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

Korey D. Conroy, Paul G. Hayes, a Warren E. Piers, b 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(tBu)CHC(tBu)N(Ar); Ar = 2,6-iPr 2 -C 6 H 3 ) and HB(C 6 F 5 ) 2 proceed through an isolable ion pair 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 kH/kD = 8.7(6) was observed for the decomposition of 2, which corroborates the proposed mechanism while also implicating a highly reactive four-membered scandocene intermediate, LSc((H)CHB(c(H)C(F)5)2). Reaction of 2 equiv of HB(C 6 F 5 ) 2 with LScR 2 yields H 2 -hydridoborate complexes [LScCH 2 ][(μ-H)B(C 6 F 5 ) 3 ] (5), while 4 equiv of borane react to afford the bis-H 2 -hydridoborate complex [LSc][(μ-H)B(C 6 F 5 ) 3 ] 2 , 6.

Introduction

The established reactivity of electrophilic boranes as cocatalysts for metal complex formation is dominated by abstraction, yielding cationic species that exhibit enhanced catalytic activity toward olefinic substrates as demonstrated by olefin polymerization and hydroamination. Typically, perfluoroaryl boranes such as B(C 6 F 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 6 F 5 ) 2, 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 2 ZrR 2 (R = CH 3 , CH 2 Ph, and CH 2 SiMe 3 ) with various equivalencies of HB(C 6 F 5 ) 2 can lead to loss of RH and formation of a reactive four-membered metallacycle, 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. Schrock’s methyl methylene tantalocene, Cp 2 Ta(=CH 2 )CH 3 , reacts with HB(C 6 F 5 ) 2 to form another borane-stabilized methylene complex (II, Chart 1).

The organometallic chemistry of the group 3 metals, while advancing rapidly, is still devoid of well-characterized examples of metal-to-element multiple-bonded compounds. Given the rich chemistry observed when HB(C 6 F 5 ) 2 was reacted with group 4 and 5 systems bearing two reactive hydrocarbyl units, and particularly the potential to generate masked alkylidynes, we have conducted a study of the reactivity of HB(C 6 F 5 ) 2 with the well-defined dimethyl scandium complex [(ArNC(tBu)CHC(tBu)N(Ar))Sc(=CH 2 )] 2 (Ar = 2,6-iPr 2 -C 6 H 3 ) to form the masked scandium methylidene species I, in hopes that a masked scandium methylidene species might be generated. While mechanistic studies implicate such a species, it is highly elusive.

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

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

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

**Results and Discussion**

**Equimolar Reactions of LScMe₂ with HB(C₆F₅)₂.** The β-diketiminato scandium dimethyl complex 1 is prepared according to literature procedures¹¹ by salt metathesis of LScCl₂ with excess LiCH₃ in toluene. Monitoring the reaction of 1 with an equimolar amount of HB(C₆F₅)₂ in d₈-toluene at 0 °C by ¹H NMR spectroscopy reveals the formation of a C₂-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 C₅ 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 C₆F₅ groups at 2.340(2) and 2.351(2) Å, which correlate with previous examples of d⁰ group 3 metals with structurally characterized ortho-fluorine contacts such as 2.390(4) Å for [(ArNC(tBu)CHC(tBu)NAr)ScCH₃][CH₃B(C₆F₅)₃]¹² and 2.366(3) Å for [C₅₂Y][MeB(C₆F₅)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 examples¹¹ of methide abstraction from 1 by B(C₆F₅)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 PMe₃ 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 to prevent any further reaction.

---

to preclude association by phosphine even when a large excess of PMe3 is employed.

While 2 exhibits C2 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-diketimino 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 1H 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 CH2 is reminiscent of the reaction of HB(C6F5)2 with Cp2ZrMe2 to produce I,\(^{60}\) the scandyclic analogue would be expected to exhibit more symmetric structural features. We thus assign 3 as the metalated species shown. The symmetry of 3, formally chiral at scandium, is also borne out in the 19F NMR spectrum as two diastereotopic C6F5 groups are observed. The 11B{1H} NMR spectrum reveals a sharp singlet in the borate region at −20.6 ppm, which splits into a doublet (\(J_{FB-H} = 68\) Hz) for the hydridoborate singlet at 1.02 ppm is assigned to the borate methyl group. The 1H NMR spectrum of \(\{\text{LSc}\}\left(\text{CH3B(C6F5)3}\right)\) 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(C6F5)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 methane unit. Heating this mixture in d8-toluene leads to quantitative conversion to the thermodynamic product 3. Furthermore, 3 was derivatized through reaction with the anilinium salt [PhNH(H)Me2][B(C6F5)4] in d8-toluene, affording a \(C_{2v}\)-symmetric scandium cation, 4, with no evidence for PhNMe2 coordination (Scheme 2). The 1H NMR spectrum of 4 shows only one isopropyl methyne singlet, one singlet for the tert-butyl groups, and two doublets for the isopropyl methyl substituents. One additional broad singlet at 1.02 ppm is assigned to the borate methyl group. The 1H spectral features of 4 are analogous to the previously reported [LSc][CH2B(C6F5)3].\(^{11}\)

The 19F NMR spectrum exhibits two distinct borate groups present in a 1:2 ratio. The tetrakis-pentafluorophenyl borate has sharp multiplets, whereas the methylylidridoborate anion exhibits broad unresolved signals presumably due to hindered rotation induced by strong ortho-fluorine contacts at scandium. Reaction of 1 with [Ph3C][B(C6F5)4] forms the previously reported scandium monocation, which, when treated with HB(C6F5)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 metatation with a half-life of 0.5 h at 65 °C,\(^{11}\) while cationic [LScMe][MeB(C6F5)3] exhibits a half-life for methane release of 1.83 h at 35 °C.\(^{16}\) This suggests that a direct ligand metatation 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 1H NMR spectroscopy. Monitoring in situ prepared solutions of 2 in d8-benzene at 29 °C shows clean first-order conversion with a rate of 4.16 \(\times 10^{-4}\) 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 (\(\Delta H^\ddagger = -13(2)\) ev; \(\Delta S^\ddagger = 18.3(6)\) kcal mol\(^{-1}\); \(\Delta G^\ddagger = 22.2\) kcal mol\(^{-1}\)). Cyclometalation in a related scandium borate,\(^{17}\) III, exhibits a

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|}
\hline
compd & \(T\) (°C) & \(k_{\text{ab}}\) (s\(^{-1}\)) & \(t_{1/2}\) (h) \\
\hline
1 & 65 & 3.50 \times 10^{-4} & 0.53 \\
2 & 9.6 & 4.83 \times 10^{-5} & 4.28 \\
3 & 21 & 1.64 \times 10^{-4} & 1.27 \\
4 & 29 & 4.16 \times 10^{-4} & 0.53 \\
5 & 43 & 1.07 \times 10^{-3} & 0.15 \\
6 & 29 & 4.76 \times 10^{-5} & 4.23 \\
III & 35 & 9.77 \times 10^{-5} & 1.32 \\
\hline
\end{tabular}
\caption{1H NMR spectrum of the methyne region of 3 at room temperature in d8-toluene. The broad multiplet (\(\phi\)) at \(-2.68\) ppm is part of the quartet (\(J_{H-H} = 68\) Hz) for the hydridoborate (CH3(H)B(C6F5)2).}
\end{table}


Activation parameters obtained: $\Delta G^\ddagger = 13.2$ kcal mol$^{-1}$; $\Delta H^\ddagger = 18.3$ kcal mol$^{-1}$; $\Delta S^\ddagger = 22.2$ kcal mol$^{-1}$.

Figure 3. Eyring plot for the thermal decomposition of 2. Activation parameters obtained: $\Delta S^\ddagger = -13.2$ eu; $\Delta H^\ddagger = 18.3$ kcal mol$^{-2}$.

Figure 4. Typical first-order plots for the thermal decomposition of 2 and $d_6$-2 at 29°C and 0.0347 M.

This large $k_d/k_0$ value is not typical of “normal” $\sigma$-bond metathesis processes, but is similar to the value of 9.1(6) observed in another system where the C–H bond partnering in the methane-eliminating $\sigma$-bond metathetical event was found within a methyl borate group. 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 $k_d/k_0$ 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 isomeromers. Starting from $d_6$-2, a direct ligand metatation (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 cyclometatation of the resultant four-membered scandacycle 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 CDH$_3$.

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:CDH$_3$ ratio of 91:9, mirroring the relative rates of path B versus path A in this system. Taking into account the $k_d/k_0$ 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-bridged scandium alkylidene function.

**Synthesis of LScR$_n$[(μ-H)$_2$B(C$_6$F$_5$)$_2$]$_2$-n (n = 0, 1).** Reactions of 1 with greater than 1 equiv of HB(C$_6$F$_5$)$_2$ were also investigated. Complex 1 reacts cleanly with 2 equiv of HB(C$_6$F$_5$)$_2$ in THF to yield the well-defined (μ-H)$_2$B(C$_6$F$_5$)$_2$ product 5 (Scheme 4) in moderate yields, as well as CH$_2$B(C$_6$F$_5$)$_2$. When four or more equivalents of HB(C$_6$F$_5$)$_2$ are allowed to react with 1, both methyl groups are exchanged for dihydridoborate ligands and the bis-[μ-H$_2$]B(C$_6$F$_5$)$_2$ product, 6, is obtained. Compound 6 can also be prepared through addition of two further equivalents of HB(C$_6$F$_5$)$_2$ to 5, with loss of another CH$_2$B(C$_6$F$_5$)$_2$ molecule.

---

(20) (a) We observe no incorporation of D into the N-aryl isopropyl groups, so it is unlikely that the observed CD$_3$H arises due to some other deuterium scrambling process. (b) Feki, U.; Goldberg, K. I. J. Am. Chem. Soc. 2002, 124, 6804–6805.
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{$^{1}$H} NMR spectrum exhibits a single sharp, upfield resonance at all temperatures measured, which becomes a triplet ($^{3}$J$_{H-B}$ = 69 Hz) in the $^{1}$H-coupled experiment. The $^{1}$H 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$_{5}$)$_{3}$] ligands are present, two resonances in the room-temperature $^{11}$B{$^{1}$H} 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 $^{1}$H 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$_{5}$)$_{3}$] 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 $\beta$-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 $-90\,^\circ C$ 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](image_url)
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 1,2-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 to 2.19 Å for \([\text{Li}(_2\text{THF})_2][\text{Cp}*(\text{SiMe}_3)_2\text{ScH}]_2\) and 2.03 Å for \((\text{C}_5\text{H}_3\text{SiMe}_3)_2\text{Sc}(_2\text{BH}_4)_2\) 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(\(\text{C}_5\text{F}_3\text{H}_2\)) unit by treating with a Lewis base were unsuccessful.

In reactions of \(\text{Cp}_2\text{Zr}R_2\) with multiple equivalents of HB(\(\text{C}_5\text{F}_3\text{H}_2\)) we invoked a stepwise process involving \(\text{Cp}_2\text{Zr}R_2\) intermediates that add a second equivalent of HB(\(\text{C}_5\text{F}_3\text{H}_2\)) to give the observed \(\text{Cp}_2\text{Zr}([\mu-\text{H}]_2\text{B}(\text{C}_5\text{F}_3\text{H}_2)_2)\) products. This is unlikely to be the case in these scandium 1,2-diketiminato systems, since all attempts to generate hydridocyclopentadienyl complexes supported by this ligand system have led to ligand fragmentation processes initiated by hydride transfer to an imino carbon. It thus seems likely that the pathway by which compound 5 forms involves interaction of the second borane equivalent with 2 directly, possibly by hydride abstraction from the \([\text{H}](\text{CH}_3)_2\text{B}(\text{C}_6\text{F}_5)_2\) 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 and stored in evacuated bombs. Bromobenzene and \(d_5\)-bromobenzene were predried over CaH\(_2\), and hexamethyldisiloxane, \(d_5\)-THF, \(d_5\)-benzene, and \(d_5\)-toluene were dried and stored over sodium/benzophenone. All were distilled prior to use.

The following reagents were synthesized using literature protocols: \(\text{Li}[\text{Cp}*(\text{SiMe}_3)_2\text{ScH}]_2\) and \(\text{DB}(\text{C}_5\text{F}_3\text{H}_2)_2\) 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 a Bruker AMX-500 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified. \(^1\)H and \(^{13}\)C were referenced to Si(CH\(_3\)_4 through 300 and DRX-400 spectrometers at room temperature unless otherwise specified.
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%). 1H NMR (C6D6): δ 6.99 (t, 2H; CH, JH–H = 7.7 Hz), 6.87–6.83 (m, 4H; CH2H), 5.55 (s, 1H; CH), 3.08 (sp, 2H; CHMe2), 2.52 (sp, 2H; CHMe2), 2.48 (q, 4H; Sc([μ-H])2B(C6F5)2], JH–H = 67 Hz), 1.34 (d, 6H; CHMe2), 1.13 (d, 6H; CHMe2), 1.04 (d, 6H; CHMe2), 1.00 (d, 6H; CHMe2), 0.82 (s, 18H; NCCMe3). 13C([1H] NMR (C6D6): δ 177.0 (NCCMe3), 142.4 (Cipso), 141.0, 140.6, 128.3, 125.3, 124.7 (C2H3), 82.2 (CH), 45.0 (CMe3), 31.6 (CHMe3), 30.7 (CMe3), 28.7 (CHMe2), 25.8, 25.4, 25.1, 24.6 (CHMe2). 19F NMR (C7D8): δ −127.5, −130.3 (o-F), −156.6, −156.8 (p-F), −162.3, −163.4 (m-F). 11B NMR (C6D6): δ −13.6 (t, 1B; JH–B = 67 Hz), −15.5 (t, 1B; JH–B = 67 Hz). Anal. Calc. for C93H93N3BF20Sc: 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 1H NMR spectroscopy. A 5 mm NMR tube was charged with 1 or 6-1 (0.01 g, 1.74 μmol) and HB(C6F5)2 (0.006 g, 1.74 μmol), sealed with a rubber septum, and cooled to −78 °C. d6-Benzene (0.5 mL) was added via syringe, yielding 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 California) 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 Steinhauser 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.