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Functionalization of Alkanes by Isolated Transition Metal Boryl Complexes

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Abstract: We report the photochemical reaction of transition metal boryl complexes of the type $Cp^*M(CO)_nB(OR)_2$ (M = Fe, Ru, W) with alkanes to form alkylboronate esters in yields as high as 85% for reaction of $Cp^*W(CO)_3[Bcat(Me)_2]$ $\{[Bcat(Me)_2] = B\text{-}1,\ 2\text{-}O_2C_6H_2\text{-}3,\ 5\text{-}Me_2\}$ with pentane. Synthesis of a series of Cp and Cp* catecholboryl complexes showed that sterically blocking or eliminating sp^2 positions on the metal boryl complex was important for alkane functionalization to occur. The metal boryl complexes reacted exclusively at the terminal C−H position of alkanes. Functionalization of 2-methylbutane occurred preferentially at the least sterically hindered terminal position with a selectivity of 10:1. This selectivity data, in addition to kinetic isotope effects measured for reaction of metal boryls with a mixture of pentane and pentane-d_{12}, argues against radical chemistry. Several experiments were conducted to probe for CO dissociation. An experiment employing added ^{13}CO, one conducted under 2 atm pressure of CO, and one conducted in the presence of PMe_3 indicated that the mechanism involves CO dissociation to form a 16-electron intermediate that reacts faster with alkane solvent than it recoordinates CO. The effect of boryl electronics on the functionalization of alkanes was studied by examining the reactions of ruthenium dialkylboryl, dithioboryl, and dialkoxyboryl complexes with pentane. The dialkoxyboryl complexes gave the highest yields of functionalized product. A comparison between reactions of the different boryl complexes in arene and alkane solvents showed that the electronic properties of the boryl group had a greater effect on the reaction of the unsaturated intermediate with alkane than they did on the generation of the intermediate.

Introduction

The efficient conversion of alkanes to products with functionality at the terminal position is a long-standing synthetic problem.[1−3] Hydrocarbons are typically considered inert due to their high C−H bond strength and low acidity. Thus, reagents or catalysts that are reactive enough to cleave C−H bonds often react unselectively or at the weakest C−H bonds, which are the internal ones.[1] Few reagents and even fewer catalysts *selectively* cleave primary C−H bonds. Metal-catalyzed oxidation of linear alkanes is typically unselective. With only recent exceptions[4−6] involving shape-selective catalysts, the most selective reactions have occurred at the weakest tertiary C−H bonds.[7,8] In contrast, homogeneous transition-metal systems which react stoichiometrically with C−H bonds through oxidative addition or σ-bond metathesis pathways generally show reactivity at primary, over secondary and tertiary, C−H bonds.[9]

While many homogeneous metal systems are known that cleave C−H bonds regiospecifically at primary positions,[10−12] few functionalize the alkane directly. One of the simplest ways to functionalize alkanes is through dehydrogenation, which recently has been reported to form terminal olefins regioselectively in the presence of a second olefin as hydrogen acceptor.[13] Internal olefins were formed in the absence of acceptor,[14] or at long reaction times with acceptor. Metal-catalyzed carbonylation of pentane is also selective for the primary position,[15,16] but the chemoselectivity for aldehyde product and the alkane conversion were low. Shilov showed that chloroplatinum salts could react with alkanes in aqueous solution to form alcohols and alkyl halides.[17] In this case the reactions occur preferentially at the primary position, but the selectivity for primary vs secondary positions in linear alkanes, such as pentane and hexane, is only on the order of 3:1.[18] The oxidation of alkanes by electrophilic metal systems has been enhanced through the use

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

(2) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2180−2192.

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

(4) Thomas, J. M.; Raja, R.; Sankar, G.; Bell, R. G. *Nature* **1999**, *398*, 227−230.

(5) Raja, R.; Sankar, G.; Thomas, J. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2313−2316.

(6) Dugal, M.; Sankar, G.; Raja, R.; Thomas, J. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2310−2313.

(7) *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; John Wiley and Sons: New York, 1989.

(8) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds: Mechanistic Principles and Synthetic Methodology Including Biochemical Processes*; Academic Press: New York, 1981.

(9) *Selective Hydrocarbon Activation*; Davies, J. A., Watson, P. L., Liebman, J. F., Greenberg, A., Eds.; Wiley-VCH: New York, 1990.

(10) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562−563.

(11) Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 4358−4359.

(12) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1997**, *119*, 10696−10719.

(13) Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086−4087.

(14) Xu, W.; Rosini, G. P.; Gupta, M.; Jensen, C. M.; Kaska, W. C.; Krogh-Jespersen, K.; Goldman, A. S. *Chem. Commun.* **1997**, 2273−2274.

(15) Sakakura, T.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1987**, 758−759.

(16) Rosini, G. P.; Zhu, K. M.; Goldman, A. S. *J. Organomet. Chem.* **1995**, *504*, 115−121.

(17) Gol'dshleger, N. F.; Es'kova, V. V.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim. (Engl. Transl.)* **1972**, *46*, 785−786.

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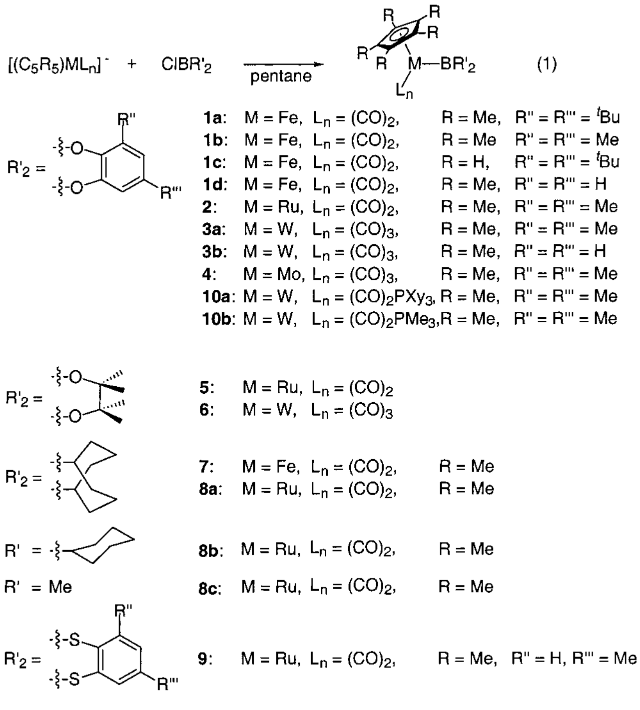
of strongly acidic media.[2,19] Sen used this chemistry to develop the Pd-mediated oxidation of methane in trifluoroacetic acid.[20,21] This process was made catalytic by use of hydrogen peroxide as the stoichiometric oxidant in trifluoroacetic anhydride.[22] The selective oxidation of methane also was carried out using 5% Pd/C as catalyst, dioxygen as oxidant, and soluble copper salts as cocatalyst in a mixture of trifluoroacetic acid and water.[23] Periana has developed a Pt system which converts methane to methyl bisulfate in fuming sulfuric acid in high yield and high selectivity.[24] We recently reported the selective catalytic photochemical[25] and thermal[26] borylation of alkanes to produce alkylboronate esters, and these discoveries stemmed from our initial report of selective, stoichiometric borylation of alkanes.[27] The organoboron products are versatile synthetic intermediates that provide access to a variety of functionalized organic compounds, such as alcohols, amines, ketones, aldehydes, and alkyl halides.[28] We report here a systematic synthetic and mechanistic account of the photochemical functionalization of alkanes by isolated transition metal boryl complexes.

Results

Synthesis and Characterization of Transition Metal Boryl Complexes. The transition metal boryl complexes used for this work on alkane functionalization were prepared by reacting the appropriate metal carbonyl anion with haloborane in toluene or pentane solvent (eq 1). The metal carbonyl anions were prepared by Na/Hg reduction of the corresponding dimers, and the metal phosphine carbonyl anions were prepared by deprotonation of the metal hydride using *n*-butyllithium. The pinacolboryl complexes were prepared from the metal anion and *B*-chloropinacolborane, which was prepared and used in situ. The reactions were monitored by ^{11}B NMR spectroscopy,[29] which showed the disappearance of haloborane and the formation of the metal boryl complexes. The dialkoxyboryl, dialkylboryl, and dithioboryl complexes resonated between δ 45 and 58, between δ 117 and 126, and at δ 78, respectively. The metal boryl complexes were isolated from boron and metal impurities by recrystallization and in some cases by sublimation.



In most cases, the ^{1}H and ^{13}C NMR spectra of the compounds were straightforward. In all cases we observed free rotation about the M−B bond on the NMR time scale. In the case of the tungsten monophosphine complex Cp*W(CO)$_2$PXy$_3$[Bcat(Me)$_2$], we observed hindered rotation about the M−P bond on the ^{1}H and ^{13}C NMR time scale. Instead of a single resonance that would be expected for the six *ortho* aromatic hydrogens of the xylyl group, two resonances with an intensity ratio of 2:1 were observed. In addition, the 18 protons of the xylyl methyl groups appeared as two resonances, again with a 2:1 ratio of integrated intensity. The ^{1}H NMR spectrum of the molybdenum analogue showed a similar pattern at room temperature; however, the spectrum at 64 °C showed a single set of ligand aromatic resonances, indicating that rotation around the W−P bond occurred rapidly on the NMR time scale at this elevated temperature. A possible structure of these complexes at room temperature would contain one xylyl group aligned with the metal Cp* axis and the other two xylyl groups canted symmetrically from the axis.

Table 1. Carbonyl-Stretching Frequencies for Ruthenium Boryl, Alkyl, and Hydride Complexes[a]

compound	ν_{CO} (cm^{-1})
Cp*Ru(CO)$_2$[Bcat(Me)$_2$] (**2**)	2012, 1952
Cp*Ru(CO)$_2$BS$_2$Tol (**9**)	2007, 1948
Cp*Ru(CO)$_2$Bpin (**5**)	2002, 1940
Cp*Ru(CO)$_2$H[b]	2000, 1941
Cp*Ru(CO)$_2$Me[c]	1998, 1935
Cp*Ru(CO)$_2$BBN (**8a**)	1994, 1931
Cp*Ru(CO)$_2$BCy$_2$ (**8b**)	1984, 1921

[a] All IR spectra were recorded in benzene, except for **2** and **5** which were recorded in benzene-*d*$_6$. [b] From ref 76. [c] From ref 31.

IR spectra of the complexes revealed electronic effects of the metal boryl substituents. Table 1 provides IR stretching frequencies for the various complexes, with some benchmarks for the analogous alkyl and hydrido species. These data indicate that the dialkylboryl groups are the strongest electron donors overall, whereas the catecholboryl groups are the weakest electron donors. The dithio- and pinacolboryl groups were intermediate donors, with the pinacolboryl the stronger donor of the two. The dialkylboryl groups appear to be stronger donors and the dithio- and dialkoxyboryl groups weaker donors than the methyl or hydride groups in Cp*Ru(CO)$_2$Me and Cp*Ru(CO)$_2$H. The pinacolboryl complex showed the closest ν_{CO} values to those of Cp*Ru(CO)$_2$H and Cp*Ru(CO)$_2$Me.

Photochemical Reaction of Transition Metal Boryl Complexes with Alkanes. Reaction of Metal Catecholboryl Complexes with Pentane. Using our previous results on arene functionalization as a starting point,[30] we sought complexes that

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[18] Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97−143.

[19] Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550−557.

[20] Sen, A. *Acc. Chem. Res.* **1988**, *21*, 421−428.

[21] Sen, A.; Gretz, E.; Oliver, T. F.; Jiang, Z. *New J. Chem.* **1989**, *13*, 755−760.

[22] Kao, L.; Hutson, A. C.; Sen, A. *J. Am. Chem. Soc.* **1991**, *113*, 700−701.

[23] Lin, M.; Hogan, T.; Sen, A. *J. Am. Chem. Soc.* **1997**, *119*, 6048−6053.

[24] Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560−564.

[25] Chen, H.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 3391−3393.

[26] Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995−1997.

[27] Waltz, K. M.; Hartwig, J. F. *Science* **1997**, *277*, 211−213.

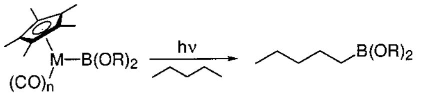
[28] Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: New York, 1988.

[29] 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.

Table 2. Yields of 1-Pentylboronate Ester and 1-Pentylborane from Photochemical Reaction of Transition Metal Boryl Complexes with Pentane

compound	% yield
$CpFe(CO)_2(Bcat)$	<1
$Cp^*Fe(CO)_2[Bcat(^tBu)_2]$ (**1a**)	15
$Cp^*Fe(CO)_2[Bcat(Me)_2]$ (**1b**)	20
$CpFe(CO)_2[Bcat(^tBu)_2]$ (**1c**)	<1
$Cp^*Fe(CO)_2(Bcat)$ (**1d**)	<1
$Cp^*Ru(CO)_2[Bcat(Me)_2]$ (**2**)	40
$Cp^*W(CO)_3[Bcat(Me)_2]$ (**3a**)	85
$Cp^*W(CO)_3Bcat$ (**3b**)	20
$Cp^*Mo(CO)_3[Bcat(Me)_2]$ (**4**)	7
$Cp^*Ru(CO)_2Bpin$ (**5**)	78
$Cp^*W(CO)_3Bpin$ (**6**)	72
$Cp^*Fe(CO)_2BBN$ (**7**)	20
$Cp^*Ru(CO)_2BBN$ (**8a**)	8
$Cp^*Ru(CO)_2BCy_2$ (**8b**)	<1
$Cp^*Ru(CO)_2BMe_2$ (**8c**)	<1
$Cp^*Ru(CO)_2BS_2Tol$ (**9**)	<1
$Cp^*W(CO)_2(PXy_3)[Bcat(Me)_2]$ (**10a**)	59
$Cp^*W(CO)_2(PMe_3)[Bcat(Me)_2]$ (**10b**)	32

would react with alkanes and that would allow for an understanding of the factors that controlled their reactivity and selectivity toward alkane substrates. Our results on the development of isolated boryl complexes that functionalize alkanes are summarized in eq 2 and Table 2. Transition metal boryl



(2)

complexes of the type $(Cp')M(CO)_nB(OR)_2$ ($Cp' = Cp$ or Cp^*) were irradiated with a medium pressure mercury arc lamp in pentane solvent. The alkylboronate ester products from these reactions were identified by comparison of spectral data of the functionalized products to those of samples synthesized independently by hydroboration of the corresponding alkenes. The initial metal-containing products were the metal hydrides $Cp'M(CO)_nH$. At early reaction times, $Cp^*Ru(CO)_2H$[31] and $Cp^*W(CO)_3H$[32] were observed by ^1H NMR spectroscopy. These complexes are photochemically unstable and decompose upon irradiation into the dimeric species $[Cp'M(CO)_n]_2$,[33−35] which were the metal products observed after all of the starting complex had reacted.

Our studies were initiated with $CpFe(CO)_2$−boryl complexes, and this chemistry revealed structural features that were important for observing chemistry with alkanes. In contrast to its reaction with unsaturated hydrocarbons, irradiation of the metal boryl complex $CpFe(CO)_2Bcat$ in alkane did not produce functionalized product. The iron complex reacted completely, but no dominant main group product was observed. In contrast, the related complex $Cp^*Fe(CO)_2[Bcat(^tBu)_2]$ (**1a**) [$Bcat(^tBu)_2 = B\text{-}1,2\text{-}O_2C_6H_2\text{-}3,5\text{-}^tBu_2$] reacted with pentane under photochemical conditions to form 1-pentylboronate ester in 15% yield. This complex, and therefore the entire system, contains no accessible aromatic C−H bonds. As a result, reaction of the metal complex with alkane is observed. The complex **1b** with the smaller methyl groups to block the catecholate aromatic C−H bonds gave a similar 20% yield. Only primary alkylboronate esters were formed from reaction of either **1a** or **1b**; no products from functionalization at the secondary positions were observed by GC. The 2- and 3-pentylboronate ester products were prepared independently as a mixture of the two isomers from hydroboration of 2-pentene. To determine if the blocking groups were necessary on both Cp and catecholate moieties, the complexes $CpFe(CO)_2[Bcat(^tBu)_2]$ (**1c**) and $Cp^*Fe(CO)_2Bcat$ (**1d**) were prepared. Neither of these species reacted with pentane.

To improve the yield of alkylboronate ester, the ruthenium analogues of iron complexes **1a** and **1b** were prepared. $Cp^*Ru(CO)_2[Bcat(^tBu)_2]$ was difficult to isolate because of its high solubility, but $Cp^*Ru(CO)_2[Bcat(Me)_2]$ (**2**) [$Bcat(Me)_2 = B\text{-}1,2\text{-}O_2C_6H_2\text{-}3,5\text{-}Me_2$] was less soluble and more readily isolated. Complex **2** reacted photochemically with pentane to give the 1-pentylboronate ester in 40% yield. This yield was measurably higher than that for reaction of the analogous iron complex **1b**.

Because the second-row ruthenium complex gave higher yields of functionalized alkane than the first-row iron complex, a third-row analogue was sought. Because $Cp^*W(CO)_3^-$ is more accessible than $Cp^*Os(CO)_2^-$,[36,37] we studied boryl complexes derived from the tungsten anion. The tungsten complex $Cp^*W(CO)_3[Bcat(Me)_2]$ (**3a**) showed remarkably high reactivity toward pentane and formed 1-pentylboronate ester in 85% yield with exclusive selectivity for reaction at the terminal position of the alkane.

To determine if blocking groups were also important in this highly reactive tungsten system, $Cp^*W(CO)_3Bcat$ (**3b**) was prepared. This complex did react with pentane, but the pentylboronate ester was formed in only 20% yield. Again, this yield was much lower than that obtained from reaction of the catecholate-substituted complex **3a**.

To compare metal boryl complexes of the chromium triad directly with those of the iron triad, the molybdenum complex $Cp^*Mo(CO)_3[Bcat(Me)_2]$ (**4**) was prepared. This complex reacted with pentane to give pentylboronate ester in only 7% yield. This yield is much lower than that obtained from reaction of the analogous second-row ruthenium complex **2**. This result suggests that the lower-coordinate complexes of the iron triad are more reactive toward alkanes than are the higher-coordinate complexes in the chromium triad.

Reaction of Pinacol-, Dialkyl-, and Dithioboryl Complexes with Pentane. To determine which features of the boryl complexes lead to the alkane functionalization chemistry, we prepared boryl complexes containing several different substituents with varying electronic properties. These studies focused on the ruthenium system because substantially lower or higher yields versus those of dimethylcatecholate complex **2** could be observed. In selected cases the iron and tungsten analogues also were evaluated. Yields for reactions of these complexes are included in Table 2.

The pinacolboryl complex $Cp^*Ru(CO)_2Bpin$ ($pin = 1,2\text{-}O_2C_2Me_4$) (**5**), which is analogous to the catecholboryl complex **2**, reacted photochemically with pentane to form the pentylboronate ester in 78% yield. This value is significantly higher than that for reaction of **2**. To determine if the reactivity of the tungsten pinacolboryl complex toward alkane was also high, Cp*W-

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(30) Waltz, K. M.; Muhoro, C. N.; Hartwig, J. F. *Organometallics* **1999**, *18*, 3383−3393.

(31) Stasunik, A.; Wilson, D. R.; Malisch, W. *J. Organomet. Chem.* **1984**, *270*, C18−22.

(32) Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 6005−15.

(33) Alt, H. G.; Mahmoud, K. A.; Rest, A. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 544−545.

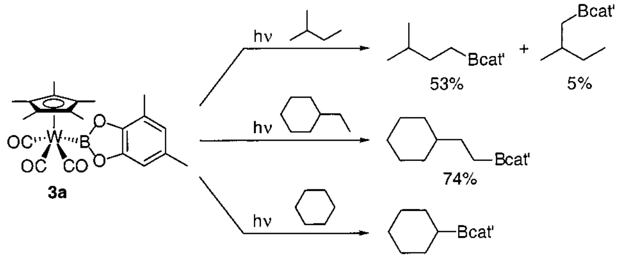
(34) Mahmoud, K. A.; Rest, A. J.; Alt, H. G. *J. Chem. Soc., Dalton Trans.* **1984**, 187−197.

(35) Shackleton, T. A.; Mackie, S. C.; Fergusson, S. B.; Johnston, L. J.; Baird, M. C. *Organometallics* **1990**, *9*, 2248−2253.

(36) Kawano, Y.; Tobita, H.; Ogino, H. *Organometallics* **1994**, *13*, 3849−3853.

(37) Hoyano, J. K.; May, C. J.; Graham, W. A. G. *Inorg. Chem.* **1982**, *21*, 3095−3099.

Scheme 1



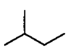
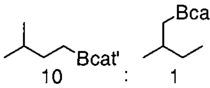
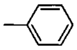
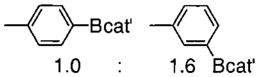
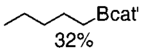
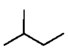
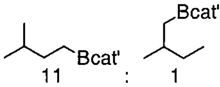
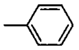
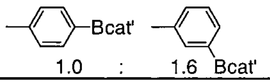
(CO)$_3$Bpin (**6**) was prepared and irradiated in pentane solvent. The tungsten pinacolboryl complex **6** reacted with pentane in 72% yield, which is similar in magnitude to that of tungsten catecholboryl **3a**.

Dialkylboryl complexes were much less reactive toward alkanes. The ruthenium complex **8a** containing a BBN (BBN = 9-borabicyclo[3.3.1]nonyl) group reacted with pentane in a low 8% yield. This product was identified by comparison of spectral data with that of a sample prepared independently by hydroboration of 1-pentene. Moreover, the dicyclohexyl and dimethyl boryl complexes **8b** and **8c** did not produce any alkane functionalization product, although the starting boryl complexes were fully consumed within 1 h of irradiation. No dominant boron-containing product was observed from these reactions. We were concerned that the low yield resulted from metal-catalyzed decomposition of the trialkylborane product. To check the stability of the product, pure pentylBBN was irradiated in benzene-d_6 in the presence of [Cp*Ru(CO)$_2$]$_2$. No decomposition was observed after 2 h of irradiation, which was the time required for reaction of **8a**. To determine if the low yields were specific for the ruthenium system, the iron complex Cp*Fe(CO)$_2$BBN (**7**) was reacted with pentane under photochemical conditions. This reaction formed pentylBBN in 20% yield, which is slightly higher than that for the ruthenium BBN complex, but similar to that for the iron catecholboryl complexes.

To compare the reactivity of a boryl complex with a structure more similar to the catecholboryl complex **2**, but with increased Lewis acidity, the dithioboryl complex Cp*Ru(CO)$_2$BS$_2$Tol (**9**) (BS$_2$Tol = B-1,2-S$_2$C$_6$H$_3$-4-Me) was prepared. Upon irradiation in pentane, the dithioboryl complex did not form pentylboronate ester. To distinguish between low reactivity of the intermediate formed from photolysis and low yield for formation of the intermediate, complex **9** was irradiated in benzene-d_6. In this case, complex **9** produced phenyl-d_5 dithioborane in 57% yield. This arene functionalization product was identified by comparison with an independently prepared sample.[38] To test again the product stability toward the reaction conditions and medium, the phenylboronate dithioester was irradiated in the presence of [Cp*Ru(CO)$_2$]$_2$. Again, no significant decomposition occurred after 1 h (the time scale of the reaction), but extended irradiation for 12 h did result in decomposition of about half of the phenylboronate dithioester.

Reaction of Cp*W(CO)$_3$[Bcat(Me)$_2$] with Nonlinear Alkanes and Arenes. The reaction of tungsten complex **3a** with several nonlinear alkanes was studied, as shown in Scheme 1. Reaction of **3a** with 2-methylbutane resulted in functionalization of the least hindered terminal position of the alkane in 53% yield. A small amount of functionalization at the more hindered terminal position was observed. The ratio of these two products was 11(±1):1. Reaction of **3a** with ethylcyclohexane resulted in functionalization of the terminal position of the ethyl group in 74% yield and showed no functionalization of the cyclohexyl ring. Reaction of **3a** with cyclohexane gave the cyclohexylboronate ester in only 22% yield. Reaction of **3a** with arenes occurred in high yields. Irradiation in benzene produced 86% yield of phenylboronate ester.

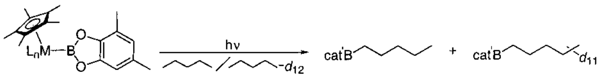
Table 3. Photochemical Reaction of Cp*W(CO)$_2$L[Bcat(Me)$_2$] Complexes with Hydrocarbons

L	Substrate	% Yield or Isomer Ratio of Products
PXy$_3$ (**10a**)		 Bcat' 59%
		 Bcat' Bcat' 10 : 1
		 Bcat' Bcat' 1.0 : 1.6
PMe$_3$ (**10b**)		 Bcat' 32%
		 Bcat' Bcat' 11 : 1
		 Bcat' Bcat' 1.0 : 1.6

Reaction of Cp*W(CO)$_2$L[Bcat(Me)$_2$] (L = phosphine) with Alkanes and Arenes. Tungsten boryl complexes containing one phosphine ligand were also capable of functionalizing a variety of branched or unbranched aliphatic and aromatic hydrocarbons, as shown in Tables 2 and 3. Cp*W(CO)$_2$(PXy$_3$)[Bcat(Me)$_2$] (**10a**), which contains a bulkier triarylphosphine, reacted with pentane to give functionalized product in 59% yield, which is lower than that for reaction of tricarbonyl complex **3a**. Cp*W(CO)$_2$(PMe$_3$)[Bcat(Me)$_2$] (**10b**), which contains the smaller, more basic PMe$_3$ ligand, produced the 1-pentyl boronate ester in an even lower 32% yield. Complexes **10a** and **10b** showed similar selectivity upon reaction with 2-methylbutane, forming the two terminally functionalized isomers in a 10(±1):1 ratio, with functionalization favoring the less sterically hindered terminal methyl group.

To determine if the low yield from reaction of **10b** with pentane was due to low reactivity of the intermediate formed from photolysis or low yield for formation of the intermediate, complex **10b** was irradiated in benzene-d_6. Phenyl-d_5Bcat(Me)$_2$ was formed in 54% yield. For comparison, the tungsten tricarbonyl boryl **3a** was also photolyzed in benzene-d_6, affording the arylboronate ester in a considerably higher 84% yield. Reaction of either **10a** or **10b** with toluene formed the same 1:6:1 ratio of *meta* and *para* functionalized products, uncorrected for the different number of *meta* and *para* C−H bonds.

Mechanistic Studies. To obtain mechanistic information, kinetic isotope effects were measured for several of the metal boryl complexes, as shown in Table 4. Photochemical reaction of the metal boryl complexes with an equimolar mixture of pentane and pentane-d_{12} resulted in a mixture of pentyl[Bcat(Me)$_2$] and pentyl-d_{11}[Bcat(Me)$_2$], as shown in eq 3. The ratio of these products, which was measured by GC/MS, provides



(3)

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(38) Wieber, M.; Künzel, W. *Z. Anorg. Allg. Chem.* **1974**, *403*, 107−115.

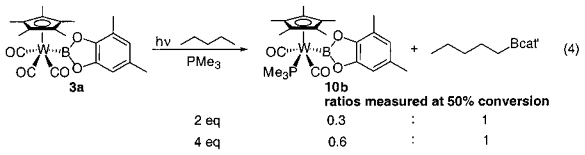
Table 4. Kinetic Isotope Effects for Photochemical Reaction of Metal Boryl Complexes with Pentane/Pentane-d_{12}

metal boryl complex	k_H/k_D
Cp*Fe(CO)$_2$[Bcat(Me)$_2$ (**1b**)	1.9
Cp*Ru(CO)$_2$[Bcat(Me)$_2$] (**2**)	2.2
Cp*W(CO)$_3$[Bcat(Me)$_2$] (**3a**)	5.1
Cp*W(CO)$_2$PXy$_3$[Bcat(Me)$_2$] (**10a**)	4.9
Cp*W(CO)$_2$PMe$_3$[Bcat(Me)$_2$] (**10b**)	5.1

the k_H/k_D for reaction of the photochemically generated intermediate with alkane. All of the boryl systems showed primary kinetic isotope effects. The iron and ruthenium complexes **1b** and **2** showed values close to 2. For tungsten complexes **3a**, **10a**, and **10b**, an isotope effect of 5.0 ± 0.1 was observed, regardless of whether CO, PMe$_3$, or PXy$_3$ was the third dative ligand.

Several experiments were performed to probe for reversible CO dissociation. Tungsten boryl complex **3a** was photolyzed in pentane solvent under 2 atm of CO side by side with an identical sample without added CO. The reactions showed the same conversions as a function of irradiation time; thus, no inhibition was observed in the presence of added CO. Complex **3a** was also irradiated in pentane solvent with 2 atm of added ^{13}CO gas. After half of the starting material had been consumed, labeled CO was not observed in the remaining starting material, but was detected in the metal carbonyl products Cp*W(CO)$_3$H and [Cp*W(CO)$_3$]$_2$. This incorporation of labeled CO into the products may occur through CO dissociation during the reaction or from CO exchange with the tungsten hydride product. Photolysis of Cp*W(CO)$_3$H alone in pentane in the presence of ^{13}CO resulted in formation of labeled Cp*W(CO)$_3$H and [Cp*W(CO)$_3$]$_2$. Thus, ^{13}CO may be incorporated before or after the formation of Cp*W(CO)$_3$H.

Irradiation of **3a** was performed with added phosphine to provide more definitive evidence for or against CO dissociation. Photolysis of tungsten boryl complex **3a** in pentane solvent in the presence of PMe$_3$ resulted in formation of phosphine complex **10b** and pentyl[Bcat(Me)$_2$]. A side-by-side photolysis of **3a** in pentane with 2 equiv and 4 equiv of PMe$_3$ resulted in roughly twice the amount of **10b** when the concentration of PMe$_3$ was doubled, as shown in eq 4. These ratios were measured when half of the starting material had reacted, and these data provide strong evidence for reaction that is initiated by dissociation of CO, as detailed in the Discussion section. The identity of **10b** was confirmed by independent synthesis and complete characterization. A single CO resonance in its ^{13}C NMR spectrum, along with a higher frequency symmetric CO band of medium intensity and a lower frequency asymmetric band of stronger intensity,[39] suggested the *trans* geometry. This complex could exist as a mixture of rapidly interconverting *cis* and *trans* isomers; however, this process is slow for similar CpW(CO)$_2$PR$_3$X complexes, and we observed only one set of infrared CO bands.



In addition to studies on selectivities of **3a**, **10a**, and **10b**, we performed reactions with added phosphine that were aimed at determining if the phosphine or carbonyl group dissociated from **10b**. Reaction in the presence of 10 equiv of added PMe$_3$ led to slightly lower conversions as a function of time than a side-by-side reaction in the absence of added PMe$_3$. More striking, the sample with added phosphine gave much lower yields of functionalized product. After consumption of **10b**, no major species that could be attributed to a bisphosphine complex Cp*W(CO)(PMe$_3$)$_2$[Bcat(Me)$_2$] were observed.

Discussion

Effect of Boryl Group on Reactivity. Steric Effects. Studies on metal boryl complexes that photochemically functionalize arenes[30] were used as a starting point to develop complexes that would react with alkanes to form alkylboronate esters. Simple metal catecholboryl complexes with the formula CpM(CO)$_n$Bcat did not react with alkanes. Attack of one metal boryl complex on the sp^2-hybridized C−H bonds of the catecholate or cyclopentadienyl groups of another metal boryl complex would explain the lack of reactivity of CpFe(CO)$_2$Bcat and related compounds with alkanes.

To prevent this reactivity at sp^2-hybridized C−H bonds, Cp* was used as ligand, and a 3,5-dialkylcatecholate substituent was placed on the boryl group. The presence of only aromatic C−H bonds with two *ortho* substituents should prevent reaction at the catecholate group. Metal catecholboryl complexes, such as CpFe(CO)$_2$Bcat, were shown to react with substituted arenes predominantly in the *m*- and *p*- positions.[30] Two *ortho* substituents may be necessary because the position *ortho* to an oxygen substituent is unusually reactive toward certain metal-boryl complexes. For example, CpFe(CO)$_2$Bcat reacted with anisole at the *ortho*, *meta*, and *para* positions, and Re(CO)$_5$Bcat reacted preferentially at the *ortho* position.[30] As designed, Cp*Fe(CO)$_2$[Bcat(^{t}Bu)$_2$], Cp*Fe(CO)$_2$[Bcat(Me)$_2$], Cp*Ru(CO)$_2$[Bcat(Me)$_2$], and Cp*W(CO)$_3$[Bcat(Me)$_2$] all reacted with alkanes to form alkylboronate esters.

To test whether blocking of the sp^2-hybridized positions was truly the important factor that allowed for reactivity with alkanes, a variety of boryl complexes with different substitution patterns were prepared and reacted photochemically with pentane solvent. Within the set of complexes CpFe(CO)$_2$[Bcat(^{t}Bu)$_2$] (**1c**), Cp*Fe(CO)$_2$Bcat (**1d**), and Cp*Fe(CO)$_2$[Bcat(^{t}Bu)$_2$] (**1a**), only complex **1a,** with both cyclopentadienyl and catecholate blocking groups, resulted in functionalization of pentane. In addition, a comparison of the reactions of pentane with tungsten dimethylcatecholboryl complex **3a** and with complex **3b**, which contains unsubstituted catecholate, showed that **3a** gave a high yield of pentylboronate ester, but **3b** gave low yields of the functionalized product. The high reactivity of the tungsten complex toward alkanes, in conjunction with the vast difference in concentration of alkane versus catecholate C−H bonds, did allow for some functionalization of alkane C−H bonds by compound **3b**.

These experiments were more revealing than those directed toward isolating or detecting borylated metal complex in reaction mixtures. Although the experiments below argue strongly that accessible sp^2 sites on the metal boryl complex interfere with alkane functionalization, the products formed by the proposed borylation of the catecholate ring of CpFe(CO)$_2$Bcat, **1d**, or **3b** were not observed directly. Of course, this borylated metal boryl species would most likely display similar photochemistry to that of the starting complex, and complex reaction mixtures would result. In a related system, however, borylation of the cyclopentadienyl ligands of CpM(CO)$_3$ catalysts was observed. The irradiation of CpRe(CO)$_3$ with B$_2$pin$_2$ in pentane[25] formed the

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(39) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley & Sons: New York, 1988; pp 1035−1037.

product from borylation of the cyclopentadienyl ring of CpRe$(CO)_3$, in addition to forming alkylboronate ester. Similar borylation of a cyclopentadienyl group was observed in analogous reactions mediated by $(MeCp)Mn(CO)_3$. In these cases the borylated metal complexes were stable enough to be identified in the reaction mixture by GC/MS.[25]

Electronic Effects. In addition to probing the ability of steric effects to inhibit reaction at aromatic C−H bonds, we studied the influence of the boryl groups' electronic properties on alkane functionalization. One might propose that the boryl complexes are highly reactive toward alkane C−H bonds because the boryl groups are strong σ-donors; alternatively, one might propose that they are reactive because of Lewis acidic character. To address these issues, the reactivities of metal boryl complexes containing the groups $B(OR)_2$, $B(SR)_2$, and BR_2 ($R =$ alkyl) were examined. The electron-donating ability of these boryl groups can be gauged by the CO stretching frequencies of their complexes with $Cp^*Ru(CO)_2$, shown in Table 1. As mentioned in the Results section, the dialkylboryl groups are apparently the strongest electron donors, while the catecholboryl group is the weakest electron donor. The electron-donating ability of the dialkylboryl complexes presumably results from strong σ-donation. The electronics of the boryl groups can also be ordered according to Lewis acidity, based on conventional properties of the analogous boranes. The dialkylboryl groups would be the most Lewis acidic, while the pinacolboryl groups would be the least Lewis acidic.

To evaluate the electronic effects of the boryl group, we focused on the ruthenium boryl complexes. The ruthenium pinacolboryl complex **5** reacted with pentane in twice the yield as the catecholboryl complex **2**. This large increase in yield may result from either the increased electron donation or decreased Lewis acidity of the pinacolboryl moiety relative to the catecholboryl group. A similar comparison between tungsten pinacolboryl **6** and catecholboryl **3a** showed that both complexes provided clean reactions with alkanes.

In contrast to catecholboryl **2**, tungsten dithiocatecholboryl **9** did not form any pentylboronate ester upon irradiation in pentane. Yet, complex **9** did react photochemically with benzene to form $PhBS_2Tol$ in moderate yield. The functionalization of benzene by **9** shows that the reactive intermediate was successfully formed upon irradiation; thus, the inability of **9** to functionalize alkanes most likely results from low reactivity of the metal boryl intermediate toward alkane C−H bonds, and not from a low yield for formation of the reactive intermediate.

In addition to pinacol- and dithioboryl ligands, we studied dialkylboryl groups that would be more electron-donating, and also more Lewis acidic, than catecholboryl ligands. The lack of C−H bonds of sp^2-hybridized sites on these ligands should make them suitable components of complexes that functionalize alkanes. However, the BBN complex **8a** was the only dialkylboryl complex among the ruthenium dialkylboryl series that formed any pentylboronate ester, and even this complex formed functionalized product with yields that were much lower than those obtained with the catecholboryl complex **2**. The analogous iron BBN complex **7** also gave low yields upon photochemical reaction with pentane. Yet, complex **7** reacted with arenes to form arylboranes,[30] again demonstrating that the photochemistry generates a 16-electron intermediate, but that the intermediate is unreactive toward alkanes. The low yields for reactions of all iron boryl complexes with alkanes precluded any firm conclusions concerning the effect of electronic variations on the reactions of the iron complexes.

Although we cannot provide detailed arguments for the differences in reactivity between complexes of all the boryl groups, several general conclusions can be drawn from the studies of electronic effects using the ruthenium complexes. First, the electronic properties of the boryl group did not dramatically alter the photochemical generation of the proposed 16-electron intermediate. Instead, the electronic properties of the boryl ligands influenced the reactivity of the intermediate toward alkane substrate. Second, a highly Lewis acidic boryl group is not necessary for alkane functionalization; among the ruthenium complexes, the least Lewis acidic boryl complex, pinacolboryl **5**, gave the highest yields of functionalized alkane.

Effect of Dative Ligands on Reactivity. In addition to examining the effect of the boryl group on reactivity, we examined the effect of altering the dative ligand. The reactions of tungsten tricarbonyl and phosphine carbonyl complexes **3a**, **10a**, and **10b** with several substrates were examined. The reactions could occur through dissociation of one dative ligand, followed by C−H bond cleavage and B−C bond formation. If phosphine complexes **10a** and **10b** undergo dissociation of phosphine, the same 16-electron intermediate $Cp^*W(CO)_2[Bcat(Me)_2]$ would be formed as in reactions of complex **3a**. In this case, all three complexes would show similar selectivities, particularly if these selectivities were determined by steric effects. Moreover, added phosphine should inhibit the formation of pentylboronate ester. If the reaction proceeds through CO dissociation, three different 16-electron intermediates of the general formula $Cp^*W(CO)(L)[Bcat(Me)_2]$ would be formed, where $L = CO$, PMe_3, and PXy_3. In this case, the three different intermediates would give different selectivities because of the large difference in steric properties between CO, PMe_3, and PXy_3. Moreover, added phosphine should convert **10b** into the bis-phosphine complex $Cp^*W(CO)(PMe_3)_2[Bcat(Me)_2]$ in competition with formation of pentylboronate ester.

Previous studies of the photochemistry of mixed carbonyl phosphine systems suggest that the lability of the CO or phosphine ligand upon irradiation depends on the identity of the metal and covalent ligand. Photolysis of $Cp^*Re(CO)_2(PMe_3)$ led to CO dissociation, but irradiation of $Cp^*Re(CO)(PMe_3)_2$ led to phosphine dissociation.[11] Photolysis of $CpFe(CO)(PPh_3)$-$(COMe)$ resulted in CO dissociation,[40] but irradiation of the analogous tungsten acetyl complex $CpW(CO)_2(PPh_3)(COMe)$ resulted in phosphine dissociation.[41] Moreover, the Cp*, instead of Cp analogue of the iron acetyl complex, and the methyl, instead of acetyl, analogue underwent phosphine dissociation upon photolysis.[40] Thus, it is difficult to predict if CO or phosphine will dissociate from complexes **10a** and **10b**.

Our experiments suggest that the functionalization chemistry of **3a**, **10a**, and **10b** occurred predominantly through the same $Cp^*W(CO)_2[Bcat(Me)_2]$ intermediate, which would be formed by CO, PMe_3, or PXy_3 dissociation. The reaction of PXy_3 and PMe_3 complexes **10a** and **10b** with isopentane gave similar ratios of isomeric products as those obtained from reactions of **3a** with isopentane. Moreover, the *m*-:*p*- ratios from reaction of **10a** and **10b** with toluene were identical. Complexes **3a**, **10a**, and **10b** also gave isotope effects that were indistinguishable from each other when these three complexes were photolyzed with a mixture of pentane and pentane-d_{12}. Finally, the presence of added PMe_3 in photochemical reactions of **10b** in pentane did not lead to the formation of the bis-phosphine complex

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(40) Aplin, R. T.; Booth, J.; Compton, R. G.; Davies, S. G.; Jones, S.; McNally, J. P.; Metzler, M. R.; Watkins, W. C. *J. Chem. Soc., Perkin Trans. 2* **1999**, *5*, 913−922.

(41) Tyler, D. R. *Inorg. Chem.* **1981**, *20*, 2257−2261.

Cp*W(CO)(PMe$_3$)$_2$[Bcat(Me)$_2$] and led to lower yields of functionalized product.

However, the variation in reaction yield suggests that a parallel path involving CO dissociation from **10a** and **10b** leads to a reduction in yield. Reactions of **10a**, **10b**, and **3a** showed significant differences in yields, but similar regioselectivities and isotopic effects. Although there are other explanations for the effect of dative ligands, these results may be rationalized by competitive formation of Cp*W(CO)$_2$[Bcat(Me)$_2$] and Cp*W(CO)(L)[Bcat(Me)$_2$] as intermediates and by a low reactivity of Cp*W(CO)(PR$_3$)[Bcat(Me)$_2$] toward alkanes. If Cp*W(CO)(PR$_3$)[Bcat(Me)$_2$] is unreactive toward alkanes then the regioselectivities and isotope effects for formation of functionalized product by **3a**, **10a**, and **10b** would not be perturbed by generation of the unsaturated, phosphine-ligated intermediate, but the reaction yields would.

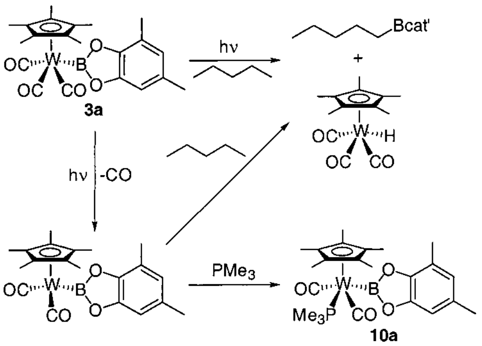
Photochemical reactions of **3a** and **10b** with benzene-d_6 are consistent with this conclusion. Tricarbonyl boryl **3a** reacted with benzene-d_6 in higher yield than did the monophosphine boryl **10b**. In addition, the yield for reaction of **10b** with arene is higher than that for its reaction with alkane. The yields for reaction of **3a** with alkanes and arenes are similar. These data are consistent with a similar high yield for reaction of the Cp*W(CO)$_2$[Bcat(Me)$_2$] intermediate with alkanes and arenes, but substantially higher yields for reaction of the Cp*W(CO)(L)[Bcat(Me)$_2$] intermediate with arenes than with alkanes. The greater yields for reaction of Cp*W(CO)(L)[Bcat(Me)$_2$] with alkanes when L=CO instead of a phosphine run counter to the general observation that increased electron density at the metal favors oxidative addition. However, these reactions may be highly sensitive to steric effects and cyclometalation of the phosphine may compete with the intermolecular C−H activation.

Mechanistic Considerations. Probe for Radical Chemistry. Additional mechanistic information was obtained through measurement and comparison of kinetic isotope effects for reaction of the iron, ruthenium, and tungsten [Bcat(Me)$_2$] complexes **1b**, **2**, and **3a** with a mixture of pentane and pentane-d_{12}. If the functionalization were to occur through a free [Bcat(Me)$_2$] radical, then the values for the isotope effect would be the same for all three systems, because the reactivity of the boryl radical should be independent of its origin. The different values obtained for reactions of complexes **1b**, **2**, and **3a** indicate that the alkane functionalization does not occur by reaction of a free boryl radical with free alkane.

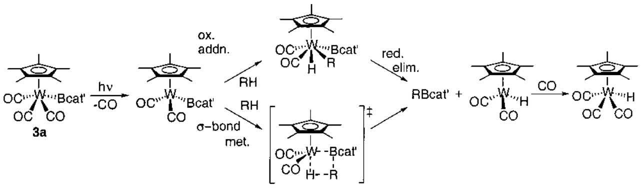
The exceptional selectivity of metal boryl complexes toward C−H bonds of terminal, unhindered methyl groups also provides mechanistic information. C−H activation processes that occur through radical pathways typically show the highest reactivity at tertiary C−H bonds at tertiary sites, followed by secondary, and finally primary. All of the reactions of metal boryl complexes with alkanes show functionalization exclusively at the C−H bonds of primary carbons. In the absence of primary C−H bonds, complex **3a** does react with secondary C−H bonds but in low yields. This observed selectivity argues against a pathway involving radical chemistry and supports the conclusion of a nonradical mechanism drawn from the kinetic isotope effects.

Probe for CO Dissociation. The reaction mechanism can be envisioned to occur through CO dissociation to form a 16-electron intermediate or through a direct sigma bond metathesis. A series of experiments were conducted to determine if CO dissociation occurred on the reaction pathway. Reaction of Cp*W(CO)$_3$[Bcat(Me)$_2$] (**3a**) with pentane in the presence of added CO showed no difference in the conversion to pentylboronate ester as a function of irradiation time. Moreover, irradiation of **3a** in pentane in the presence of ^{13}CO showed no formation of labeled starting material Cp*W(CO)$_2$(^{13}CO)[Bcat(Me)$_2$]. One could argue that the lack of CO inhibition and incorporation could be the result of poor CO solubility in alkane solvent. The solubility of 1 atm of CO in heptane at room temperature has been reported as 0.012 M.[42] Our experiments used 2 atm of CO, and the concentration of tungsten boryl was about 0.018 M. We estimate that only 10% incorporation of labeled CO would be necessary to detect ^{13}CO incorporation by ^{13}C NMR spectroscopy. We observed labeled CO in two different metal products, and their concentrations were less than the concentration of the remaining tungsten boryl after 50% conversion. Thus, we would detect reversible CO dissociation with this experiment, and our experiments indicate that CO does not dissociate from **3a** reversibly.

Scheme 2



Scheme 3



However, the formation of pentylboronate ester and phosphine complex **10b** upon photolysis of tungsten complex **3a** in the presence of PMe$_3$ in pentane indicated that irreversible dissociation of CO did occur. The ratio of **10a** to alkylboronate ester depended directly on the concentration of added phosphine. Because the amounts of these products depended on the amount of added phosphine, the pentylboronate ester and trapped intermediate **10b** most likely originate from the same intermediate, as summarized in Scheme 2. The likely intermediate is the 16-electron species Cp*W(CO)$_2$[Bcat(Me)$_2$]. The trapped complex **10b** reacted photochemically with pentane, but this process was inhibited by the presence of added phosphine. Thus, the pentylboronate ester, formed in competition with **10b** in the presence of PMe$_3$, originated predominately from reaction of the starting material **3a** with alkane.

The most plausible mechanistic pathway suggested by these data is described in Scheme 3 using **3a** as an example. Photochemical CO dissociation occurs to form the reactive 16-electron intermediate Cp*W(CO)$_2$[Bcat(Me)$_2$]. This 16-electron intermediate reacts with substrate much faster than it reassociates CO. The 16-electron species most likely undergoes addition of an alkane C−H bond to form an unusual cyclopentadienyl tungsten (IV) carbonyl complex, which would reductively eliminate alkylboronate ester. The remaining metal hydride fragment Cp*W(CO)$_2$H would then recombine with CO to form the observed metal product Cp*W(CO)$_3$H.

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[42] Gerrard, W. *Solubility of Gases and Liquids*; Plenum Press: New York, 1976; p 73.

Alternatively, the 16-electron intermediate could react with an alkane C−H bond through σ-bond metathesis.[12] This type of mechanism is typical of early transition metal, lanthanide, and actinide systems which cannot undergo oxidative addition.[3] Although a σ-bond metathesis mechanism is unconventional for mid- to late-metal systems, the electrophilicity of boron may allow this main group site to play the role of the early transition metal center, resulting in a σ-bond metathesis with the opposite regiochemistry of conventional σ-bond metatheses.

Nevertheless, we favor a mechanism involving oxidative addition. Bergman has reported the low-temperature activation of alkanes by $[Cp^*Ir(PMe_3)(CH_3)]^+$.[43] Theoretical calculations on a model of this complex showed that oxidative addition is a low-energy pathway for reaction of Ir(III) to form Ir(V), and that σ-bond metathesis is unlikely to occur.[44] Bergman's direct observation of C−H oxidative addition at an Ir(III) center to form an isolable Ir(V) species has provided further experimental evidence to support these calculations.[45]

Conclusions

We conclude by reflecting on the features of the boryl group that allow transition metal boryl complexes to functionalize alkanes, while the analogous metal alkyl complexes do not. Upon irradiation of metal alkyl complexes containing β-hydrogens, β-H elimination of the alkyl group is known to occur after CO dissociation.[32,46,47] The pinacol and catecholboryl complexes, which provided the best yields of functionalized alkane, cannot undergo β-hydrogen elimination. Irradiation of metal alkyl complexes is also known to generate alkyl radicals.[46,48,49] We showed previously that metal−boron bonds are unusually strong[50] and in the present work that metal boryl complexes do not react through radical chemistry. It is likely that the strong metal−boron bond prevents the generation of boryl radicals. Thus, the major pathways for decomposition of metal−carbonyl alkyl complexes are inaccessible for metal boryl complexes.

We propose that the modest electrophilic properties of the boron in the boryl group assist in providing favorable kinetics for B−C bond formation. The coupling of electrophilic and nucleophilic groups from a metal center are favorable. For example, acyl−alkyl couplings are faster than alkyl−alkyl couplings.[51] Favorable matching of nucleophile and electrophile have also been demonstrated in C−N, C−S, and C−O coupling processes.[52−54] Thus, the electrophilicity of the boron may make coupling of the alkyl and boryl groups facile. Rapid B−C bond formation has been implied by a number of experimental observations in other systems.[55,56] Alkylmetal boryl complexes are unknown, and aryl or vinylmetal boryl complexes are rare.[57,58]

Finally, the thermodynamics for alkane borylation are unusually favorable. Because all transformations appear to occur thermally after photochemical ligand dissociation, an examination of the bond dissociation energies (BDEs) involved, albeit for the saturated 18-electron analogue of the 16-electron intermediate, can reveal why alkane borylation is favorable thermodynamically. The BDEs for W−H, C−B, and C−H bonds have been measured or calculated previously, and a value for the W−B bond may be estimated based on the reported 5 kcal/mol difference in Ir−B and Ir−H bond energies.[50] For this analysis, only relative BDEs are important; thus, the roughly 5 kcal/mol difference estimated between the W−B and W−H BDEs is the important value, not the absolute BDE. The total energy of the bonds that are formed [68 kcal/mol (W−H)[59] + 112 kcal/mol (C−B)[50]] is then 9 kcal/mol greater than the energy of the bonds that are broken [∼73 kcal/mol (W−B) + 98 kcal/mol (C−H)[60]]. Thus, the strength of the B−C bond dominates the thermodynamics and provides the driving force for the reactivity of the boryl complexes with alkanes. Even if the oxidative addition of a C−H bond to the Fe(II), Ru(II), or W(II) intermediate is endothermic, the highly exothermic combination of reductive elimination to form the B−C bond and reassociation of CO would make the overall reaction exothermic.

On the basis of this logic, the thermal dissociation of a dative ligand would provide a route to alkane functionalization that occurs in the absence of photochemical irradiation. This prediction was recently fulfilled by the development of a rhodium complex which catalyzes the borylation of alkanes under purely thermal conditions.[26]

Experimental Section

General Methods. Unless otherwise noted, all manipulations were conducted in an inert atmosphere glovebox or by using standard Schlenk techniques. ^{1}H NMR spectra were recorded on either a General Electric QE-300 or Bruker AM-500 NMR spectrometer, and ^{11}B- and ^{31}P{H} NMR spectra were recorded on an Omega 300 NMR spectrometer. ^{11}B- and ^{31}P{H} chemical shifts are reported in parts per million relative to external standards of $BF_3 \cdot Et_2O$ and 85% H_3PO_4, respectively. Resonances downfield of the standard are assigned positive chemical shifts. Proton chemical shifts are reported in ppm relative to residual protiated solvent as internal standard. Gas chromatography was performed on an HP5890A GC fitted with a 30 m × 0.25 mm ID capillary column coated with a 0.25 μm film of EC-5 and connected to a 2 m deactivated fused silica guard column. The GC was connected to an HP5971A mass spectrometer. Runs were ramped from 50 to 210 °C at 10 °C/min. UV/vis spectra were acquired on a Cary 3E UV/vis spectrophotometer. Pentane, THF, benzene, and toluene solvents were distilled from sodium/benzophenone ketyl prior to use. Alkanes for use as substrates were treated with concentrated sulfuric acid to remove olefin impurities and then washed with a saturated $NaHCO_3$ solution and water. The olefin-free alkanes were dried first with $MgSO_4$ and then with sodium/benzophenone ketyl, and were finally transferred by vacuum techniques and degassed. Benzene-d_6 was dried over sodium/benzophenone ketyl and degassed before use. The complexes $CpFe(CO)_2Bcat$, $Cp^*Fe(CO)_2Bcat$ (**1d**),[30] $[Cp^*Fe(CO)_2]_2$,[61] $[Cp^*Ru(CO)_2]_2$,[62,63]

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(43) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970−1973.

(44) Strout, D. L.; Zarié, S.; Niu, S.; Hall, M. B. *J. Am. Chem. Soc.* **1996**, *118*, 6068−6069.

(45) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *2000*, 1816−1817.

(46) Alt, H. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 766−782.

(47) Mahmoud, K. A.; Rest, A. J.; Alt, H. G.; Eichner, M. E.; Jansen, B. M. *J. Chem. Soc., Dalton Trans.* **1984**, 175−186.

(48) Giese, G.; Thoma, G. *Helv. Chim. Acta* **1991**, *74*, 1143−1155.

(49) Gismondi, T. E.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *284*, 59−71.

(50) Rablen, P. R.; Hartwig, J. F.; Nolan, S. P. *J. Am. Chem. Soc.* **1994**, *116*, 4121−4122.

(51) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, 1987; pp 332−333.

(52) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 8232−8245.

(53) Barañano, D.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 2937−2938.

(54) Widenhoefer, R. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 6504−6511.

(55) Baker, R. T.; Calabrese, J. C.; Westcott, S. A.; Marder, T. B. *J. Am. Chem. Soc.* **1995**, *117*, 8777−8784.

(56) Baker, R. T.; Calabrese, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 4367−4368.

(57) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1110−1113.

(58) Knorr, J. R.; Merola, J. S. *Organometallics* **1990**, *9*, 3008−3010.

(59) Barbini, D. C.; Tanner, P. S.; Francone, T. D.; Furst, K. B.; Jones, J., Wayne E. *Inorg. Chem.* **1996**, *35*, 4017−4022.

(60) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493−532.

(61) Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 1094−1100.

(62) Nelson, G. O.; Sumner, C. E. *Organometallics* **1986**, *5*, 1983−1990.

$Cp^*Ru(CO)_2H$,[31] $Cp^*W(CO)_3H$,[32] $Cp^*Mo(CO)_3H$,[64] $Li[Cp^*W(CO)_2PMe_3]$,[65] $Cl[Bcat(^tBu)_2]$,[66] $ClBS_2Tol$,[67] $PhBS_2Tol$,[38,68] 3,5-dimethylcatechol,[69] and PXy_3[70] were prepared according to literature procedures. All other chemicals were used as received from commercial suppliers. We report the ^1H NMR spectrum of $PhBcatS_2Tol$ in benzene-d_6, complete with coupling constants, which have not appeared previously in the literature. Photolyses were carried out with a medium pressure 450-W Hanovia mercury arc lamp in a quartz immersion well using Pyrex reaction vessels placed flush with the immersion well, approximately 0.75 in. from the lamp.

Preparation of Anionic Metal Complexes in THF. $Na[CpFe(CO)_2]$, $Na[Cp^*Fe(CO)_2]$, and $Na[Cp^*W(CO)_3]$. The appropriate metal dimer was dissolved in THF and reacted with 1% sodium−mercury amalgam (2.5 equiv of Na) for 12 h with vigorous stirring. The solution was removed from the amalgam and filtered through Celite to remove a gray, powdery solid. The THF was removed as described below, resulting in quantitative yield of the orange/brown sodium salts.

$KCp^*Ru(CO)_2$. $[Cp^*Ru(CO)_2]_2$ (1.60 g, 2.74 mmol) was suspended in THF and refluxed with K metal (535.0 mg, 13.68 mmol) under nitrogen for 12 h with stirring, as reported in the literature.[71] The K metal was removed by filtration, and the THF was removed as described below. The resulting solid was washed with toluene to remove dark brown impurities, affording the yellow potassium salt in 86% yield (1.5673 g).

$LiCp^*W(CO)_3$. $LiCp^*$, which was generated in situ from Cp^*H (1 mL, 6.39 mmol) and *n*-BuLi (2.6 mL of a 2.46 M solution in *n*-hexane, 6.40 mmol) at −78 °C in 30 mL of THF, was refluxed with $W(CO)_6$ (2.4786 g, 7.04 mmol) in 30 mL of THF for 2 d as reported in the literature.[72] The THF was removed as described below, resulting in quantitative yield of the yellow/orange lithium salt (3.0831 g).

Removal of THF from Metal Salts. Because the presence of THF led to the decomposition of the metal boryl complexes, it was necessary to remove as much THF from the metal anions as possible. Thorough removal of THF was achieved by first removing the solvent under vacuum to yield a sticky solid which was ground into a fine powder in the presence of toluene. A suspension of this powder in toluene was heated to 80 °C under vacuum until all of the solvent had been removed. This procedure was repeated three times. The resulting solid was washed with toluene to remove dimeric impurities, affording the metal salt.

Independent Synthesis of Organoboronate Esters and Organoboranes. Catalytic Hydroboration of Alkene. The following compounds were prepared by rhodium-catalyzed hydroboration of alkene in THF according to the literature procedure using Wilkinson's catalyst.[73,74]

1-$[Bcat(Me)_2]$-3-methylbutane: ^1H NMR (C_6D_6) δ 6.83 (s, 1H), 6.51 (s, 1H), 2.25 (s, 3H), 2.11 (s, 3H), 1.46 (m, 3H), 1.13 (m, 2H), 1.84 (m, 6H); ^{11}B NMR (C_6D_6) δ 36; GC/MS: (15.51 min) $m/z = 218$ (M^+), 203, 175, 160, 148, 133, 91.

1-$[Bcat(Me)_2]$ethylcyclohexane: ^1H NMR (C_6D_6) δ 6.84 (s, 1H), 6.51 (s, 1H), 2.25 (s, 3H), 2.10 (s, 3H), 1.80−1.45 (m, 7H), 1.30−1.00 (m, 6H), 0.82 (t, $J = 12$ Hz, 2H); ^{11}B NMR (C_6D_6) δ 36; GC/MS: (20.69 min) $m/z = 258$ (M^+), 175, 160, 148, 133, 91.

1-$[Bcat(^tBu)_2]$pentane: ^1H NMR (C_6D_6) δ 7.22 (d, $J = 1.6$ Hz, 1H), 7.19 (d, $J = 1.6$ Hz, 1H), 4.27 (s, 5H), 1.52 (s, 9H), 1.35−1.13 (m, 15H), 1.60 (t, $J = 7.3$ Hz, 2H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 149.48, 146.12, 144.93, 135.22, 116.66, 108.43, 35.41 (4 °C of ^tBu), 35.08 (CH_2), 34.95 (4 °C of ^tBu), 32.29 (3 Me of ^tBu), 30.33 (3 Me of ^tBu), 24.32 (CH_2), 23.18 (CH_2), 14.58 (CH_3), 11.33 (CH_2B); ^{11}B NMR (C_6D_6) δ 36.

Direct Hydroboration of Alkene. The following compounds were prepared by heating borane in neat alkene according to the literature procedure.[75]

1-$[Bcat(Me)_2]$pentane: ^1H NMR (C_6D_6) δ 6.83 (s, 1H), 6.51 (s, 1H), 2.25 (s, 3H), 2.10 (s, 3H), 1.56 (m, 2H), 1.35−1.08 (m, 6H), 0.83 (t, $J = 6$ Hz, 3H); ^{11}B NMR (C_6D_6) δ 37; GC/MS (16.07 min) $m/z = 218$ ((M^+), 173, 160, 148, 133, 91. HRMS (EI) calcd for $C_{13}H_{19}BO_2$: 218.1478. Found: 218.1470.

Mixture of 2-$[Bcat(Me)_2]$pentane and 3-$[Bcat(Me)_2]$pentane: ^{11}B NMR (C_6D_6) δ 37; GC/MS Two distinct peaks were observed. (15.15 min) $m/z = 218$ (M^+), 176, 161, 148, 133. (15.39 min) $m/z = 218$ (M^+), 173, 162, 148, 133, 91.

Cyclohexyl$[Bcat(Me)_2]$: ^1H NMR (C_6D_6) δ 6.83 (s, 1H), 6.50 (s, 1H), 2.25 (s, 3H), 2.10 (s, 3H), 1.90 (m, 2H), 1.60 (m, 5H), 1.45−1.15 (m, 4H); ^{11}B NMR (C_6D_6) δ 37; GC/MS (18.02 min) $m/z = 230$ (M^+), 173, 159, 148, 133, 91. HRMS (EI) calcd for $C_{14}H_{19}BO_2$: 230.1478. Found: 230.1474.

1-$[Bcat(Me)_2]$-2-methylbutane: ^1H NMR (C_6D_6) δ 6.82 (s, 1H), 6.50 (s, 1H), 2.25 (s, 3H), 2.11 (s, 3H), 1.45−1.03 (m, 5H), 0.97 (d, $J = 6$ Hz, 3H), 0.83 (t, $J = 6$ Hz, 3H); ^{11}B NMR (C_6D_6) δ 37; GC/MS (15.38 min) $m/z = 218$ (M^+), 203, 189, 173, 161, 148, 133, 91.

1-BBNpentane: ^1H NMR (C_6D_6) δ 2.00−1.10 (m, 22H), 0.93 (t, $J = 6$ Hz, 3H); ^{11}B NMR (C_6D_6) δ 89.

$H[Bcat(Me)_2]$. A solution of 3,5-dimethylcatechol (4.0882 g, 0.0296 mol) in 15 mL of ether was added slowly to a stirred solution of $BH_3 \cdot Me_2S$ (2.81 mL, 0.0296 mol) in 10 mL of ether at 0 °C. After complete addition of the catechol, the reaction was stirred at room temperature for 3 h. Volatile materials were removed under vacuum, resulting in a sticky white solid in 96% yield (4.22 g) that was suitably pure for the hydroboration reaction. ^1H NMR (C_6D_6) δ 6.75 (s, 1H), 6.47 (s, 1H), 2.17 (s, 3H), 2.06 (s, 3H); ^{11}B NMR (C_6D_6) δ 28.4 (d, $J = 195.4$ Hz).

$Cl[Bcat(Me)_2]$. A three-necked round-bottom flask equipped with a stirbar and nitrogen inlet was charged with 3,5-dimethylcatechol (3.82 g, 0.0277 mol) in 200 mL of pentane and submerged in an ice bath. Neat BCl_3 (5 mL) was added via cannula with vigorous stirring, resulting in rapid gas evolution. After complete addition of BCl_3, the reaction was stirred at room temperature for 3 h. Volatile materials were removed under vacuum, resulting in a white solid in 96% yield (4.82 g) which was spectroscopically pure. ^1H NMR (C_6D_6) δ 6.56 (s, 1H), 6.38 (s, 1H), 2.04 (s, 3H), 1.99 (s, 3H); ^{11}B NMR (C_6D_6) δ 29.2.

$Cp^*Fe(CO)_2[Bcat(^tBu)_2]$ (1a). A solution of $ClBcat(^tBu)_2$ (209 mg, 0.785 mmol) in 5 mL of toluene was added to a stirred suspension of $Na[Cp^*Fe(CO)_2]$ (213.6 mg, 0.791 mmol) in 10 mL of toluene. After 30 min of stirring, all of the $ClBcat(^tBu)_2$ had been consumed. The solvent was removed under reduced pressure, and the residue was extracted with pentane. The extracts were filtered through glass wool, condensed under vacuum, and crystallized at −30 °C. Two additional recrystallizations were necessary to remove colored impurities, affording a pale yellow crystalline solid in 30% yield (108 mg). ^1H NMR (C_6D_6) δ 7.26 (d, $J = 1.9$ Hz, 1H), 7.15 (d, $J = 1.9$ Hz, 1H), 1.610 (s, 9H), 1.605 (s, 15H), 1.30 (s, 9H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 216.51, 151.66, 147.18, 144.74, 133.75, 115.43, 107.52, 95.89, 35.35, 34.97, 32.41, 30.43, 10.35; ^{11}B NMR (C_6D_6) δ 53.7; IR (pentane) ν_{CO} 2003 (s), 1949 (s) cm^{-1}. Anal. calcd for $C_{26}H_{35}BO_4Fe$: C, 65.30; H, 7.38. Found: C, 64.97; H, 7.47.

$Cp^*Fe(CO)_2[Bcat(Me)_2]$ (1b). A solution of $ClBcat(Me)_2$ (215.0 mg, 1.178 mmol) in 5 mL of pentane was added to a stirred suspension of $Na[Cp^*Fe(CO)_2]$ (327.4 mg, 1.213 mmol) in 10 mL of pentane. After 15 min of stirring, all of the $ClBcat(Me)_2$ had been consumed. The reaction mixture was filtered through glass wool, condensed under vacuum, and crystallized at −30 °C for 15 min, resulting in yellow crystalline product. Crystallization for longer periods of time resulted

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(63) King, R. B.; Iqbal, M. Z.; King, J., A. D. *J. Organomet. Chem.* **1979**, *171*, 53−63.

(64) Kubas, G. J.; Kiss, G.; Hoff, C. D. *Organometallics* **1991**, *10*, 2870−2876.

(65) Schmitzer, S.; Weis, U.; Käb, H.; Buchner, W.; Malisch, W.; Polzer, T.; Posset, U.; Kiefer, W. *Inorg. Chem.* **1993**, *32*, 303−309.

(66) He, X.; Hartwig, J. F. *Organometallics* **1996**, *15*, 400−407.

(67) Srivastava, G. *J. Chem. Soc., Perkin Trans. 1* **1974**, *8*, 916−917.

(68) Goetze, R.; Nöth, H.; Pommerening, H.; Sedlak, D.; Wrackmeyer, B. *Chem. Ber.* **1981**, *114*, 1884−1893.

(69) Weller, D. D.; Stirchak, E. P. *J. Org. Chem.* **1983**, *48*, 4873−4879.

(70) Culcasi, M.; Berchadsky, Y.; Gronchi, G.; Tordo, P. *J. Org. Chem.* **1991**, *56*, 3537−3542.

(71) Guerchais, V.; Lapinte, C.; Thépot, J.-Y.; Toupet, L. *Organometallics* **1988**, *7*, 604−612.

(72) Lindsell, W. E.; McCullough, K. J.; Plancq, S. *J. Organomet. Chem.* **1995**, *491*, 275−287.

(73) Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957−5026.

(74) Mannig, D.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 878−879.

(75) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 5249−5255.

(76) Nelson, G. O. *Organometallics* **1983**, *2*, 1474−1475.

in concurrent crystallization of yellow Cp*Fe(CO)$_2$Bcat with red [Cp*Fe(CO)$_2$]$_2$ impurity. An additional recrystallization was necessary to remove colored impurities, affording a yellow crystalline solid (239 mg). Additional pure material was obtained from the mother liquor after two recrystallizations. The total yield of recrystallized product was 81% (374 mg). ^{1}H NMR (C$_6$D$_6$) δ 6.89 (s, 1H), 6.51 (s, 1H), 2.34 (s, 3H), 2.15 (s, 3H), 1.58 (s, 15H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 216.52, 151.11, 147.99, 131.05, 124.00, 120.82, 110.04, 96.11, 21.69, 15.26, 10.31; ^{11}B NMR (C$_6$D$_6$) δ 54; IR (C$_6$D$_6$) ν_{CO} 1996 (s), 1939 (s) cm^{-1}; UV/vis (pentane) $\lambda_{max} = 277$ nm; $\epsilon_{277} = 6000$ cm^{-1} M^{-1}. Anal. calcd for $C_{20}H_{23}BO_4Fe$: C, 60.96; H, 5.88. Found: C, 61.06; H, 5.71.

CpFe(CO)$_2$[Bcat(^{t}Bu)$_2$] (1c). A solution of ClBcat(^{t}Bu)$_2$ (274 mg, 1.03 mmol) in toluene was added to a suspension of NaCpFe(CO)$_2$ (205 mg, 1.03 mmol) in toluene and stirred for 1 h. The toluene solvent was removed under vacuum, and the resulting residue was extracted with pentane. These pentane extracts were condensed under vacuum, filtered through glass wool, and crystallized at -30 °C to give a pale yellow solid. A second crop was obtained from the mother liquor. An additional recrystallization of both crops gave pure pale yellow product in 69% yield (289 mg). ^{1}H NMR (C$_6$D$_6$) δ 7.25 (d, $J = 1.91$ Hz, 1H), 7.16 (d, $J = 1.94$ Hz, 1H), 4.27 (s, 5H), 1.58 (s, 9H), 1.31 (s, 9H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 214.55, 151.31, 146.87, 145.16, 134.00, 115.71, 107.53, 84.22, 35.39, 35.03, 32.41, 30.36; ^{11}B NMR (C$_6$D$_6$) δ 51; IR (pentane) ν_{CO} 2022 (s), 1969 (s) cm^{-1}. Anal. calcd for $C_{21}H_{25}BO_4Fe$: C, 61.81; H, 6.17. Found: C, 61.85; H, 6.12.

Cp*Ru(CO)$_2$[Bcat(Me)$_2$] (2). A solution of ClBcat(Me)$_2$ (145.0 mg, 0.795 mmol) in 5 mL of pentane was added to a stirred suspension of K[Cp*Ru(CO)$_2$] (264.3 mg, 0.798 mmol) in 10 mL of pentane. After an hour of stirring, all of the ClBcat(Me)$_2$ had been consumed. The reaction mixture was filtered through glass wool, and the solid residue was extracted with 50 mL of pentane. The filtrate and pentane extracts were combined, condensed under vacuum, and crystallized at -30 °C. An additional recrystallization failed to remove all boron impurities which appear at δ 23 in the ^{11}B NMR spectrum. These impurities were sublimed overnight (45−55 °C, 0.01 Torr) from the recrystallized material, leaving a slightly impure ruthenium boryl compound which was recrystallized from pentane to give pure, pale yellow product in 40% yield (140.0 mg). ^{1}H NMR (C$_6$D$_6$) δ 6.90 (s, 1H), 6.52 (s, 1H), 2.35 (s, 3H), 2.15 (s, 3H), 1.71 (s, 15H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 203.29, 150.76, 147.64, 131.11, 124.05, 120.89, 110.16, 100.61, 21.70, 15.25, 10.79; ^{11}B NMR (C$_6$D$_6$) δ 48; IR (C$_6$D$_6$) ν_{CO} 2012 (s), 1952 (s) cm^{-1}. Anal. calcd for $C_{20}H_{23}BO_4Ru$: C, 54.69; H, 5.28. Found: C, 54.77; H, 5.15.

Cp*W(CO)$_3$[Bcat(Me)$_2$] (3a). A pentane solution of ClBcat(Me)$_2$ (206.6 mg, 1.13 mmol) was added to a suspension of NaCp*W(CO)$_3$ (482.3 mg, 1.13 mmol) in pentane. After an hour of stirring, the reaction mixture was filtered through glass wool, and the solid residue was extracted with 50 mL of pentane. The filtrate and pentane extracts were combined, condensed under vacuum, and crystallized at -30 °C. A second recrystallization afforded pure, amber crystalline material in 67% yield. Additional material was obtained from the mother liquor. ^{1}H NMR (C$_6$D$_6$) δ 6.83 (s, 1H), 6.49 (s, 1H), 2.30 (s, 3H), 2.13 (s, 3H), 1.82 (s, 15H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 224.07, 219.67, 151.45, 148.48, 131.57, 124.19, 121.16, 110.29, 104.65, 21.63, 15.17, 11.17; ^{11}B NMR (pentane) δ 53; IR (benzene) ν_{CO} 2002 (m), 1920 (s), 1900 (vs) cm^{-1}; UV/vis (pentane) $\lambda_{max} = 246$, 286, 295 nm; $\epsilon_{246} = 13\,000$ cm^{-1} M^{-1}. Anal. calcd for $C_{21}H_{23}BO_5W$: C, 45.81; H, 4.21. Found: C, 45.69; H, 4.17.

Cp*W(CO)$_3$Bcat (3b). A solution of ClBcat (373.1 mg, 2.416 mmol) in toluene was added to a stirred suspension of LiCp*W(CO)$_3$ (1.001 g, 2.443 mmol) in 15 mL of toluene. The reaction was monitored by ^{11}B NMR spectroscopy, and after 1 h all of the ClBcat was consumed. The reaction mixture was filtered through glass wool to remove all solids, and the toluene solvent was removed under vacuum. The residue was extracted with pentane, and the resulting solution was condensed under vacuum. Crystallization at -30 °C afforded beige crystals. Several more recrystallizations from pentane were necessary to remove all traces of colored metal impurity and boron impurities which resonate at δ 23 in the ^{11}B NMR spectrum. Cp*W(CO)$_3$Bcat was isolated as a light beige solid in 47% yield (591.3 mg). ^{1}H NMR (C$_6$D$_6$) δ 7.10 (m, 2H), 6.76 (m, 2H), 1.77 (s, 15H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 223.93, 219.59, 151.80, 122.40, 111.98, 104.56, 11.14; ^{11}B NMR (C$_6$D$_6$) δ 52.4; IR (pentane) ν_{CO} 2010 (s), 1931 (s), 1914 (s) cm^{-1}. Anal. calcd for $C_{19}H_{19}BO_5W$: C, 43.72; H, 3.67. Found: C, 43.91; H, 3.72.

LiCp*Mo(CO)$_3$. A 2.5 M solution of *n*-BuLi in *n*-hexane (1.3 mL, 3.25 mmol) was added dropwise to a stirred solution of Cp*Mo(CO)$_3$H (1.0047 g, 3.18 mmol) in 15 mL of pentane. Upon addition, the clear yellow solution turned bright cloudy yellow. After 1 h of stirring, the reaction mixture was filtered, and the solid residue was washed several times with pentane. The bright yellow lithium salt was obtained in quantitative yield (1.0923 g).

Cp*Mo(CO)$_3$[Bcat(Me)$_2$] (4). A solution of ClBcat(Me)$_2$ (179.5 mg, 0.984 mmol) in 5 mL of pentane was added to a suspension of LiCp*Mo(CO)$_3$ (318.7 mg, 0.990 mmol) in 5 mL of pentane. After 1.5 h of stirring, the solution was filtered through glass wool, and the solid residue was extracted with at least 30 mL of pentane. The filtrate and extracts were combined, condensed, and recrystallized at -30 °C. Two additional recrystallizations gave pure, pale yellow crystalline product in 32% yield (144.7 mg). ^{1}H NMR (C$_6$D$_6$) δ 6.82 (s, 1H), 6.48 (s, 1H), 2.29 (s, 3H), 2.12 (s, 3H), 1.75 (s, 15H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 233.48, 227.98, 151.29, 148.37, 131.68, 124.43, 121.20, 110.30, 106.06, 21.62, 15.14, 11.21; ^{11}B NMR (C$_6$D$_6$) δ 55.4; IR (C$_6$D$_6$) ν_{CO} 2009 (s), 1920 (s), cm^{-1}. Anal. calcd for $C_{21}H_{23}BO_5Mo$: C, 54.58; H, 5.02. Found: C, 54.72; H, 5.06.

Cp*Ru(CO)$_2$Bpin (5). A 1.0 M solution of BCl$_3$ in heptane (1.8 mL, 1.8 mmol) was added via syringe to a vigorously stirred solution of pinacol (142.0 mg, 1.20 mmol) in pentane (40 mL) at 0 °C. After all of the BCl$_3$ was added, the reaction was stirred at room temperature for 1 h. The solution was condensed under vacuum until a few mL's of liquid remained in the flask. It was important not to condense to dryness because ClBpin is volatile. ^{11}B NMR spectroscopy of this crude reaction mixture confirmed the clean formation of ClBpin, which resonates at δ 28. The mixture was filtered through glass wool to remove white insoluble impurities and was used immediately to avoid thermal decomposition of ClBpin. The crude pentane solution of ClBpin was added to a stirred suspension of KCp*Ru(CO)$_2$ (400.0 mg, 1.21 mmol) in pentane. After 45 min of stirring, the ClBpin was completely consumed as determined by ^{11}B NMR spectroscopy. The reaction mixture was filtered through glass wool to remove all solids, and the pentane solution was condensed under vacuum. Crystallization at -30 °C produced yellow crystals, which were then recrystallized to remove colored metal impurities and boron impurities which resonate at δ 23 in the ^{11}B NMR spectrum. Pure Cp*Ru(CO)$_2$Bpin was isolated as an off-white crystalline solid (138.4 mg). Additional material was obtained from the mother liquor by sublimation (25 °C, 0.01 Torr) for at least 1 d, followed by recrystallization from pentane at -30 °C to remove yellow impurities. The total yield of pure material was 36% (183.4 mg). ^{1}H NMR (C$_6$D$_6$) δ 1.79 (s, 15H), 1.16 (s, 12H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 204.24, 99.96, 82.46, 25.61, 10.91; ^{11}B NMR (C$_6$D$_6$) δ 44.7; IR (Nujol) ν_{CO} 2009(s), 1950(s), 1920(w) cm^{-1}. Anal. calcd for $C_{18}H_{27}BO_4Ru$: C, 51.56; H, 6.49. Found: C, 51.61; H, 6.47.

Cp*W(CO)$_3$Bpin (6). The same procedure was followed as for the preparation of Cp*Ru(CO)$_2$Bpin, except that LiCp*W(CO)$_3$ (516.0 mg, 1.26 mmol) was reacted with the ClBpin generated in situ from 1.0 M BCl$_3$ (1.8 mL, 1.8 mmol) and pinacol (144.0 mg, 1.22 mmol). Four recrystallizations were necessary to remove boron impurities and orange metal impurities, affording pure, pale yellow boryl complex. Additional material was obtained from the mother liquor by sublimation (45 °C, 0.01 Torr) overnight, followed by recrystallization from pentane at -30 °C. The total yield of pure product was 10% (64.1 mg). ^{1}H NMR (C$_6$D$_6$) δ 1.85 (s, 15H), 1.14 (s, 12H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 224.66, 220.52, 104.36, 83.92, 24.87, 11.18. ^{11}B NMR (C$_6$D$_6$) δ 50; IR (pentane) ν_{CO} 1999 (s), 1916 (m), 1900 (s) cm^{-1}. Anal. calcd for $C_{19}H_{27}BO_5W$: C, 43.05; H, 5.13. Found: C, 42.94; H, 5.00.

Cp*Fe(CO)$_2$BBN (7). A solution of BrBBN (185.6 mg, 0.925 mmol) in 5 mL of pentane was added to a stirred suspension of Na[Cp*Fe(CO)$_2$] (258.7 mg, 0.959 mmol) in 10 mL of pentane. After an hour of stirring, all of the BrBBN had been consumed. The reaction mixture was filtered through glass wool, condensed under vacuum, filtered again to remove dark red [Cp*Fe(CO)$_2$]$_2$, and crystallized at -30 °C. Two additional recrystallizations were necessary to remove colored impurities, affording a yellow/orange crystalline solid in 21% yield (72.8 mg). ^{1}H NMR (C_6D_6) δ 2.68 (s, 2H), 1.95−2.20 (m, 10H), 1.56 (s, 15H), 1.47 (m, 2H); ^{13}C{^{1}H} NMR (C_6D_6) δ 218.26, 96.28, 43.77, 34.05, 23.86, 10.40; ^{11}B NMR (C_6D_6) δ 125.6; IR (pentane) ν_{CO} 1981, 1927 cm^{-1}; UV/vis (pentane) $\lambda_{max} = 253$, 332 nm; $\epsilon_{253} = 7000$ cm^{-1} M^{-1}. Anal. calcd for $C_{20}H_{29}BO_2Fe$: C, 65.26; H, 7.94. Found: C, 64.99; H, 8.00.

Cp*Ru(CO)$_2$BBN (8a). A solution of BrBBN (301.0 mg, 1.50 mmol) in 5 mL of pentane was added to a stirred suspension of K[Cp*Ru(CO)$_2$] (501.4 mg, 1.51 mmol) in 15 mL of pentane. After 5 min of stirring, all of the BrBBN was consumed. The reaction mixture was filtered through glass wool, condensed under vacuum, and crystallized at −30 °C. Two additional recrystallizations were necessary to remove colored impurities, affording a yellow crystalline solid in 28% yield (171.5 mg). ^{1}H NMR (C_6D_6): δ 2.62 (s, 2H), 1.90−2.20 (m, 10H), 1.67 (s, 15H), 1.46 (m, 2H); ^{13}C{^{1}H} NMR (C_6D_6): δ 205.41, 100.81, 43.49, 33.41, 23.94, 10.74; ^{11}B NMR (C_6D_6): δ 117; IR (pentane): ν_{CO} 2002 (s), 1944 (s) cm^{-1}; UV/VIS (pentane): $\lambda_{max} = 270$ nm; $\epsilon_{270} = 7000$ cm^{-1}M^{-1}; Anal. Calc'd for $C_{20}H_{29}BO_2Ru$: C, 58.12; H, 7.07. Found: C, 58.09; H, 7.13.

Cp*Ru(CO)$_2$BCy$_2$ (8b). A 1.0 M solution of ClBCy$_2$ (0.97 mL, 0.97 mmol) in hexanes was added to a stirred suspension of KCp*Ru(CO)$_2$ (337.3 mg, 1.02 mmol) in 10 mL of pentane. The reaction was monitored by ^{11}B NMR spectroscopy and stirred for 2 h until all of the ClBCy$_2$ was consumed. The reaction mixture was filtered through glass wool to remove all solids, and the resulting pentane solution was condensed under vacuum. Crystallization at −30 °C afforded 314 mg of pale yellow crystals. Two more recrystallizations from pentane were necessary to remove all traces of colored metal impurity. Cp*Ru(CO)$_2$BCy$_2$ was isolated as a pale yellow crystalline solid in 55% yield (250.3 mg). ^{1}H NMR (C_6D_6) δ 2.35 (tt, J = 2.8 Hz, 12.0 Hz, 2H), 1.68 (s, 15H), 1.4−2.0 (m, 20H); ^{13}C{^{1}H} NMR (C_6D_6) δ 206.50, 100.73, 48.31, 28.39, 28.05, 28.01, 10.79; ^{11}B NMR (C_6D_6) δ 120; IR (Nujol) ν_{CO} 1989 (s), 1929 (s) cm^{-1}. Anal. calcd for $C_{24}H_{37}BO_2Ru$: C, 61.41; H, 7.94. Found: C, 61.59; H, 7.67.

Cp*Ru(CO)$_2$BMe$_2$ (8c). Neat BrBMe$_2$ (0.092 mL, 0.943 mmol) was added to a stirred suspension of KCp*Ru(CO)$_2$ (313.7 mg, 0.947 mmol) in pentane. After 45 min of stirring, the reaction mixture was filtered through glass wool, condensed, and crystallized at −30 °C, producing a dark red solid which contained no ^{11}B NMR signals. The mother liquor was condensed and crystallized again, this time affording a lighter-colored solid containing boron, as determined by ^{11}B NMR spectroscopy. Sublimation (70 °C, 0.01 Torr) of this solid separated a yellow solid from red impurities. Two recrystallizations of this yellow solid from pentane removed most of the Cp*Ru(CO)$_2$H and colored impurities. The product was obtained as a very pale yellow, slightly impure solid. ^{1}H NMR (C_6D_6) δ 1.60 (s, 15H), 1.58 (s, 6H); ^{13}C{^{1}H} NMR (C_6D_6) δ 205.14, 99.51, 28.19, 10.52; ^{11}B NMR (C_6D_6) δ 118.7.

Cp*Ru(CO)$_2$BS$_2$Tol (9). A solution of ClBS$_2$Tol (198.5 mg, 0.991 mmol) in pentane was added to a stirred suspension of KCp*Ru(CO)$_2$ (330.3 mg, 0.997 mmol) in 15 mL of pentane. The reaction was monitored by ^{11}B NMR spectroscopy and stirred for 30 min until all of the ClBS$_2$Tol was consumed. The reaction mixture was filtered through glass wool to remove all solids, and the pentane solvent was condensed under vacuum. Crystallization at −30 °C afforded pale yellow crystals. Two more recrystallizations from pentane were necessary to remove all traces of colored metal impurity. Cp*Ru(CO)$_2$BS$_2$Tol was isolated as an off-white solid in 34% yield (155 mg). ^{1}H NMR (C_6D_6) δ 7.58 (d, J = 8.0 Hz, 1H), 7.48 (s, 1H), 6.74 (d, J = 8.0 Hz, 1H), 2.04 (s, 3H), 1.63 (s, 15H); ^{13}C{^{1}H} NMR (C_6D_6) δ 203.32, 147.13, 143.88, 134.54, 126.17, 125.65, 124.71, 100.30, 21.22, 10.61; ^{11}B NMR (C_6D_6) δ 78; IR (pentane) ν_{CO} 2014(s), 1962(s) cm^{-1}; UV/vis (pentane) $\lambda_{max} = 247$, 286, 295 nm; $\epsilon_{247} = 16\,000$ cm^{-1} M^{-1}. Anal. calcd for $C_{19}H_{21}BO_2S_2Ru$: C, 49.90; H, 4.63. Found: C, 49.88; H, 4.68.

PhBS$_2$Tol. This complex was prepared according to the literature,[38] except that benzene solvent was used instead of methylene chloride. ^{1}H NMR data is reported in the literature,[68] but the aromatic resonances were not resolved. ^{1}H NMR (C_6D_6) δ 7.88 (d, J = 6.7 Hz, 2H), 7.39 (d, J = 8.1 Hz, 1H), 7.26 (s, 1H), 7.13 (m, 3H), 6.72 (d, J = 8.1 Hz, 1H), 1.99 (s, 3H). ^{11}B NMR (C_6D_6) δ 59.6.

Cp*W(CO)$_2$PXy$_3$H. A glass reaction vessel fused to a Kontes vacuum adaptor was equipped with a stirbar and charged with Cp*W(CO)$_3$H (563.6 mg, 1.395 mmol) and PXy$_3$ (663.0 mg, 1.92 mmol) dissolved in 20 mL of benzene. The solution was heated at 140 °C for 3 d and monitored by ^{1}H and ^{31}P{^{1}H} NMR. After all of the tungsten hydride was consumed, the volatile materials were removed under vacuum, and the oily residue was washed with several 2 mL portions of pentane to solidify the product and remove unreacted PXy$_3$. Additional free phosphine was removed by sublimation for 2 d (50 °C, 0.01 Torr). The remaining yellow solid was recrystallized from pentane at −30 °C, affording pure, yellow crystalline product in 60% yield (604.0 mg). ^{1}H NMR (C_6D_6) δ 7.36 (d, J = 11.0 Hz, 6H), 6.70 (s, 3H), 2.05 (s, 18H), 1.88 (s, 15H), −5.91 (d, J = 67.8 Hz, 1H); ^{13}C{^{1}H} NMR (C_6D_6) δ 139.46 (d, J_{CP} = 48.3 Hz, ipso C), 137.79 (d, J_{CP} = 10.3 Hz, *m*-), 132.22 (d, J_{CP} = 12.0 Hz, *o*-), 131.71(*p*-), 101.32, 21.76, 11.79, the CO resonance was not observed at room temperature; ^{31}P{^{1}H} NMR (C_6D_6) δ 43.7 (s, J_{PW} = 268.6 Hz); IR (C_6D_6) ν_{CO} 1920 (s), 1834 (m) cm^{-1}. Anal. calcd for $C_{36}H_{43}O_2PW$: C, 59.84; H, 6.00. Found: C, 59.78; H, 5.86.

LiCp*W(CO)$_2$PXy$_3$. A 2.46 M solution of *n*-BuLi in hexanes (0.075 mL, 0.185 mmol) was added dropwise to a stirred solution of Cp*W(CO)$_2$PXy$_3$H (133.5 mg, 0.185 mmol) in pentane. After 1 min, the clear yellow solution turned cloudy. After 20 min of stirring, the reaction mixture was filtered, and the solid residue was washed with pentane. The bright yellow lithium salt was obtained in quantitative yield (134.2 mg). Immediate refrigeration at −30 °C was necessary to prevent decomposition to a brown solid. ^{1}H NMR (THF-d_8) δ 7.23 (d, J = 9.8 Hz, 6H), 6.72 (s, 3H), 2.18 (s, 18H), 1.81 (s, 15H); ^{31}P{^{1}H} NMR (THF-d_8) δ 58.8 (s, J_{PW} = 468.8 Hz); IR (THF) ν_{CO} 1775 (m), 1655 (s), cm^{-1}.

***trans*-Cp*W(CO)$_2$PXy$_3$[Bcat(Me)$_2$] (10a).** A solution of ClBcat(Me)$_2$ (86.0 mg, 0.471 mmol) in 5 mL of pentane was added to a stirred suspension of Li[Cp*W(CO)$_2$PXy$_3$] (343.7 mg, 0.472 mmol) in 10 mL of pentane. After 30 min of stirring, the reaction mixture was filtered, and the solid residue was extracted with at least 50 mL of pentane. The filtrate and pentane extracts were combined, and the pentane solvent removed under vacuum. The residue was recrystallized twice from toluene layered with pentane at −30 °C. Another recrystallization from toluene at −30 °C over the course of several days resulted in yellow crystalline material that contained traces of toluene solvent. Removal of toluene was achieved by lyophilizing the product in frozen benzene, resulting in a yellow powder in 20% yield (51.5 mg). ^{1}H NMR (C_6D_6) δ 7.88 (d, J = 11.6 Hz, 2H), 7.37 (d, J = 11.1 Hz, 4H), 6.97 (s, 1H), 6.75 (s, 3H), 6.56 (s, 1H), 2.43 (s, 3H), 2.22 (s, 3H), 2.20 (s, 6H), 2.06 (s, 12H), 1.96 (s, 15H); ^{13}C{^{1}H} NMR (C_6D_6) δ 230.68 (d,$^{2}J_{CP}$ = 19.4 Hz, CO), 152.10 (**C**-O in catechol), 149.18 (**C**-O in catechol), 138.05 (d, J_{CP} = 10.8 Hz, *m*- C), 136.67 (d, J_{CP} = 43.0 Hz, ipso C), 133.09 (d, J_{CP} = 10.1 Hz, *o*-), 132.41 (d, J = 12.0 Hz, *o*-), 132.20 (*p*-), 130.58 (**C**-Me in cat), 123.52 (**C**-H in cat), 120.36 (**C**-Me in cat), 109.92 (**C**-H in cat), 102.66 (Cp*), 21.95 (Me on cat), 21.72 (Me in PXy$_3$), 15.57 (Me on cat), 11.58 (Cp*); ^{11}B NMR (C_6D_6) δ 58; ^{31}P{^{1}H} NMR (C_6D_6) δ 42.4 (s, J_{PW} = 289.3 Hz); IR (C_6D_6) ν_{CO} 1914 (m), 1832 (s) cm^{-1}. Anal. calcd for $C_{44}H_{50}BO_4PW$: C, 60.85; H, 5.80. Found: C, 61.10; H, 6.05.

***trans*-Cp*W(CO)$_2$(PMe$_3$)[Bcat(Me)$_2$] (10b).** A solution of ClBcat(Me)$_2$ (120.0 mg, 0.658 mmol) in 5 mL of pentane was added to a stirred suspension of Li[Cp*W(CO)$_2$PMe$_3$] (304.0 mg, 0.664 mmol) in 10 mL of pentane. After 2 h of stirring, the reaction mixture was filtered, and the solid residue was extracted with at least 50 mL of pentane. The filtrate and pentane extracts were combined, condensed, and crystallized at −30 °C. One additional recrystallization from pentane afforded a pure, bright yellow crystalline solid in 38% yield (148 mg). ^{1}H NMR (C_6D_6) δ 6.90 (s, 1H), 6.52 (s, 1H), 2.40 (s, 3H), 2.15 (s, 3H), 1.92 (s, 15H), 1.29 (d, J_{HP} = 8.9 Hz, 9H); ^{13}C{^{1}H} NMR (C_6D_6) δ 229.63 (d,$^{2}J_{CP}$ = 19.7 Hz, $^{1}J_{CW}$ = 143.0 Hz), 152.03, 149.03, 130.43, 123.37, 120.23, 109.96, 102.65, 21.74, 20.35 (d, J_{CP} = 33.0 Hz), 15.42, 11.79; ^{11}B NMR (C_6D_6) δ 58; ^{31}P{^{1}H} NMR (C_6D_6) δ -10.61 (s, J_{PW} = 273.4 Hz); IR (C_6D_6) ν_{CO} 1906 (m), 1823 (s) cm^{-1}. Anal. calcd for $C_{23}H_{32}BO_4PW$: C, 46.19; H, 5.39. Found: C, 46.30; H, 5.39.

$Cp^*Mo(CO)_2(PXy_3)H$. A glass reaction vessel fused to a Kontes vacuum adaptor was equipped with a stirbar and charged with $Cp^*Mo(CO)_3H$ (442.0 mg, 1.40 mmol) and PXy_3 (502.4 mg, 1.45 mmol) dissolved in 20 mL of benzene. The solution was heated at 100 °C for 4 d and monitored by ^1H and $^{31}P\{^1H\}$ NMR, after which time approximately 75% of the starting material had been consumed. The reaction was driven to completion by heating for an additional day at 140 °C. The volatile materials were removed under vacuum, and the residue was extracted with several portions of pentane. The pentane extracts were combined and filtered through glass wool, and the solvent was removed under vacuum. Unreacted hydride and PXy_3 were removed by sublimation for 2 d (50 °C, 0.01 Torr). The remaining yellow solid was recrystallized twice from pentane at −30 °C, affording pure, yellow crystalline product. Additional material was obtained from the mother liquor, for a total yield of 33% (290.0 mg). ^1H NMR (C_6D_6) δ 7.37 (d, $J = 11.0$ Hz, 6H), 6.72 (s, 3H), 2.06 (s, 18H), 1.82 (s, 15H), −4.56 (d, $J = 64.4$ Hz, 1H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 139.25 (d, $J_{CP} = 38.8$ Hz, ipso C), 137.86 (d, $J_{CP} = 9.5$ Hz, *m*-), 132.02 (d, $J_{CP} = 12.2$ Hz, *o*-), 131.64 (*p*-), 102.80, 21.74, 11.76; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 72.6; IR (C_6D_6) ν_{CO} 1928 (s), 1846 (ms) cm^{-1}. Anal. calcd for $C_{36}H_{43}O_2PMo$: C, 68.13; H, 6.83. Found: C, 68.01; H, 6.72.

$Li[Cp^*Mo(CO)_2PXy_3]$. A 2.46 M solution of *n*-BuLi in hexanes (0.13 mL, 0.32 mmol) was added dropwise to a stirred solution of $Cp^*Mo(CO)_2(PXy_3)H$ (193.8 mg, 0.305 mmol) in 20 mL of pentane. After a few seconds, the clear yellow solution turned bright cloudy yellow. After 30 min of stirring, the reaction mixture was filtered, and the solid residue was washed several times with pentane. The bright yellow lithium salt was obtained in 94% yield (184.5 mg). Immediate refrigeration at −30 °C was necessary to prevent decomposition to a brown solid.

***trans*-$Cp^*Mo(CO)_2(PXy_3)[Bcat(Me)_2]$.** A solution of $Cl[Bcat(Me)_2]$ (51.2 mg, 0.281 mmol) in 5 mL of pentane was added to a stirred suspension of $Li[Cp^*Mo(CO)_2PXy_3]$ (180 mg, 0.281 mmol) in 5 mL of pentane. The mixture changed color from bright yellow to a darker yellow. After 30 min of stirring, the reaction was complete as determined by ^{11}B NMR spectroscopy. The mixture was filtered, and the solid residue was extracted with at least 50 mL of pentane. The filtrate and pentane extracts were combined, and the pentane solvent was removed under vacuum. The residue was crystallized from toluene layered with pentane at −30 °C. The product was recrystallized from toluene at −30 °C over the course of several days, resulting in yellow crystalline material which contained traces of toluene solvent. The toluene was removed by lyophilizing the product in frozen benzene, resulting in a yellow powder in 25% yield (55.0 mg). This material appeared clean by spectroscopic analysis, but attempts to obtain satisfactory analytical data after repeated recrystallizations were unsuccessful. ^1H NMR (C_6D_6) δ 7.85 (d, $J = 11.5$ Hz, 2H), 7.39 (d, $J = 10.9$ Hz, 4H), 6.96 (s, 1H), 6.76 (s, 3H), 6.55 (s, 1H), 2.42 (s, 3H), 2.20 (s, 9H), 2.07 (s, 12H), 1.91 (s, 15H); ^1H NMR (64 °C, C_6D_6) δ 7.25−7.80 (broad, 6H), 6.91 (s, 1H), 6.80 (s, 3H), 6.54 (s, 1H), 2.41 (s, 3H), 2.21 (s, 3H), 2.14 (broad s, 18H), 1.92 (s, 15H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 237.54 (d, $^2J_{CP} = 26.5$ Hz, 2 CO), 151.81 (**C**-O in catechol), 148.99 (**C**-O in catechol), 138.10 (d, $J_{CP} = 8.4$ Hz, *m*-), 136.75 (d, $J_{CP} = 36.7$ Hz, ipso), 132.65 (d, $J_{CP} = 11.7$ Hz, *o*-), 132.35 (d, $J = 12.1$ Hz, *o*-), 132.16 (*p*-), 130.70 (**C**-Me in cat), 123.64 (**C**-H in cat), 120.46 (**C**-Me in cat), 109.90 (**C**-H in cat), 104.00 (Cp*), 21.89 (Me on cat), 21.74 (Me in PXy_3), 21.71 (Me in PXy_3), 15.56 (Me on cat), 11.58 (Me in Cp*); ^{11}B NMR (C_6D_6) δ 58; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 71.6; IR (C_6D_6) ν_{CO} 1916 (ms), 1834 (s) cm^{-1}.

General Procedure for Photochemical Reaction of Metal Boryl Complexes with Alkane Substrates. The metal boryl complex (5 mg) was dissolved in 0.5 mL of neat substrate and transferred to an NMR tube. ^{11}B NMR spectra were recorded for the starting material. The sample was irradiated with periodic monitoring of the reaction by ^{11}B NMR spectroscopy.

Measurement of Yields of Organoboron Compounds. The metal boryl complex (5 mg) and dodecahydrotriphenylene (1−2 mg) as an internal standard were dissolved in 0.8 mL of neat substrate. Half of this solution was transferred to an NMR tube. ^{11}B NMR spectra were recorded for the starting material. The sample was irradiated with periodic monitoring of the reaction by ^{11}B NMR spectroscopy. After the reaction was judged to be complete, the ratio of organoborane to standard was determined by either GC or ^1H NMR spectroscopy. The other half of the original solution was reduced to dryness under vacuum, and the residue was dissolved in C_6D_6. A ^1H NMR spectrum of this sample was recorded to obtain the ratio of the standard to the metal boryl starting material.

Isotope Effect Measurements. The metal boryl complex (1 mg) was added as a solid to an NMR sample tube, which was capped with a rubber septum. Equimolar amounts of pentane (0.10 mL) and pentane-d_{12} (0.10 mL) were added to the tube by syringe. The sample was irradiated until all starting material was consumed as determined by ^{11}B NMR spectroscopy. The solution inside the tube was analyzed by GC/MS to determine the ratio of protiated and deuterated alkylboronate esters by the abundance of their molecular ions.

Irradiation of 3a in the Presence of CO. Tungsten boryl complex **3a** (6 mg) was dissolved in pentane (1 mL) and the solution added to two NMR tubes (0.4 mL in each). Carbon monoxide (2 atm) was introduced into one of the tubes. ^{11}B NMR spectra of the two samples were recorded before irradiation side by side. During the course of irradiation, ^{11}B NMR spectra of both samples were periodically recorded, and the amount of product was qualitatively evaluated at each time point.

Irradiation of 3a in the Presence of ^{13}CO. Tungsten boryl complex **3a** (5 mg) was dissolved in pentane and transferred to a Young NMR tube. ^{13}CO (2 atm) was introduced into the tube. ^{11}B and ^{13}C NMR spectra of the starting material were recorded. The solution was irradiated until roughly half the starting material remained as monitored by ^{11}B NMR spectroscopy. ^{13}C NMR spectroscopy of this sample showed no incorporation of the labeled CO into the starting material.

Irradiation of 3a in the Presence of PMe_3. Tungsten boryl complex **3a** (5 mg) was dissolved in pentane (0.5 mL), and the solution was added to a Young NMR tube. Using vacuum techniques, 2 equiv of PMe_3 were condensed into the tube. A ^{11}B NMR spectrum of the starting material was recorded. The solution was irradiated and periodically monitored by ^{11}B NMR spectroscopy until half of the starting material remained. The volatile materials were removed using vacuum techniques, and the residue was dissolved in C_6D_6. The ratio of $Cp^*W(CO)_2PMe_3Bcat(Me)_2$ and $pentylBcat(Me)_2$ was determined by ^1H NMR spectroscopy. This procedure was repeated with 4 equiv of PMe_3.

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