connectivity in **3** was determined on the basis of a single-crystal X-ray diffraction experiment (Figure 2),[13b,d] thereby establishing this complex as the first cationic member of a very limited class of isolable complexes featuring an η^2-BH monoborane ligand.[3,4] Complex **3** can be viewed as adopting a piano-stool structure, in which the Cp*Ru$^+$ fragment is supported by three neutral two-electron donors: the P^{i}Pr$_3$ coligand as well as two dative interactions involving the bis(η^2-BH)-ligating MesBH$_2$ group, giving an 18-electron configuration. Notably, the bis(η^2-BH) motif in **3** has only been observed in one other complex [Ru(H)$_2$(PCy$_3$)$_2$-(BH$_2$Mes), **4**], recently reported by Sabo-Etienne and coworkers.[3a]While the presence of Ru−H coligands in the neutral complex **4** is of considerable interest in relation to σ-complex-assisted metathesis processes,[1a] the absence of such coligands in the cationic species **3** provides an opportunity to examine bis(η^2-BH) ligation free of potential secondary Ru−H···BMesH$_2$ or other interligand interactions.[1a,3b] The Ru−H [1.61(3) and 1.60(3) Å] and B−H [1.31(3) and 1.28(3) Å] distances in **3** are comparable to those found in **2**, suggesting significant B−H interactions that would appear to be inconsistent with an alternative description of **3** as being the dihydridoborylene species [Cp*(P^{i}Pr$_3$)(H)$_2$Ru=BMes]$^+$B(C$_6$F$_5$)$_4^-$. Notably, the Ru···B contact [1.921(2) Å] in **3** is significantly shorter than that in the precursor **2**; indeed, the Ru···B distance in **3** is statistically equal to that observed in **4** [1.938(4) Å], which represents the shortest reported Ru−B

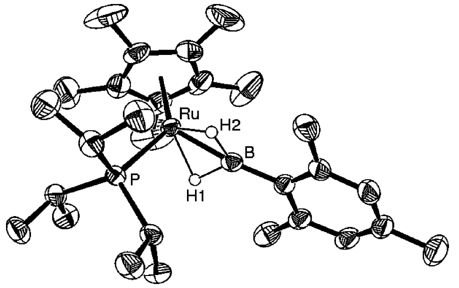


Figure 2. ORTEP diagram of **3** shown with 50% ellipsoids. Selected H atoms and the counteranion have been omitted. Selected interatomic distances (Å) and angles (deg): Ru−P 2.3911(6); Ru···B 1.921(2); Ru−H1 1.61(3); Ru−H2 1.60(3); B−H1 1.31(3); B−H2 1.28(3); B−C 1.522(3); Ru−B−C 172.24(17); P−Ru−B 97.88(7); H1−Ru−H2 79.1(14); H1−B−H2 104.5(17); H1−B−C 126.9(11); H2−B−C 125.3(13).

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(15) We have not been able to observe ^{11}B NMR resonances for **3**, despite prolonged acquisition times using either variable-temperature ^{11}B{^{1}H} NMR methods or ^{1}H−^{11}B HSQC NMR techniques and by employing baseline correction routines. Furthermore, we have thus far not been able to obtain satisfactory IR data for **3** owing to the air sensitivity of the complex.

linkage.[3a] The sum of the H−B−H and H−B−C angles (ca. 357°), as well as the observed Ru−B−C angle [172.24(17)°], is in keeping with bis(η^2-BH) monoborane ligation within the cationic complex **3**. The rare and unusual bis(η^2-BH) coordination featured in **3** can be viewed as providing empirical support for the viability of putative platinum group [(alkane)ML_n]$^+X^-$ species that that feature multiple σ-CH interactions.[2,16]

In a preliminary reactivity survey, heating of **3** in fluorobenzene at 50 °C resulted in clean conversion to the Lewis adduct $^iPr_3P\cdot BH_2Mes$ (**5**; ^{11}B and ^{31}P NMR). In examining the ability of **3** to insert unsaturated substrates, this complex was treated with styrene or diphenylacetylene (1 or 10 equiv); no reaction was observed at ambient temperature, and heating of these reaction mixtures at 50 °C afforded **5** as a major product (^{31}P NMR). By comparison, [Cp*(P^{i}Pr$_3$)(H)$_2$-Ru=SiHR]$^+X^-$ complexes react with α-olefins to afford Si−H insertion products.[10]

In summary, the synthesis and characterization of **3** establishes for the first time the feasibility of η^2-BH monoborane ligation within the coordination sphere of a cationic metal complex. Given the significant insights that have been gained over the past 2 decades through the study of neutral and cationic complexes featuring η^2-HH[7] or η^2-SiH[8] ligands,[17] it is evident that similar comparative reactivity studies involving η^2-BH complexes [including cationic bis(η^2-BH) species such as **3**] could figure importantly in advancing our understanding of this rather poorly explored class of complexes. We are currently developing variants of **3**, in an effort to evaluate how altering the substituents at Ru and B can be exploited as a means of initiating new and interesting reactivity involving the Ru(H)$_2$B core. The results of these and related investigations featuring other cationic platinum group metal η^2-BH complexes will be the focus of future reports.

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Supporting Information Available: Experimental details and characterization data, including X-ray crystallographic information files (CIF) for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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