8422 *J. Am. Chem. Soc.* **2001,** *123,* 8422−8423

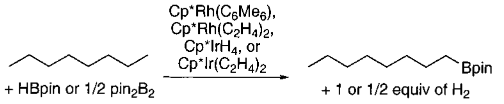
Isolated Ir(V) Boryl Complexes and Their Reactions with Hydrocarbons

Kazumori Kawamura and John F. Hartwig*

Department of Chemistry, Yale University
P.O. Box 208107, New Haven, Connecticut 06520-8107

Received April 9, 2001
Revised Manuscript Received July 6, 2001

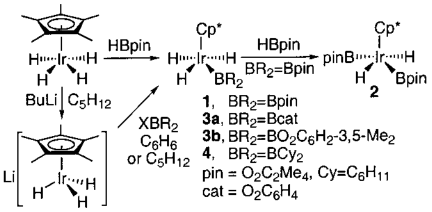
Transition metal−boryl compounds[1,2] are intermediates in a variety of catalytic processes,[3−5] including the regiospecific functionalization of alkanes.[6−8] We recently showed that pentamethylcyclopentadienyl rhodium and iridium complexes with labile dative ligands catalyze under thermal conditions the regiospecific borylation of alkanes at the terminal position (eq 1).[6] We proposed that high-valent Rh(V) and Ir(V) boryl complexes were intermediates in these reactions. The high reactivity of the rhodium boryl compounds and the high temperatures thus far required to form them have prevented isolation of rhodium intermediates in pure form. Thus, we have targeted potential intermediates in the iridium-catalyzed process. In particular, we have sought Ir(V) hydrido boryl complexes.[9] We report our recent success in the generation and the isolation of a series of Ir(V) boryl polyhydrides, including X-ray structural characterization of one example. These compounds are the first fully characterized complexes that react regiospecifically with alkanes to produce free functionalized products.



(1)

Scheme 1 shows our synthetic routes to the Ir(V) boryl complexes. Thermolysis of Cp^*IrH_4[10] with a small excess of pinacolborane (HBpin, 2 equiv) at 80 °C for 50 h in octane formed the monoboryl trihydride **1** in 81% yield after sublimation. Reaction of **1** with a large excess (7−20 equiv) of HBpin for 50 h at 100 °C produced bisboryl dihydride **2** in 74% yield after sublimation. The ^{11}B NMR signals of these materials were singlets and were located at 33.4 and 33.5 ppm. These chemical shifts are slightly downfield of those for pinacolborane and chloropinacolborane and are similar to the chemical shifts of other dioxaborolanyl complexes of iridium.[11−13] Monoboryl **1** displayed a single hydride resonance at room temperature, but the two hydrides were observed as a second-order A_2B pattern at −40 °C, indicating that site exchange of the hydrides occurred on the NMR time scale at room temperature. Similar behavior was observed for the related silyl compound.[10] The dihydrido bisboryl **2** showed a sharp hydride resonance.

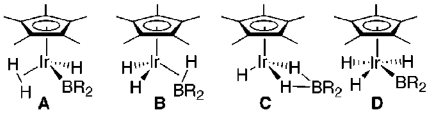
Scheme 1



Reaction of $Li[Cp^*IrH_3]$[10] with haloboranes provided an alternative route to the monoboryl species. This reaction was more convenient for generation of **1** and allowed for the synthesis of Ir(V) boryl complexes with different substituents at boron. Analytically pure **1** was prepared in 87% yield, and catecholboryl complexes **3a** and **3b** were prepared in 83−91% yield. Pure dialkyl boryl **4** was isolated in 85% yield. Compounds **3a** and **3b** showed NMR features similar to those of **1** and **2**: a singlet ^{11}B NMR chemical shift near the corresponding borane and a single hydride signal in the ^1H NMR spectrum at room temperature, which broadened at low temperatures and became resolved into two signals at −30 °C. Important for the discussion below, the two hydride signals showed similar line widths at this low temperature. Compound **4** displayed an ^{11}B NMR chemical shift of 72.1. This shift was significantly upfield of the typical chemical shifts for dialkylboryl compounds,[14,15] even those of iridium,[16] but, like **1**−**3** was similar in chemical shift to that of the haloborane.

Several possible binding modes for **1**−**4** are shown below. These complexes may exist as dihydrogen complexes (**A**), as borane complexes (**B**), as hydridoborate complexes (**C**), or as classical Ir(V) complexes (**D**). Cp^*IrH_4 is an Ir(V) tetrahydride[10] and $Cp^*Ir(H)_2(SiEt_3)_2$ is an Ir(V) bissilyl dihydride.[17,18]

Thus, we disfavor formulating **1**−**4** as Ir(III) dihydrogen complexes. Unfortunately T_1 measurements that have been used to distinguish classical from nonclassical structures[19] would be affected in this case by the quadrupolar boron and would be uninformative.[20] We and others have previously characterized complexes of types **B**−**D** with different metal centers. These data provide a spectroscopic and structural platform to interpret our data for **1**−**4**.



The spectroscopic features expected for a borane complex (**B**)[21−23] are not consistent with the data for **1**−**4**. A borane complex would show $^1H-^{11}B$ coupling in the form of a doublet

---

(1) 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.

(2) Braunschweig, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1786.

(3) Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957.

(4) Han, L.-B.; Tanaka, M. *Chem. Commun.* **1999**, 395.

(5) Smith, M. R., III *Prog. Organomet. Chem.* **1999**, *48*, 505.

(6) Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995.

(7) Chen, H.; Hartwig, J. F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3391.

(8) Waltz, K. M.; Hartwig, J. F. *Science* **1997**, *277*, 211.

(9) For a reaction of phosphine-ligated Ir(III) boryl compounds with arenes and catalytic borylation of arenes with 3 turnover numbers see: Iverson, C. N.; Smith, M. R., III *J. Am. Chem. Soc.* **1999**, *121*, 7696.

(10) Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3508.

(11) Clegg, W.; Lawlor, F. J.; Marder, T. B.; Nguyen, P.; Norman, N. C.; Orpen, A. G.; Quayle, M. J.; Rice, C. R.; Robins, E. G.; Scott, A. J.; Souza, F. E. S.; Stringer, G.; Whittell, G. R. *J. Chem. Soc., Dalton Trans.* **1998**, 301.

(12) Knorr, J. R.; Merola, J. S. *Organometallics* **1990**, *9*, 3008.

(13) Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Can. J. Chem.* **1993**, *71*, 930.

(14) Hartwig, J. F.; Huber, S. *J. Am. Chem. Soc.* **1993**, *115*, 4908.

(15) Waltz, K. M.; Muhoro, C. N.; Hartwig, J. F. *Organometallics* **1999**, *18*, 3383.

(16) Baker, R. T.; Ovenall, D. W.; Calabrese, J. C.; Westcott, S. A.; Taylor, N. J.; Williams, I. D.; Marder, T. B. *J. Am. Chem. Soc.* **1990**, *112*, 9399.

(17) Ricci, J. S., Jr.; Koetzle, T. F.; Fernandez, M.-J.; Maitlis, P. M.; Green, J. C. *J. Organomet. Chem.* **1986**, *299*, 383.

(18) Fernandez, M.-J.; Bailey, P. M.; Bentz, P. O.; Ricci, J. S.; Koetzle, T. F.; Maitlis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 5458.

(19) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126.

(20) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173.

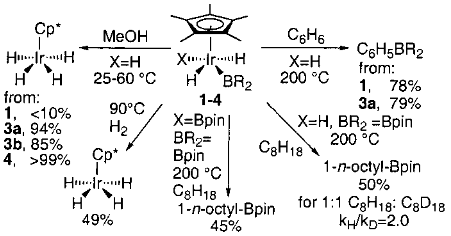
(21) Schlecht, S.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 9435.

(22) Muhoro, C. N.; He, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 5033.

(23) Muhoro, C. N.; Hartwig, J. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1510.

10.1021/ja015975d CCC: $20.00

Scheme 2



^{11}B NMR signal[21] and/or a broad ^1H resonance[22,23] due to coupling with the quadrupolar ^{11}B nucleus; hydrides cis and trans to the boryl group would show different line widths. In addition, Mn borane complexes have shown increasingly broadened ^1H NMR signals at low temperature due to increased coupling.[21] In contrast, the hydride resonances for **1**−**4** were all sharp at temperatures low enough to stop site exchange on the NMR time scale.

A hydridoborate structure (**C**) would also generate broad resonances due to coupling to the quadrupolar nucleus and would display different line widths for the terminal and bridging hydrides[24] when the site exchange is slow on the NMR time scale. Moreover, this structural class would generate ^{11}B NMR signals that are upfield of those for related boryl complexes. The ^{11}B NMR signals of **1** and **3** were located at chemical shifts similar to those of other iridium dioxaborolanyl compounds. Thus, the formulation of **1** and **3** as Ir(V) complexes is the most consistent with our data. Although the upfield boron shift of **4** vs those of previous dialkylboryl complexes[14−16] suggests that this complex may possess some hydridoborate character, this character was not reflected in the hydride line widths.

X-ray structural analysis also supports this formulation, even though the hydride ligands were not located. Ir boryl complexes show M−B distances of 1.99−2.09 Å, and metal hydroborate complexes have longer distances than boryl complexes.[25−27] Moreover, our Mn−borane complexes also showed longer M−B distances than those for related boryl complexes. The Ir−B distance in **1** was 2.047(7) Å (see Supporting Information for details), which falls in the range of Ir−B distances noted above for iridium boryl complexes.[21]

The reactivity of the boryl compounds toward protic reagents, dihydrogen, and hydrocarbons is summarized in Scheme 2. The reactivity toward protic reagents varied dramatically. Pinacolboryl complexes did not react within 12 h with alcohols to form the tetrahydride, even at 100 °C, but the more electrophilic compounds **3a**,**b** and **4** did form Cp^*IrH_4 in 84−100% yield at 50−60 °C and at room temperature, respectively. Complex **1** reacted with dihydrogen at 90 °C to form Cp^*IrH_4 in 49% yield after 72 h under 2 atm of H_2.

Dioxaborylanes **1**−**3** reacted with hydrocarbons to give functionalized products, and **1** and **2** reacted with alkanes. For each reaction with octane, Cp^*IrH_4 was observed at early reaction times, but this species decomposes at the temperatures and times of the reaction (vide infra). Reaction of **1** and **3a** in benzene-d_6 formed $C_6D_5BR_2$ in 78 and 79% yield, respectively. Heating of an octane solution of **1** at 200 °C for 2 d completely consumed **1** and formed the functionalized product in 50% yield. Reaction of **2** formed 2 equiv of octylboronate ester in 45% yield. In general, boron oxide pinBOBpin was formed early in the reaction, presumably from trace amounts of water. After this time, the yields of octylboronate ester were high. The rate for reaction of **2** with octane was similar to that for reaction of **1**. Although it reacted with benzene, complex **3** did not react with octane. Instead the boryl complex in these reactions decomposed to bridging oxo compounds catBOBcat. Likewise, complex **4** formed $(Cy_2B)_2O$, and did not react with either benzene or octane solvent to form phenyl- or octylborane products.

Heating of an octane solution of **1** at 110 °C for 10 d instead of 200 °C for 2 d eventually consumed **1**, but did not form the functionalized product. In this case several new iridium boryl complexes were formed, as indicated by ^{11}B and ^1H NMR spectrometry. We have not been able to isolate these materials in pure form, but heating of this solution at 200 °C for 140 h generated octylboronate ester in 47% yield based on starting **1**. Thus, these compounds may be intermediates in the high-temperature transformation of **1**. Alternatively, they may be formed reversibly by elimination of H_2 and may have structures that are similar to those of dimeric Cp*Ir polyhydrides.[28] These compounds were not observed in the reactions with benzene and were detected only at early reaction times for the reactions of **1** with octane at 200 °C.

Reactions of **1** with deuterated hydrocarbons provided mechanistic insight. Reactions in deuterated benzene led to deuterium incorporation into the Cp* and hydride groups, with faster incorporation into the hydride. ^1H NMR integration of the hydride and Cp* signals showed a decrease in intensity relative to that of the boryl group signal. After 16 h at 80 °C, a deuteride signal for $Cp^*IrH_{3-n}D_n(Bpin)$ was observed by ^2H NMR spectrometry. H/D exchange with octane also occurred, but was much slower than exchange with benzene. After 24 h at 110 °C the hydride signal had decreased in intensity, and a deuteride signal was observed by ^2H NMR spectrometry.

A kinetic isotope effect was observed for the reaction of octane with **1**. Reaction of **1** with a 1:1 mixture of octane and octane-d_{18} showed a k_H/k_D of 2.0. Although qualitative, the reaction of **1** in octane was faster than the separate reaction in octane-d_{18}, suggesting that the intermediate that reacts with alkane is formed reversibly and/or that generation of this intermediate involves cleavage of an Ir−H bond. Reaction of **1** with a 1:1 mixture of C_6H_6 and C_6D_6 was uninformative because of isotope scrambling in the free arene. With the caveat that H/D exchange can be mediated by heterogeneous iridium, the H/D exchange of the iridium hydride along with the primary isotope effect suggests reversible addition of the hydrocarbon during the reaction.

A comparison of the reactivity of **1** with that of Cp^*IrH_4 and $Cp^*IrH_2(SiEt_3)_2$ demonstrates the unusual property of the boryl group to induce C−H activation and functionalization. The tetrahydride decomposes before undergoing H/D exchange with octane. The more thermally stable $Cp^*IrH_2(SiEt_3)_2$ is also inert toward alkanes, even after 20 h at 200 °C. No $DSiEt_3$ or octyl triethylsilane was observed. Thus, the boryl ligand generates compounds that are distinct from both hydride and silyl complexes in their ability to undergo reactions with alkanes. To date, boryl complexes are unique in their reactivity toward regiospecific replacement of a terminal hydrogen in an alkane with a functional group that is present in the ligand of a transition metal complex.[29−32]

Acknowledgment. We thank the NSF for support of this work. K.K. thanks the JSPS for postdoctoral fellowship support. We thank Huiyuan Chen for initially observing the clean reaction of Cp^*IrH_4 with HBpin.

Supporting Information Available: Experimental procedures and characterization of compounds **1**−**4** and X-ray structural data for **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA015975D

---

(24) Empsall, H. D.; Hyde, E. M.; Mentzer, E.; Shaw, B. L.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2069.

(25) Hartwig, J. F.; De Gala, S. R. *J. Am. Chem. Soc.* **1994**, *116*, 3661.

(26) Lantero, D. R.; Motry, D. H.; Ward, D. L.; Smith, M. R., III *J. Am. Chem. Soc.* **1994**, *116*, 10811.

(27) Lantero, D. R.; Miller, S. L.; Cho, J.-Y.; Ward, D. L.; Smith, M. R., III *Organometallics* **1999**, *18*, 235.

(28) Jones, W. D.; Chin, R. M. *J. Am. Chem. Soc.* **1994**, *116*, 198.

(29) Nucleophilic attack on a metal alkyl species is an alternative approach to alkane functionalization and is described in the following three references. This reaction has been shown to occur in Shilov processes, but with lower regioselectivity than the chemistry here.

(30) Nelson, A. P.; DiMagno, S. G. *J. Am. Chem. Soc.* **2000**, *122*, 8569.

(31) Williams, B. S.; Holland, A. W.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 252.

(32) Luinstra, G. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 3004.