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Hydrocarbon Functionalization by Transition Metal Boryls

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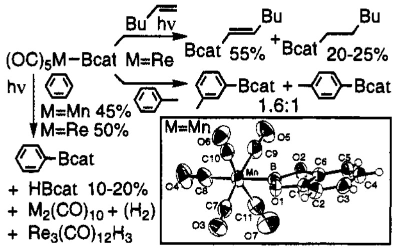
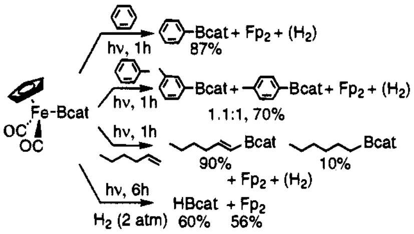
We report the functionalization of hydrocarbons by the reactions of arenes and alkenes with $(CO)_5MnBcat$ (cat = $O_2C_6H_4$) (**1**), $(CO)_5ReBcat$ (**2**), and $CpFe(CO)_2Bcat$ (**3**). The activation of unreactive C−H bonds has been one of the major goals of transition metal chemistry,[1] and systems have been discovered that oxidatively add even alkane C−H bonds.[2] However, few systems activate and *functionalize* any type of hydrocarbon.[1c,3] We have found that irradiation of metal boryl complexes **1**−**3** in the presence of arenes and alkenes leads to the selective, high-yield formation of aryl- and vinylboranes. This C−H activation chemistry is an unusual route to important synthetic intermediates. It is well known that such organoboranes can be readily converted to alcohols, amines, aldehydes, and organic halides. Further, they can be used as nucleophiles for additions to organic electrophiles by uncatalyzed or palladium-catalyzed chemistry.[4]

The synthesis and hydrocarbon functionalization chemistry of $(CO)_5MBcat$ (M = Mn, **1**; Re, **2**) is displayed in Scheme 1, and the analogous chemistry for $CpFe(CO)_2Bcat$ (**3**) is outlined in Scheme 2. The manganese boryl compound **1** was prepared in 72% yield by the addition of ClBcat to $Na[Mn(CO)_5]$[5] in toluene solvent and was crystallized at −30 °C from the reaction solution after filtration and layering with pentane. The boryl complex of rhenium carbonyl was prepared by an analogous method, except two recrystallizations were required to obtain analytically pure boryl complex (30% yield). The synthesis and structure of iron complex **3** have been reported previously.[6] Boryl complexes of manganese carbonyl and $CpFe(CO)_2$ have been reported.[7] However, the ^{11}B NMR chemical shifts of these compounds[8] are much different from those characterized crystallographically in this paper and another.[6]

Scheme 1



Scheme 2



A crystal structure of **1** is provided in Scheme 1. The Mn−B distance is 2.108(6) Å, longer than the metal−boron distances in related metal carbonyl boryl complexes $CpFe(CO)_2Bcat$ (**3**) (1.959(6) Å),[6] and $(CO)_4Fe(Bcat\text{-}t\text{-}Bu)_2$ (2.028(7) Å).[9] In the compounds $(CO)_5MR$ (M = Re, Mn; R = alkyl, H),[10] the M−CO bond located trans to the alkyl or hydride ligand is shorter than the other four CO distances. A different influence of the trans ligand on the M−CO bond length is observed in compound **1**, as the metal−carbonyl bond length trans to the boryl (1.841(6) Å) falls in the range of the other four M−CO distances (1.832(8)−1.870(7) Å).

Irradiation of a solution of **1** in benzene solvent for 6 h with a medium-pressure Hanovia mercury arc lamp led to the decay of the starting complex and the formation of PhBcat, a borane formed by functionalization of the solvent, in 45% yield by NMR spectroscopy versus an internal standard. HBcat (10−20%) was formed competitively with PhBcat. The transition metal product was $Mn_2(CO)_{10}$, as determined by IR spectroscopy of the reaction mixture. The phenyl boronate ester product was identified by its ^{11}B NMR resonance at δ 32, by its ^1H NMR spectrum after solvent removal, and by its GC/MS spectrum that showed a clear molecular ion. These spectroscopic data were all identical with those for a sample prepared independently by addition of catechol to Cl_2BPh. HBcat was identified by its characteristic doublet centered at δ 29 in the ^{11}B NMR spectrum and by comparison of the ^1H NMR spectrum with that of an authentic sample.

Irradiation of the rhenium compound **2** for 3 h in benzene solvent also provided PhBcat in 50% yield. Traces (5−10%) of HBcat were again formed. The major rhenium product was $Re_2(CO)_{10}$, although $Re_3(CO)_{12}H_3$[11] was also formed. Infrared spectroscopy of reaction solutions, as well as a ^1H NMR signal at δ −17.4 for $Re_3(CO)_{12}H_3$ identified these products. Irradiation of **2** in toluene solvent led to the formation of the meta and para isomeric aryl boronate esters in Scheme 1 in a 1.6:1 ratio (57% combined yield) and the same metal-containing species as from reactions in benzene. The two isomeric aryl

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(1) (a) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (c) Hill, C. L. In *Activation and Functionalization of Alkanes*; Shilov, A. E., Ed.; John Wiley and Sons, Inc.: New York, 1989.

(2) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929; (b) **1982**, *104*, 352. (c) Jones, W. D.; Feher, F. *J. Am. Chem. Soc.* **1985**, *107*, 620. (d) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7433; 7436. (e) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449. (f) Hackett, M.; Ibers, J. A.; Whitesides, G. *J. Am. Chem. Soc.* **1988**, *110*, 1436. (g) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190. (h) Sanner, R. D.; Miller, F. D. *Organometallics* **1988**, *7*, 818.

(3) (a) Jones, W. D.; Foster, G. P.; Putinas, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5047. (b) Fisher, B. J.; Eisenberg, R. *Organometallics* **1983**, *2*, 764. (c) Kunin, A. J.; Eisenberg, R. *Organometallics* **1988**, *7*, 2124; (d) *J. Am. Chem. Soc.* **1986**, *108*, 535. (e) Sakakura, T.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1987**, 758. (f) Maguire, J. A.; Boese, W. T.; Goldman, A. S. *J. Am. Chem. Soc.* **1989**, *111*, 7088. (g) Maguire, J. A.; Goldman, A. S. *J. Am. Chem. Soc.* **1991**, *113*, 6706. (h) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025. (i) Baudry, D.; Ephritikine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1980; (j) **1982**, 606.

(4) (a) Brown, H. C. *Organic Synthesis via Boranes*; Wiley: New York, 1975. (b) Brown, H. C. *Boranes in Organic Chemistry*; Cornell University Press: Ithaca, NY, 1972. (c) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: New York, 1988.

(5) The solid anions used in this chemistry were prepared by Na/Hg reduction of the dimers and were heated and washed with toluene to remove as much THF as possible.

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

(7) Schmid, G. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 819.

(8) A list of the chemical shifts of the previously reported compounds is included in the following: Nöth, H.; Wrackmeyer, B. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: New York, 1978; Vol. 14, p 271.

(9) $Fe(CO)_5$ adds Cat*BBCt* to form $Fe(CO)_4(BCat^*)_2$: He, X.; Hartwig, J. F. *Organometallics*, in press.

(10) (a) Davies, J. A.; El-Ghanam, M.; Pinkerton, A. A. *J. Organomet. Chem.* **1991**, *409*, 367−376. (b) LaPlaca, S. J.; Hamilton, W. C.; Ibers, J. A.; Davison, A. *Inorg. Chem.* **1969**, *8*, 1928. (c) Lee, G.-H.; Peng, S.-M.; Yang, G.-M.; Lush, S.-F.; Liu, R.-S. *Organometallics* **1989**, *8*, 1106−1111. (d) Lindner, E.; Pabel, M.; Fawzi, R.; Mayer, H. A.; Wurst, K. *J. Organomet. Chem.* **1992**, *435*, 109−121. (e) Masters, A. P.; Richardson, J. F.; Sorensen, T. S. *Can. J. Chem.* **1990**, *68*, 2221.

(11) Andrews, M. A.; Kirtley, S. W.; Kaesz, H. D. *Inorg. Synth.* **1977**, *17*, 66.

0002-7863/95/1517-11357$09.00/0

boronate esters were independently generated from ClBcat and the appropriate Grignard reagent. Compound **2** also underwent high-yield dehydrogenative borylation of alkenes. For example, irradiation of **2** in 1-hexene provided the terminal, trans vinylborane in 55% yield by NMR spectroscopy. Only minor amounts of other vinylborane isomers were detected by GC/MS. Most of the remaining material (20–25% yield) was the hydroborated alkene, as determined from ^{11}B NMR spectroscopy and GC/MS. This *n*-hexylborane product was independently prepared by hydroboration of 1-hexene with HBcat at 110 °C and was presumably formed in the reaction mixture by photochemical, metal-catalyzed hydroboration with HBcat formed in competition with the vinylborane.[12] The trans vinylborane was identified by comparison of the ^{1}H and ^{11}B NMR spectra of reaction solutions to those of an independently prepared sample from $Cp_2Ti(CO)_2$-catalyzed addition of HBcat to 1-hexyne.[13] The rhenium product mixture was complex. A single hydride resonance at δ −14.5 was observed that accounted for roughly 25% of the C−H bonds cleaved, and products from alkene coordination may be formed. The hydride resonance did not correlate with any hydrides of solely rhenium carbonyl structures, and firm identification of the rhenium products awaits further study.

These results suggested to us that $CpFe(CO)_2Bcat$ (**3**) might also activate and functionalize hydrocarbons under photochemical conditions. Indeed, irradiation of a solution of compound **3** for 1 h in benzene solvent provided PhBcat in 80–90% yield, and $[CpFe(CO)_2]_2$ was the only iron product. As in all of the reactions, no Ph−Ph product was detected by GC. Irradiation of **3** in toluene solvent led to formation of a 1.1:1 ratio of meta and para isomers of tolylBcat. No orthofunctionalized products were observed, consistent with low yields of arylborane products from reactions in *p*-xylene solvent. The reaction of **3** in 1-hexene gave the terminal trans vinylborane isomer in 85–90% yield along with roughly 10% *n*-hexylborane product.

The more active nonpolar bond of molecular hydrogen also underwent reaction with **3** under photochemical conditions. Irradiation of a sample of **3** in pentane solvent under 2 atm of hydrogen for 6 h gave HBcat as the major product in 40–50% yield. Again, $[CpFe(CO)_2]_2$ was the major organometallic product, although a small hydride resonance for $CpFe(CO)_2H$ was observed under the H_2 atmosphere. The manganese boryl compound also reacted with hydrogen, but with much lower yields, and an accurate measurement of the reaction yield was not performed.

The aryl boronate ester products were converted to the corresponding alcohols directly in the reaction mixture by typical oxidation procedures. We conducted oxidations of reaction solutions generated from photolysis of **3** in arenes. Reaction of **3** with benzene, followed by oxidation, gave 70% overall conversion of benzene to phenol and 65% overall conversion of toluene to *m*- and *p*-cresol.

The C−H activation and functionalization chemistry could be envisioned to occur by either a photochemically activated transition metal boryl compound or a photochemically generated free boryl radical, since irradiation of the alkyl complexes $CpFe(CO)_2R$, $(CO)_5MnR$, and $(CO)_5ReR$ is known to provide competitive extrusion of CO and alkyl radicals.[14] A comparison of the selectivities for reactions of the three boryl complexes would probe for a common boryl radical intermediate. Similar selectivities would support the presence of a common intermediate, while different selectivities would argue against one. Our data indicate that the arene and alkene activation and functionalization reactions involve a metal boryl complex, rather than a catecholboryl radical that would be formed as a common intermediate by irradiating each of **1**–**3**.

The selectivities observed for reactions of the $Mn(CO)_5$, $Re(CO)_5$, and $CpFe(CO)_2$ systems were all different. PhBcat was formed exclusively from irradiation of $CpFe(CO)_2Bcat$, while PhBcat and HBcat were formed competitively from reaction of $(CO)_5MnBcat$ and $(CO)_5ReBcat$. Perhaps more striking, the ratios of *m*- and *p*-isomers of the aryl boronate esters resulting from toluene activation were clearly different for reaction of FpBcat and $(CO)_5ReBcat$.

The selectivity for reaction with C_6H_6 and C_6D_6 would further probe for a common intermediate. Consistent with C−H activation and functionalization occurring with an intermediate that is a metal boryl complex, the observed isotope effects for **1**–**3** were distinct. Complexes **1**–**3** were irradiated in 1:1 mixtures of benzene and benzene-d_6 solvent, and the ratios of PhBcat and PhBcat-d_5 products were determined by GC/MS. The isotope effect k_H/k_D observed for reaction of **3** was 3.3 ± 0.4, that for reaction of **2** was 5.4 ± 0.4, and that for reaction of **1** was 2.1 ± 0.1. These differences in isotope effects, along with differences in PhBcat/HBcat, and the meta/para toluene activation products, essentially rule out a common boryl radical intermediate. These single isotope effect experiments, however, do not allow for discrimination between various mechanisms for the C−H cleavage, including reaction by a 16-electron intermediate formed by photochemical ejection of CO or reaction by a photochemically generated exited state of intact **1**–**3**.

Although the dehydrogenative borylation of benzene has not been observed previously, dehydrogenative borylation of alkenes has been observed in catalytic chemistry.[15] The replacement of a vinyl hydrogen by a boryl group has been rationalized by reversible alkene insertion. It is possible that hexene undergoes a photochemically initiated insertion into the metal−boryl bond[16] of **2** and **3**, followed by C−H bond cleavage as a β-hydrogen elimination. However, it is less likely that benzene undergoes insertion into the metal−boryl linkage. A potentially relevant silylation of benzene was observed during studies of tetraalkyldisiloxane oligomerizations, albeit in low yield,[17] and our chemistry alludes to an arylation of an electrophilic carborane by benzene observed recently.[18]

It is clear from these results that the polarity of transition metal−boron covalent bonds, which is opposite to that of typical metal−ligand bonds, can produce highly unusual chemistry. Further, the formation of strong[19] but reactive B−C bonds allows for useful functionalization reactions. We are now investigating methods for catalytic functionalization of arene solvents and for boryl complexes that react with alkanes.

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Supporting Information Available: Spectroscopic and analytical data for **1** and **2**; X-ray crystallographic results for **1** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[12] Essentially all commercially available metal carbonyl compounds catalyze hydroborations by HBcat under photolytic conditions. He, X.; Hartwig, J. F., unpublished results.

[13] He, X.; Hartwig, J. F., submitted.

[14] (a) Alt, H. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 766–782. (b) Giese, B.; Thoma, G. *Helv. Chim. Acta* **1991**, *74*, 1143–1155. (c) Gismondi, T. E.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *284*, 59–71.

[15] (a) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 8863–8869. (b) Burgess, K.; van der Donk, W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, G. C. *J. Am. Chem. Soc.* **1992**, *114*, 9350. (c) Brown, J. M.; Lloyd-Jones, G. C. *J. Chem. Soc., Chem. Commun.* **1993**, 710.

[16] Westcott, S. A.; Marder, T. B.; Baker, R. T. *Organometallics* **1993**, *12*, 975.

[17] Gustavson, W. A.; Epstein, P. S.; Curtis, M. D. *Organometallics* **1982**, *1*, 884.

[18] Hawthorne, M. F.; Mavunkal, I. J.; Knobler, C. B. *J. Am. Chem. Soc.* **1992**, *114*, 4427.

[19] Rablen, P. R.; Hartwig, J. F.; Nolan, S. P. *J. Am. Chem. Soc.* **1994**, *116*, 4121.