*Inorg. Chem.* **2008**, *47*, 7471−7473

Inorganic Chemistry
Communication

# Synthesis and Characterization of a Cationic Ruthenium Complex Featuring an Unusual Bis($\eta^2$-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*

Received July 10, 2008

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 $\eta^2$-BH monoborane ligand, as well as a rare example of bis($\eta^2$-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, $\eta^2$-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 $\sigma$-CH intermediates in hydrocarbon activation chemistry.[2] However, isolable examples of such $\eta^2$-BH complexes remain quite rare,[3−6] especially in comparison to related complexes featuring $\eta^2$-HH[7] and $\eta^2$-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 $\eta^2$-BH monoborane ligands have appeared thus far in the literature.[3,4]

Coordinatively unsaturated species of the type $\mathrm{[Cp^*RuP_{\mathit{n}}]^+X^-}$ ($\mathrm{Cp^*} = \eta^5$-$\mathrm{C_5Me_5}$) exhibit rich and diverse reactivity,[9] including reactions with organosilanes leading to isolable $\eta^2$-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 $\mathrm{[Cp^*RuP_{\mathit{n}}]^+X^-}$ complexes. Herein we report on the reaction of Cp*Ru-

---

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

[†] Dalhousie University.

[‡] University of Alberta.

(1) For selected reviews, see: (a) Perutz, R. N.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 2578. (b) Stephens, F. H.; Pons, V.; Baker, R. T. *Dalton Trans.* **2007**, 2613. (c) Braunschweig, H.; Kollann, C.; Rais, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 5254. (d) Aldridge, S.; Coombs, D. L. *Coord. Chem. Rev.* **2004**, *248*, 535. (e) Braunschweig, H.; Colling, M. *Coord. Chem. Rev.* **2001**, *223*, 1. (f) Piers, W. E. *Angew. Chem., Int. Ed.* **2000**, *39*, 1923. (g) Braunschweig, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1786. (h) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685. (i) Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957.

(2) For selected reviews pertaining to the metal-mediated C−H activation of hydrocarbons, see: (a) Crabtree, R. H. *J. Organomet. Chem.* **2004**, *689*, 4083. (b) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (c) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154.

(3) Ruthenium examples: (a) Alcaraz, G.; Clot, E.; Helmstedt, U.; Vendier, L.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **2007**, *129*, 8704. (b) Lachaize, S.; Essalah, K.; Montiel-Palma, V.; Vendier, L.; Chaudret, B.; Barthelat, J.-C.; Sabo-Etienne, S. *Organometallics* **2005**, *24*, 2935. (c) Montiel-Palma, V.; Lumbierres, M.; Donnadieu, B.; Sabo-Etienne, S.; Chaudret, B. *J. Am. Chem. Soc.* **2002**, *124*, 5624.

(4) Non-ruthenium examples: (a) Crestani, M. G.; Muñoz-Hernández, M.; Arévalo, A.; Acosta-Ramírez, A.; García, J. J. *J. Am. Chem. Soc.* **2005**, *127*, 18066. (b) Schlecht, S.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 9435. (c) Muhoro, C. N.; He, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 5033.

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

(6) Related borate complexes of the type $\mathrm{(BH_4)ML_{\mathit{n}}}$ are well established. For a review, see: (a) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263. (b) For $\mathrm{ML_{\mathit{n}} = Cp^*RuP^+}$ see: Suzuki, H.; Lee, D. H.; Oshima, N.; Moro-oka, Y. *Organometallics* **1987**, *6*, 1569.

(7) (a) Heinekey, D. M.; Oldham, W. J., Jr *Chem. Rev* **1993**, *93*, 913. (b) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155.

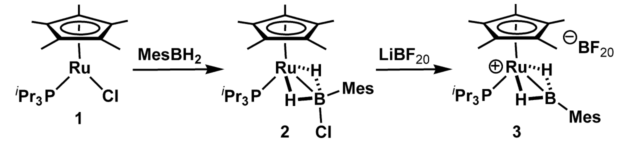
(8) (a) Lachaize, S.; Sabo-Etienne, S. *Eur. J. Inorg. Chem.* **2006**, 2115. (b) Nikonov, G. I. *Adv. Inorg. Chem.* **2005**, *53*, 217. (c) Lin, Z. *Chem. Soc. Rev.* **2002**, *31*, 239. (d) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

(9) (a) Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Eur. J. Inorg. Chem.* **2004**, 17. (b) Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Inorg. Chem.* **1990**, *30*, 1.

(10) Glaser, P. B.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 13640.

10.1021/ic801300m CCC: $40.75

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



[a] $\mathrm{LiBF_{20}} = \mathrm{LiB(C_6F_5)_4 \cdot 2.5OEt_2}$; Mes = 2,4,6-trimethylphenyl.

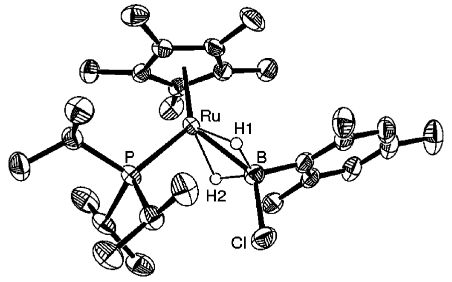


**Figure 1.** ORTEP diagram of **2** shown with 50% ellipsoids. Selected H atoms have been omitted. Selected interatomic distances (Å) and angles (deg): Ru−P 2.3589(6); Ru···B 2.162(3); Ru−H1 1.63(3); Ru−H2 1.71(3); B−H1 1.29(2); B−H2 1.30(3); B−Cl 1.887(3); B−C 1.586(3); Ru−B−C 123.13(16); P−Ru−B 98.63(7);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

$(\mathrm{P}^i\mathrm{Pr}_3)\mathrm{Cl}$ (**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 $[\mathrm{Cp^*Ru(P^iPr_3)(BH_2Mes)}]^+\mathrm{B(C_6F_5)_4}^-$ (**3**). Notably, **3** represents the first reported cationic complex to feature an $\eta^2$-BH monoborane ligand, as well as a rare example of bis($\eta^2$-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 $\mathrm{LiB(C_6F_5)_4 \cdot 2.5OEt_2}$ 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 $\eta^2$-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($\eta^2$-BH)-ligating MesBH$_2$ group, giving an 18-electron configuration. Notably, the bis($\eta^2$-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 $\sigma$-complex-assisted metathesis processes,[1a] the absence of such coligands in the cationic species **3** provides an opportunity to examine bis($\eta^2$-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 $[\mathrm{Cp^*(P^iPr_3)(H)_2Ru{=}BMes}]^+\mathrm{B(C_6F_5)_4}^-$. 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

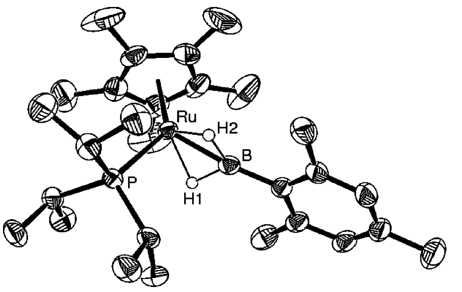


**Figure 2.** ORTEP diagram of **3** shown with 50% ellipsoids. Selected H atoms and the counteranion have been omitted. Selected interatomic distances (Å) and angles (deg): Ru−P 2.3911(6); Ru···B 1.921(2); Ru−H1 1.61(3); Ru−H2 1.60(3); B−H1 1.31(3); B−H2 1.28(3); B−C 1.522(3); Ru−B−C 172.24(17); P−Ru−B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

---

(11) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *Chem. Commun.* **1988**, 278.

(12) Smith, K.; Pelter, A.; Jin, Z. *Angew. Chem. Int. Ed.* **1994**, *33*, 851.

(13) (a) Full experimental details are provided in the Supporting Information. (b) ORTEP-3 for Windows version 1.074: Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565. All Ru−$H$−B positions were located in the Fourier difference map and refined freely. (c) Crystal data for **2** (193 K): monoclinic ($P2_1/c$); $a = 16.007(2)$ Å; $b = 10.4284(14)$ Å; $c = 18.504(3)$ Å; $\beta = 106.1982(16)$ Å; $V = 2966.1(7)$ Å$^3$; $Z = 4$; GOF = 1.063; R1 = 0.0302; wR2 = 0.0761. (d) Crystal data for **3** (193 K): orthorhombic ($Pbca$); $a = 18.8734(15)$ Å; $b = 18.0950(15)$ Å; $c = 30.283(3)$ Å; $V = 10341.9(15)$ Å$^3$; $Z = 8$; GOF = 1.047; R1 = 0.0342; wR2 = 0.0900.

(14) Kawano, Y.; Shimoi, M. *Chem. Lett.* **1998**, 935.

(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($\eta^2$-BH) monoborane ligation within the cationic complex **3**. The rare and unusual bis($\eta^2$-BH) coordination featured in **3** can be viewed as providing empirical support for the viability of putative platinum group $[(\text{alkane})\text{ML}_n]^+\text{X}^-$ species that that feature multiple $\sigma$-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 $^i\text{Pr}_3\text{P}\cdot\text{BH}_2\text{Mes}$ (**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, $[\text{Cp}^*(\text{P}^i\text{Pr}_3)(\text{H})_2\text{Ru}{=}\text{SiHR}]^+\text{X}^-$ 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 $\eta^2$-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 $\eta^2$-HH[7] or $\eta^2$-SiH[8] ligands,[17] it is evident that similar comparative reactivity studies involving $\eta^2$-BH complexes [including cationic bis($\eta^2$-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 $\eta^2$-BH complexes will be the focus of future reports.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada and Dalhousie University for their generous support of this work. We also thank Drs. Michael Lumsden and Katherine Robertson (Atlantic Region Magnetic Resonance Center, Dalhousie University) for assistance in the acquisition of NMR data.

**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.

IC801300M

---

(16) For the relevance of such species in metal-mediated hydrocarbon C−H activation chemistry, see: Jones, W. D. *Acc. Chem. Res.* **2003**, *36*, 140.

(17) Kubas, G. J. *Adv. Inorg. Chem.* **2004**, *56*, 127.