Intermolecular β -Hydrogen Abstraction in Ytterbium, Calcium, and Potassium Tris(dimethylsilyl)methyl Compounds

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S Supporting Information

ABSTRACT: A series of organometallic compounds containing the tris(dimethylsilyl)methyl ligand are described. The potassium carbanions $KC(SiHMe_2)_3$ and $\{KC(SiHMe_2)_3$ -TMEDA $\}_2$ are synthesized by deprotonation of the hydrocarbon HC(SiHMe_2)_3 with potassium benzyl. $\{KC(SiHMe_2)_3$ -TMEDA $\}_2$ crystallizes as a dimer with two types of three-center–two-electron K–H–Si interactions: side-on coordination of SiH ($\angle K$ –H–Si = 102(2)°) and more obtuse K–H–Si structures ($\angle K$ –H–Si \approx 150°). The divalent calcium and ytterbium



compounds $M\{C(SiHMe_2)_3\}_2L$ (M = Ca, Yb; L = 2THF, TMEDA) are prepared from MI₂ and 2 equiv of KC(SiHMe_2)₃. Low ${}^1J_{SiH}$ coupling constants in the NMR spectra, low-energy ν_{SiH} bands in the IR spectra, and short M–Si distances and small M–C–Si angles in the crystal structures suggest β -agostic interactions on each C(SiHMe_2)₃ ligand. The IR assignments of M{C(SiHMe_2)_3}_2L (L = 2THF, TMEDA) are supported by DFT calculations. The compounds $M\{C(SiHMe_2)_3\}_2L$ react with 1 or 2 equiv of $B(C_6F_5)_3$ to give the 1,3-disilacyclobutane {Me_2SiC(SiHMe_2)_2}_2 and MC(SiHMe_2)_3HB(C_6F_5)_3L or M{HB(C_6F_5)_3}_2L, respectively. In addition, M{C(SiHMe_2)_3}_2L compounds react with BPh₃ to give β -H abstracted products. The compounds M{C(SiHMe_2)_3}_2THF_2 react with SiMe_3I to yield Me_3SiH and disilacyclobutane as the products of β -H abstraction, while M{C(SiHMe_2)_3}_2TMEDA and Me_3SiI form a mixture of Me_3SiH and the alkylation product Me_3SiC(SiHMe_2)_3 in a 1:3 ratio.

INTRODUCTION

Isolable and thermally robust organotransition-metal compounds tend to lack β -hydrogen-containing alkyl ligands, as these groups are susceptible to intramolecular reaction pathways, including β -hydrogen elimination and β -hydrogen abstraction.¹ However, this easily identified structural feature is not the only requirement for classical intramolecular β -H elimination; at least one vacant orbital or coordination site must be located *cis* to the alkyl ligand, the accepting orbital must have the appropriate energy, the symmetry of the orbitals involved should be matched throughout the reaction, and the overall thermodynamics must favor elimination and/or subsequent products. The pathway for β -hydrogen elimination of an alkyl ligand is the microscopic reverse of olefin insertion, and thus both the forward and reverse directions of these reactions are chemically important.²

Likewise, there are specific requirements for β -hydrogen abstraction. Intramolecular β -hydrogen abstraction requires a sufficiently basic X⁻ ligand, also located *cis* to the alkyl ligand, to allow the conjugate acid HX to be a leaving group. Note that β -elimination and intramolecular β -abstraction are electronically dissimilar in terms of the formal polarization of the β -hydrogen: a hydride is transferred to the metal center in the former reaction, whereas a proton is transferred in the latter transformation. In an interesting contrast to transition-metal chemistry, many main-group and rare-earth-metal alkyls are reticent to undergo β -hydrogen eliminations and abstractions despite highly polarized

M–C bonds that give strongly basic ligands, potentially open coordination sites resulting from flexible coordination geometries, labile metal–ligand interactions, and often highly Lewis acidic metal centers.

For example, β -hydrogen elimination of alkyllithiums takes place at 130–150 °C in refluxing hydrocarbons;³ the sodium congeners react more rapidly, requiring less forcing conditions,⁴ while compounds such as tert-butylpotassium readily eliminate isobutylene as one of a number of reaction pathways.⁵ Likewise, β -H-containing dialkylmagnesium compounds form olefins upon thermolysis; however, n-butylcalcium chloride persists in refluxing tetrahydrofuran.⁶ Coordinatively unsaturated organolanthanides also undergo β -elimination less readily than organotransition-metal analogues.⁷ In a representative example, isobutylene elimination from isolable Cp2ErCMe3(THF) is facilitated by LiCl at elevated temperatures.⁸ Despite the hints that group 1, group 2, and rare-earth-metal alkyls containing β -hydrogen are metastable, most main-group- and rareearth-metal organometallic compounds still avoid gratuitous β -hydrogen in their ligands.⁹ Thus, β -hydrogen-free benzyl,¹⁰ allyl,¹¹ CH₂SiMe₃,¹² CH(SiMe₃)₂,¹³ and the ultrabulky trisyl $C(SiMe_3)_3$ ligands¹⁴ and their derivatives are commonly

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Received: October 30, 2012 Published: February 22, 2013 Scheme 1. Main-Group-Metal- and Rare-Earth-Metal-Catalyzed (A) Meerwein–Ponndorf–Verley Reduction/Oppenauer Oxidation and (B) Tishchenko Ester Formation That Are Proposed To Involve β -Hydrogen Abstractions



employed in starting material syntheses and in the preparation of homoleptic alkyl compounds. Such ligands have allowed the preparation of dialkyl calcium and ytterbium compounds, such as Ca{C(SiMe₃)₃}₂,¹⁵ Yb{C(SiMe₃)₃}₂,¹⁶ Ca{C(SiMe₃)₂Ph}₂,¹⁰ Ca{CH(SiMe₃)₂}₂(C₄H₂O₂)₂,¹⁷ and Yb{C(SiMe₃)₂SiMe₂X}₂ (X = OMe, CH₂CH₂OEt, CH=CH₂, hexahydro-2*H*-pyrimido-[1,2-*a*]pyrimidine).¹⁸

However, β -hydrogens are important in chemical transformations, particularly catalytic reactions involving β -hydrogen abstraction such as Meerwein–Ponndorf–Verley carbonyl reductions, Oppenauer alcohol oxidations, and Tishchenko ester syntheses (Scheme 1).¹⁹

These reactions involve β -hydrogen on main-group- and rare-earth-metal alkoxides rather than alkyls. The important point here is that β -hydrogens are particularly reactive, even though the elimination pathway is not facile in such maingroup- and rare-earth-metal alkoxides. Second, β -agostic alkyl compounds provide key information as models for intermediates in olefin insertion reactions.²⁰ β -Hydrogen-containing silazides, such as N(SiHMe₂)*t*-Bu and N(SiHMe₂)₂, have rich rare-earth- and early-transition-metal chemistry that centers on the spectroscopic and structural features and reactivity of the SiH moiety.^{21–23} Thus, a significant amount of chemistry comes from β -SiH-containing amido, β -CH-containing alkoxide, and β -CH-containing alkyl compounds.

Fewer alkyl groups contain β -SiH moieties, and therefore we targeted ligands for rare-earth- and main-group-metal compounds that contain M–C bonds and β -SiH groups. Lappert described the preparation and the reaction of Me₂HSiCH₂-MgBr and RhCl(PPh₃)₃ that gives RhH(PPh₃)₄.²⁴ Eaborn has prepared analogues of trisyl (HC(SiMe₃)₃) containing dimethyl-silyl groups such as HC(SiHMe₂)₃ and HC(SiHMe₂)(SiMe₃)₂.²⁵ Ladipo demonstrated that the central CH of HC(SiHMe₂)₃ is acidic and readily deprotonated by lithium diisopropylamide.²⁶

Recently, we reported the homoleptic tris(alkyl)yttrium complex Y{C(SiHMe₂)₃}₃ and bis(alkyl)calcium(II) and -ytterbium(II) compounds M{C(SiHMe₂)₃}₂THF₂ (M = Ca, Yb) containing the C(SiHMe₂)₃ ligand.²⁷ These molecules contain spectroscopic and structural signatures associated with β -agostic Si-H-M interactions but do not undergo β -H elimination even though they are (at least formally) coordinatively unsaturated. Upon thermolysis to 100 °C, only HC(SiHMe₂)₃ is observed. Although the classical intramolecular β -hydrogen elimination is inhibited in the sterically hindered -C(SiHMe₂)₃, addition of external Lewis acids results in abstraction of the β -hydrogen rather than the C(SiHMe₂)₃ group. This abstraction is distinguished from the intramolecular β -hydrogen abstraction described above, in that the hydrogen is formally removed as a hydride rather than as a proton.

A few examples of intermolecular β -hydrogen abstractions from alkyl ligands have been reported, particularly for aluminum and zinc alkyls.²⁸ Recently, β -hydrogen abstractions from zinc alkyls were shown to be favored by pre-coordination of the organometallic compound and the Lewis acid.²⁹ Therefore, we wanted to explore the structures of starting materials and β -abstraction products as well as the effects of the Lewis acid and ancillary ligands in our calcium and ytterbium system. We have observed interesting structural and spectroscopic effects in these organometallic compounds containing the C(SiHMe₂)₃ ligands, and we have discovered that the M–C bond (rather than the β -SiH) reactivity is enhanced by TMEDA as an ancillary ligand.

RESULTS AND DISCUSSION

1. Synthesis of KC(SiHMe₂)₃ and {KC(SiHMe₂)₃TMEDA₂. The reaction of HC(SiHMe₂)₃ and potassium benzyl in THF for 18 h provides KC(SiHMe₂)₃ (1) as a red solid (eq 1). The red material is insoluble in pentane, and the compound solidifies upon washing with that solvent.

$$HC(SiHMe_{2})_{3} + KCH_{2}C_{6}H_{5} \xrightarrow{} KC(SiHMe_{2})_{3} + C_{6}H_{5}CH_{3}$$
(1)
THF, 18 h 1

The ¹H NMR spectrum of KC(SiHMe₂)₃ contained resonances at 4.59 ppm (¹ $J_{SiH} = 154$ Hz) and 0.46 ppm (³ $J_{HH} = 3.2$ Hz) assigned to SiH and SiMe groups, respectively, the ¹³C{¹H} NMR spectrum contained signals at 2.61 and 5.19 ppm, and the ²⁹Si{¹H} NMR spectrum contained one signal at -23.3 ppm. Signals for residual or coordinated THF are not detected, and combustion analysis is consistent with the formulation KC(SiHMe₂)₃. Thus, NMR spectroscopy is consistent with the presence of a C_3 axis that relates the three SiHMe₂ groups in 1. The unexpected red color, the slightly low ¹ J_{SiH} coupling constant, and the IR spectrum with ν_{SiH} bands at 2108 and 1973 cm⁻¹ hint at an interesting structure. A UV–vis spectrum of 1 dissolved in benzene contained a stronger band (λ_{max} 352 nm, $\varepsilon = 450$ L mol⁻¹ cm⁻¹) and a broad and weaker band better described as a shoulder that tails from 450 to 550 nm ($\varepsilon = 32.1$ L mol⁻¹ cm⁻¹ at 480 nm).

 ${KC(SiHMe_2)_3TMEDA}_2$ (${1\cdot TMEDA}_2$) is prepared by the addition of TMEDA to $KC(SiHMe_2)_3$ in benzene, and this compound is a red solid that is soluble in pentane and benzene. The solution-phase NMR spectra are incommensurate with the results of an X-ray structure determination (the solid-phase structure is shown in eq 2), and this discrepancy suggests a fluxional solution-phase structure.



As in 1, the ¹H, ¹³C{¹H}, and ²⁹Si NMR spectra of (1.TMEDA)₂ suggest a 3-fold rotation axis that relates the SiHMe₂ groups in the alkyl ligand. Thus, the ¹H NMR spectrum of (1.TMEDA)₂ contained resonances at 4.80 ppm $({}^{1}J_{\text{SiH}} = 154 \text{ Hz})$ and 0.52 ppm $({}^{3}J_{\text{SiH}} = 3.5 \text{ Hz})$, the ${}^{13}\text{C}\{{}^{1}\text{H}\}$ NMR spectrum contained signals at 5.32 and 5.19 ppm, assigned to SiMe and KC groups, respectively, and the ²⁹Si{¹H} NMR spectrum contained one signal at -23.7 ppm. As in the TMEDA-free potassium alkyl, the ¹H NMR data (${}^{1}J_{SiH}$ = 154 Hz) and FTIR ν_{SiH} bands (2105, 2035, 1962 cm⁻¹ in KBr) suggest potassium-silylhydride interactions. Assignment of the $\nu_{\rm SiH}$ signals was facilitated by the corresponding spectrum of $(1-d_2 \cdot \text{TMEDA})_2$, in which new peaks at 1533, 1462, and 1414 cm⁻¹ were observed and the bands assigned to $\nu_{\rm SiH}$ were absent. However, ¹H NMR spectra acquired even at 185 K were broad, and a spectrum consistent with a static structure was not observed.

X-ray-quality crystals are grown from concentrated pentane solution, and a solution from the diffraction study reveals that $(1 \cdot TMEDA)_2$ is dimeric in the solid state (Figure 1). The two $KC(SiHMe_2)_3$ units of the dimer are related by a crystallographically imposed inversion center. Each potassium center is



Figure 1. ORTEP diagram of $\{KC(SiHMe_2)_3TMEDA\}_2$ ($\{1\cdotTMEDA\}_2$). Ellipsoids are plotted at 35% probability. Hydrogen atoms bonded to carbon are not illustrated. Hydrogen atoms bonded to silicon were located objectively in the Fourier difference map. Significant interatomic distances (Å): K1–C1, 3.030(5); K1–H3s, 2.80(5); K1–Si3, 3.450(2); K1–Si1#, 3.983(2); K1–H1s#, 2.68(5); K1–Si2#, 4.096(2); K1–H2s#, 2.85(4). Significant interatomic angles (deg): K1–C1–Si1, 95.8(2); K1–C1–Si2, 98.1(2); K1–C1–Si3, 87.2(2); K1–H1s#–Si1#, 156(3); K1–H2s#–Si2#, 149(3); K1– H3s–Si3, 102(2).

coordinated by a bidentate TMEDA ligand, the central carbon and one "side-on" Si–H moiety from the $C(SiHMe_2)_3$ ligand and two hydrogens from two H–Si groups in the second $C(SiHMe_2)_3$ group of the dimer.

The potassium–carbon distance of 3.030(5) Å is shorter than the related distance in potassium trisyl KC(SiHMe₂)₃ of 3.10(1) Å; the structure of KC(SiMe₃)₃ consists of linear chains of alternating C(SiMe₃)₃ groups and K atoms.^{14c} The K–C distance in chains of KC(SiHMe₂)(SiPhMe₂)₂ of 3.167(8) Å is also longer;^{25b} in that compound, there are close potassium contacts to the silicon (K···Si, 3.457 Å) and hydrogen (K···H, 2.57(9) Å). The potassium in the literature compound is also coordinated by two phenyl groups of the next alkylpotassium repeat unit. The K–C interatomic distances in these compounds are within the sum of van der Waals radii of C and K (4.45 Å).³⁰ The central carbons are typically planar in tris(silyl) carbanions as well as phenyl-substituted carbanions;³¹ thus, the carbon and three substituents are nearly planar in (1·TMEDA)₂₁ and the sum of the Si–C–Si angles is 358.8° .

There are three non-equivalent close contacts between potassium and hydrogen (bonded to silicon) in $\{1\text{-TMEDA}\}_2$. The side-on interaction involves short K…H and short K…Si interatomic distances of 2.80(5) and 3.450(2) Å. For comparison, the sum of H and K van der Waals radii is 3.84 Å, and the sum of H and K covalent radii is 2.34 Å.³² Likewise, the sum of Si and K van der Waals radii is 4.85 Å, and the sum of Si and K van der Waals radii is 4.85 Å, and the sum of Si and K covalent radii is 3.23 Å. The side-on interaction is further identified by an acute K1–C1–Si3 angle of 87.2(2)°, while the other K1–C1–Si1 and K1–C1–Si2 angles are greater than 90° at 95.8(2) and 98.1(2)°. As a result, the plane of the CSi₃ moiety is tilted toward the agostic SiH with respect to the potassium–carbon vector.

Four K···H-Si end-on interactions connect the two $KC(SiHMe_2)_3$ units to form the dimeric structure of $(1 \cdot \text{TMEDA})_2$, and two of these interactions are equivalent to the two other interactions by crystallographically imposed symmetry. Thus, the K1–Si1# distance is 3.983(2) Å, and the K1–Si2# distance is 4.096(2) Å. The bridging hydrogen atoms were located in the electron-density map, and the related K1-H1s# and K1-H2s# distances are 2.68(5) and 2.85(5) Å. The K1–H1s#–Si1# angle of $156(3)^{\circ}$ is greater than the K1– H2s#-Si2# angle of $149(3)^{\circ}$. Thus, the potassium compound $(1 \cdot \text{TMEDA})_2$ contains two types of potassium-hydrosilyl interactions that are best described as SiH analogues of agostic and anagostic structures.³³ The two potassium atoms of the dimer are separated by a distance of 4.890(2) Å, which is within the sum of van der Waals radii (5.50 Å) but longer than the sum of covalent radii (4.06 Å); a K–K bond is not chemically reasonable in (**1**·TMEDA)₂.

The connectivity of this structure contrasts with that of LiC(SiHMe₂)₃THF₂ and LiC(SiMe₃)₃TMEDA, which are disproportionated Li dimers $[Li(L)_4][Li(C(SiHMe_2)_3)_2]$.^{14b,26} The potassium alkyl KC(SiHMe₂)(SiMe₂Ph)₂ contains a similar K(η^2 -SiH) interaction with a K···H distance of 2.57(9) A.^{25b}

2. Synthesis of M{C(SiHMe₂)₃}₂(THF)₂ and M{C(SiHMe₂)₃}₂-TMEDA (M = Ca, Yb). Bis(tris(dimethylsilyl)methyl)calcium and -ytterbium compounds are synthesized by salt metathesis reactions of MI₂ and KC(SiHMe₂)₃. Reactions in tetrahydrofuran provide the THF adducts Ca{C(SiHMe₂)₃}₂(THF)₂ (2·2THF, 58.7%) and Yb{C(SiHMe₂)₃}₂(THF)₂ (3·2THF, 49.6%).^{27b} The diamine adducts Ca{C(SiHMe₂)₃}₂TMEDA (2·TMEDA, 23.7%) and Yb{C(SiHMe₂)₃}₂TMEDA (3. TMEDA, 29.8%) are prepared from MI_2 , 2 equiv of $KC(SiHMe_2)_3$, and excess TMEDA in benzene (eq 3).



In general, the spectroscopic properties of $M{C(SiHMe_2)_3}_2$ -TMEDA and $M{C(SiHMe_2)_3}_2THF_2$ are similar, but a few features associated with the Si-H groups appear to be influenced by the donor ligand and metal center. The ¹H NMR spectra for $M{C(SiHMe_2)_3}_2TMEDA$ (M = Ca, Yb) each contained one SiH resonance (Ca, δ 4.81, ${}^{1}J_{SiH}$ = 154 Hz; Yb, δ 4.76, ${}^{1}J_{SiH} = 148$ Hz), and these spectral features are similar to those of the THF analogues $M\{C(SiHMe_2)_3\}_2THF_2$ (Ca, δ 4.78, ${}^{1}J_{\text{SiH}} = 152$ Hz; Yb, δ 4.78, ${}^{1}J_{\text{SiH}} = 150$ Hz). The lowest ${}^{1}J_{SiH}$ coupling constant was detected for the ytterbium compound 3. TMEDA, while the largest ${}^{1}J_{SiH}$ was observed for the calcium compound 2. TMEDA. Although these values are likely affected by several time-averaged factors resulting from fluxional exchange, 3. TMEDA consistently exhibits the extreme of spectroscopic values (see below). The ²⁹Si NMR spectra of TMEDA and bis(tetrahydrofuran) compounds 3 and 4 each contained a single resonance at ~ -20 ppm. Additionally, singlet resonances in both ¹H and ¹³C{¹H} NMR spectra of 2. TMEDA and 3. TMEDA, assigned to the N-methyl and methylene groups of the TMEDA ligand, suggested bidentate coordination of TMEDA to ytterbium and calcium metal centers, respectively.

Three slightly broad bands were observed in the IR spectra of 2. TMEDA and 3. TMEDA in the region associated with SiH stretching modes (Table 1). Three bands are in contrast to the two ν_{SiH} bands for KC(SiHMe₂)₃. The IR spectra of 2- d_6 ·TMEDA and 3- d_6 ·TMEDA provide further support for the ν_{SiH} assignments (see Table 1). Additionally, the NMR spectra suggest equivalent SiHMe₂ groups; the comparison of IR and NMR spectra indicates fluxionality on the NMR time scale. We assigned the two higher energy bands to terminal and weakly activated Si-H, whereas the lowest energy bands are associated with the Si-H bonds of silicon and hydrogen atoms that most closely approach the metal centers. These assignments are supported by DFT calculations (see below). The frequencies of the terminal SiH (high ν_{SiH}) are approximately constant for all compounds, but the low-energy $\nu_{\rm SiH}$ bands vary significantly. The signals are similar for THF-coordinated Ca and Yb compounds (~1900 cm⁻¹), lower energy in $Ca{C(SiHMe_2)_3}_2TMEDA$ (1861 cm⁻¹), and lowest in Yb{C- $(SiHMe_2)_3$ ₂TMEDA (1846 cm⁻¹). On the basis of the inequivalent SiH bands in the IR spectra, we attempted to resolve the ¹H NMR spectra of 2.2THF, 3.2THF, 2.TMEDA, and 3. TMEDA with variable-temperature measurements from 185 to 298 K in toluene- d_8 . However, spectra acquired even at 195 K contained equivalent and broad resonances associated with the SiHMe₂ groups.

Recrystallization of Yb{ $C(SiHMe_2)_3$ }_TMEDA from a concentrated pentane solution at -30 °C provides X-rayquality crystals, and an ORTEP diagram is shown in Figure 2. Although the previously reported THF adducts 2.2THF and 3.2THF have structures similar to the ytterbium diamine adduct described here, the features of the M- $C(SiHMe_2)_3$

Table 1. Infrared Spectroscopic Data for Tris(dimethylsilyl)methylpotassium, -calcium, and -ytterbium with THF and TMEDA Ligands (KBr, cm⁻¹)

compd	high $ u_{\rm SiH}$	intermediate ν_{SiH}	low ν_{SiH}
$HC(SiHMe_2)_2^{25a}$	2090	n.a.	n.a.
$HC(SiDMe_2)_3$	1534	n.a.	n.a.
$KC(SiHMe_2)_3$ (1)	2108	n.a.	1973
$KC(SiDMe_2)_3$ (1- d_3)	1532	n.a.	1417
${KC(SiHMe_2)_3TMEDA}_2 ({1 \cdot TMEDA}_2)$	2105	2035	1962
$ \begin{array}{l} \{ \text{KC}(\text{SiDMe}_2)_3 \text{TMEDA} \}_2 \\ (\{ 1 - d_3 \cdot \text{TMEDA} \}_2) \end{array} $	1533	1462	1414
$Ca{C(SiHMe_2)_3}_2THF_2$ (2·2THF)	2107	2066	1905
$Ca{C(SiDMe_2)_3}_2THF_2$ (2- d_6 ·2THF)	1530	1493	1409
$\begin{array}{c} Ca\{C(SiHMe_2)_3\}_2THF_2\\ (2_{calc}\cdot 2THF \ C_1) \end{array}$			
sym	2087	2050	1887
asym	2090	2050	1881
$Yb{C(SiHMe_2)_3}_2THF_2$ (3·2THF)	2101	2065	1890
$Yb{C(SiDMe_2)_3}_2THF_2$ (3- d_6 ·2THF)	1506 sh	1492	1410
Yb{ $C(SiHMe_2)_3$ } ₂ THF ₂ (3_{calc} ·2THF C_1)			
sym	2074	2047	1893
asym	2090	2051	1878
2·TMEDA	2105	2038	1861
2- <i>d</i> ₆ ·TMEDA	1510 sh	1493	1411
3.TMEDA	2080	2038	1846
3-d ₆ ·TMEDA	1505 sh	1494	1380
CaC(SiHMe ₂) ₃ HB(C ₆ F ₅) ₃ THF ₂ (4·2THF)	2077	2042	1957
$YbC(SiHMe_2)_3HB(C_6F_5)_3THF_2 (5 \cdot THF)$	2074	n.a.	1921
4·TMEDA	2094	2026	1918
5·TMEDA	2094	2027	1899

interactions (Tables 2 and 3) interestingly correlate with spectroscopic trends (Table 1) for the THF and TMEDA adducts.

The formally four-coordinate ytterbium center adopts a distorted-tetrahedral geometry containing an acute ∠N-Yb-N angle of $71.5(3)^{\circ}$ and an obtuse $\angle C - Yb - C$ angle of $121.8(3)^{\circ}$. All of the SiHMe₂ groups in the $C(SiHMe_2)_3$ ligands are oriented with hydrogen directed toward the interior of the molecule and the methyl groups pointing outward. The hydrogen atoms bonded to silicon were located objectively in the difference Fourier map; the positions of the SiMe₂ atoms and the electron density map provide a reasonable estimate of the hydrogen positions, subject to the normal limitations associated with X-ray diffraction. Still, the angles and distances of the C(SiHMe₃)₃ ligands show distortions associated with β -agostic type structures. In particular, three categories of Yb-Si distances are easily identified as long (\sim 4 Å), intermediate (3.4–3.5 Å), and short (3.14-3.19 Å). For comparison, the Yb-Si distance in Cp*YbSi(SiMe₃)₃ is 3.032(2) Å.³⁴ The Yb-C-Si angles in 3. TMEDA may also be categorized as obtuse ($\sim 120^{\circ}$), intermediate (95-102), and acute (86-88°), and these angles correlate with the Yb-Si distances. However, the C-Si distances in the CSi₃ moieties (C7-Si1, C7-Si2, C7-Si3 and C14–Si4, C14–Si5, C14–Si6) are identical within 3σ error.

In 3·TMEDA, the SiHMe₂ groups associated with the most acute M–C–Si angles, Yb–C7–Si2 and Yb–C14–Si6, also have small Yb–C–Si–H torsion angles, showing that the Yb–C and Si–H bonds are coplanar. In particular, the Yb1–C14–Si6–H6s torsion angle is 3.75° and Yb1–C7–Si2–H2s is 3.31° . The other Yb–C–Si–H torsion angles are greater than



Figure 2. ORTEP diagram of $Yb{C(SiHMe_2)_3}_2$ TMEDA (3·TMEDA). Carbon atoms on the TMEDA are plotted as points, and hydrogen atoms on TMEDA and silv methyl groups are not illustrated. Interatomic distances (Å): Yb1-C7, 2.68(1); Yb1-C14, 2.67(1); Yb1-Si1, 3.374(4); Yb1-Si2, 3.191(4); Yb1-Si3, 3.977(4); Yb1-Si4, 3.559(4); Yb1-Si5, 4.002(4); Yb1-Si6, 3.142(4); Yb1-H2s, 2.4(1); Yb1-H6s, 2.5(1). Interatomic angles (deg): N1-Yb1-N2, 71.5(3); C7-Yb1-C14, 121.8(3); Si1-C7-Si2, 116.7(6); Si1-C7-Si3, 117.2(6); Si2-C7-Si3, 114.4(6); Si4-C14-Si5, 114.0(6); Si4-C14-Si6, 113.2(2); Si5-C15-Si6, 114.8(6); Yb1-H2s-Si2, 44(4); Yb1-H6s-Si6, 52(4).

Table 2. Significant Interatomic Distances (Å) from the Single-Crystal Diffraction Studies of $Ca{C(SiHMe_2)_3}_2THF_2$ (2·2THF), $Yb{C(SiHMe_2)_3}_2THF_2$ (3·2THF), $Yb{C(SiHMe_2)_3}_2TMEDA$ (3·TMEDA), $CaC(SiHMe_2)_3HB(C_6F_5)_3THF_2$ (4·2THF), and $YbC(SiHMe_2)_3HB(C_6F_5)_3THF_2$ (5·2THF), as well as from Density Functional Theory Modeling of $Ca{C(SiHMe_2)_3}_2THF_2$ (2_{calc}·2THF) and $Yb{C(SiHMe_2)_3}_2THF_2$ (3_{calc}·2THF) and $Yb{C(SiHMe_2)_3}_2THF_2$ (3_{calc}·2THF)

compd	agostic M–Si	intermediate M–Si	long M–Si	M-C bond
$Ca{C(SiHMe_2)_3}_2THF_2$ (2·2THF)	Ca1-Si2: 3.216(2)	Ca1-Si3: 3.571(2)	Ca1-Si1: 3.642(3)	Ca1-C7: 2.616(7)
2 _{calc} ·2THF	3.209	3.660	3.721	2.579
$Yb{C(SiHMe_2)_3}_2THF_2$ (3.2THF)	Yb1-Si1: 3.180(1)	Yb1-Si3: 3.515(2)	Yb1-Si2: 3.617(2)	Yb1-C1: 2.596(4)
3_{calc} ·2THF C_1	3.272, 3.286	3.624, 3.654	3.785, 3.699	2.602, 2.598
$Yb{C(SiHMe_2)_3}_2TMEDA$ (3·TMEDA)	Yb1-Si6: 3.142(4)	Yb1-Si1: 3.374(4)	Yb1-Si3: 3.977(4)	Yb1-C7: 2.68(1)
	Yb1-Si2: 3.191(4)	Yb1-Si4: 3.559(4)	Yb1-Si5: 4.002(4)	Yb1-C14: 2.67(1)
CaC(SiHMe ₂) ₃ HB(C ₆ F ₅) ₃ THF ₂ (4·2THF)	Ca1-Si3: 3.097(1)	Ca1-Si2: 3.097(1)	Ca1-Si1: 3.912(1)	Ca1-C1: 2.566(3)
$YbC(SiHMe_2)_3HB(C_6F_5)_3THF_2 (5.2THF)$	Yb1-Si1: 3.1016(7)	Yb1-Si2: 3.0925(7)	Yb1-Si3: 3.937(1)	Yb1-C27: 2.593(2)

Table 3. Significant Interatomic Angles (deg) from the Single-Crystal Diffraction Studies of $Ca{C(SiHMe_2)_3}_2THF_2$ (2·2THF), $Yb{C(SiHMe_2)_3}_2THF_2$ (3·2THF), $Yb{C(SiHMe_2)_3}_2TMEDA$ (3·TMEDA), $CaC(SiHMe_2)_3HB(C_6F_5)_3THF_2$ (4·2THF), and $YbC(SiHMe_2)_3HB(C_6F_5)_3THF_2$ (5·2THF), as well as from Density Functional Theory Modeling of $Ca{C(SiHMe_2)_3}_2THF_2$ (2_{calc}·2THF) and $Yb{C(SiHMe_2)_3}_2THF_2$ (3_{calc}·2THF) and $Yb{C(SiHMe_2)_3}_2THF_2$ (3_{calc}·2THF)

compd	agostic M–C–Si	intermediate M–C–Si	obtuse M–C–Si
$Ca{C(SiHMe_2)_3}_2THF_2$ (2·2THF)	Ca1-C7-Si2: 90.7(3)	Ca1-C7-Si3: 105.1(3)	Ca1-C7-Si1: 108.4(3)
$Ca{C(SiHMe_2)_3}_2THF_2$ (2 _{calc} ·2THF)	90.730	109.358	111.747
$Yb{C(SiHMe_2)_3}_2THF_2$ (3·2THF)	Yb1-C1-Si1: 90.6(1)	Yb1-C1-Si3: 103.9(2)	Yb1-C1-Si2: 108.7(2)
$Yb{C(SiHMe_2)_3}_2THF_2$ (3 _{calc} ·2THF) C_1	92.407, 93.037	106.949, 108.099	113.896, 110.556
$Yb{C(SiHMe_2)_3}_2TMEDA (3 \cdot TMEDA)$	Yb1-C14-Si6: 86.2(4)	Yb1-C7-Si1: 95.1(5)	Yb1-C7-Si3: 120.7(5)
	Yb1-C7-Si2: 88.1(4)	Yb1-C14-Si4: 102.0(5)	Yb1-C14-Si5: 123.3(5)
$CaC(SiHMe_2)_3HB(C_6F_5)_3THF_2$ (4·2THF)	Ca1-C1-Si3: 88.2(1)	Ca1-C1-Si2: 88.1(1)	Ca1-C1-Si1: 125.2(1)
$YbC(SiHMe_2)_3HB(C_6F_5)_3THF_2$ (5.2THF)	Yb1-C27-Si1: 87.43(9)	Yb1-C27-Si2: 87.22(9)	Yb1-C27-Si3: 125.3(1)

20°. Together, short Yb–Si distances and acute Yb–C–Si angles, along with small Yb–C–Si–H torsion angles and short Yb–H distances, provide structural support for two mono-agostic $C(SiHMe_2)_3$ ligands bonded to the ytterbium center in 3·TMEDA. Similar features are observed in 2·2THF and 3·2THF.

In fact, comparisons with THF adducts of Ca and Yb reveal that the ytterbium TMEDA adduct contains shorter M–Si distances, even though the ionic radius of six-coordinate Ca(II) (1.00 Å) is 0.02 Å shorter than that of Yb(II) (1.02 Å).³⁵ For example, the shortest Yb–Si distance in 3·TMEDA is 3.142(4) Å, whereas the shortest M–Si distances in THF adducts are 3.216(2) Å (Ca) and 3.180(1) Å (Yb). Likewise, the most acute

M−C−Si angle is found in the ytterbium TMEDA adduct of 86.2(4)° in comparison to the Ca value of 90.7(3)° and Yb angle of 90.6(1)° in the THF adducts. These structural features nicely parallel the trends observed in the IR, where 3 TMEDA contains the lowest energy ν_{SiH} . The M−C distances, however, are long in the TMEDA adduct (Yb−C7, 2.68(1) Å; Yb−C14, 2.67(1) Å). These interatomic distance are longer by ~0.2 Å than those found in the corresponding C(SiMe₃)₃ compound Yb{C(SiMe₃)₃} (2.490(8) and 2.501(9) Å)¹⁶ and even ~0.1 Å longer than in Yb{C(SiHMe₂)₃}₂THF₂ (2.596(4) Å).

Clearly, the donor ligands THF and TMEDA influence the spectroscopic and structural properties of compounds **2** and **3**, particularly the characteristics associated with the tris(dimethylsilyl)methyl-metal interaction. We were therefore curious which donor would bind preferentially. Reaction of 1 equiv of TMEDA and 2.2THF in benzene- d_6 quantitatively provides 2.TMEDA and 2 equiv of THF (eq 4).



In contrast, addition of excess THF (>5 equiv) to 3-TMEDA provides the mixed donor compound $\{Yb[C(SiHMe_2)_3]_2-THF\}_2TMEDA$ ({3·THF}₂TMEDA), which is also isolated in quantitative yield (eq 5).



The thermal stabilities of 3. TMEDA and 3.2THF were examined to further compare the effects of THF and TMEDA as ligands in these bis(alkyl) divalent metal compounds. Thermolysis of both compounds at 120 °C in benzene-d₆ yields the hydrocarbon HC(SiHMe₂)₃ as the only ¹H NMR spectroscopically active material; however, 3. TMEDA is consumed in 6 h, whereas the THF adduct requires 96 h to form HC(SiHMe₂)₃. The source of the hydrogen $HC(SiHMe_2)_3$ is unknown. The deuterated solvent is dried and distilled from NaK alloy prior to thermolysis, and the interior surface of a Teflon-sealed J. Young style NMR tube is silvlated with CHCl₃/ Me₃SiCl. These compounds are highly air- and moisture sensitive, and benzene- d_6 solutions are 90% decomposed to $HC(SiHMe_2)_3$ upon 30 s of air exposure. Their persistence in sealed NMR tubes at room and moderate temperatures (60 °C) argues against adventitious hydrolysis in the hightemperature reactions. Thermolysis of 3.2THF- d_8 provides $HC(SiHMe_2)_{3}$, ruling out THF as the source of hydrogen. Thermolysis of $Yb\{C(SiDMe_2)_3\}_2THF_2$ affords HC- $(SiDMe_2)_3$; this experiment rules out the silicon hydride as the source of hydrogen by intramolecular or intermolecular β -hydrogen abstraction. A related decomposition of Cp*La(CH- $(SiMe_3)_2)_2$ THF produces $H_2C(SiMe_3)_2$, in which the proton source is proposed to be the C5Me5 ligand; that is not a possibility in this case.³⁶

3. Density Functional Theory Calculations of Ca{C-(SiHMe₂)₃}₂THF₂ and Yb{C(SiHMe₂)₃}₂THF₂. Both Ca{C-(SiHMe₂)₃}₂THF₂ (2·2THF) and Yb{C(SiHMe₂)₃}₂THF₂

(3.2THF) were modeled using density functional theory (DFT) employing the B3LYP functional. DFT optimizations were performed for gas-phase species and compared with solidstate results to help elucidate the locations of the hydrogens. The calculations also facilitate assignments of infrared bands to particular structural motifs; indeed, the calculations show that the SiH groups with short M-SiH distances also have lowenergy $\nu_{\rm SiH}$ bands. The large size of the compounds limits the methods available for the calculations; X-ray coordinates were used as the starting geometries for optimizations. Our first calculations employed the constraint of C_2 symmetry. C_2 -optimized structures contain very small imaginary frequencies in the Hessian calculations (2_{calc}·2THF, -19, -28 cm⁻¹; 3_{calc}·2THF, $-20, -24, -38 \text{ cm}^{-1}$). These imaginary frequencies correspond to a rotational motion of the $SiH(CH_3)_2$ groups around the C–Si bonds that results in breaking of the C_2 symmetry. The Yb complex 3_{calc}·2THF, reoptimized without symmetry constraints $(C_1 \text{ symmetry})$ to examine the effect of this rotation, retains the imaginary frequencies $(-35, -23, \text{ and } -18 \text{ cm}^{-1})$. Further geometry optimizations were not performed because the magnitudes of the imaginary frequencies are small and the computational cost for these calculations is great. Furthermore, the small magnitude of the imaginary frequencies indicates that this region of the potential energy surface is relatively flat; thus, a structure with a positive definite Hessian is difficult to locate. Also, because the potential energy surface (PES) is relatively flat, the imaginary modes introduce only a small error in the calculated energy. Finally, the C_1 -optimized Yb complex and C_2 -optimized 3_{calc} ·2THF have similar ν_{SiH} values, similar Si-H distances, and similar Si-C distances.

Despite these minor difficulties, the optimized gas-phase structures reproduce the general features of the structures obtained from crystallography (see Tables 2 and 3 for crystallographic and DFT-calculated distances and angles). Each $C(\text{SiHMe}_2)_3$ ligand contains one SiHMe₂ group with short M–H and M–Si distances and acute M–C–Si angles consistent with a β -agostic SiH. The optimized Ca–C distance of 2.58 Å is shorter than the experimental distance in 2.2THF of 2.616(7) Å (see Table 2), whereas the calculated Yb–C distance (2.60 Å) is similar to the experimental distance 2.596(4) Å. The shortest optimized M–Si distances in each molecule are reproduced well for Ca and are slightly longer than experiment for Yb (Ca–Si, calcd 3.21 Å, exptl 3.216(2) Å; Yb–Si, calcd 3.27 Å, exptl 3.180(1) Å).

The DFT calculations support a relationship between Si–H and Yb–H distances (Table 4). The calculation of 2_{calc} ·2THF clearly shows a long Si–H distance is associated with a short Ca–H distance; likewise, 3_{calc} ·2THF contains long Si–H distances for the hydrogen atoms that have close contacts to the ytterbium center. Furthermore, the calculated vibrational frequencies (see Table 1) show that the longest Si–H distances are the moieties with the lowest energy ν_{SiH} . However, the Si–H distances in the X-ray structures are identical within 3σ error. Although 3·2THF contains a seemingly long Si–H distance for the hydrogen that has a short Yb–H distance, that observation may be fortuitous.

For comparison, in-depth studies of monoagostic and diagostic tetramethyldisilazide compounds of lanthanum, lutetium, yttrium, and scandium reveal ~0.05 Å lengthened Si–H distances.^{23d} In computationally modeled compounds such as $\{H_2Si(C_5H_4)_2\}LaN(SiHMe_2)_2$, the β -diagostic interaction is described as a donor–acceptor pair, with both the Si and H

Table 4. M–H and Si–H Distances (Å) in 2·2THF, 2_{calc}·2THF, 3·2THF, 3_{calc}·2THF, and 3·TMEDA

compd	Si-H	M-H
2·2THF	Si1-H1s: 1.42(6)	Ca1-H1s: 3.37(2)
	Si2-H2s: 1.39(6)	Ca1-H2s: 2.53(7)
	Si3-H3s: 1.46(6)	Ca1-H3s: 3.86(6)
$2_{calc} \cdot 2THF (C_2 \text{ sym})$	1.541	2.562
	1.507	3.936
	1.500	3.744
3·2THF	Si1-H1s: 1.48(3)	Yb1-H1s: 2.50(3)
	Si2-H2s: 1.36(4)	Yb2-H2s: 3.56(4)
	Si3-H3s: 1.42(4)	Yb3-H3s: 3.59(4)
$3_{calc} \cdot 2THF (C_1 \text{ sym})$	1.541, 1.538	2.651, 2.679
	1.500, 1.502	3.881, 3.665
	1.506, 1.507	3.916, 3.991
3. TMEDA	Si1-H1s: 1.6(1)	Yb1-H1s: 2.9(1)
	Si4-H4s: 1.4(1)	Yb1-H4s: 3.4(1)
	Si2-H2s: 1.5(1)	Yb1-H2s: 2.4(1)
	Si6-H6s: 1.6(1)	Yb1-H6s: 2.5(1)
	Si3-H3s: 1.4(1)	Yb1-H3s: 4.2(1)
	Si5-H5s: 1.6(1)	Yb1-H5s: 4.0(1)

contributing to the donor orbitals and the lanthanum s and d orbitals as the acceptor.

In the present system, the Kohn–Sham orbitals show that the HOMO and HOMO-1 (-0.1828 and -0.1919 hartree) are largely centered on the carbon bonded to the calcium center. An Edminston–Ruedenberg energy localization of the orbitals provides a localized orbital picture (the HOMO is shown in Figure 3a).³⁷ The next lower set of orbitals involves bonding



Figure 3. Rendered images of localized orbitals of the HOMO (**A**) and occupied Si–H bonding orbital associated with the β -agostic SiH (**B**). Ca, Si, C, O, and H are shown as light green, teal, gray, red, and white, respectively. The localized orbital is shown in green.

from the central carbon to the silicon centers, followed by Si–C bonding to the methyl groups. The Si–H bonding orbitals are still lower in energy. The Kohn–Sham canonical orbitals corresponding to terminal silicon–hydrogen bonding are grouped by energy into two sets (-0.4790 and -0.4779 hartree; -0.3147 and -0.3136 hartree); the Si–H bonds associated with the β -agostic structures are barely stabilized versus the latter set (-0.3231 and -0.3175 hartree) and have significantly higher energy than the former.

4. β -Hydrogen Abstraction Reactions. The identity of the organic thermolysis product as HC(SiHMe₂)₃ argues against β -hydrogen elimination as the kinetically favored reaction pathway. While β -hydrogen eliminations are notoriously slow for rare-earth- and main-group-metal compounds as noted in the Introduction, 2·2THF, 3·2THF, 2·TMEDA, and 3·TMEDA contain (presumably) a hydridic β -hydrogen bonded to silicon and Lewis acid sites on the metal that might act as intramolecular hydride acceptors via β -elimination or through intermolecular reactions involving β -hydride abstraction. Therefore, reactions of 2·2THF, 3·2THF, 2·TMEDA, and 3·TMEDA, and 3·TMEDA with the Lewis acids B(C₆F₅)₃, BPh₃, and Me₃SiI were explored to test the nucleophilicity of the central carbanion versus that of the peripheral β -hydrogen.

Reactions of M{*C*(*SiHMe*₂)₃/₂*L*₂ and *B*(*C*₆*F*₅)₃. Reactions of **2**·2THF, 3·2THF, and B(C₆F₅)₃ occur through β-hydrogen abstraction to form MC(SiHMe₂)₃HB(C₆F₅)₃THF₂ (M = Ca (4·2THF); Yb (5·2THF)), as previously communicated.^{27b} Similarly, the TMEDA adducts and B(C₆F₅)₃ react to give MC(SiHMe₂)₃HB(C₆F₅)₃TMEDA (M = Ca (4·TMEDA); Yb (5·TMEDA)) and 0.5 equiv of 1,3-disilacyclobutane {Me₂SiC-(SiHMe₂)₂}₂, which is the head-to-tail dimer of the silene Me₂Si=C(SiHMe₂)₂ (eq 6).

These reactions are best monitored initially by ¹¹B NMR spectroscopy, in which sharp upfield doublet resonances (4.2THF, -21.3 ppm, ${}^{1}J_{BH}$ = 76.2 Hz; 4 TMEDA, -21.8 ppm, ${}^{1}J_{BH} = 75.0 \text{ Hz}; \text{ } \text{5} \cdot 2 \text{THF}, -20.8 \text{ ppm}, {}^{1}J_{BH} = 72.8 \text{ Hz}; \text{ } \text{5} \cdot \text{TMEDA},$ -21.4 ppm, ${}^{1}J_{BH} = 71.6$ Hz) are consistent with formation of an anionic, four-coordinate boron center that is bonded to hydrogen. In the ${}^{1}H{}^{11}B{}$ NMR spectra, singlets were assigned to the boron hydride (4·2THF, 2.63 ppm; 4·TMEDA, 2.64 ppm; 5·TMEDA, 3.22 ppm), and cross-peaks in ¹H-¹¹B HMQC experiments supported these assignments. The general NMR features of the $C(SiHMe_2)_3$ ligand were similar in 4.2THF, 5.2THF, 4.TMEDA, and 5. TMEDA. In the ¹H NMR spectra, upfield doublets (~0.3 ppm, ${}^{3}J_{SiH} \approx 3$ Hz) were assigned to methyl groups of the SiHMe2, whereas the SiH multiplets were characterized by signals from 4.4 to 4.6 ppm (${}^{1}J_{SiH} = 145-149$ Hz). Table 5 gives the SiH resonances and ${}^1\!J_{
m SiH}$ coupling constants for the dialkyl compounds and the (alkyl)hydridoborate complexes for comparison. The signals in the zwitterionic compounds are ca. 0.2 ppm upfield in comparison to those of the dialkyl compounds, and the coupling constants are reduced by ~5 Hz.



Table 5. Spectroscopic Features of Dialkyl and Monoalkyl Ytterbium and Calcium Compounds

compd	δ(SiH), ppm	¹ J _{SiH} , Hz	compd	$\delta(SiH),$ ppm	¹ J _{SiH} , Hz
$2 \cdot 2 \text{THF}$	4.78	152.1	4·2THF	4.55	148.9
3·2THF	4.78	150.4	5·3THF	4.61	146.4
2. TMEDA	4.81	154	4.TMEDA	4.44	144.9
3-TMEDA	4.76	148	5. TMEDA	4.51	147.0

Interestingly, the trend in the IR spectra is somewhat opposite to that of the NMR, in that the $\nu_{\rm SiH}$ bands in the zwitterionic compounds appeared at higher energy relative to their dialkyl precursors (see Table 1). Three $\nu_{\rm SiH}$ signals were observed in 4·2THF, 4·TMEDA, and 5·TMEDA, but only two bands were observed for 5·2THF. As in the dialkyl compounds, the lowest energy bands were assigned to the β -agostic SiH. The spectrum for the ytterbium compound 5·TMEDA contained the lowest energy band, and the trend of stretching frequency for the zwitterionic compounds 5·TMEDA < 4·TMEDA \approx 5·2THF < 4·2THF is similar to that of the dialkyl compounds, 3·TMEDA < 2·TMEDA < 3·2THF.

X-ray-quality crystals were obtained for 4.2THF and 5.2THF, and the general structural features and connectivities of these zwitterionic compounds are similar (see Figure 4 for the ORTEP diagram of 4.2THF).^{27b} On the basis of the similar structural features of these two crystallographically characterized compounds and the similar overall spectroscopic features for 4.2THF, 5.2THF, 4.7MEDA, and 5.7MEDA, the connectivity of these compounds is assigned as shown in eq 6.

The solid-state structure of 4·2THF confirms that calcium interacts with one HB(C_6F_5)₃ group and one tris(dimethylsily)methyl ligand, as well as two THF ligands. The Ca–C distance for 4·2THF (2.566(3) Å) is 0.05 Å shorter than for the neutral compound 2·2THF (2.616(7) Å). This is in contrast to the pair of Yb analogues, in which the Yb–C distances are identical in the neutral and zwitterionic compounds. Additionally, the zwitter-ionic nature of 4·2THF affects Ca–Si and Ca–O distances. For example, the Ca1–Si3 distance of 3.097(1) Å (associated with the proposed β -agostic structure) is ~0.1 Å shorter than that of the agostic Ca1–Si2 distance in 2.2THF (3.216(2) Å). The hydrogen bonded to silicon (H3s) was located in the Fourier difference map at the position expected for a roughly tetrahedral silicon center. SiH is directed toward the Ca center such that the Ca1–C1–Si3–H3s torsion angle is $-3(1)^\circ$. Furthermore, a second short calcium–silicon distance (Ca1–Si2 = 3.097(1) Å) is also observed; however, in this case, the torsion angle is $37(1)^\circ$.

The Ca center is further coordinated by two *ortho*-F atoms from two C_6F_5 groups in a bidentate $HB(C_6F_5)_3$ ligand, with Ca–F distances of 2.412(2) and 2.437(2) Å. The hydrogen bonded to boron was located objectively in the difference Fourier map, and its position is consistent with that expected for a tetrahedral boron center. From this, the H1g–Ca1 distance of 2.45(3) Å is significantly (0.45 Å) longer than the sum of covalent radii of Ca and H (1.99 Å), suggesting that the Ca–H interaction is likely weak. The ν_{BH} values in this series of compounds (Table 6)

Table 6. Comparison of B–H Stretching Bands (KBr, cm⁻¹) from IR Spectra of Mono- and Bis(hydridoborate) Compounds

$MC(SiHMe_2)_3 \{HB(C_6F_5)_3\}L_2$	$ u_{ m BH}$	$M\{HB(C_{6}F_{5})_{3}\}_{2}L_{2}$	$ u_{\rm BH} $
4·2THF	2329	6·2THF	2308
5·2THF	2310	7·2THF	2377
4·TMEDA	2302	6-TMEDA	2383
5. TMEDA	2293	7. TMEDA	2305

also suggested weak M···H···B interactions (see below). A similar structural motif was reported for the coordination of HB(C₆F₅)₃ to a samarium(III) center in Cp*₂Sm{ κ^3 -H,F,F-HB(C₆F₅)₃}.³⁸ In that compound, the Sm–H distance is 2.45(5) Å, the B–H distance is 1.18(5) Å, and the infrared spectrum contains a ν_{BH} band at 2290 cm⁻¹.

Reactions of 2·2THF or 3·2THF with 2 equiv of $B(C_6F_5)_3$ in benzene provide $M\{HB(C_6F_5)_3\}_2(THF)_2$ (M = Ca (6·2THF), Yb (7·2THF)) along with 1 equiv of the 1,3-disilacyclobutane



Figure 4. ORTEP diagram of $CaC(SiHMe_2)_3\{\kappa^3-H, o-F, o-F-HB(C_6F_5)_3\}(THF)_2$ (4·2THF). See Tables 2–4 for significant interatomic distances and angles.



Figure 5. ORTEP diagram of $Yb{\kappa^3-HB(C_6F_5)_3}_2TMEDA$ (7·TMEDA). Ellipsoids are plotted at 35% probability, and hydrogen atoms on the TMEDA ligand are not illustrated for clarity.

 ${\text{Me}_2\text{SiC}(\text{SiHMe}_2)_2}_2$ (eq 7). The "dizwitterionic" TMEDA adducts **6**·TMEDA and 7·TMEDA are prepared analogously from **2**·TMEDA and **3**·TMEDA. These products are consistent with β -abstraction of one hydrogen from each C(SiHMe_2)_3 ligand. Expectedly, the monoalkyl compounds **4** and **5** react with 1 equiv of B(C₆F₅)₃ to provide **6** and 7.

The TMEDA adducts of $\mathbf{6}$ and 7 precipitate from benzene, whereas $\{Me_2SiC(SiHMe_2)_2\}_2$ is soluble, thus allowing facile separation of products. However, the poor solubility of $\mathbf{6}$ ·TMEDA and 7·TMEDA in aromatic and aliphatic solvents limits solution-phase characterization.

The ν_{BH} stretching frequencies in monoalkyl hydridoborate compounds 4 and 5 and bis(hydridoborates) 6 and 7 vary from 2293 to 2383 cm⁻¹ (Table 6). For comparison, the ν_{BH} value in Cp*₂Sc(κ^2 -C₆F₅)BH(C₆F₅)₂ is 2410 cm⁻¹,³⁹ and in that compound an X-ray structural analysis indicates that the boron-hydrogen distance is to long to allow a scandiumhydrogen bonding interaction. The ν_{BH} values are generally blue-shifted in the bis(hydridoborate) compounds versus the mono(hydridoborate) compounds. The exception is 6-2THF, in which the ν_{BH} value is 21 cm⁻¹ lower in energy. The variation in the ν_{BH} values suggests that there is some M···H···B interaction in these compounds (which is also suggested by X-ray crystallography). However, the fluxionality of these compounds limits further conclusions on the strength of the interaction.

Both bis(hydridoborate) Yb complexes 7.2THF and 7.TMEDA crystallize from benzene solution. X-ray crystallog-raphy reveals that the Yb center is coordinated to four *o*-F

atoms from four C_6F_5 rings (two from each $HB(C_6F_5)_3$ ligand) as well as a bidentante TMEDA ligand or two THF ligands in the two compounds (Figure 5). As in the mono(hydridoborate) structures discussed above, the boron-hydrogen group points toward the ytterbium centers. The crystallographically characterized calcium analogue **6**·2THF is isostructural with 7·2THF.

The SiH groups in 2.2THF, 3.2THF, 2.7MEDA, and 3.7MEDA have sufficient nucleophilic character to react with the strong Lewis acid $B(C_6F_5)_3$, but the SiH moieties do not react with calcium(II) or ytterbium(II) centers in any of the neutral, cationic, or dicationic compounds 2.2THF-7.2THF or 3.7MEDA-7.7MEDA even though the THF and TMEDA ligands are sufficiently labile to undergo substitution. The only hint of possible β -elimination comes from the thermolysis of 4.2THF, which gives HC(SiHMe₂)₃ and the disilacyclobutane species in a 4:3 ratio after 5 days at 80 °C. Disilacyclobutane could form through a β -elimination process, although dissociation of $B(C_6F_5)_3$ from $(Me_2HSi)_3CCaHB(C_6F_5)_3$ followed by β -abstraction is more likely.

Reactions of $M{C(SiHMe_2)_3}_{2L_2}$ and 1 equiv of BPh₃. Compounds 2.2THF, 3.2THF, 2.TMEDA, and 3.TMEDA also react with the much weaker Lewis acid BPh₃. This observation is unexpected because, as noted above, the calcium(II) and ytterbium(II) centers in 2–7 are not sufficient Lewis acids to mediate β -hydrogen elimination or abstraction. The M(HBPh₃) and MHB(C₆F₅)₃ products from the abstractions have dissimilar connectivities in the solid state (see below). BPh₃ abstractions afford a mixture of species, whereas B(C₆F₅)₃



4

Βĺ

C6

H1ŀ

N1

Figure 6. ORTEP diagram of Yb(HBPh₃)₂TMEDA (9·TMEDA). Ellipsoids are plotted at 35% probability, and hydrogen atoms bonded to C₆H₅ and TMEDA groups are not drawn for clarity. Selected interatomic distances (Å): Yb1–H1b, 2.22(5); Yb1–H2b, 2.39(4); Yb1–C6, 2.772(4); Yb1–C25, 2.667(4); Yb1–C26, 2.843(4); B1–H1b, 1.19(5); B2–H2b, 1.22(5); Yb1–B1, 2.930(5); Yb1–B2, 3.065(4); B1–C6, 1.643(6); B1–C7, 1.621(6); B1–C13, 1.600(6); B2–C19, 1.623(6); B2–C25, 1.648(6); B2–C31, 1.624(6).

Yb

H2b

B2

 c_{2}

C26



Figure 7. ORTEP diagram of Yb(HBPh₃)₂THF (9·THF). Ellipsoids are plotted at 35% probability, and hydrogen atoms bonded to C₆H₅ and THF groups are not drawn for clarity. Selected interatomic distances (Å): Yb1–H1b, 2.45(3); Yb1–H2b, 2.22(3); Yb1–B1, 2.675(3); Yb1–B2, 2.675(3); Yb1–C5, 2.871(3); Yb1–C6, 2.793(3); Yb1–C18, 2.614(3); Yb1–C24, 2.705(3); Yb1–C36, 2.780(3); B1–C6, 1.642(4).

Article



provides a single product. In addition, the product distributions from reactions of BPh₃ and 2·TMEDA and 3·TMEDA in comparison to 2·2THF and 3·2THF and BPh₃ are different. For example, 3·TMEDA and BPh₃ react in benzene to give 0.5 equiv of Yb(HBPh₃)₂TMEDA (9·TMEDA), leaving 0.5 equiv of 3·TMEDA unreacted (eq 8). In contrast, 2·2THF and 3·2THF and 1 equiv of BPh₃ react to give a mixture of dialkyl starting material, MC(SiHMe₂)₃(HBPh₃)(THF)_n (10·*n*THF and 11·*n*THF), and M(HBPh₃)₂THF (8·THF and 9·THF) in a 1:2:1 ratio, along with disilacyclobutane (eq 9).

The products 8·TMEDA and 9·TMEDA precipitate or crystallize from the reaction mixtures and are isolated by filtration. Unfortunately, the compounds 8·TMEDA and 9·TMEDA are insoluble in pentane, benzene, toluene, and THF, precluding characterization in those solvents. In contrast to the IR spectra of the HB(C₆F₅)₃ compounds, the IR spectra of 8·TMEDA and 9·TMEDA contained four ν_{BH} bands (8·TMEDA 2059, 2027, 2008, and 1943 cm⁻¹; 9·TMEDA, 2054, 2024, 2006, and 1940 cm⁻¹). Despite the relatively simple X-ray structure (see below), these signals suggest there are multiple types of M···H···B interactions in these two compounds in the solid state.

X-ray-quality crystals of 9. TMEDA are obtained from the reaction mixture, and an X-ray diffraction study confirmed the identity of the product (Figure 6). The structure of 9.TMEDA contains a bidentate TMEDA ligand and two HBPh₃ ligands that have short distances to ytterbium through hydrogen and boron as well as ipso- and o-aryl carbons. Interestingly, the related THF adduct 9. THF contains only one molecule of THF coordinated to ytterbium (Figure 7). The HBPh₃ytterbium close interatomic contacts in 9. THF include the H on boron (Yb1-H1b, 2.45(3) Å; Yb1-H2b, 2.22(3) Å), the boron center (Yb1-B1 and Yb1-B2, 2.675(3) Å), and two of the three ipso carbons in each HBPh₃ group (Yb1-C6, 2.793(3) Å; Yb1-C18, 2.614(3) Å; Yb1-C24, 2.750(3) Å; Yb1-C36, 2.780(3) Å). Coordination of an anion to BPh₃ tends to lengthen the B–C bonds from 1.58 Å in BPh₃ by 0.05 Å.^{40–42} This lengthening effect is further enhanced for the phenyl groups of 9. TMEDA and 9. THF, in which there is a $Yb-C_{ipso}$ close contact. In 9. TMEDA, for example, the pendant phenyl group has a B-C13 distance of 1.600(6) Å, whereas the B-C6 distance for the coordinated phenyl is 1.643(6) Å. Likewise, in 9. THF, coordinated (B2-C36) and noncoordinated (B2-C30) phenyls have distances of 1.648(4) and 1.608(4) Å, respectively.

We know of only two other structurally characterized compounds that contain the [HBPh₃] unit. Reaction of $(C_5H_3-t-Bu_2)_2$ CeH and BPh₃ gives $(C_5H_3-t-Bu_2)_2$ CeHBPh₃,

which contains a Ce–H–B angle of 139(1)°, a Ce…B distance of 3.423(3) Å, and a B–H distance of 1.26 Å.⁴² Additionally, the ruthenium compound Ru(η^6 -C₆H₅)(BHPh₃)(PMe₃)₃ contains a terminal boron hydrogen; the IR in that case reveals a band at 2270 cm⁻¹ assigned to ν_{BH} .⁴³

Additionally, a number of BPh₄⁻-containing ytterbium(II) and calcium(II) compounds are known,⁴⁴ and BPh₄⁻ is often non-coordinating in these compounds. However, BPh₄⁻ is known to coordinate to Yb(II) in Yb(η^6 -C₆H₅)(η^4 -C₆H₅)BPh₂type structures, where the shortest Yb–C distance is 2.833(3) Å.⁴⁵ In Yb{N(SiMe₃)(SiMe₂CH₂BPh₂(η^2 -C₆H₅)₂)}THF₂, short Yb–C_{ipso} distances (2.635(3) and 2.792(3) Å) are similar to the Yb^{II}–C distance in 9·TMEDA.⁴⁵ Deacon pointed out that these Yb^{II}–C_{ipso} distances are in the range observed for bridging Yb–Ph–Yb.⁴⁶

The monoalkyl compounds $10 \cdot n$ THF and $11 \cdot n$ THF are not isolable but are characterized in solution by ¹H NMR signals that are distinct from those of the isolable and fully characterized 2·2THF and 3·2THF. In particular, the ¹H NMR spectrum of calcium $10 \cdot n$ THF contained resonances at 4.51 ppm (¹J_{SiH} = 152.7 Hz) and 0.41 ppm (³J_{HH} = 3.5 Hz), assigned to the SiH and SiMe₂ groups, respectively.

The species 8·THF and 9·THF are independently prepared by the reactions of 2 equiv of BPh₃ and 3·2THF and 4·2THF (eq 10). Unlike the insoluble TMEDA adducts, 8·THF and 9·THF are soluble in benzene.

The best procedure to isolate 8·THF and 9·THF involves evaporation of the reaction mixture followed by pentane washes to remove the 1,3-disilacyclobutane {Me₂SiC(SiHMe₂)₂}₂ byproduct. One broad resonance was observed in the ¹¹B NMR spectra of 8·THF (-6.0 ppm), while a broad doublet was detected for 9·THF (-4.0 ppm, ¹J_{BH} = 56 Hz). In the ¹H{¹¹B} NMR spectrum, singlet resonances were assigned to the boron hydride (8·THF, 3.18 ppm; 9·THF, 3.66 ppm), and cross-peaks in ¹H-¹¹B HMQC experiments supported these assignments. Two ν_{BH} bands (2021 and 1936 cm⁻¹) were observed in the IR spectrum for 8·THF, but only one ν_{BH} band (2003 cm⁻¹) was detected for 9·THF.

Reaction of $M\{C(SiHMe_2)_3\}_2L_2$ and Me_3SiI . As with borane Lewis acids, reactions of 2.2THF or 3.2THF and 1 equiv of Me_3SiI in benzene- d_6 results in β -hydrogen abstraction, yielding HSiMe₃ and the disilacyclobutane (eq 11). The HSiMe₃ is characterized by a multiplet at 4.18 ppm and a doublet at 0.01 ppm in ¹H NMR spectra of reaction mixtures. Only half of the dialkyl starting material is consumed in the reaction, and a white precipitate is formed that is likely a THF adduct of YbI₂



Figure 8. ORTEP diagram of $K\{HB(C_6F_5)_3\}TMEDA_2$ (13-2TMEDA). Ellipsoids are plotted at 35% probability, and hydrogen atoms on the TMEDA ligands are not illustrated for clarity.

on the basis of the reaction stoichiometry and the observations for the transformations involving BPh₃.

Notably, neither Me₃SiC(SiHMe₂)₃ nor the silvl ether iodide Me₃SiO(CH₂)₄I product from THF ring opening are formed in these reactions. Alternatively, Cp*La{CH(SiMe₃)₂}₂THF and Me₃SiI were reported to react to give Me₃SiO(CH₂)₄I and Cp*La{CH(SiMe₃)₂}₂.³⁶ The observation of HSiMe₃ and disilacyclobutane indicates that Me₃SiI reacts with the β -H rather than the carbanion C(SiHMe₃)₃ through β -H abstraction, similar to reactions with boron-based Lewis acids.

Interestingly, the reaction of Me₃SiI and 2·TMEDA or 3·TMEDA provides Me₃SiC(SiHMe₂)₃ as the major organic product (eq 12). HSiMe₃ and the disilacyclobutane {Me₂SiC(SiHMe₂)₂}₂ are formed as minor products (5:2:1), as determined by integration of ¹H NMR spectra of reaction mixtures. Again, an insoluble white precipitate is formed (likely MI₂), and only half of the dialkyl starting material is consumed.

Thus, the central carbon of the $-C(SiHMe_2)_3$ ligands in the TMEDA adducts are accessible for interaction with Me₃SiI. In

the ytterbium case, TMEDA adduct contained shorter Yb–Si distances and a longer Yb–C distance than the corresponding THF adducts. Furthermore, the lowest energy ν_{SiH} bands were observed with 3·TMEDA in comparison to 2·2THF and 3·2THF. However, 2·TMEDA also gives Si–C bond formation, even through that compound contains distances and spectroscopic features similar to those of the THF adducts.

Reaction of $KC(SiHMe_2)_3$ and $B(C_6F_5)_3$. The bonding interactions between the tris(dimethylsilyl)methyl ligand and calcium(II) or ytterbium(II) have significant polarity. The potassium compound **1** is also highly polar, and its reactions with $B(C_6F_5)_3$ and Me_3SiI were investigated for comparison with the calcium and ytterbium compounds.

 β -Hydrogen abstraction readily occurs in the reaction of B(C₆F₅)₃ and KC(SiHMe₂)₃ to yield the benzene-insoluble pink solid KHB(C₆F₅)₃ (13) and disilacyclobutane {Me₂SiC-(SiHMe₂)₂}₂ (eq 13). The product readily dissolves in THF, and 13 was characterized in that solvent. Resonances at 3.71 and -27.3 ppm (¹J_{BH} = 93 Hz) in the ¹H{¹¹B} and ¹¹B NMR spectra were assigned to the hydrogen bonded to boron and

Scheme 2. β -Hydrogen Elimination and Intermolecular β -Abstraction



the boron center, respectively, and these data are consistent with a hydridoborate moiety. In the IR spectrum, a peak at 2382 cm^{-1} was detected that is similar to the boron–hydrogen stretching frequencies in the calcium and ytterbium hydridoborate compounds described above.

Furthermore, reaction of KHB(C_6F_5)₃ and 2 equiv of TMEDA provides the monomeric species KHB(C_6F_5)₃TMEDA₂ (**13**·2TMEDA). The TMEDA ligand gives solubility to the potassium salt, allowing characterization in benzene- d_6 . The β -SiH abstraction product is evident, as the ¹¹B NMR spectrum revealed a doublet resonance at -24.7 ppm (¹ J_{BH} = 85 Hz), while the hydrogen bonded to boron was assigned to a resonance at 3.46 ppm in the ¹H NMR spectrum. The ν_{BH} band at 2381 cm⁻¹ is almost identical with that of the TMEDA-free **13**. The monomeric nature of **13**·2TMEDA in the solid state has been unambiguously demonstrated by an X-ray crystallographic structure determination (Figure 8).

The K center is coordinated to two *o*-F from the two C_6F_5 rings to form a zwitterionic complex. The structural features of the metal—hydridoperfluorophenylborate interaction to ytterbium, calcium, and potassium are similar in dicationic 7·TMEDA, monoalkyl 5·2THF, and 13·2TMEDA. Thus, the reactivity of B(C_6F_5)₃ and ionic (tris(dimethylsilyl)methyl) metal compounds involves abstraction of β -hydrogen to give the κ^3 -*H*,*F*,*F*-HB(C_6F_5)₃M compounds.

Because the ytterbium compound 3 TMEDA and the lithium alkyl LiC(SiHMe₂)₃ provide silicon–carbon bond formation upon reaction with Me₃Sil or Me₃SiCl,²⁶ respectively, and KC(SiHMe₂)₃ reacts with MI₂ to give M–C bond formations, the reaction of the potassium alkyl and Me₃Sil was investigated. However, the reaction of KC(SiHMe₂)₃ and Me₃Sil gives HSiMe₃ and disilacyclobutane as the soluble products; Me₃Si–C(SiHMe₂)₃ is not formed.

CONCLUSION

The β -hydrogen in the tris(dimethylsilyl)methide ligand influences the reaction pathways in reactions of its organometallic compounds with Lewis acids. Two pathways have been observed: β -hydrogen abstraction and ligand group transfer. The favored pathway depends strongly on the identity of the Lewis acid center, but it is also influenced by ancillary ligands and the metal center(s) involved. Thus, reactions of KC-(SiHMe₂)₃ and MI₂ salts (M = Ca, Yb) result in ligand transfer through salt metathesis. M{C(SiHMe₂)₃}_TMEDA and Me₃SiI give a mixture of alkylation and β -hydrogen abstraction, whereas M{C(SiHMe₂)₃}_THF₂ and Me₃SiI react solely through the β -abstraction pathway. Borane electrophiles, such as B(C₆F₅)₃ and BPh₃, react with the SiH. The alkylation pathways appear most facile when the partners are sterically less hindered (i.e., MI₂ salts), and β -hydrogen abstraction occurs with bulky Lewis acids (i.e., B(C₆F₅)₃). Recently, we have observed a similar effect in the reactions of β -hydrogen containing silazides such as LiN(SiHMe₂)₂ and LiN(SiHMe₂)-*t*-Bu with zirconium halides, where the sterically most hindered reaction partners give zirconium hydride products rather than silazido zirconium species.⁴⁷

There are similarities between these intermolecular abstraction reactions and intramolecular β -elimination: both form metal hydrides, and both result in the expulsion of an unsaturated organic fragment from the metal alkyl. In the current transformations, calcium and ytterbium hydridoborates are the products, and dissociation of B(Aryl)₃ from the M–H– B(Aryl)₃ species would provide a metal hydride, to give final products equivalent with intramolecular β -elimination. Furthermore, it is worth noting that the B(C₆F₅)₃ and BPh₃ Lewis acids provide the needed empty orbital which is apparently not present in the calcium or ytterbium alkyl compounds that would allow intramolecular β -elimination or a bimolecular β -abstraction. Considering these points, this abstraction of a β -hydrogen by an external Lewis acid can also be described as a Lewis acid mediated β -hydrogen elimination (Scheme 2).

Thus, structural models for intermediates in these β -abstraction reactions are important for understanding the reaction pathway. Intramolecular three-center-two-electron interactions between the β -CH bond and metal centers (i.e., β -agostic interactions) are proposed to provide insight into the pathway for β -elimination and its microscopic reverse, olefin insertion. As noted in the Introduction, these abstraction reactions have features similar to those of intramolecular elimination reactions, as they provide metal hydride and unsaturated organic products. Thus, it is interesting to consider the role of the β -agostic interactions in the potassium, calcium, and ytterbium tris(dimethylsilyl)methyl compounds in the intermolecular β -abstraction reaction. The bridging Si–H groups in the dimeric potassium compound {KC(SiHMe₂)₃TMEDA}₂, where a third SiH group approaches a potassium center in a side-on β -agostic type interaction, provides a structural model for an arrested intermolecular β -hydrogen abstraction. The "intramolecular" β -agostic interaction in this structure does not interact with the second potassium center, and this may suggest that the reactions of Lewis acids with the ytterbium and calcium alkyl compounds involve abstraction of the terminal SiH groups, rather than the SiH's involved in side-on coordination. The presence of the intramolecular silicon-hydrogen-calcium close contacts in this structure, however, may be significant, either for increasing the nucleophilicity of the remaining SiH groups or simply serving as a spectroscopic and structural marker that shows significant nucleophilic character of all the SiH groups in these hydrosilylalkyl ligands.

EXPERIMENTAL SECTION

General Procedures. All reactions were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox unless otherwise indicated. Dry, oxygen-free solvents were used throughout. Benzene, toluene, pentane, and tetrahydrofuran were degassed by sparging with nitrogen, filtered through activated alumina columns, and stored under N_2 . Benzene- d_6 , toluene- d_{8} , and THF- d_{8} were vacuum -transferred from Na/K alloy and stored under N₂ in the glovebox. Anhydrous CaI₂ was purchased from Aldrich and used as received. All organic reagents were purchased from Aldrich. Anhydrous $YbI_{2'}^{48}$ B(C₆F₅)₃,⁴⁹ and HC(SiHMe₂)₃^{25a} were prepared as described in literature procedures. We previously reported the following compounds in the Supporting Information of ref 27 in initially communicated work: KC(SiHMe₂)₃ (1), Ca{C- $(SiHMe_2)_3\}_2THF_2$ (2·2THF), Yb{C(SiHMe_2)_3}_2THF_2 (3·2THF), $\label{eq:cac(SiHMe_2)_3[HB(C_6F_5)_3]THF_2} (4.2THF), YbC(SiHMe_2)_3[HB-(C_6F_5)_3]THF_2 (4.2THF), Ca{HB(C_6F_5)_3}_2THF_2 (6.2THF), Yb{HB-$ (C₆F₅)₃}₂THF₂ (7·2THF), and Yb(HBPh₃)₂THF (9·THF). 1,1,3,3-Tetramethyl-2,2,4,4-tetrakis(dimethylsilyl)-1,3-disilacyclobutane was identified by comparison with literature values²⁶ and X-ray crystallography (see the Supporting Information of ref 27b). ¹H, ¹³C{¹H}, ¹¹B, ¹⁹F, and ²⁹Si NMR spectra were collected on Agilent MR-400, Bruker DRX-400, Bruker AVIII 600, and Bruker AVII 700 spectrometers. ¹⁵N chemical shifts were determined by ¹H-¹⁵N HMBC experiments on a Bruker AVII 600 spectrometer with a Bruker Z-gradient inverse TXI ¹H/¹³C/¹⁵N 5 mm cryoprobe. ²⁹Si{¹H} NMR spectra were recorded using DEPT experiments, and assignents were verified by ¹H COESY, ¹H-¹³C HMQC, ¹H-¹³C HMBC, and ¹H-²⁹Si HMBC experiments. UV-vis spectral data were measured on a Shimadzu 3101 PC spectrophotometer. Elemental analysis was performed using a Perkin-Elmer 2400 Series II CHN/S by the Iowa State Chemical Instrumentation Facility.

Computational Details. All electronic structure calculations were performed with the NWChem computational chemistry software suite.⁵⁰ The 6-311++G** basis set was used for H, C, N, O, and Ca.⁵¹ The small-core Stuttgart relativistic effective core potential (RECP) and associated basis set were used for Yb,⁵² and the large-core Stuttgart RECP and associated basis set were used for Si.⁵³ Density functional theory with the B3LYP⁵⁴ functional was used for both the geometry optimizations and the Hessian (frequency) calculations. The vibrational frequencies were calculated with the harmonic oscillator approximation. C_1 and C_2 symmetries were used in the geometry optimization calculations.

HC(SiDMe₂)₃. Lithium aluminum deuteride (1.548 g, 36.88 mmol) was suspended in diethyl ether (50 mL) in a 100 mL Schlenk flask, and the reaction vessel was cooled to 0 °C. A diethyl ether solution (20 mL) of HC(SiBrMe₂)₃ (5.249 g, 12.29 mmol) was added slowly. After the addition, the reaction mixture was stirred at room temperature for 12 h and then heated to reflux for 2.5 h. Saturated ammonium chloride solution (15 mL) was added slowly at 0 °C to quench the reaction mixture. The resulting mixture was filtered to remove insoluble salts. The organic phase was separated, washed with water (2 × 10 mL) and brine (1 × 10 mL), and dried with anhydrous sodium sulfate. Evaporation of diethyl ether provided HC(SiDMe₂)₃ as a spectroscopically pure colorless oil (2.252 g, 11.6 mmol, 94.7%). ²H NMR (CDCl₃, 93.0 MHz, 25 °C): δ 4.15 (br s, SiD).

Tris(dimethylsily!)methylpotassium-d₃. KC(SiDMe₂)₃ (1-d₃). The procedure for the synthesis of KC(SiHMe₂)₃ was followed:²⁷ THF (30 mL) was added to a mixture of HC(SiDMe₂)₃ (1.841 g, 9.51 mmol) and KCH₂Ph (1.239 g, 9.51 mmol) in a 100 mL Schlenk flask. The dark red mixture was stirred at room temperature for 12 h, and all volatile materials were removed under reduced pressure. The resulting reddish brown gummy solid was dissolved in a minimal amount of toluene and cooled to -30 °C to afford KC(SiDMe₂)₃ (1.910 g, 8.25 mmol, 86.7%) as red needles. ²H NMR (benzene-H₆, 93.0 MHz, 25 °C): δ 4.59 (br s, SiD). IR (KBr, cm⁻¹): 1532 (ν_{SiD}), 1417 (ν_{SiD}). **{KC(SiHMe₂)₃TMEDA}₂ ({1-TMEDA}₂).** Excess TMEDA (0.35 mL)

{KC(SiHMe₂)₃TMEDA}₂ ({1·TMEDA}₂). Excess TMEDA (0.35 mL, 2.33 mmol) was added to KC(SiHMe₂)₃ (0.175 g, 0.77 mol) dissolved in benzene. The red mixture was stirred for 30 min at room temperature. The volatiles were evaporated under reduced pressure, and

the resulting gummy solid was extracted with pentane (10 mL). The pentane extract was concentrated and cooled to -30 °C for recrystallization to obtain yellow needles of {KC(SiHMe₂)₃TMEDA}₂ ({1·TMEDA}₂; 0.093 g, 0.271 mmol, 35.2%). ¹H NMR (benzene-*d*₆, 400 MHz, 25 °C): δ 4.80 (m, 3 H, ¹*J*_{SiH} = 154 Hz, SiH), 1.78 (s, 4 H, NCH₂), 1.74 (s, 12 H, NMe₂), 0.52 (d, 18 H, ³*J*_{HH} = 3.5 Hz, SiMe₂). ¹³C{¹H} NMR (benzene-*d*₆, 100 MHz, 25 °C): δ 57.33 (CH₂), 45.68 (NCH₃), 14.69 (KC), 5.33 (SiCH₃). ²⁹Si{¹H} NMR (benzene-*d*₆, 79.5 MHz, 25 °C): δ -23.7 (*Si*HMe₂). IR (KBr, cm⁻¹): 2946 s, 2828 m, 2105 m (ν _{SiH}), 2035 m br (ν _{SiH}), 1962 m (ν _{SiH}), 1580 w, 1469 m, 1361 w, 1296 w, 1250 s, 1154 w, 1000 s br, 895 s, 781 s, 699 w, 665 w. Anal. Calcd for C₁₃H₃₇KSi₃N₂: C, 45.28; H, 10.82; N, 8.12. Found: C, 44.95; H, 11.32; N, 7.28. Mp: 47–53 °C.

{KC(SiDMe₂)₃TMEDA}₂ ({1-d₃·TMEDA}₂). The procedure for {KC(SiHMe₂)₃TMEDA}₂ was followed, using KC(SiDMe₂)₃ (0.168 g, 0.724 mmol) and TMEDA (0.33 mL, 2.18 mmol) to give KC-(SiDMe₂)₃TMEDA (0.144 g, 0.414 mmol, 57.5%). ²H NMR (benzene-H₆, 93.0 MHz, 25 °C): δ 4.83 (br s, SiD). IR (KBr, cm⁻¹): 1533 (ν _{SiD}), 1462 (ν _{SiD}), 1414 (ν _{SiD}).

Ca{C(SiHMe₂)₃}₂TMEDA (2·TMEDA). CaI₂ (0.384 g, 1.31 mmol) and KC(SiHMe₂)₃ (0.598 g, 2.62 mmol) were suspended in benzene (10 mL), and TMEDA (0.39 mL, 2.62 mmol) was added. The mixture was stirred at room temperature for 12 h. Evaporation of the benzene, extraction of the residue with pentane $(2 \times 10 \text{ mL})$, concentration in vacuo, and cooling to -30 °C overnight provided yellow crystals of Ca{C(SiHMe₂)₃}₂TMEDA (2·TMEDA; 0.166 g, 0.310 mmol, 23.7%). Alternatively, 2. TMEDA can be prepared from CaI_2 (0.165 g, 0.562) mmol) and 1 TMEDA (0.388 g, 1.124 mmol) in benzene (10 mL); stirring for 12 h followed by an identical workup gave 51.7% yield (0.156 g, 0.291 mmol). ¹H NMR (benzene- d_{67} 600 MHz, 25 °C): δ 4.81 (m, 3 H, ${}^{1}J_{SiH}$ = 154 Hz, SiHMe₂), 1.80 (s, 12 H, NCH₃), 1.76 (s, 4 H, NCH₂), 0.53 (d, 18 H, ${}^{3}J_{HH}$ = 3.3 Hz, SiCH₃). ${}^{13}C{}^{1}H$ NMR (benzene- d_{6} , 150 MHz, 25 °C): δ 57.3 (NCH₂), 45.7 (NCH₃), 5.34 (¹ J_{SiC} = 47 Hz, SiCH₃), 2.48 (CaC). ²⁹Si{¹H} NMR (benzene- d_{6} , 119.3 MHz, 25 °C): δ –23.6 (SiHMe₂). IR (KBr, cm⁻¹): 2949 s br, 2896 s br, 2828 m, 2105 m br ($\nu_{\rm SiH}$), 2038 m br ($\nu_{\rm SiH}$), 1861 m br $(\nu_{\rm SiH})$, 1599 w, 1468 s, 1297 m, 1249 s, 942 s br, 889 s br, 836 s br, 775 s, 670 s. Anal. Calcd for $C_{20}H_{58}$ Si₆N₂Ca: C, 44.88; H, 10.92; N, 5.23. Found: C, 44.77; H, 10.83; N, 5.23. Mp 138-140 °C.

Ca{C(SiDMe_2)_3}_2THF_2 (2-*d***_6-2THF).** The procedure was similar to that for the preparation of Ca{C(SiHMe_2)_3}_2THF_2,^{27b} using CaI₂ (0.157 g, 0.535 mmol) and KC(SiDMe_2)_3 (0.248 g, 1.07 mmol) to give Ca{C(SiDMe_2)_3}_2THF_2 (0.205 g, 0.360 mmol, 67.4%). ²H NMR (benzene-H₆, 93.0 MHz, 25 °C): δ 4.71 (br s, SiD). IR (KBr, cm⁻¹): 1530 (ν _{SiD}), 1493 (ν _{SiD}), 1409 (ν _{SiD}).

Yb[**C**(**SiDMe**₂)₃]₂**THF**₂ (**3**-*d*₆·**2THF**). The procedure was similar to that for Yb{C(SiHMe₂)₃}₂THF₂.^{27b} using YbI₂ (0.145 g, 0.340 mmol) and KC(SiDMe₂)₃ (0.158 g, 0.680 mmol) to give Yb{C-(SiDMe₂)₃}₂THF₂ (0.163 g, 0.234 mmol, 68.9%). ²H NMR (benzene-H₆, 93.0 MHz, 25 °C): δ 4.77 (br s, SiD). IR (KBr, cm⁻¹): 1506 (ν_{SiD}), 1492 (ν_{SiD}), 1410 (ν_{SiD}).

Ca{C(SiDMe₂)₃}₂TMEDA (2-*d*₆-TMEDA). The procedure was similar to that for Ca{C(SiHMe₂)₃}₂TMEDA using CaI₂ (0.143 g, 0.485 mmol), KC(SiDMe₂)₃ (0.225 g, 0.970 mmol), and TMEDA (0.15 mL, 0.970 mmol) to give Ca{C(SiDMe₂)₃}₂TMEDA (0.232 g, 0.434 mmol, 89.4%). ²H NMR (benzene-H₆, 93.0 MHz, 25 °C): δ 4.71 (br s, SiD). IR (KBr, cm⁻¹): 1510 sh (ν_{SiD}), 1493 (ν_{SiD}), 1411 (ν_{SiD}).

Yb{C(SiHMe₂)₃/₂TMEDA (**3·TMEDA**). A mixture of KC(SiHMe₂)₃ (0.580 g, 2.54 mmol) and YbI₂ (0.542 g, 1.27 mmol) in benzene was allowed to react in the presence of TMEDA (0.38 mL, 2.5 mmol). A workup procedure similar to that described above for **2**·TMEDA provided a deep red pentane extract; crystallization at -30 °C afforded red crystals of Yb{C(SiHMe₂)₃/₂TMEDA (**3**·TMEDA) (0.253 g, 0.379 mmol, 29.8%). **3**·TMEDA can also be prepared from YbI₂ (0.339 g, 0.795 mmol) and **1**·TMEDA (0.548 g, 1.590 mmol) in an improved yield of 70.5% (0.375 g, 0.560 mmol). ¹H NMR (benzene-*d*₆, 600 MHz, 25 °C): δ 4.76 (m, 3 H, ¹*J*_{SiH} = 148 Hz, SiHMe₂), 1.99 (s, 12 H, NMe), 1.72 (s, 4 H, NCH₂), 0.492 (d, 18 H, ³*J*_{HH} = 2.8 Hz, SiMe₂). ¹³C{¹H} NMR (benzene-*d*₆, 150 MHz, 25 °C): δ 57.38 (NCH₂), 47.11 (NMe), 11.94 (YbC), 4.82 (¹*J*_{SiC} = 50 Hz, SiMe₂). ²⁹Si{¹H</sup>

NMR (benzene-*d*₆, 119.3 MHz, 25 °C): δ –17.9 (*Si*HMe₂, *J*_{YbSi} = 9.1 Hz). IR (KBr, cm⁻¹): 2949 s br, 2895 s br, 2843 m, 2802 m, 2080 s br (*ν*_{SiH}), 2038 s br (*ν*_{SiH}), 1846 s br (*ν*_{SiH}), 1584 w, 1468 s, 1248 s, 1029 s, 938 s br, 884 s br, 835 s br, 773 s, 670 s. Anal. Calcd for C₂₀H₅₈ Si₆N₂Yb: C, 35.95; H, 8.75; N, 4.19. Found: C, 35.81; H, 8.74; N, 4.42. Mp 90–95 °C.

Yb{C(SiDMe₂)₃}₂TMEDA (3-*d*₆-**TMEDA).** The procedure was similar to that for Yb{C(SiHMe₂)₃}₂TMEDA using YbI₂ (0.143 g, 0.335 mmol), KC(SiDMe₂)₃ (0.155 g, 0.670 mmol), and TMEDA (0.10 mL, 0.670 mmol) to give Yb{C(SiDMe₂)₃}₂TMEDA (0.164 g, 0.244 mmol, 72.8%). ²H NMR (benzene-H₆, 93.0 MHz, 25 °C): δ 4.79 (br s, SiD). IR (KBr, cm⁻¹): 1505 (ν_{SiD}), 1494 (ν_{SiD}), 1380 (ν_{SiD}).

{Yb[C(SiHMe2)3]2THF}2TMEDA ({3·THF}2TMEDA). Excess THF (0.45 mL, 5.60 mmol) was added to a benzene solution (5 mL) of 3. TMEDA (0.375 g, 0.560 mol) at room temperature. The red mixture was stirred for 30 min. Evaporation of the volatile materials provided a gummy solid of ({3·THF}2TMEDA) (0.381 g, 0.558 mmol, 99.6%). ¹H NMR (benzene- d_{6} , 600 MHz, 25 °C): δ 4.70 (m, 6 H, ¹ J_{SiH} = 148 Hz, SiHMe₂), 3.67 (br s, 4 H, OCH₂CH₂), 1.97 (s, 6 H, NMe), 1.77 (s, 2 H, NCH₂), 1.36 (br s, 4 H, OCH₂CH₂), 0.49 (d, 36 H, ${}^{3}J_{\text{HH}} = 2.1 \text{ Hz}, \text{ SiMe}_{2}$). ${}^{13}\text{C}\{{}^{1}\text{H}\} \text{ NMR} (\text{benzene-}d_{6}, 150 \text{ MHz}, 25 °C)$: δ 69.46 (OCH₂), 57.46 (NCH₂), 46.88 (NMe), 25.68 (OCH₂CH₂), 11.81 (YbC), 4.70 (${}^{1}J_{\text{SiC}} = 50 \text{ Hz}$, SiMe₂). ${}^{29}\text{Si}\{{}^{1}\text{H}\}$ NMR (benzene- d_{67} 119.3 MHz, 25 °C): δ –18.4. IR (KBr, cm⁻¹): 2951 s, 2896 s, 2802 m, 2095 s br (ν_{SiH}), 2039 s br sh (ν_{SiH}), 1850 m br (ν_{SiH}), 1598 w, 1493 m, 1468 w, 1249 s, 1028 s br, 937 s br, 890 s br, 834 s br, 773 s, 670 s. Anal. Calcd for C₂₁H₅₈Si₆NOYb: C, 36.97; H, 8.57; N, 2.05. Found: C, 37.04; H, 9.01; N, 1.95.

CaC(SiHMe₂)₃{HB(C₆F₅)₃}TMEDA (4·TMEDA). Benzene (5 mL) was added to a mixture of $Ca\{C(SiHMe_2)_3\}_2TMEDA$ (0.052 g, 0.097 mmol) and $B(C_6F_5)_3$ (0.050 g, 0.097 mmol). The mixture was stirred for 45 min, and then the volatile components were evaporated under reduced pressure. The yellow solid was washed with pentane $(3 \times 5 \text{ mL})$ and dried under vacuum to yield $CaC(SiHMe_2)_3\{HB(C_6F_5)_3\}$ -TMEDA as a white solid (0.055 g, 0.064 mmol, 65.7%). 1 H NMR (benzene- d_{6} , 600 MHz, 25 °C): δ 4.44 (m, ${}^{1}J_{SiH}$ = 144.9 Hz, 3 H, SiH), 3.00–2.27 (br q, 1 H, HB), 1.70 (br s, 12 H, NMe), 1.51 (br s, 4 H, NCH₂), 0.30 (d, ${}^{3}J_{HH} = 3.4$ Hz, 18 H, SiMe₂). ${}^{1}H{}^{11}B{}$ NMR (benzene- d_{6} , 600 MHz, 25 °C): δ 2.64 (br s, HB) (the other signals were unchanged from coupled ¹H NMR spectrum). ¹³C{¹H} NMR (benzene-d₆, 150 MHz, 25 °C): δ 149.78 (br, C₆F₅), 148.30 (br, C_6F_5), 138.83 (br, C_6F_5), 137.12 (br, C_6F_5), 56.72 (NCH₂), 46.37 (br, NMe), 11.69 (CaC), 2.15 (SiMe₂). ¹¹B NMR (benzene- d_6 , 119.3 MHz, 25 °C): $\delta -21.8$ (d, ${}^{1}J_{BH} = 75.0$ Hz). ${}^{19}F$ NMR (benzene- d_{8} , 376 MHz, 25 °C): δ -134.9 (br, 6 F, o-F), -159.0 (br, 3 F, p-F), -163.2 (6 F, *m*-F). ²⁹Si{¹H} NMR (benzene- d_{6} , 119.3 MHz, 25 °C): δ –18.9. IR (KBr, cm $^{-1}$): 2962 m, 2897 m, 2851 m, 2302 m br ($\nu_{\rm BH}$), 2094 m br (ν_{SiH}), 2026 m br (ν_{SiH}), 1918 m br (ν_{SiH}), 1646 m, 1603 w, 1517 s br, 1467 s br, 1373 m, 1283 s, 1253 m, 1124 s, 1078 s, 1024 m, 965 s br, 835 s, 790 s. Anal. Calcd for BC₃₁F₁₅H₃₈Si₃N₂Ca: C, 43.36; H, 4.46; N, 3.26. Found: C, 43.15; H, 4.38; N, 3.24. Mp: 137-140 °C.

YbC(SiHMe₂)₃{HB(C₆F₅)₃}TMEDA (5·TMEDA). The procedure was similar to that for the calcium analogue 4.TMEDA above, with Yb{C(SiHMe₂)₃}₂TMEDA (0.083 g, 0.124 mmol) and $B(C_6F_5)_3$ (0.063 g, 0.124 mmol) affording 5.TMEDA as a yellow solid (0.075 g, 0.076 mmol, 61.2%). ¹H NMR (benzene- d_6 , 600 MHz, 25 °C): δ 4.51 $(m, {}^{1}J_{SiH} = 147.0 \text{ Hz}, 3 \text{ H}, \text{SiH}), 3.67-2.82 \text{ (br q, 1 H, HB)}, 1.71 \text{ (br s,}$ 12 H, NMe), 1.55 (br s, 4 H, NCH₂), 0.33 (d, ${}^{3}J_{HH}$ = 2.9 Hz, 18 H, SiMe₂). ¹H{¹¹B} NMR (benzene- d_{6} , 600 MHz, 25 °C): δ 3.22 (br s, HB) (all other resonances were identical to the ¹H NMR spectrum). ¹³C{¹H} NMR (benzene- d_{6} , 150 MHz, 25 °C): δ 149.88 (br, C₆F₅), 148.34 (br, C_6F_5), 140.84 (br, C_6F_5), 138.93 (br, C_6F_5), 137.17 (br, C₆F₅), 56.65 (NCH₂), 46.18 (br, NMe), 17.41 (YbC), 2.15 (SiMe₂). ¹¹B NMR (benzene- d_{6} , 119.3 MHz, 25 °C): δ –21.4 (d, ¹ J_{BH} = 71.6 Hz). ¹⁹F NMR (benzene- d_6 , 376 MHz, 25 °C): δ –134.7 (br, 6 F, o-F), -159.3 (br, 3 F, p-F), -163.7 (6 F, m-F). ²⁹Si{¹H} NMR (benzene- d_{6} , 119.3 MHz, 25 °C): δ –18.0. IR (KBr, cm⁻¹): 2961 m, 2895 m, 2849 m, 2293 m br (ν_{BH}), 2094 m br (ν_{SiH}), 2027 m br (ν_{SiH}), 1899 m br (ν_{SiH}), 1645 m, 1602 w, 1516 s, 1466 s br, 1373 m, 1326 vw, 1282 m, 1253 m, 1110 s, 1076 s, 1024 m, 965 s br, 894 s br, 837 s, 789 m. Anal. Calcd for $BC_{31}F_{15}H_{38}Si_3N_2Yb:$ C, 37.54; H, 3.86; N, 2.82. Found: C, 37.59; H, 3.61; N, 2.75. Mp: 120–125 $^\circ C.$

Ca{HB(C_6F_5)₃}₂TMEDA (6·TMEDA). Ca{C(SiHMe₂)₃}₂TMEDA (0.095 g, 0.177 mmol) and B(C₆F₅)₃ (0.190 g, 0.371 mmol) were allowed to react in benzene (5 mL). As the mixture was stirred, a light vellow solid precipitated, and the mixture was stirred for an additional 10 min. The solid was isolated by filtration, washed with benzene (2 \times 4 mL) and pentane (1 \times 4 mL), and dried under reduced pressure to yield Ca{HB(C₆F₅)₃}₂TMEDA as a white solid (0.147 g, 0.124 mmol, 70.3%). ¹H NMR (THF-*d*₈, 600 MHz, 25 °C): δ 4.02–3.33 (br q, 1 H, HB), 2.31 (br s, 4 H, NCH₂), 2.15 (br s, 12 H, NMe). ¹H{¹¹B} NMR (THF- d_8 , 600 MHz, 25 °C): δ 2.64 (br s, HB) (resonances assigned to TMEDA are identical in ¹H and ¹H{¹¹B} NMR spectra). ¹³C{¹H} NMR (THF- d_{8} , 150 MHz, 25 °C): δ 150.05 (br, C_6F_5), 148.47 (br, C_6F_5 , 139.37 (br, C_6F_5), 138.14 (br, C_6F_5), 136.14 (br, C_6F_5), 58.86 (NCH₂), 46.23 (br, NMe). ¹¹B NMR (THF-*d*₈, 119.3 MHz, 25 °C): δ –27.3 (d, ¹J_{BH} = 93.2 Hz). ¹⁹F NMR (THF- d_8 , 376 MHz, 25 °C): δ -136.8 (d, ${}^{3}J_{FF} = 20.4$ Hz, 12 F, o-F), -169.5 (t, ${}^{3}J_{FF} = 17.7$ Hz, 6 F, p-F), -172.1 (t, ${}^{3}J_{FF} = 22.0$ Hz, 12 F, m-F). IR (KBr, cm⁻¹): 2965 m, 2383 m br ($\nu_{\rm BH}$), 1665 m, 1606 m, 1515 s, 1466 s br, 1373 m, 1274 s, 1113 s, 1086 s, 965 s br, 913 m, 828 m, 789 m, 768 m, 685 m, 666 m. Anal. Calcd for B₂C₄₂F₃₀H₁₈N₂Ca: C, 42.67; H, 1.53; N, 2.37. Found: C, 43.09; H, 1.79; N, 2.00. Mp: 205-211 °C.

Yb{HB(C₆F₅)₃}₂TMEDA (7·TMEDA). The procedure was similar to that for 6.TMEDA, using Yb{C(SiHMe₂)₃}₂TMEDA (0.095 g, 0.143) mmol) and $B(C_6F_5)_3$ (0.153 g, 0.299 mmol) to yield Yb(HB- $(C_6F_5)_3)_2$ TMEDA as an off-white solid (0.158 g, 0.120 mmol, 84.1%). ¹H NMR (THF- d_{8} , 600 MHz, 25 °C): δ 4.03–3.32 (br q, 1 H, HB), 2.37 (s, 4 H, NCH₂), 2.19 (s, 12 H, NMe). ${}^{1}H{}^{11}B{}$ NMR (THF- d_{8} , 600 MHz, 25 °C): δ 2.64 (br s, HB) (resonances assigned to TMEDA are identical in ¹H and ¹H $\{^{11}B\}$ NMR spectra). ¹³C $\{^{1}H\}$ NMR (THF- d_{8} , 150 MHz, 25 °C): δ 150.04 (br, C₆F₅), 148.51 (br, C₆F₅), 139.45 (br, C₆F₅), 138.10 (br, C₆F₅), 136.52 (br, C₆F₅), 58.55 (NCH₂), 46.05 (br, NMe). ¹¹B NMR (THF- d_8 , 119.3 MHz, 25 °C): δ –27.3 (d, ¹ J_{BH} = 93.3 Hz). ¹⁹F NMR (THF- d_8 , 376 MHz, 25 °C): δ –136.9 (d, ³ J_{FF} = 20.9 Hz, 12 F, o-F), -169.2 (t, ${}^{3}J_{FF} = 20.2$ Hz, 6 F, p-F), -171.9 (t, ${}^{3}J_{\text{FF}} = 19.1 \text{ Hz}, 12 \text{ F}, m-\text{F}$). IR (KBr, cm⁻¹): 3094 w, 2974 w, 2900 w, 2305 m br ($\nu_{\rm BH}$), 1647 m, 1606 m, 1517 s, 1466 s br, 1374 m, 1281 m, 1123 s br, 1083 s, 957 s, 898 m, 789 m, 769 m, 754 m, 685 m, 673 m. Anal. Calcd for B₂C₄₂F₃₀H₁₈N₂Yb: C, 38.36; H, 1.38; N, 2.13. Found: C, 38.69; H, 1.24; N, 1.94. Mp: 163-170 °C.

Ca(HBPh₃)₂TMEDA (8·TMEDA). Benzene (3 mL) was added to a mixture of Ca{C(SiHMe₂)₃}₂TMEDA (0.077 g, 0.144 mmol) and BPh₃ (0.070 g, 0.290 mmol). The colorless solution mixture was thoroughly mixed and allowed to stand at room temperature for 10 h to yield white crystals. The solution was decanted, and the off-white crystals were washed with benzene (3 mL) and pentane (2 × 3 mL) and dried under vacuum to give 8·TMEDA as a white, crystalline, benzene-insoluble solid (0.060 g, 0.094 mmol, 65.2%). IR (KBr, cm⁻¹): 3056 m, 2998 m, 2059 m (ν_{BH}), 2027 m (ν_{BH}), 2008 m (ν_{BH}), 1943 s (ν_{BH}), 1577 m, 1478 m br, 1428 m, 1284 m, 1168 m br, 1066 m, 1027 m, 788 m, 734 s, 707 vs br. Anal. Calcd for B₂C₄₂H₄₈N₂Ca: C, 78.51; H, 7.53; N, 4.36. Found: C, 77.97; H, 7.90; N, 3.60. Mp: 240–245 °C dec.

Yb(HBPh₃)₂TMEDA (9-TMEDA). The procedure followed that for the calcium analogue 8·TMEDA, using Yb{C(SiHMe₂)₃}₂TMEDA (0.087 g, 0.130 mmol) and BPh₃ (0.063 g, 0.261 mmol) to give 9·TMEDA as a red, insoluble, crystalline solid (0.074 g, 0.095 mmol, 73.2%). IR (KBr, cm⁻¹): 3059 s, 3040 s, 2995 s, 2880 m, 2054 s (ν_{BH}), 2024 s (ν_{BH}), 2006 s (ν_{BH}), 1940 s (ν_{BH}), 1582 m, 1464 s, 1428 s, 1284 w, 1158 s br, 1065 m, 943 s, 786 m, 733 s br, 706 s br. Anal. Calcd for B₂C₄₂H₄₈N₂Yb: C, 65.05; H, 6.24; N, 3.61. Found: C, 64.84; H, 6.04; N, 3.59. Mp: 140–150 °C.

Ca(HBPh₃)₂THF (8·THF). The procedure followed that for the calcium TMEDA adduct 8·TMEDA, with Ca{C(SiHMe₂)₃}₂THF₂ (0.072 g, 0.127 mmol) and BPh₃ (0.062 g, 0.255 mmol) providing 8·THF as a white solid (0.057 g, 0.095 mmol, 74.5%). ¹H NMR (benzene- d_{6} , 600 MHz, 25 °C): δ 7.64 (br, 12 H, *m*-C₆H₅), 7.24 (br, 12 H, *o*-C₆H₅), 7.16 (br, 6 H, *p*-C₆H₅), 3.23 (m, 4 H, CH₂CH₂O), 1.15 (m, br, 4 H, CH₂CH₂O). ¹H{¹¹B} NMR (benzene- d_{6} , 600 MHz, 25 °C): δ 3.18 (br, HB). ¹³C{¹H} NMR (benzene- d_{6} , 150 MHz,

25 °C): δ 155.2 (*ipso*-CH), 139.3 (*m*-CH), *o*-CH and *p*-CH overlapped with C₆D₆, 69.8 (CH₂CH₂O), 25.4 (CH₂CH₂O). ¹¹B NMR (benzened₆, 119.3 MHz, 25 °C): δ –6.0 (br). IR (KBr, cm⁻¹): 3058 m, 2992 m, 2021 m br ($\nu_{\rm BH}$), 1936 m br ($\nu_{\rm BH}$), 1581 m, 1481 m, 1429 m, 1257 w, 1184 m br, 1021 m, 978 m, 880 m br, 737 s, 703 vs Anal. Calcd for B₂C₄₀H₄₀OCa: C, 80.28; H, 6.74. Found: C, 76.09; H, 7.21. Mp: 113–116 °C.

 $KHB(C_6F_5)_3$ (13). Benzene (5 mL) was added to a mixture of KC-(SiHMe₂)₃ (0.107 g, 0.469 mmol) and B(C₆F₅)₃ (0.252 g, 0.492 mmol), and the solution was stirred for 10 min. The orange color quickly faded away, and a pale pink crystalline solid precipitated. The benzene solution was filtered, and the solid was washed with benzene $(2 \times 5 \text{ mL})$ and pentane $(1 \times 4 \text{ mL})$. The volatiles were evaporated under reduced pressure to yield a white solid (0.168 g, 0.303 mmol, 64.7%). ¹H NMR (THF- d_{s} , 600 MHz, 25 °C): δ 4.04–3.38 (br q, 1 H, HB). ¹³C{¹H} NMR (THF-*d*₈, 150 MHz, 25 °C): δ 150.1 (br, C₆F₅), 148.5 (br, C₆F₅), 139.5 (br, C_6F_5), 137.9 (br, C_6F_5), 136.5 (br, C_6F_5). ¹¹B NMR (THF- d_{80} 119.3 MHz, 25 °C): δ –27.3 (d, ${}^{1}J_{\rm BH}$ = 92.5 Hz). 19 F NMR (THF- d_{sv} 376 MHz, 25 °C): δ –136.7 (d, ${}^{3}J_{\rm FF}$ = 21.6 Hz, 6 F, *o*-F), –169.8 (t, ${}^{3}J_{FF} = 20.2$ Hz, 3 F, p-F), -172.3 (t, ${}^{3}J_{FF} = 18.9$ Hz, 6 F, m-F). IR (KBr, $\rm cm^{-1}):~3092$ w, 3037 w, 2964 w, 2819 w, 2586 vw, 2382 s br $(\nu_{\rm BH})$, 2224 vw, 2178 vw, 2132 vw, 2093 vw, 2027 vw, 1644 vs, 1606 m, 1511 vs, 1450 vs, 1407 m, 1324 vw, 1273 vs, 1114 vs, 1086 vs, 1021 m, 945 vs, 914 vs, 886 s, 843 w, 785 m, 769 s, 752 s, 733 w, 720 vw, 666 s. Anal. Calcd for BC18F15HK: C, 39.16; H, 0.18. Found: C, 40.15; H, 0.26. Mp: 290-292 °C dec.

KHB $(C_6F_5)_3$ **TMEDA**₂ (14). KHB $(C_6F_5)_3$ (0.090 g, 0.162 mmol) was suspended in benzene (2 mL), and excess TMEDA (73 mL, 0.486 mmol) was added to yield a clear solution. The mixture was stirred for 10 min, and the volatiles were evaporated under reduced pressure to give KHB(C_6F_5)₃TMEDA₂ as a white solid (0.125 g, 0.159 mmol, 98.1%). X-ray-quality crystals can be grown from a toluene solution of KHB(C_6F_5)₃TMEDA₂ at -30 °C for 3 days. ¹H NMR (benzene- d_{60} 600 MHz, 25 °C): δ 3.84–3.08 (br q, 1 H, HB), 1.90 (s, 8 H, NCH₂), 1.82 (s, 24 H, NCH₃). ¹³C{¹H} NMR (benzene-*d*₆, 150 MHz, 25 °C): δ 150.0 (br, C₆F₅), 148.5 (br, C₆F₅), 140.1 (br, C₆F₅), 138.5 (br, C_6F_5), 136.9 (br, C_6F_5), 57.5 (NCH₂), 45.4 (NMe). ¹¹B NMR (benzene- d_6 , 119.3 MHz, 25 °C): δ -24.7 (d, ${}^1J_{BH}$ = 83.1 Hz). ${}^{19}F$ NMR (benzene- d_6 , 376 MHz, 25 °C): δ –135.9 (d, ${}^{3}J_{FF}$ = 21.8 Hz, 6 F, o-F), -163.2 (t, ${}^{3}J_{FF} = 20.6$ Hz, 3 F, p-F), -170.0 (t, ${}^{3}J_{FF} =$ 21.8 Hz, 6 F, *m*-F). IR (KBr, cm⁻¹): 2948 m, 2872 m, 2832 m, 2792 m, 2712 m, 2381 m br ($\nu_{\rm BH}$), 1643 m, 1514 s, 1461 s, 1364 m, 1297 m, 1278 m, 1099 s, 969 s, 907 m, 782 m, 764 m. Calcd for BC₃₀F₁₅H₃₃K: C, 45.93; H, 4.24; N, 7.14. Found: C, 46.02; H, 3.84; N, 6.87. Mp: 90-92 °C.

ASSOCIATED CONTENT

Supporting Information

CIF files giving X-ray crystallographic data for the compounds $\{KC(SiHMe_2)_3TMEDA\}_2$ ($\{1\cdotTMEDA\}_2$), $Yb\{C(SiHMe_2)_3\}_2$ -TMEDA ($3\cdotTMEDA$), $CaC(SiHMe_2)_3\{HB(C_6F_5)_3\}THF_2$ ($4\cdot2THF$), 27b Yb{ κ^3 -HB(C_6F_5)_3\}_2THF_2 ($7\cdot2THF$), Yb{ κ^3 -HB-(C_6F_5)_3\}_2TMEDA ($7\cdotTMEDA$), Yb(HBPh_3)_2TMEDA ($9\cdotTMEDA$), Yb(HBPh_3)_2THF ($9\cdotTHF$), and KHB(C_6F_5)_3-TMEDA₂ ($13\cdot2TMEDA$) and tables giving initial and optimized geometries and minimized total energies of Ca(C(SiHMe_2)_3)_2THF_2 and Yb(C(SiHMe_2)_3)_2THF_2. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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