Experimental and Computational Evidence for a Boron-Assisted, σ-Bond Metathesis Pathway for Alkane Borylation

Charles Edwin Webster,[†] Yubo Fan,[†] Michael B. Hall,*,[†] Doris Kunz,[‡] and John F. Hartwig*,[‡]

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255, and Department of Chemistry, 225 Prospect Street, P.O. Box 208107, Yale University, New Haven, Connecticut 06520-8107

Received September 3, 2002 ; E-mail: hall@mail.chem.tamu.edu

Dioxaboryl transition-metal complexes efficiently and selectively induce both catalytic and stoichiometric regiospecific functionalization at alkane C−H bonds.[1] Reactions of the first and mechanistically best-characterized system that functionalizes alkanes with terminal regiospecificity begin with photodissociation of one CO from $Cp*M(CO)_{n+1}BR_2$ ($n = 1$: M = Fe, Ru; $n = 2$: M = Mo, W; R_2 = catecholate or pinacolate) to generate a coordinatively unsaturated 16 e$^-$ intermediate as shown in eq 1.[2] This metal−boryl intermediate can be trapped with phosphine; but, in the absence of phosphine, it readily cleaves and functionalizes the terminal alkane C−H bond. The mechanism of the C−H bond cleavage and B−C bond formation events could not be determined experimentally. We show here by a combination of experimental and theoretical studies[3] that the formally unoccupied p orbital of a cyclic dioxaboryl ligand is intimately involved in the C−H bond activation step and that this step occurs by σ-bond metathesis.[4]

(1)
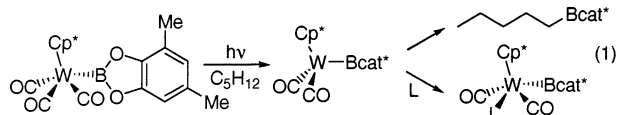
Published chemistry of $CpM(CO)_nR$ complexes with R = alkyl or aryl groups is manifold but has not encompassed intermolecular C−H bond activation of arenes or alkanes. To determine rigorously if the intermolecular C−H activation by analogous boryl compounds is truly distinct from that reported previously for related $CpM(CO)_n$ complexes of alkyl and aryl ligands, we prepared $CpM(CO)_n(p$-Tol$)$ with M = Fe (**1**) and M = W (**2**). The reactions of these complexes with arenes to form a new aryl complex and free toluene would be thermoneutral and cannot be prevented by reaction thermodynamics. These and related reactions (below) are summarized in Scheme 1.

Scheme 1
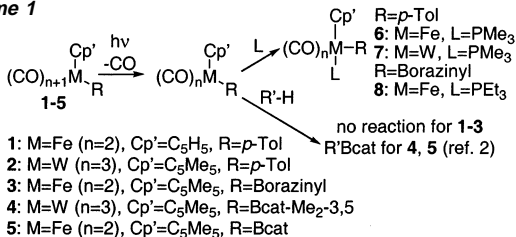
Complexes **1** and **2** were generated by a palladium-catalyzed process reported by Beletskaya.[5] Irradiation of the tungsten complex **2** at room temperature in benzene did not lead to C−H activation, and little conversion of the starting complex to any new material occurred. Irradiation of iron complex **1** generated only traces of the corresponding phenyl complex $CpFe(CO)_2Ph$ and formed predominantly $[CpFe(CO)_2]_2$.

---

† Texas A&M University.
‡ Yale University.

Although little or no C−H activation occurred, the 16 e$^-$ intermediate, which would be analogous to the boryl intermediate that cleaves C−H bonds, was formed reversibly. Irradiation of either the iron or tungsten complex under 1 atm of ^{13}CO for 20 min led to incorporation of the labeled CO into the starting complex, as determined by ^{13}C NMR spectroscopy. Irradiation of iron complex **1** in the presence of 1 equiv of trimethylphosphine formed monophosphine complex **6** in 92% yield by NMR spectroscopy after 20 min, and irradiation of tungsten complex **2** formed a 1.3:1 ratio of the cis and trans isomers of the phosphine product **7** in 83% yield after 25 min.

To determine if the unoccupied p orbital on boron was required for the C−H activation, we prepared borazinyl complex **3** from the ferrate complex and trimethyltrichloroborazine.[6] The p orbital of this boryl ligand is less available to participate in the reaction because it lies in an aromatic π-system. In contrast to the dioxaboryl complexes, **3** was stable toward 1 h of irradiation. However, **3** again formed a coordinately unsaturated 16 e$^-$ intermediate readily and reversibly. It reacted with triethylphosphine in 25 min to form 41% yield (by NMR spectroscopy) of the phosphine adduct **8**.

To understand this dramatic difference in activation energies between the 16 e$^-$ intermediates containing aryl and borazinyl ligands instead of dioxaboryl ligands, we computed the energetics of several reaction mechanisms. A general mechanism for the lowest-energy pathway is shown in Scheme 2, and the relative energies of the Fe and W species are provided in Table 1. Initial formation of an alkane σ-complex (**9**) is followed by transfer of a hydrogen from the coordinated alkyl group to the boron through a σ-bond metathesis transition state (**10-TS**). The cis disposition of the boron and hydrogen atom of the metal-bound alkane permits the empty boron p orbital to assist the metal in the C−H bond cleavage step. This σ-bond metathesis mechanism avoids a W(IV) or an unusual organometallic Fe(IV) complex en route to the stable intermediate borane complex **11**.

Scheme 2. Proposed General Reaction Path for $CpM(CO)_n(B(OCH_2)_2)$ Reacting with Alkane
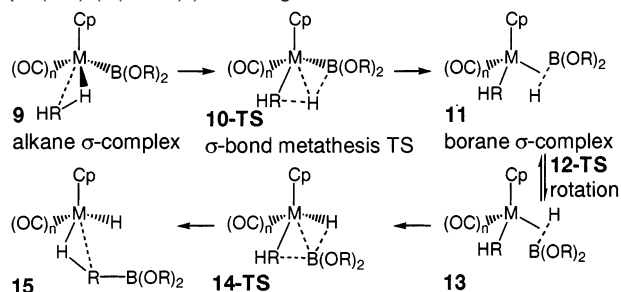
This complex cannot undergo direct formation of the final alkylboronate ester because the alkyl and boryl groups are located trans to each other. This alkyl σ-borane complex could dissociate borane, but this dissociation is calculated to be thermodynamically

Table 1. Calculated Relative Energies of Species in Boron-Assisted σ-Bond Metathesis (kcal mol^{-1})^a

	9	10-TS	11	12-TS	13	14-TS	15	R-Prod	H-Prod
	CpFe(CO)$_2$(B(OCH$_2$)$_2$)								
$\Delta H^{[\circ,\ddagger]}$	−6.1	+1.3	−5.4	+0.8	−5.5	−5.1	−8.0	−0.5	+7.8
$\Delta G^{[\circ,\ddagger]}$	+3.6	+13.2	+6.1	+13.5	+6.9	+7.5	+2.9	−2.1	+7.6
	CpW(CO)$_3$(B(OCH$_2$)$_2$)								
$\Delta H^{[\circ,\ddagger]}$	−3.7	+4.3	−3.1	+0.9	+0.8	+0.9	−6.8	−1.0	+4.5
$\Delta G^{[\circ,\ddagger]}$	+6.1	+15.8	+9.0	+14.6	+12.8	+14.6	+2.0	−2.1	+5.0

^{a} Relative energies compared to separated reactants, CpM(CO)$_n$(B(O-CH$_2$)$_2$), the coordinatively unsaturated 16 e$^-$ complex (where $n = 1$ for Fe and $n = 2$ for W), and CH$_4$.
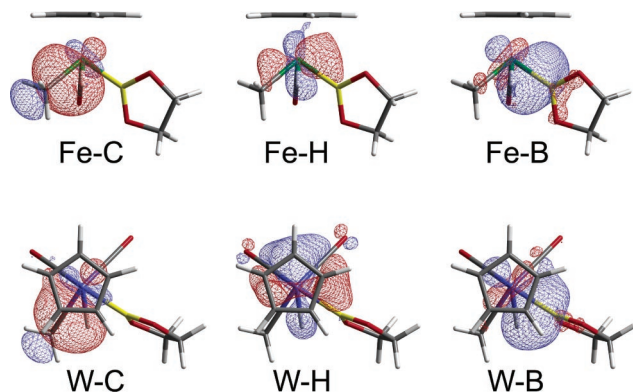

Figure 1. Boys localized molecular orbitals representing the boron-assisted, metal-mediated, hydrogen-transfer transition states (**10-TS**) for the Fe [top: CpFe(CO)CH$_3$(H)(B(OCH$_2$)$_2$)] and W [bottom: CpW(CO)$_2$CH$_3$(H)-(B(OCH$_2$)$_2$)] systems. Only one of the representative "M-H" orbitals is pictured.

unfavorable (**H-Prod** in Table 1). Thus, the complex undergoes a more thermodynamically favorable reaction sequence that does generate the alkylboronate ester product. This calculated reaction pathway occurs by rotation about the (H−B)−M axis (**12-TS**) from intermediate **11** to **13**, which possesses cis disposed alkyl and boryl groups. With the open side of the boron and the alkyl carbon oriented cis, B−C bond formation occurs through a σ-bond metathesis transition state **14-TS**. Elimination of alkylboronate ester from **15** is calculated to be thermodynamically favorable and produces the experimentally observed product (**R-Prod** in Table 1). Full details of an alternative higher-energy pathway[7] involving the oxidative addition of alkane (as seen in late metals[8]) followed by the reductive elimination of the alkylboronate ester and the effect of conjugated, nonconjugated, and noncyclic ligands on the reaction barrier will be reported in a subsequent publication.

Boys localization[9] of the molecular orbitals of the σ-bond metathesis transition states (**10-TS**) for the Fe and W systems reveals the nature of this boron-assisted, metal-mediated hydrogen transfer (see Figure 1). The labels "M-C", "M-H", and "M-B" denote the localized orbitals involving the metal−carbon, metal−hydrogen, and metal−boron interactions. If one ignores the "M-H" orbitals, which are mainly metal with only a little H character, the transferring hydrogen is protonic, and the transfer occurs through a three-center four-electron interaction involving H as the central atom between the M−C and M−B orbitals. If one focuses on the small H character in the "M-H" orbitals, then transition state **10-TS** has a small amount of oxidative-addition character. Yet, this structure remains a transition state and is not an Fe(IV) or W(IV) intermediate. Mulliken population analysis of the fragments comprising the iron intermediate **11** show that the unoccupied boron p orbital plays a role in lowering the energy of iron **10-TS** and iron intermediate **11** by accepting 0.4 and 0.2 e$^-$ from the metal, respectively. As shown in structure **I** (below), the electropositive

nature of the boron causes the electron pair in the M−B bond to attack the H; the attack is supported by (1) transfer of the electron pair from R−H to the new M−C bond and (2) back donation of electrons on the M into the boron p orbital.
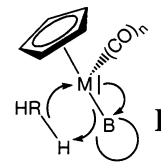
Supporting Information Available: Synthesis, photochemistry, and spectral data for **1−3** and **6−8**, structures of **9−15**, percentage atomic character in Boys localized orbitals, and details of the Mulliken population analysis (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995−1997.
(2) Waltz, K. M.; Hartwig, J. F. *Science* **1997**, *277*, 211−213. Waltz, K. M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 11358−11369.
(3) Gaussian 98[10] implementation of B3LYP[11, 12] density functional theory;[13] energies: pruned fine grids; gradients and Hessians: pruned course grids (unpruned for iron and tungsten); geometry optimization SCF convergence: 10^{-8}; geometries: fully optimized and analytical frequencies; basis sets: iron (341/341/41) and tungsten (341/341/21): Couty and Hall modification[14] of Hay and Wadt LANL2DZ[15] with effective core potentials; metal-bound carbons, borons, and hydrogens and all oxygens: Dunning's cc-pVDZ[16] (redundant functions removed and linearly transformed);[17] all other carbon and hydrogen: D95.[18]
(4) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491−6493. Steigerwald, M. L.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 308−311.
(5) Artamkina, G. A.; Mil'chenko, A. Yu.; Bunagin, N. A.; Beletskaya, I. P.; Reutov, O. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 700−701.
(6) Braunschweig, H.; Kollann, C.; Müller, M. *Eur. J. Inorg. Chem.* **1998**, 291−293.
(7) The barriers are 11 and 4 kcal mol^{-1} higher for Fe and W, respectively.
(8) Niu, S.; Hall, M. B. *Chem. Rev.* **2000**, *100*, 353−406 and references therein.
(9) Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 296−299. Boys, S. F. In *Quantum Theory of Atoms, Molecules, and the Solid State*; Löwdin, P. O. Ed.; Academic Press: New York, 1966; pp 253−262.
(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revisions A.6, A.7, and A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
(11) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(12) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.
(13) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
(14) Couty, M.; Hall, M. B. *J. Comput. Chem.* **1996**, *17*, 1359−1370.
(15) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270−283. Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284−298.
(16) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007−1023.
(17) Davidson, E. R. *Chem. Phys. Lett.* **1996**, *260*, 514−518.
(18) Dunning, T. H.; Hay, P. J. *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1976; pp 1−28.
(19) POV-Team co/ Hallam Oaks P/L, P.O. Box 407, Williamstown, Victoria, 3016 Australia; http://www.povray.org.

JA028394C