Accelerated Ligand Metalation in a β-Diketiminato Scandium Dimethyl Complex Activated with Bis(pentafluorophenyl)borane

Korey D. Conroy, Paul G. Hayes,‡ Warren E. Piers,* and Masood Parvez

Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, Alberta, T2N 1N4, Canada

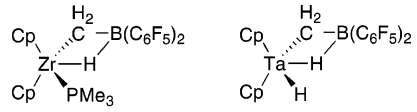
Received May 3, 2007

Equimolar reactions of $LScMe_2$ (L = (Ar)NC(*t*Bu)CHC(*t*Bu)N(Ar); Ar = 2,6-*i*Pr_2-C_6H_3) and $HB(C_6F_5)_2$ proceed through an isolable ion pair **2** to a metalated scandium borate **3** with loss of methane. Multinuclear NMR experiments confirm the proposed structure, which was also verified by synthesis via alternative routes and derivatization. Deuterium labeling studies offer insight into the mechanism of methane loss, which occurs through C−H activation of an abstracted methide rather than the direct intramolecular metalation commonly observed for β-diketiminato scandium alkyl complexes. A large primary kinetic isotope effect of $k_H/k_D = 8.7(6)$ was observed for the decomposition of **2**, which corroborates the proposed mechanism while also implicating a highly reactive four-membered scandocycle intermediate, $LSc((H)CH_2B(C_6F_5)_2)$. Reaction of 2 equiv of $HB(C_6F_5)_2$ with $LScR_2$ yields μ_2-hydridoborate complexes $[LScCH_3][(\mu\text{-}H)_2B(C_6F_5)_2]$ (**5**), while 4 equiv of borane react to afford the bis-μ_2-hydridoborate complex $[LSc][(\mu\text{-}H)_2B(C_6F_5)_2]_2$, **6**.

Introduction

The established reactivity of electrophilic boranes[1] as co-catalyst activators for early metal organometallic compounds is dominated by abstraction, yielding cationic species that exhibit enhanced catalytic activity toward olefinic substrates as demonstrated by olefin polymerization[2] and hydroamination.[3] Typically, perfluoroaryl boranes such as $B(C_6F_5)_3$ are employed, due to their high Lewis acidity and the weakly coordinating nature of the resultant anions. On the other hand, use of the bis-pentafluorophenyl borane, $HB(C_6F_5)_2$,[4] gives ion pairs that are less chemically innocent due to the presence of a reactive H−B function and the tighter ion-pairing allowed due to the lower steric bulk of the anion. For example, treatment of Cp_2ZrR_2 (R = CH_3, CH_2Ph, and CH_2SiMe_3) with various equivalencies of $HB(C_6F_5)_2$ can lead to loss of RH[5] and formation of a reactive four-membered metallocycle, which can be stabilized by PMe_3 (**I**, Chart 1). Analogous chemistry with dialkyl titanocenes resulted in redox processes and generation of Ti(III) complexes.[6] Schrock's methyl methylidene tantalocene complex, $Cp_2Ta(=CH_2)CH_3$,[7] reacts with $HB(C_6F_5)_2$ to form another d^0 borane-stabilized methylidene complex (**II**, Chart 1).[8]

Chart 1



I II

The organometallic chemistry of the group 3 metals, while advancing rapidly,[9] is still devoid of well-characterized examples of metal-to-element multiple-bonded compounds.[10] Given the rich chemistry observed when $HB(C_6F_5)_2$ was reacted with group 4 and 5 systems bearing two reactive hydrocarbyl units, and particularly the potential to generate masked alkylidenes, we have conducted a study of the reactivity of $HB(C_6F_5)_2$ with the well-defined dimethyl scandium complex [(ArNC(*t*Bu)CHC(*t*Bu)NAr)]$Sc(CH_3)_2$ (Ar = 2,6-*i*Pr_2-C_6H_3), **1**,[11] in the hopes that a masked scandium methylidene species might be generated. While mechanistic studies implicate such a species, it is highly

* To whom correspondence may be addressed. Tel: 403-220-5746. E-mail: wpiers@ucalgary.ca.

‡ Current address: Department of Chemistry and Biochemistry, University of Lethbridge, E866 University Hall, Lethbridge, Alberta, T1K 3M4, Canada.

(1) Piers, W. E. *Adv. Organomet. Chem.* **2005**, *52*, 1−77.

(2) (a) Chen, E.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391−1434. (b) Hou, Z.; Luo, Y.; Li, X. *J. Organomet. Chem.* **2006**, *691*, 3114−3121. (c) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255−270. (d) Arndt, S.; Okuda, J. *Adv. Synth. Catal.* **2005**, *347*, 339−354. (e) Hou, Z.; Wakatsuki, Y. *Coord. Chem. Rev.* **2002**, *231*, 1−22. (f) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325−87. (g) Bochmann, M. *J. Organomet. Chem.* **2004**, *689*, 3982−3998. (h) Kretschmer, W. P.; Meetsma, A.; Hessen, B.; Schmalz, T.; Qayyum, S.; Kempe, R. *Chem.−Eur. J.* **2006**, *12*, 8969−8978.

(3) (a) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675−703. (b) Beller, M.; Seayad, J.; Tillack, A.; Jiao, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 3368−3398. (c) Hultzsch, K. C. *Adv. Synth. Catal.* **2005**, *347*, 367−391. (d) Bambirra, S.; Tsurugi, H.; van Leusen, D.; Hessen, B. *Dalton Trans.* **2006**, 1157−1161.

(4) (a) Parks, D. J.; Spence, R. E. v H.; Piers, W. E. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 809−811. (b) Parks, D. J.; Piers, W. E.; Yap, G. P. A; *Organometallics* **1998**, *17*, 5492−5503. (c) In benzene solution, bis-pentafluorophenyl borane exhibits a dimer/monomer equilibrium. Since it reacts via the monomer, we write its formula this way throughout the present article.

(5) (a) Spence, R. E. v. H.; Parks, D. J.; Piers, W. E.; MacDonald, M. A.; Zaworotko, M. J.; Rettig, S. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1230−1233. (b) Spence, R. E. v. H.; Piers, W. E. *Organometallics* **1995**, *14*, 4617−4624. (c) Spence, R. E. v. H.; Piers, W. E.; Sun, Y.; Parvez, M.; MacGillivray, L. R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 2459−2469.

(6) Chase, P. A.; Piers, W. E.; Parvez, M. *Organometallics* **2000**, *19*, 2040−2042.

(7) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389−2399.

(8) Cook, K. S.; Piers, W. E.; Rettig, S. J. *Organometallics* **1999**, *18*, 1575−1577.

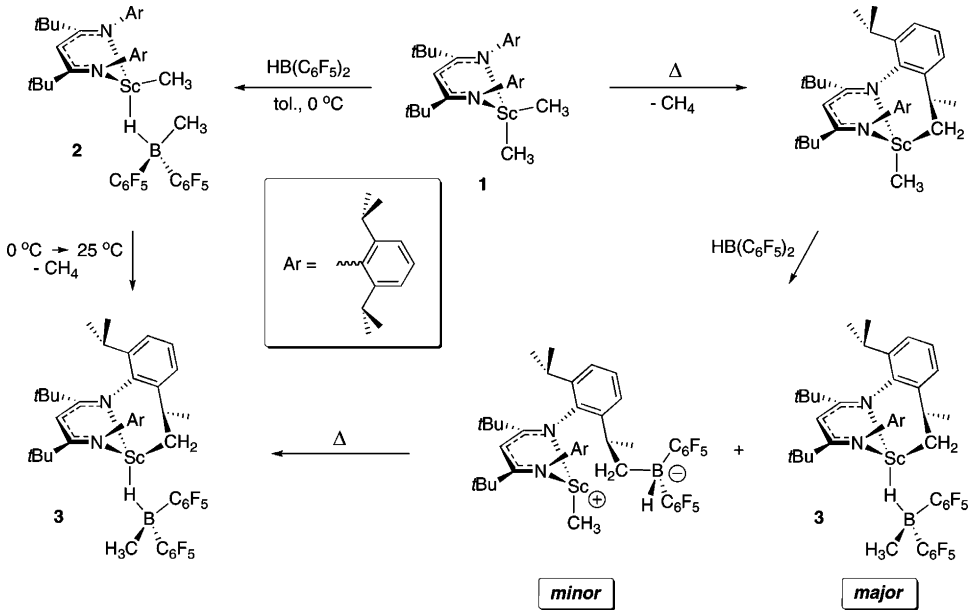
(9) (a) Skinner, M. E. G.; Tyrrell, B. R.; Ward, B. D.; Mountford, P. *J. Organomet. Chem.* **2002**, *647*, 145−150. (b) Zeimentz, P. M.; Arndt, S.; Elvidge, B. R.; Okuda, J. *Chem. Rev.* **2006**, *106*, 2404−2433. (c) Mountford, P.; Ward, B. D. *Chem. Commun.* **2003**, 1797−1803. (d) Emslie, D. J.; Piers, W. E. *Coord. Chem. Rev.* **2002**, *233−34*, 129−155.

(10) Giesbrecht, G. R.; Gordon, J. C. *Dalton Trans.* **2004**, 2387−2393.

(11) Hayes, P. G.; Piers, W. E.; Lee, L. W. M.; Knight, L. K.; Parvez, M.; Elsegood, M. R. J.; Clegg, W. *Organometallics* **2001**, *20*, 2533−2544.

10.1021/om700435v CCC: $37.00
Publication on Web 07/25/2007

Scheme 1



reactive and rapidly activates a C−H bond in an N-aryl isopropyl group of the ligand framework.

Results and Discussion

Equimolar Reactions of $LScMe_2$ with $HB(C_6F_5)_2$. The *β*-diketiminato scandium dimethyl complex **1** is prepared according to literature procedures[11] by salt metathesis of $LScCl_2$ with excess $LiCH_3$ in toluene. Monitoring the reaction of **1** with an equimolar amount of $HB(C_6F_5)_2$ in d_8-toluene at 0 °C by ^1H NMR spectroscopy reveals the formation of a C_2-symmetric product, **2**, corresponding to the ion pair resulting from methide abstraction from **1** by the highly Lewis acidic borane, and no observable byproducts (Scheme 1). Complex **2** is stable for a number of hours at 0 °C; however, raising the solution temperature to 25 °C facilitates the clean conversion of **2** to a new C_s symmetric product, assigned as **3** (*vide infra*), with observed loss of methane (0.16 ppm) over a period of 1 h.

X-ray quality crystals of ion pair **2** were obtained from concentrated hexane solutions at −35 °C, and the structure is shown in Figure 1. The structure of **2** depicts a six-coordinate distorted octahedral scandium center with two *ortho* fluorine contacts from the C_6F_5 groups at 2.340(2) and 2.351(2) Å, which correlate with previous examples of d^0 group 3 metals with structurally characterized *ortho*-fluorine contacts such as 2.390(4) Å for $[(ArNC(tBu)CHC(tBu)NAr)ScCH_3][CH_3B(C_6F_5)_3]$[12] and 2.366(3) Å for $[Cp_2Y][MeB(C_6F_5)_3]$.[13] The scandium lies out of the plane of the ligand by over 1.1 Å, which is a general feature of scandium *β*-diketiminato complexes,[11] and the degree of this out-of-plane bonding provides qualitative insight into the degree of steric congestion at scandium. As expected, the sterically more demanding substituent occupies the less congested *exo* position, allowing for further electronic stabilization through Sc−F interactions, while the scandium methyl occupies the more crowded *endo* site. Previous examples[11] of methide abstraction from **1** by $B(C_6F_5)_3$ reveal contact ion pairs via coordination of the abstracted methyl group at scandium as well as by an *ortho*-fluorine. In the less sterically encumbered **2**, the greater donating ability of the fluorine lone pairs and the strongly donating hydride effectively exclude any contact between scandium and the C−H bonds of the abstracted methide. The scandium hydride distance is quite elongated at 2.08(2) Å, implying that the hydride is covalently bound to boron (cf. B−H1 = 1.24 Å) and donating *σ*-electron density to scandium.

It is evident that the strong ion pairing persists in solution, as treatment of **2** with PMe_3 at 0 °C, followed by warming to room temperature, proceeds smoothly to **3** and uncoordinated phosphine exclusively, with no appreciable change in reaction rate. Apparently, the alkylhydridoborate binds strongly enough

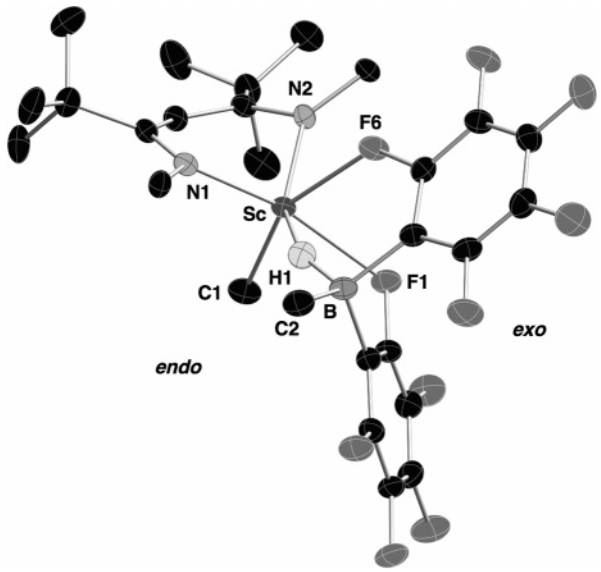


Figure 1. Thermal ellipsoid diagram of **2**. Ligand aromatic carbons and all hydrogen atoms except H1 are removed for clarity. Selected bond distances (Å): Sc−N1, 2.151(2); Sc−N2, 2.060(2); Sc−C1, 2.193(3); Sc−F1, 2.351(2); Sc−F6, 2.340(2); Sc−H1, 2.08(2). Distance of Sc from N1−C4−C5−C6−N2 mean plane (Å): 1.13(2). Selected bond angles (deg): N1−Sc−N2, 94.28(8); N1−Sc−C1, 103.63(10); N2−Sc−B1, 107.30(9); C1−Sc−F1, 153.36(9); C1−Sc−F6, 79.99(9); N1−Sc−H1, 86.7(7); N2−Sc−H1, 143.4(6).

(12) Hayes, P. G.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 2132−2133.

(13) Song, X. J.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **1998**, *17*, 1004−1006.

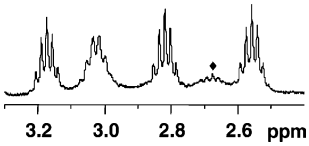


Figure 2. 300 MHz NMR spectrum of the methyne region of **3** at room temperature in d_8-toluene. The broad multiplet (◆) at ~2.68 ppm is part of the quartet ($^1J_{H-B}$ = 68 Hz) for the hydridoborate ($CH_3(H)B(C_6F_5)_2$).

to preclude association by phosphine even when a large excess of PMe_3 is employed.

While **2** exhibits C_2 symmetry in solution, the NMR features of **3** are decidedly more complex. Compound **3** is formed as a kinetic mixture of two isomers in a ratio of 85:15 (determined from integrating the β-diketiminato backbone proton of the two species), possibly representing the *exo* and *endo* cyclometalated positions.[11,14] Heating the mixture at 50 °C for 1 h converts the minor isomer to the major isomer quantitatively, which is stable for hours at temperatures > 80 °C. The ^{1}H NMR spectrum of the major isomer of **3** exhibits four distinct resonances: three septets and one multiplet for the four methyne C−H's from the isopropyl groups (Figure 2). Furthermore, there are two singlets corresponding to the *tert*-butyl groups and an additional broad resonance upfield of 0 ppm, which integrates as three hydrogens. Although the observed loss of CH_4 is reminiscent of the reaction of $HB(C_6F_5)_2$ with Cp_2ZrMe_2 to produce **I**,[5c] the scandocyclic analogue would be expected to exhibit more symmetric structural features. We thus assign **3** as the metalated species shown. The asymmetry of **3**, formally chiral at scandium, is also borne out in the ^{19}F NMR spectrum as two diastereotopic C_6F_5 groups are observed. The ^{11}B{^{1}H} NMR spectrum reveals a sharp singlet in the borate region at −20.6 ppm, which splits into a doublet ($^1J_{B-H}$ = 68 Hz) in the ^{1}H-coupled experiment.

Two-dimensional NMR experiments were also performed, with the most informative data emanating from a ^{1}H−^{11}B HMQC experiment; two distinct B−H cross-peaks are observed corresponding to the borohydride at 2.95 ppm and a broad upfield resonance at −0.13 ppm. In the section of the ^{1}H NMR spectrum shown in Figure 2, one of the quartets of borohydride multiplets is evident at 2.68 ppm, the rest being buried under the isopropyl methyne resonances. The ^{13}C DEPT-135 spectrum exhibits one inverted CH_2 group at 33 ppm, and the ^{1}H−^{1}H COSY has no off-diagonal peaks associated with the broad singlet at −0.13 ppm. Unfortunately, all attempts to obtain X-ray quality crystals by exhaustive manipulation of solvent systems and experimental conditions were unsuccessful, and so the structural assignment of the major isomer of **3** as depicted in Scheme 1 is not absolutely proven.

The identity of **3** was further confirmed by its independent preparation; reaction of the metalated derivative of **1**[11] with $HB(C_6F_5)_2$ (Scheme 1) provides a mixture of two products, the major one of which was clearly identified as **3**. The minor component was assigned to the product resulting from abstraction of the metalated isopropyl methylene unit. Heating this mixture in d_8-toluene leads to quantitative conversion to the thermodynamic product **3**. Furthermore, **3** was derivatized through reaction with the anilinium salt $[PhN(H)Me_2][B(C_6F_5)_4]$ in d_8-toluene, affording a C_{2v}-symmetric scandium cation, **4**, with no evidence for $PhNMe_2$ coordination (Scheme 2). The ^{1}H NMR spectrum of **4** shows only one isopropyl methyne septet, one singlet for the *tert*-butyl groups, and two doublets

Scheme 2

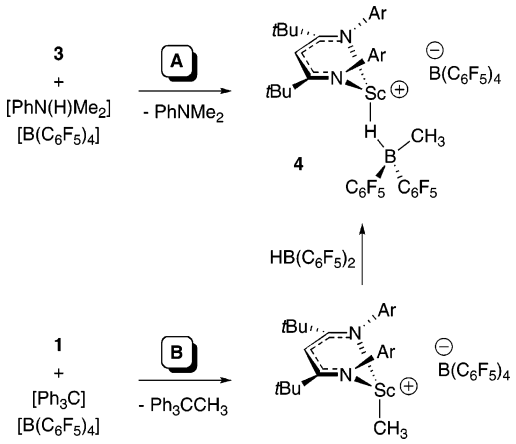


Table 1. k_{obsd} and Half-Lives for Methane Loss

compd	T (°C)	k_{obsd} (s^{-1})	$t_{1/2}$ (h)
1	65	3.59×10^{-4}	0.53
2	9.6	4.83×10^{-5}	4.28
2	21	1.64×10^{-4}	1.27
2	29	4.16×10^{-4}	0.53
2	43	1.67×10^{-3}	0.15
***d*$_6$-2**	29	4.76×10^{-5}	4.23
III	35	9.77×10^{-5}	1.32

for the isopropyl methyl substituents. One additional broad singlet at 1.02 ppm is assigned to the borate methyl group. The ^{1}H spectral features of **4** are analogous to the previously reported $[LSc][CH_3B(C_6F_5)_3]_2$.[11]

The ^{19}F NMR spectrum exhibits two distinct borate groups present in a 1:2 ratio. The tetrakis-pentafluorophenyl borate has sharp multiplets, whereas the methylhydridoborate anion exhibits broad unresolved signals presumably due to hindered rotation induced by strong *ortho*-fluorine contacts at scandium. Reaction of **1** with $[Ph_3C][B(C_6F_5)_4]$ forms the previously reported scandium monocation, which, when treated with $HB(C_6F_5)_2$, also affords **4** (Scheme 2). Samples of **4** prepared by either route depicted in Scheme 2 are spectroscopically identical with the exception of residual triphenylethane present in samples prepared by route B.[15]

Mechanistic Studies. Qualitatively, the rate of conversion of **2** to **3** is significantly faster than methane-releasing metalative process in closely related systems. For example, neutral complex **1** undergoes ligand metalation with a half-life of 0.5 h at 65 °C,[11] while cationic $[LScMe][MeB(C_6F_5)_3]$ exhibits a half-life for methane release of 1.83 h at 35 °C.[16] This suggests that a direct ligand metalation mechanism may not be occurring in the conversion of **2** to **3**, so the reaction was examined in more detail via a series of kinetic experiments in which the process was followed by ^{1}H NMR spectroscopy. Monitoring *in situ* prepared solutions of **2** in d_6-benzene at 29 °C shows clean first-order conversion with a rate of 4.16×10^{-4} s^{-1} and a half-life of 0.5 h (Table 1) by integrating the baseline-resolved ligand backbone signals. The conversion of **2** to **3** was monitored at a variety of temperatures (10−43 °C), and an Eyring plot (Figure 3) was constructed, affording activation parameters ($\Delta S^{\ddagger}$ = −13(2) eu; $\Delta H^{\ddagger}$ = 18.3(6) kcal mol^{-1}; $\Delta G^{\ddagger}$ = 22.2 kcal mol^{-1}). Cyclometalation in a related scandium borate,[17] **III**, exhibits a

(14) Knight, L. K.; Piers, W. E.; Fleurat-Lessard, P.; Parvez, M.; McDonald, R. *Organometallics* **2004**, *23*, 2087−2094.

(15) Dicationic organoscandium derivatives: Ward, B. D.; Bellemin-Laponnaz, S.; Gade, L. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 1668−1671.

(16) Hayes, P. G.; Piers, W. E.; Parvez, M. *Organometallics* **2005**, *24*, 1173−1183.

(17) Hayes, P. G. Ph.D. Thesis, University of Calgary, 2004.

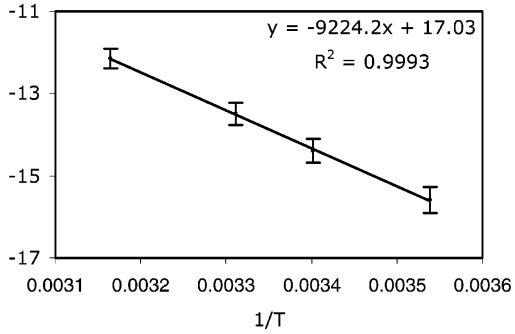


Figure 3. Eyring plot for the thermal decomposition of **2**. Activation parameters obtained: $\Delta S^{\ddagger} = -13(2)$ eu; $\Delta H^{\ddagger} = 18.3(6)$ kcal mol^{-1}; $\Delta G^{\ddagger} = 22.2$ kcal mol^{-1}.

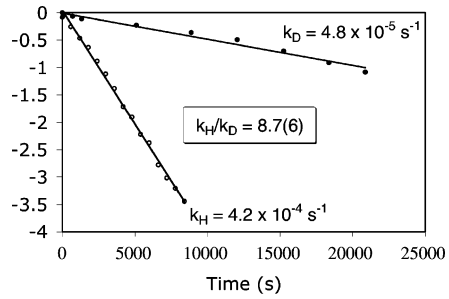
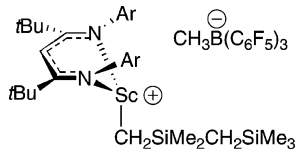


Figure 4. Typical first-order plots for the thermal decomposition of **2** and ***d*$_6$-2** at 29 °C and 0.0347 M.

slightly higher enthalpy of activation (i.e., 21.5(2) kcal mol^{-1}), while the entropies of activation observed for these two systems are slightly different (i.e., −7.0(7) eu versus −13(2) eu for **2**), with the more negative value for **2** implying a somewhat more ordered transition state. Both sets of data are consistent with a σ-bond metathesis transformation involving C−H cleavage/formation processes. However, deuterium labeling experiments suggest that the mechanism of methane loss in **2** does not involve direct metalation of the Sc−C bond with an isopropyl C−H bond. Deuterium labeled ***d*$_6$-1** was prepared in an

Chart 2



III

analogous fashion to **1** with the exception that $LiCD_3 \cdot LiI$ was used in place of $LiCH_3$. The ^{1}H NMR spectrum of **1** and ***d*$_6$-1** in d_8-toluene are identical notwithstanding the absence of the scandium methyl peak at 0.00 ppm in ***d*$_6$-1**, which is present in the ^{2}H NMR spectrum taken in C_7H_8. Qualitatively, it is immediately apparent that reaction of ***d*$_6$-1** with $HB(C_6F_5)_2$, affording ***d*$_n$-3**, is much slower than in the unlabeled system; under the same conditions where **3** is produced quantitatively (i.e., 80 min at room temperature), ***d*$_6$-2** underwent <10% conversion to ***d*$_2$-3**. However, heating a sample of ***d*$_6$-2** in d_6-benzene at 47 °C for ∼30 min resulted in clean, complete conversion to ***d*$_2$-3**. Quantitatively, a primary kinetic isotope effect of 8.7(6) (Figure 4) was observed when the two reactions were followed side by side.

This large k_H/k_D value is not typical of "normal" σ-bond metathesis processes,[18] but is similar to the value of 9.1(6) observed in another system where the C−H bond partnering in the methane-eliminating σ-bond metathetical event was found within a methyl borate group.[19] In that instance, the large magnitude of the KIE was rationalized on the basis of it being a composite of both primary and secondary isotope effects. Whatever the explanation, the large k_H/k_D observed here is indicative of methane loss via cleavage of a borate methyl C−H/D bond, as depicted in Scheme 3. This intimate mechanism of methane loss is supported by monitoring the deuterium incorporation into the evolved methane and complex **3** isotopomers. Starting from ***d*$_6$-2**, a direct ligand metalation (path A) would yield CHD_3 and have no proton resonance for the resultant methyl group on the borate (i.e., ***d*$_3$-3** would be the expected product). In contrast, cleavage of one of the C−D bonds of the abstracted borate methyl with the remaining methyl group on scandium to produce methane should extrude CD_4 exclusively (path B). Rapid cyclometalation of the resultant four-membered scandocycle to form ***d*$_2$-3** would thus exhibit a proton resonance that integrates as 1H for the borate methyl group. The aforementioned primary kinetic isotope effect is suggestive that path B is operative, as no C−D bonds are broken in path A.

To ensure reproducibility, a number of experiments monitoring the decomposition of ***d*$_6$-2** each provided clear evidence that path B is dominant at room temperature, although because of the large isotope effect on path B, path A is detectably competitive via the observation of CD_3H.[20] Nonetheless integration of the methane and borate methyl resonances in the ^{1}H NMR spectrum (employing a 15 s relaxation delay to allow for complete relaxation of the methane protons) gives a ***d*$_2$-2**:CD_3H ratio of 91:9, mirroring the relative rates of path B versus path A in this system. Taking into account the k_H/k_D, in the all-proteo system, path B dominates by about 2 to 3 orders of magnitude.

While the scandocycle **IV** is not observed directly, its presence, as implied by the spectroscopic evidence supporting path B, is interesting. The fact that no appreciable amount of **IV** accumulates during the course of the reaction implies that, even though it is masked as a borane adduct, the "Sc=CH_2" moiety is a very reactive species. Installation of a more metalation-resistant ancillary may permit isolation of this borane-ligated scandium alkylidene function.

Synthesis of $LScR_n[(\mu\text{-}H)_2B(C_6F_5)_2]_{2-n}$ ($n = 0, 1$). Reactions of **1** with greater than 1 equiv of $HB(C_6F_5)_2$ were also investigated. Complex **1** reacts cleanly with 2 equiv of $HB(C_6F_5)_2$ in THF to yield the well-defined $(\mu\text{-}H)_2B(C_6F_5)_2$ product **5** (Scheme 4) in moderate yields, as well as $CH_3B(C_6F_5)_2$.[21] When four or more equivalents of $HB(C_6F_5)_2$ are allowed to react with **1**, both methyl groups are exchanged for dihydridoborate ligands and the bis-$[(\mu\text{-}H)_2B(C_6F_5)_2]$ product, **6**, is obtained. Compound **6** can also be prepared through addition of two further equivalents of $HB(C_6F_5)_2$ to **5**, with loss of another $CH_3B(C_6F_5)_2$ molecule.

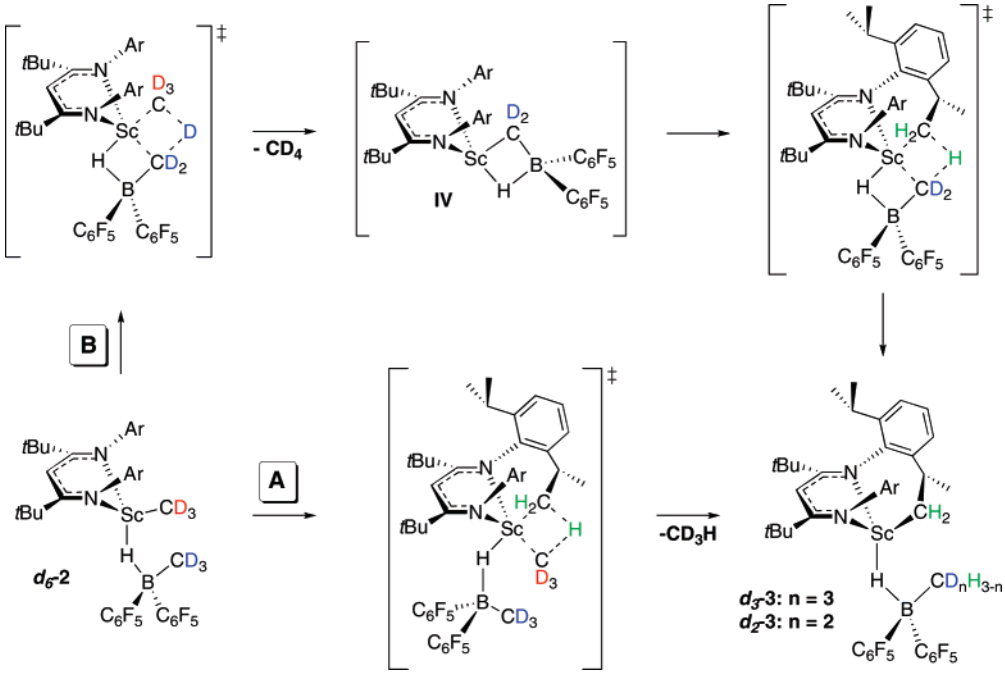
(18) Thompson. M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203−219.

(19) Zhang, S.; Piers, W. E.; Gao, X.; Parvez, M. *J. Am. Chem. Soc.* **2000**, *122*, 5499−5509.

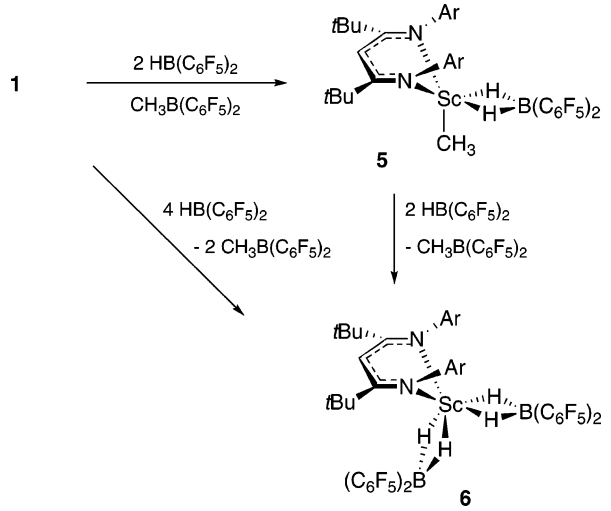
(20) (a) We observe no incorporation of D into the N-aryl isopropyl groups,[20b,c] so it is unlikely that the observed CD_3H arises due to some other deuterium scrambling process. (b) Fekl, U.; Goldberg, K. I. *J. Am. Chem. Soc.* **2002**, *124*, 6804−6805. (c) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 15286−15287.

(21) Dagorne, S.; Guzei, I. A.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 274−289.

Scheme 3



Scheme 4



Only one diastereomer of **5** is observed in solution, as determined by variable-temperature NMR spectroscopy. Presumably, the bulky hydridoborate group occupies the less sterically hindered *exo* position in compound **5**. The $^{11}B\{^1H\}$ NMR spectrum exhibits a single sharp, upfield resonance at all temperatures measured, which becomes a triplet ($^1J_{H-B} = 69$ Hz) in the ^1H-coupled experiment. The ^1H NMR indicates a ligand resonance pattern consistent with the presence of two chemically distinct nonancillary ligands. In the case of product **6**, where two diastereotopic [$(\mu$-H)$_2$B(C$_6$F$_5$)$_2$] ligands are present, two resonances in the room-temperature $^{11}B\{^1H\}$ NMR spectrum indicate that exchange of these moieties is slow on the NMR time scale. The static nature of the structure is also manifested in the ^1H NMR spectrum, where the pattern observed for the isopropyl resonances demonstrates the reduction in symmetry expected for the slow exchange regime.

Crystals of **6** suitable for X-ray diffraction analysis were grown from cold hexanes, and a CrystalMaker depiction of the structure is shown in Figure 5, along with selected metrical parameters. In addition to the four Sc−H and two Sc−N contacts, there is also a donation from F5 of the *exo* [H$_2$B(C$_6$F$_5$)$_2$] substituent to scandium at 2.370(5) Å (*vide supra*). This fluoride serves to cap one of the faces of the tetrahedron formed by the two β-diketiminato nitrogen atoms and the two hydridoborate ligands. This close contact in the *exo* site is consistent with this position being more sterically accessible than the *endo* position, where no close Sc−F interactions are observed. Again, this contact is observed exclusively in the solid state; low-temperature NMR studies at −90 °C do not exhibit coalescence of the C$_6$F$_5$ groups in the ^{19}F NMR time-averaged spectrum. The scandium center lies 1.3 Å out of the plane of

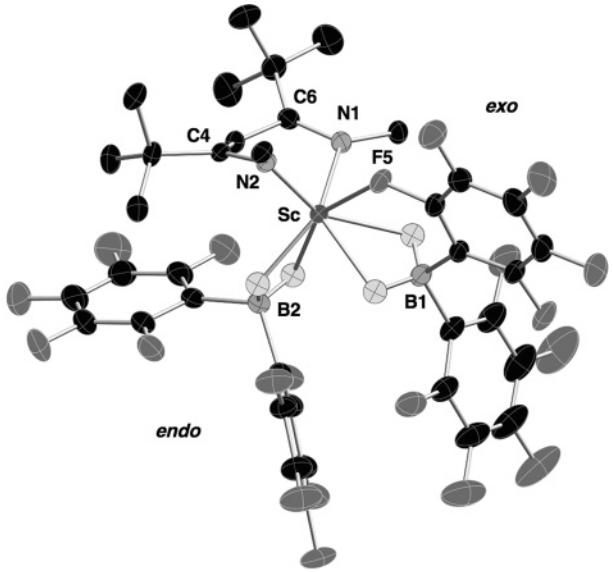


Figure 5. Thermal ellipsoid diagram of **6**. Ligand aromatic groups and all hydrogen atoms except those associated with boron are removed for clarity. Selected bond lengths (Å): Sc−N1, 2.052(2); Sc−N2, 2.148(2); Sc−F5, 2.370(5); Sc−C4, 2.591(2); Sc−C5, 2.630(2); Sc−C6, 2.764(2). Distance of Sc from N1−C4−C5−C6−N2 mean plane (Å): 1.309(2). Selected bond angles (deg): N1−Sc−N2, 96.18(6); N1−Sc−B1, 135.85(6); N1−Sc−B2, 112.48(6); N2−Sc−B1, 103.73(6); N2−Sc−B2, 114.39(6); Sc−N1−C4, 96.58(11); Sc−N2−C6, 103.54(12).

the ligand, which is 0.2 Å further than that observed for **2** and is consistent with the greater steric congestion at the metal center in **6**. Metrical parameters associated with the *β*-diketiminato ligand are unremarkable.

Three of the four bridging hydrides were located in the electron density map and exhibit Sc−H distances ranging from 2.063(1) to 2.202(1) Å. Previously reported Sc−H distances in scandium borohydride species of 2.17−2.19 Å for $[Li(THF)_2][Cp^*(C_2B_9H_{11})ScH]_2$[22] and 2.03 Å for $(C_5H_3(SiMe_3)_2)_2Sc(BH_4)$[23] suggest that the hydrides in **3** are tightly bound to the borate centers and the scandium center is best depicted as a bis-hydridoborate-stabilized dication. Attempts to remove an $HB(C_6F_5)_2$ unit by treating with a Lewis base[24] were unsuccessful.

In reactions of Cp_2ZrR_2 with multiple equivalents of $HB(C_6F_5)_2$ we invoked a stepwise path involving $Cp_2Zr(H)R$ intermediates that add a second equivalent of $HB(C_6F_5)_2$ to give the observed $Cp_2Zr[(\mu\text{-}H)_2B(C_6F_5)_2]R$ products. This is unlikely to be the case in these scandium *β*-diketiminato systems, since all attempts to generate hydrido complexes supported by this ligand system have led to ligand fragmentation processes initiated by hydride transfer to an imino carbon.[14] It thus seems likely that the path by which compound **5** forms involves interaction of the second borane equivalent with **2** directly, possibly by hydride abstraction from the $[(H)CH_3B(C_6F_5)_2]$ anion. An analogous sequence from **5** delivers compound **6**.

Experimental Section

General Procedures. All manipulations were performed either in an Innovative Technologies System One inert atmosphere glovebox or on greaseless vacuum lines equipped with Teflon needle valves (Kontes) using swivel-frit-type glassware. Toluene, THF, and hexanes were dried and purified using the Grubbs/Dow purification system[25] and stored in evacuated bombs. Bromobenzene and d_5-bromobenzene were predried over CaH_2, and hexamethyldisiloxane, d_8-THF, d_6-benzene, and d_8-toluene were dried and stored over sodium/benzophenone. All were distilled prior to use.

The following reagents were synthesized using literature protocols: $LSc(CH_3)_2$ **1**,[11] $HB(C_6F_5)_2$, and $DB(C_6F_5)_2$.[4a] $[PhN(H)Me_2][B(C_6F_5)_4]$ and $[Ph_3C][B(C_6F_5)_4]$ were received as generous gifts from NOVA Chemicals Ltd. All other materials were obtained from Aldrich and either used as received or dried and distilled prior to use.

Samples were analyzed by NMR spectroscopy on Bruker AMX-300 and DRX-400 spectrometers at room temperature unless otherwise specified. ^1H and ^{13}C were referenced to $Si(CH_3)_4$ through the residual peaks of the employed solvent, ^2H spectra to external $Si(CD_3)_4$ at 0.0 ppm, ^{11}B spectra to external $BF_3{\cdot}OEt_2$ at 0.0 ppm, and ^{19}F spectra to $CFCl_3$ using an external standard of hexafluorobenzene (δ −163.0 ppm) in C_6D_6. NMR data are provided in ppm; ^{13}C resonances for the C_6F_5 groups are not reported. The coupling constants (i.e., $^3J_{H-H}$) for the isopropyl groups on the ligand range between 6.4 and 7.2 Hz and, thus, are not reported in the NMR analysis of the compounds. Elemental analyses were performed by Mrs. Roxanna Smith and Mrs. Dorothy Fox in the microanalytical laboratory at the University of Calgary. X-ray data were collected on a Bruker P4/RA/SMART 1000 CCD diffractometer using Mo Kα radiation at −100 °C.

Synthesis of $LSc(CD_3)_2$, d_6-1. This compound was prepared in an identical fashion to that previously described for **1** with the exception that $LiCD_3{\cdot}LiI$ was used in place of $LiCH_3$.[1] The ^1H spectrum matched **1**, except no resonances were observed for the scandium methyl groups, which resonate at the same position in the ^2H NMR spectrum. ^2H NMR (C_7H_8): δ (s, 0.00).

Synthesis of $[LScCD_3][CD_3(H)B(C_6F_5)_2]$, d_6-2. A 50 mL flask charged with d_6-**1** (0.15 g, 0.26 mmol) and $HB(C_6F_5)_2$ (0.088 g, 0.26 mmol) was attached to a swivel frit apparatus. The entire assemblage was evacuated, and toluene (25 mL) was vacuum distilled into the flask. After warming to room temperature, the reaction was allowed to stir at room temperature for 20 min, whereupon an orange solution was obtained. Toluene was removed *in vacuo*, and hexamethyldisiloxane (15 mL) was added. The mixture was sonicated (15 min), cooled to − 35 °C (30 min), and filtered. The solvent was removed to give a yellow powder, which was recrystallized from hexanes (0.16 g, 0.17 mmol, 65%). ^1H NMR (C_7D_8): δ 6.91−6.77 (ov m, 6H; C_6H_3), 6.20 (s, 1H; C*H*), 3.40 (sp, 2H; C*H*Me_2), 2.97 (q, 1H; $ScCD_3(H)B(C_6F_5)_2$, $^1J_{H-B}$ = 69 Hz), 2.55 (sp, 2H; C*H*Me_2), 1.22 (d, 6H; CH*Me*$_2$), 1.15 (d, 6H; CH*Me*$_2$), 1.09−1.01 (ov m, 30H; CH*Me*$_2$, NCC*Me*$_3$). $^{13}C\{^1H\}$ NMR (C_7D_8): δ 176.4 (N*C*CMe$_3$), 149.4 (C_{ipso}), 142.5, 141.8, 141.1, 137.5 (*C*$_6$H$_3$), 96.2 (*C*H), 45.1 (*C*Me$_3$), 32.1 (C*Me*$_3$), 31.3, 30.8 (*C*HMe$_2$), 29.3, 28.4, 26.4, 25.0 (CH*Me*$_2$), 24.0 (Sc*C*D$_3$) (*C*D$_3$(H)B(C$_6$F$_5$)$_2$ not observed). ^{19}F NMR (C_7D_8): δ −131.0, (*o*-F), −158.3, (*p*-F), −162.6, (*m*-F). ^{11}B NMR (C_7D_8): δ −17.2 (d, 1B; $^1J_{H-B}$ = 69 Hz).

Synthesis of $[\kappa^3\text{-}LSc][CH_3(H)B(C_6F_5)_2]$, 3. A 50 mL flask charged with **1** (0.350 g, 0.608 mmol) and $HB(C_6F_5)_2$ (0.210 g, 0.608 mmol) was attached to a swivel frit apparatus. The entire assemblage was evacuated, and toluene (25 mL) was vacuum distilled into the flask. After warming to room temperature, the reaction was allowed to stir at room temperature for 80 min, whereupon a dark orange solution was obtained. Toluene was removed *in vacuo*, and hexamethyldisiloxane (15 mL) was added. The mixture was sonicated (15 min) and cooled to −35 °C (30 min), and the solid yellow product was removed by filtration. The product was recrystallized from hexanes (0.374 g, 0.413 mmol, 68%). ^1H NMR (C_6D_6): δ 7.11−6.64 (ov m, 6H; C_6H_3), 5.75 (s, 1H; C*H*), 3.19 (sp, 1H; C*H*Me_2), 3.09 (m, 1H; CH_2CHMe), 2.95 (q, 1H; $ScCH_3(H)B(C_6F_5)_2$, $^1J_{H-B}$ = 68 Hz), 2.82 (sp, 1H; C*H*Me_2), 2.55 (sp, 1H; C*H*Me_2), 1.45 (d, 3H; CH*Me*$_2$), 1.33 (d, 3H; CH*Me*$_2$), 1.13 (d, 3H; CH*Me*$_2$), 1.01−0.97 (ov m, 30H; CH*Me*$_2$, NCC*Me*$_3$), 0.82 (d, 3H; CH*Me*$_2$), −0.13 (br s, 3H; Sc*C*H$_3$(H)B(C$_6$F$_5$)$_2$,). $^{13}C\{^1H\}$ NMR (C_7D_8): δ 174.8, 174.5 (N*C*CMe$_3$), 145.5, 143.9 (C_{ipso}), 143.4, 137.6, 136.9, 135.3, 129.3, 128.5, 126.0, 125.7, 124.0, 122.5 (*C*$_6$H$_3$), 101.3 (*C*H), 42.9, 39.3 (*C*Me$_3$), 32,1, 31.5 (C*Me*$_3$) 21.2, 29.2, 28.4, 27.8 (*C*HMe$_2$), 25.1, 25.0, 24.8, 24.4 (2), 24.2, 23.4 (2) (CH*Me*$_2$) (*C*H$_3$(H)B(C$_6$F$_5$)$_2$ not observed). ^{19}F NMR (C_7D_8): δ −130.0, −130.5 (*o*-F), −159.9, −160.3 (*p*-F), −164.3, −164.7 (*m*-F). ^{11}B NMR (C_7D_8): δ −20.6 (d, 1B; $^1J_{H-B}$ = 68 Hz). Anal. Calcd for $C_{48}H_{56}N_2BF_{10}Sc$: C, 63.59; H, 6.23; N, 3.09. Found: C, 63.97; H, 6.19; N, 2.94.

Synthesis of $[LSc][CH_3(H)B(C_6F_5)_2][B(C_6F_5)_4]$, 4. A 5 mm NMR tube was charged with **3** (0.017 g, 0.019 mmol), and $[PhN(H)Me_2][B(C_6F_5)_4]$ and d_8-toluene (0.5 mL) were added. The tube was shaken vigorously for 10 min and then allowed to settle, whereupon a dark orange oil collected at the bottom of the tube. The d_8-toluene solution containing $PhNMe_2$ was decanted, and the oil was dissolved in d_5-bromobenzene. ^1H NMR (C_6D_5Br): δ 7.31−7.17 (ov m, 6H; C_6H_3), 6.57 (s, 1H; C*H*), 2.25 (br sp, 4H, C*H*Me_2), 1.31−1.24 (ov m, 30H; CH*Me*$_2$, NCC*Me*$_3$), 1.02 (br s, 3H; C*H*$_3$(H)B(C$_6$F$_5$)$_2$,) 0.89 (d, 6H; CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (C_6D_5Br): δ 173.2 (N*C*CMe$_3$), 152.3 (C_{ipso}), 149.9, 142.0, 141.7, 140.3, 133.8, (*C*$_6$H$_3$), 97.6 (*C*H), 47.9 (*C*Me$_3$), 47.0 (CH*Me*$_2$), 32.1 (C*Me*$_3$), 27.7

(22) Bazan, G. C.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1993**, *12*, 2126−2130.

(23) (a) Lappert, M. F.; Singh, A.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1983**, 206−207. (b) See also: Basuli, F.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2003**, *22*, 4705−4714.

(24) Hüsgen, N. S.; Luinstra, G. A. *Inorg. Chim. Acta* **1997**, *259*, 185−196.

(25) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

Table 2. Data Collection and Structure Refinement Details for 2 and 6

	2	**6**
formula	$C_{49}H_{60}BF_{10}N_2Sc$	$C_{59}H_{57}B_2F_{20}N_2Sc\cdot C_6H_{14}$
fw	922.76	1326.82
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a, Å	12.233(5)	13.4712(1)
b, Å	12.595(4)	18.5810(2)
c, Å	17.932(8)	26.1801(2)
α, deg	99.87(2)	90
β, deg	92.75(2)	90.899(1)
γ, deg	117.27(2)	90
V, Å^3	2394.1(2)	6552.3(1)
Z	2	4
T, K	173(2)	173(2)
λ, Å	0.71073	0.71073
ρ_{calc}, g/cm^3	1.280	1.345
F(000)	968	2744
μ, mm^{-1}	0.227	0.210
cryst size, mm^3	0.32 × 0.08 × 0.05	0.27 × 0.22 × 0.20
transmn factors	0.989−0.931	0.959−0.946
θ range, deg	3.2−25.0	2.5−30.0
no. of data/restraints/params	8372/0/586	18 604/0/822
GoF	1.00	1.02
R_1 ($I > 2\sigma(I)$)	0.043	0.057
wR_2 (all data)	0.097	0.144
residual density, e/Å^3	0.19 and −0.26	0.40 and −0.42

(*C*H$_3$(H)B(C$_6$F$_5$)$_2$), 25.8 (*C*HMe$_2$). ^{19}F NMR (C$_6$D$_5$Br): *δ* −129.6 (*o*-F; CH$_3$(H)B(C$_6$F$_5$)$_2$), −131.1 (*o*-F; B(C$_6$F$_5$)$_4$), −151.5 (*p*-F; CH$_3$(H)B(C$_6$F$_5$)$_2$), −157.2 (*m*-F; CH$_3$(H)B(C$_6$F$_5$)$_2$), −161.6 (*p*-F; B(C$_6$F$_5$)$_4$), −165.4 (*m*-F; B(C$_6$F$_5$)$_4$). ^{11}B{^{1}H} NMR (C$_6$D$_5$Br): *δ* −16.6 (s, 2B).

Synthesis of [LScCH$_3$][(*μ*-H)$_2$B(C$_6$F$_5$)$_2$], 5. HB(C$_6$F$_5$)$_2$ (0.160 g, 0.466 mmol) and **1** (0.135 g, 0.233 mmol) were dissolved in THF (15 mL) and stirred for 15 min, whereupon solvent was removed under vacuum to give an oily yellow solid. Hexanes (20 mL) were added and the reaction mixture was filtered. The solvent was removed *in vacuo* to afford **5** as a yellow solid, which was recrystallized from cold hexanes (0.112 g, 0.123 mmol, 53%). ^{1}H NMR (C$_7$D$_8$, 285 K): *δ* 7.17−6.81 (ov m, 6H; C$_6$H$_3$), 5.49 (s, 1H; CH), 3.46 (sp, 2H; C*H*Me$_2$), 2.77 (q, 2H; Sc[(*μ*-*H*)$_2$B(C$_6$F$_5$)$_2$], $^1J_{H-B}$ = 69 Hz), 2.61 (sp, 2H; C*H*Me$_2$), 1.46 (d, 6H; CH*Me*$_2$), 1.38 (d, 6H; CH*Me*$_2$), 1.10 (d, 6H; CH*Me*$_2$), 0.98 (d, 6H; CH*Me*$_2$), 0.87 (s, 18H; NCC*Me*$_3$), 0.18 (Sc*Me*). ^{13}C{^{1}H} NMR (C$_7$D$_8$), 285 K): *δ* 173.9 (N*C*CMe$_3$), 142.4 (C$_{ipso}$), 140.1, 139.4, 126.3, 124.2, 123.6 (*C*$_6$H$_3$), 87.8 (*C*H), 43.9 (*C*Me$_3$), 32.3 (*C*HMe$_2$), 31.0 (C*Me*$_3$), 28.1 (*C*HMe$_2$), 26.1, 25.9, 24.2, 23.7 (CH*Me*$_2$) (Sc*Me* not observed). ^{19}F NMR (C$_7$D$_8$): *δ* −131.2 (*o*-F), −157.5 (*p*-F), −163.7 (*m*-F). ^{11}B NMR (*d*$_8$-THF): *δ* −10.9 (t, 1B; $^1J_{H-B}$ = 69 Hz). Anal. Calcd for C$_{48}$H$_{58}$N$_2$BF$_{10}$Sc: C, 63.45; H, 6.43; N, 3.08. Found: C, 63.15; H, 6.29; N, 2.96.

Synthesis of [LSc][(*μ*-H)$_2$B(C$_6$F$_5$)$_2$]$_2$, 6. A 50 mL flask charged with **1** (0.058 g, 0.10 mmol) and HB(C$_6$F$_5$)$_2$ (0.140 g, 0.40 mmol) was attached to a swivel frit apparatus. The entire assemblage was evacuated, and toluene (30 mL) was vacuum distilled into the flask. After warming to room temperature, the reaction mixture was allowed to stir for 30 min and filtered and solvent removed under vacuum to afford a yellow powder. Hexanes (15 mL) were added, and the resultant suspension was sonicated for 15 min. The volume was reduced to 5 mL, cooled to −78 °C for 30 min, and back-filtered. The solvent was removed *in vacuo* to afford **6** as a light yellow powder (0.089 g, 0.072 mmol, 72%). ^{1}H NMR (C$_6$D$_6$): *δ* 6.99 (t, 2H; C$_6$*H*$_3$, J_{H-H} = 7.7 Hz), 6.87−6.83 (m, 4H; C$_6$*H*$_3$), 5.55 (s, 1H; C*H*), 3.08 (sp, 2H; C*H*Me$_2$), 2.52 (sp, 2H; C*H*Me$_2$), 2.48 (q, 4H; Sc[(*μ*-*H*)$_2$B(C$_6$F$_5$)$_2$]$_2$, $^1J_{H-B}$ = 67 Hz), 1.34 (d, 6H; CH*Me*$_2$), 1.13 (d, 6H; CH*Me*$_2$), 1.04 (d, 6H; CH*Me*$_2$), 1.00 (d, 6H; CH*Me*$_2$), 0.82 (s, 18H; NCC*Me*$_3$). ^{13}C{^{1}H} NMR (C$_7$D$_8$): *δ* 177.0 (N*C*CMe$_3$), 142.4 (C$_{ipso}$), 141.0, 140.6, 128.3, 125.3, 124.7 (*C*$_6$H$_3$), 82.2 (*C*H), 45.0 (*C*Me$_3$), 31.6 (*C*HMe$_2$), 30.7 (C*Me*$_3$), 28.7 (*C*HMe$_2$), 25.8, 25.4, 25.1, 24.6 (CH*Me*$_2$). ^{19}F NMR (C$_7$D$_8$): *δ* −127.5, −130.3 (*o*-F), −156.6, −156.8 (*p*-F), −162.3, −163.4 (*m*-F). ^{11}B NMR (C$_7$D$_8$): *δ* −13.6 (t, 1B; $^1J_{H-B}$ = 67 Hz), −15.5 (t, 1B; $^1J_{H-B}$ = 67 Hz). Anal. Calcd for C$_{59}$H$_{57}$N$_2$B$_2$F$_{20}$Sc: C, 57.12; H, 4.63; N, 2.26. Found: C, 56.81; H, 4.55; N, 2.07.

Kinetic Isotope Effect Measurements. The following is a general procedure for the kinetic measurements of conversion from **2** to **3** as monitored by ^{1}H NMR spectroscopy. A 5 mm NMR tube was charged with **1** or ***d*$_6$-1** (0.010 g, 1.74 *μ*mol) and HB(C$_6$F$_5$)$_2$ (0.006 g, 1.74 *μ*mol), sealed with a rubber septum, and cooled to −78 °C. *d*$_6$-Benzene (0.5 mL) was added via syringe, yielding a 0.0347 M solution, which was slowly warmed to room temperature, shaken briefly to facilitate mixing, and then placed in the magnet, whereupon acquisition commenced following a brief pause for temperature equilibration. Data were analyzed by monitoring the disappearance of the backbone peak of **2** relative to **3** and plotted using the first-order equation. Each experiment was repeated a minimum of two times.

Single-Crystal X-ray Analyses. Crystals of **2** and **6** were coated with Paratone 8277 oil and mounted on a glass fiber. Measurements were made on a Nonius Kappa CCD diffractometer (University of Calgary) using graphite-monochromated Mo Kα radiation for all measurements. Table 2 gives further details, and the crystallographic information files are available as Supporting Information.

Acknowledgment. Funding for this work came from the Natural Sciences and Engineering Research Council in the form of a Discovery Grant to W.E.P. and scholarships to K.D.C. (PGS-A and CGS-D) and P.G.H. (PGS-A and PGS-B). K.D.C. also thanks Alberta Ingenuity for a Studentship Award. P.G.H. acknowledges the Alberta Heritage Foundation for a Ralph Steinhauer Award and the Sir Izaak Walton Killam Foundation for Doctoral Fellowships.

Supporting Information Available: Crystallographic data (CIF) for **2** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700435V