

Communications to the Editor

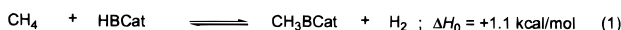
Stoichiometric and Catalytic B–C Bond Formation from Unactivated Hydrocarbons and Boranes

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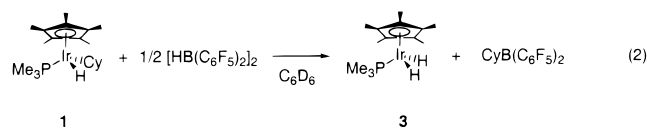
The catalytic functionalization of hydrocarbons represents a long-standing challenge in homogeneous and heterogeneous catalysis.¹ Over the past 20 years a detailed picture of metal-mediated C–H activation has emerged from intensive study by several research groups.^{2–6} While an activation step is requisite for generating species with M–C bonds, further elaboration of the M–C bond must be carefully designed to engender catalytic viability. Lewis acidic reagents are logical choices for converting activated alkyl or aryl groups to functionalized organic products since the reactive complexes and intermediates responsible for C–H activation can be coordinatively unsaturated or cationic reagents, whose reactivity may be hampered by Lewis basic substrates. For borane reagents, thermochemical and computational data establish that the reaction in eq 1 is essentially thermoneutral.⁷ Hence, catalysis is thermodynamically viable. For these reasons, we have been examining metathetic B–C bond forming reactions of B–X and M–C bonds.^{8–13} In this communication, we describe B–C bond forming chemistry for the archetypal C–H activation products, Cp*Ir(PMe₃)(H)(R),¹⁴ and demonstrate catalytic viability of eq 1 for the first time.¹⁵ In



particular, the borane substituents have significant impact on rates for B–C bond formation and are critical for effecting catalytic conversion.

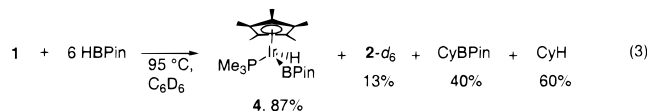
Cp*Ir(PMe₃)(H)(Cy) (**1**, Cy = *c*-C₆H₁₁) and Cp*Ir(PMe₃)(H)(Ph) (**2**, Ph = C₆H₅) reacted with HBX₂ reagents in C₆D₆ to yield

the alkylborane derivatives, CyBX₂ and PhBX₂ (X₂ = (C₆F₅)₂,¹⁶ (CH₃)₂CO–CO(CH₃)₂^{2–} ≡ Pin, O₂C₆H₄^{2–} ≡ Cat). The rates for B–C bond formation and Ir product distributions were borane dependent. For example, the reaction between [HB(C₆F₅)₂]₂ and compound **1** gave Cp*Ir(PMe₃)H₂ (**3**) and CyB(C₆F₅)₂ (eq 2).¹⁷



Conversions were quantitative, as judged by ¹H NMR, and complete within 5 min at ambient temperature. Alkane elimination from compound **1** was not observed, and Ir products from solvent activation were not detected. Characterization of CyB(C₆F₅)₂ was established by comparing ¹H and ¹¹B NMR data to an authentic sample, prepared from [HB(C₆F₅)₂]₂ and cyclohexene. The reaction between [HB(C₆F₅)₂]₂ and compound **2** gave a mixture of products.

For oxygen-substituted boranes, B–C bond formation required more forcing conditions as illustrated by the reactivity of pinacolborane (HBPin) with compound **1**. In benzene-*d*₆ solutions, this reaction yielded Cp*Ir(PMe₃)(H)(BPin) (**4**) and 2-*d*₆ as the major Ir products.¹⁸ The boryl compound, **4**, was identified by comparing ¹H, ¹¹B, and ³¹P NMR data to those for compound **4** generated from compound **3** and HBPin.¹⁹ The fate of the cyclohexyl group is revealed by the formation of CyBPin and cyclohexane. A typical product distribution obtained for the reaction of compound **1** with 6 molar equiv of HBPin at 95 °C is shown in eq 3. Although rigorous kinetic analysis was precluded



by irreproducible rate data, the qualitative rates for cyclohexane formation were much higher than expected for thermal elimination of cyclohexane from compound **1**.²⁰ Two potential mechanisms that could account for enhanced cyclohexane formation include the reaction of CyBPin and compound **3** to generate **4** and cyclohexane or pathways that involved metathesis between compound **1** and C₆D₆.²¹ Control experiments indicated that (i) CyBPin and Cp*Ir(PMe₃)H₂ do not produce cyclohexane and

(16) Parks, D. J.; von h. Spence, R. E.; Piers, W. E. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 809–811.

(17) The yields in eqs 2–5 were determined from integration of NMR spectra.

(18) Unless otherwise noted, satisfactory combustion analyses were obtained for all new Ir complexes.

(19) Compound **4** is an oil at room temperature, but satisfactory combustion analysis was obtained. Relevant spectroscopic data include the following: ¹H NMR (C₆D₆) δ -17.64 (d, 1 H, Ir–H, [²J_{H–P}] = 29 Hz), 1.17 (12 H, BO₂C₆H₁₂), 1.50 (d, 9 H, PMe₃, [²J_{H–P}] = 10 Hz), 2.10 (d, 15 H, C₅Me₅, [⁴J_{H–P}] = 2 Hz). ¹¹B NMR (C₆D₆) δ 33. ³¹P{¹H} NMR (C₆D₆) δ -42.8.

(20) Expected yields of CyH from thermal elimination from compound **1** were determined from the extrapolated rate constant at 95 °C from previously reported activation parameters: Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537–1550.

(21) Trialkylaluminum reagents react with compound **3** to yield alkanes and Ir–Al bonds: Golden, J. T.; Peterson, T. H.; Holland, P. L.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1998**, *120*, 223–224.

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(1) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154–162.

(2) For recent reviews on C–H activation see refs 3–6.

(3) Bengali, A. A.; Arndtsen, B. A.; Burger, P. M.; Schultz, R. H.; Weiller, B. H.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *Pure Appl. Chem.* **1995**, *67*, 281–288.

(4) Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 2599–2599.

(5) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879–2932.

(6) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2181–2192.

(7) Rablen, P. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 4648–4653.

(8) Some aspects of this chemistry have been highlighted,¹¹ and some preliminary findings have been presented: Iverson, C. N.; Smith, M. R., III; 216th National Meeting of the American Chemical Society, Boston, MA, August 23–27, 1998; INOR 518.

(9) Iverson, C. N.; Smith, M. R., III *J. Am. Chem. Soc.* **1995**, *117*, 4403–4404.

(10) For recent reviews of boryl complex chemistry see refs 11–13.

(11) Smith, M. R., III *Prog. Inorg. Chem.* **1999**, *48*, 505–567.

(12) Braunschweig, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1787–1801.

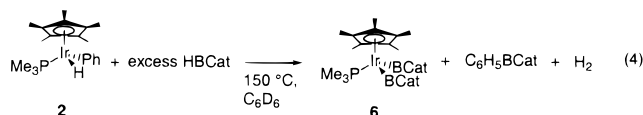
(13) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. *J. Chem. Rev.* **1998**, *98*, 2685–2722.

(14) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929–3939.

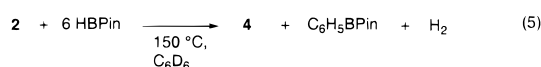
(15) For leading references to related stoichiometric C–H activation by metal boryl complexes see: Waltz, K. M.; Hartwig, J. F. *Science* **1997**, *277*, 211–213.

compound **4** and (ii) deuterium incorporation in compound **4** was insignificant.²²

The reaction between compound **1** and HBCat gave a ratio of CyBCat to cyclohexane similar to that in eq 3. In addition to Cp*Ir(PMe₃)(H)(BCat) (**5**) and compound **2**, the diboryl compound, Cp*Ir(PMe₃)(BCat)₂ (**6**), was also formed in this reaction. The boryl products were identified by comparing spectroscopic data to authentic samples prepared from compound **3** and HBCat. Reactions of compound **2** with HBPIn and HBCat required elevated temperatures. In both cases PhBX₂ was the major organoboron product. For HBCat, the diboryl compound, **6**, was the predominant Ir product (eq 4), while the reaction with HBPIn



yielded the monoboryl compound, **4** (eq 5).²³



The stoichiometric chemistry of compounds **1** and **2** suggested potential catalytic conversion of unactivated hydrocarbons to organoboranes in this system. Since B–C bond formation was most facile for reactions of compounds **1** and **2** with [HB(C₆F₅)₂]₂, catalytic viability of this borane reagent was assessed first. The dihydride product in eq 2 reacts with [HB(C₆F₅)₂]₂ to generate a borohydride complex, Cp*Ir(PMe₃)(H)(HBH(C₆F₅)₂) (**7**). At elevated temperatures, a complex mixture formed when benzene or cyclohexane solutions of compound **7** were heated with excess [HB(C₆F₅)₂]₂, eliminating the possibility of a clean thermal catalytic process. Since photolyses of compound **3** in the appropriate solvent generate compounds **1** and **2**, similar photochemical generation of compounds **1** and **2** from compound **7** would complete a photocatalytic cycle. Unfortunately, compound **7** was photochemically inert.

(22) The isotopic constitution for cyclohexane produced in reaction between compound **1** and HBPIn in toluene-*d*₈ was examined by GC/MS. Deuterium incorporation was not detected.

(23) The yield for the reaction in eq 5 cannot be determined due to catalytic B–C bond formation from C₆D₆ and HBPIn. It is noteworthy that some C₆H₆ elimination is observed under the reaction condition, while pure compound **2** does not exchange with C₆D₆ after extended thermolysis at 190 °C.

(24) Although hydroboration of benzene has been proposed to account for isotopic scrambling between B₂H₆ and C₆D₆,²⁵ we see evidence (¹¹B NMR) for exchange between HBPIn and C₆D₆. Moreover, B–C bond formation was not observed when solutions of HBPIn and C₆H₆ were heated at 150 °C.

(25) Gaines, D. F.; Heppert, J. A.; Kunz, J. C. *Inorg. Chem.* **1985**, *24*, 621–624.

(26) Conversion was judged to be nearly quantitative by ¹¹B NMR.

(27) Although photolysis of compound **4** in cyclohexane produces compound **1** and HBPIn, thermolysis of the resulting mixture does not afford the CyBPIn. We currently have no explanation for this apparent solvent effect.

(28) Periana, R. A.; Taube, D. J.; Evtit, E. R.; Loffler, D. G.; Wentreck, P. R.; Voss, G.; Masuda, T. *Science* **1993**, *259*, 340–343.

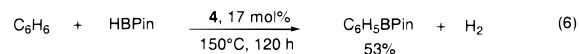
(29) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560–564.

(30) Jones, W. D.; Kosar, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5640–5641.

(31) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483.

Thermal B–H or B–B elimination from compounds **4** and **6** was assessed by heating C₆D₆ solutions of the pure compounds. After several days at 200 °C, decomposition was not evident and there was no evidence for elimination. Thus, photochemical reactivity of mono- or diboryl derivatives seemed necessary for catalytic activity. Although the diboryl compound, **6**, was photochemically inert, the phenylhydride compound, **2**, was regenerated when a benzene solution of the monoboryl compound, **4**, was photolyzed. Although less efficient, the regeneration of **1** also occurred when a cyclohexane solution of **4** was photolyzed. Thus, thermal B–C and photochemical Ir–C bond-forming events constitute a catalytic cycle for HBPIn.

To evaluate the viability of photocatalytic benzene activation, a thick-walled flask was charged with compound **3** (0.15 mol) and HBPIn (0.89 mmol) and the contents were dissolved in C₆H₆. After the solution was photolyzed to generate compound **2** (confirmed by ³¹P NMR), the flask was heated in an oil bath to convert compound **2** to compound **4** and C₆H₅BPIn. After the thermal conversion was complete, the solution was photolyzed to regenerate compound **2**. From the initial Ir and borane concentrations, full conversion should have required five thermal/photolytic cycles; however, ¹¹B NMR indicated full conversion of the borane after the third thermolysis. This observation clearly implicated a thermal catalytic process. Although we had determined that solutions of compound **4** do not react with C₆H₆, reexamination of the NMR spectra for the “stoichiometric” reaction in eq 5 indicated that the intensity of the pinacolate resonance for CyBPIn is greater than anticipated. When a solution of compound **4** and 5 molar equiv of HBPIn was heated in C₆D₆, ¹¹B NMR indicated exchange between the boron hydride and solvent deuterons after 18 h at 150 °C. Conversion to C₆D₅BPIn was quantitative after 60 h at 150 °C, as judged by ¹H and ¹¹B NMR.^{24,25} The reaction was repeated on a larger scale (**4**, 0.15 mmol; HBPIn, 0.75 mmol) in C₆H₆, and C₆H₅BPIn was isolated in 53% yield (eq 6).^{26,27}



Aside from methane-to-methanol conversion,^{28,29} catalytic C–H functionalizations for unactivated hydrocarbons are extremely rare.³⁰ Since applications of boronate esters in cross-coupling chemistry are expansive,³¹ the demonstration of catalytic viability of eq 1 is significant. Although the nature of the borane reagent is critical to catalytic viability, the role of added borane in the hydrocarbon activation by compound **4** is more important. We hope to answer this question and extend our findings to catalytic activation of hydrocarbons in related systems.

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Supporting Information Available: Synthetic and spectroscopic details for all new compounds as well as ¹H, ³¹P{¹H}, and ¹¹B NMR spectra for the crude reaction mixture corresponding to eq 1 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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