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First Transition Metal–Boryl Bond Energy and Quantitation of Large Differences in Sequential Bond Dissociation Energies of Boranes

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Transition metal catalyzed hydroboration displays potential for altering chemo-, regio-, and diastereoselectivity relative to uncatalyzed hydroborations, as well as for achieving enantioselectivity in the presence of a chiral transition metal catalyst.[1–6] Although transition metal compounds containing covalent bonds to three-coordinate boron centers (boryl complexes) are believed to be intermediates in these processes, isolated examples are rare.[5,7–11] Studies concerning the fundamental properties and reaction chemistry of well-characterized boryl complexes have been initiated only recently.

Transition metal–ligand covalent bond energies are important in understanding catalysis,[12] but no thermochemical data on transition metal–boryl complexes are known, and few data are available for boranes. It is difficult to measure borane BDEs (bond dissociation energies) experimentally, and only average bond dissociation energies are typically quoted for B–H and B–C bonds.[13–15] We have calculated B–H and B–C BDEs for a series of boranes including catecholborane, the reagent most commonly employed in metal-catalyzed processes. Our results demonstrate large differences between the first BDEs and average BDEs. With an accurate single B–H BDE for catecholborane in hand, we have measured the enthalpy for oxidative addition of a borane B–H bond to *trans*-[$Ir(CO)(PPh_3)_2Cl$] and have obtained the first estimate of a transition metal–boryl bond energy.

Table 1 displays BDEs for several boranes determined at the G-2 and CBS-4 levels. MP4 methods have been used previously to determine ΔH_f for a series of electrophilic molecules with two heavy atoms including small boranes. An isodesmic approach at the HF/6-31G* level was then used to obtain ΔH_f of larger boranes.[16,17] Reliable single BDEs, more important for thermodynamic analysis of reaction chemistry than ΔH_f, can be determined by the G-2 and CBS-4 methods.[18] G-2 theory has been shown to reproduce bond dissociation energies, proton affinities, electron affinities, and ionization potentials to an accuracy of ±2 kcal/mol for a wide variety of compounds,[19] and it allows direct, accurate determination of single BDEs by comparison of closed-shell species with the corresponding open shell species formed by homolytic bond scission. Because this method is very demanding of computational resources, our larger molecules were treated with CBS-4. This method is much less intensive computationally, but demonstrates an accuracy only modestly diminished from G-2 theory.[18] The foundation of the CBS-4 calculation is a single-point Hartree–Fock calculation with a very large basis set (6–311+G(3d2f,2df,p)) at the HF/3-21G* optimized geometry, a correction for electron correlation by adding MP2 and MP4(SDQ) calculations with much smaller basis sets, and an extrapolation to the complete basis set limit.[20,21] The values in Table 1 show that the G-2 and CBS-4 bond dissociation energies agree very closely and provide average bond energies that are close to those derived from the ΔH_f values mentioned above.[16,17,22]

Table 1. G-2 and CBS-4 Bond Dissociation Energies[a]

bond	BDE	
	G-2	CBS-4
B–H	83.7	81.6 (singlet BH)
B–H	50.0	50.8 (triplet BH)
BH–H	78.5	80.1 (singlet BH)
BH–H	112.2	110.9 (triplet BH)
BH_2–H	106.6	105.5
BF_2–H	110.3	108.6
BF–H	45.6	46.4 (singlet BF)
BFH–H	106.2	104.9
CH_3CH_2–H	102.5	101.7
B–CH_3	91.9	90.1 (singlet BCH_3)
B–CH_3	48.3	49.8 (triplet BCH_3)
BCH_3–CH_3	70.7	73.3 (singlet BCH_3)
BCH_3–CH_3	114.3	113.6 (triplet BCH_3)
$B(CH_3)_2$–CH_3		103.9
BF_2–CH_3	111.2	110.3
NH_3BH_2–H	103.6	102.6
$(HO)_2B$–H	108.9	107.2
$(HO)(CH_3O)B$–H		107.4
$(CH_3O)_2B$–H		105.2
OCH_2CH_2OB–H		110.8
OCH_2CH_2OB–CH_3		111.6
OCHCHOB–H		111.8
OCHCHOB–CH_3		112.6
$(C_6H_4O_2)B$–H		111.3
$(C_6H_4O_2)B$–Me		113.0

[a] In kcal/mol (enthalpies at 298 K; kcal/mol).

Table 2. Iridium-Mediated Hydroboration of Olefins[a]

primary reaction	ΔH (kcal/mol)
[Ir] + H(Bcat) $\rightarrow$ [Ir](H)(Bcat)	–15.1
[Ir](H)(Bcat) + CH_2CH_2 $\rightarrow$ [Ir](CH_2CH_3)(Bcat)	2
[Ir](H)(Bcat) + CH_2CH_2 $\rightarrow$ [Ir](H)(CH_2CH_2(Bcat))	–6
[Ir](CH_2CH_3)(Bcat) $\rightarrow$ [Ir] + CH_3CH_2(Bcat)	–11
[Ir](H)(CH_2CH_2(Bcat)) $\rightarrow$ [Ir] + CH_3CH_2(Bcat)	–3
H(Bcat) + CH_2CH_2 $\rightarrow$ CH_3CH_2(Bcat)	–24

[a] Based on the following BDE data: C═C 163, C—C 88, C—H 98, H—Bcat 111, C—Bcat 113, H—[Ir] 60, C—[Ir] 35, [Ir] = *trans*-[$Ir(CO)(PPh_3)_2Cl$].

Although not relevant to most solution chemistry, the case of monomeric BH_3 nevertheless makes clear that the first, second, and third BDEs are strikingly different. The first BDE of 106.6 kcal/mol is similar to that in methane or benzene. However, the second BDE of 78.5 kcal/mol is significantly lower, the difference

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(22) In addition, the CBS-4 procedure reproduced the atomization energies of the 55 molecules in the G-2 test set with an average absolute error of only 1.9 kcal/mol and would be expected to reproduce experimental B–H and B–C bond dissociation energies with a similar degree of accuracy.[18]

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being due to the large singlet–triplet energy gap in BH.[23,24] This trend in sequential BDEs is repeated for trialkylboranes. The first BDE of trimethylborane is 30 kcal/mol greater than the second. The averages of the three BDEs for BMe_3 (89.1 kcal/mol) and BH_3 (89–90 kcal/mol) compare favorably with the average BDEs determined from experimental ΔH_f values. BMe_3 has a well-accepted experimental ΔH_f that gives an average BDE of 86.8 kcal/mol. The ΔH_f of diborane and its dimerization energy possess large errors and are subject to debate.[14,25,26] However, our average BDE is essentially identical to that in the JANAF tables (89 kcal/mol),[27] and the G2 level of theory should provide a dimerization energy (38.2 kcal/mol) that is closest to the actual value. Most important from these calculations is the significantly greater first bond dissociation energy than predicted from ΔH_f.

The CBS-4 method allowed an accurate determination of the B–H and B–C BDEs in catecholborane, methylcatecholborane, and analogous boranes. These values should be relatively independent of solvent since catecholborane does not form adducts even with THF, and bond strengths calculated at the HF/3-21G* level in the gas phase and with the SCRF method[28] in a medium of dielectric constant 40 are within 0.3–0.6 kcal/mol of each other. Increased BDEs were obtained for those molecules containing a ring structure. A large difference in the B–H and B–C BDEs for RBF_2 (R = alkyl, H) has been noted from electron impact data.[29] Our data for this species suggest that the values obtained in this study are larger than average BDEs of trialkylboranes due to the differences in sequential BDEs rather than to an effect of fluorine substitution. In addition to the constancy of the B–H and B–C bond strengths upon various substitution patterns, the similarity between the B–C and the B–H bond strengths is unusual, since X–H bonds tend to be stronger than the corresponding X–C bonds, as discussed recently.[30] Consistent with our calculations, experimental ΔH_f data suggested similar B–H and B–C bond strengths.[13,14]

It has been reported recently that catecholborane undergoes quantitative oxidative addition to *trans*-[$Ir(CO)(PPh_3)_2(Cl)$], forming *trans*-[$Ir(CO)(PPh_3)_2(Cl)(H)(Bcat)$].[7] By measuring the enthalpy of this oxidative addition reaction and employing the B–H BDE for catecholborane in Table 1, we determined that the sum of the iridium–hydrogen and iridium–boron bond energies is 126.4 kcal/mol. The sum of the two iridium–hydrogen bonds in *trans,cis*-[$Ir(CO)(PPh_3)_2(Cl)(H)_2$] has been determined previously to be 120 kcal/mol.[31] Thus, the iridium–boron bond strength is equal to or greater than that of the corresponding iridium–hydride. If the two Ir–H bonds in *trans,cis*-[$Ir(CO)(PPh_3)_2(Cl)(H)_2$] have comparable sequential bond energies, as was shown for $CpIr(PMe_3)H_2$,[32] then the resulting 60 kcal/mol Ir–H bond energy of the *trans*-[$Ir(CO)(PPh_3)_2ClH$] radical allows an estimate of 66 kcal/mol for the iridium–boron bond in *trans,cis*-[$Ir(CO)(PPh_3)_2(Cl)(H)(Bcat)$]. This value greatly exceeds the 35 kcal/mol bond energy for the iridium–methyl bond in *trans*-[$Ir(CO)(PPh_3)_2(Cl)(Me)(I)$].

$$\textit{trans}\text{-}[Ir(CO)(PPh_3)_2Cl]_{(soln)} + H{-}BO_2C_6H_{4(soln)} \rightarrow (PPh_3)_2Ir(CO)(Cl)(H)(BO_2C_6H_4)_{(soln)} \quad (1)$$
$$\Delta H = -15.1 \pm 0.4 \text{ kcal/mol}$$

The determination of an iridium–boron bond strength allows analysis of the various steps in transition metal catalyzed hydroboration (Table 2). Alkene insertion into the iridium hydride is slightly less favorable thermodynamically than alkene insertion into the iridium–boron bond, and the entropic term may give both processes a small, positive ΔG. The similarity in the two ΔH terms is consistent with the apparent competition between the two insertion processes[33-36] and implies that kinetic factors will dominate the selectivity between these two catalytic pathways. Importantly, boron–carbon reductive elimination of the hydroborated product after alkene insertion into the hydride is clearly exothermic. The B–C bond in methylcatecholborane is worth 113 kcal/mol and is similar to the B–H bond in catecholborane. However, the much lower Ir–C BDE relative to the Ir–H BDE makes reductive elimination rather than oxidative addition favorable enthalpically.

It has been demonstrated previously that covalent transition metal–ligand bonds correlate linearly with H–X bond strengths in the absence of strong π-effects.[37] The Ir–CH_3, Ir–H, and Ir–Bcat bond dissociation energies in Vaska-type complexes relative to H–X bond dissociation energies show a similar trend, indicating that π-interactions need not be invoked to explain the large metal–boron BDE. π-Bonding in iron and tungsten complexes has been noted by one of us recently,[8,38] although low rotational barriers indicated that the energy of this π-bond in catechol-substituted boryl systems is small.

In conclusion, we have quantitated individual borane bond dissociation energies and demonstrated the importance of employing BDEs from a single B–H bond when considering catalysis with boranes. Accurate borane BDEs allowed the first information on transition metal–boron bond strengths, and the value for the iridium–catecholboryl linkage was found to exceed those of either the corresponding alkyls or hydrides. Interestingly, the B–H oxidative addition reaction cleaves a bond that is stronger than that in methane. It is the strength of the iridium–boron bond that provides the necessary driving force for this reaction.

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Supplementary Material Available: G-2 and CBS-4 energies of borane fragments, details of the G-2 and CBS-4 calculations, and determination of ΔH for reaction 1 (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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