

Lewis Acid-Mediated β -Hydride Abstraction Reactions of Divalent $M(C(SiHMe_2)_3)_2THF_2$ ($M = Ca, Yb$)

KaKing Yan, Brianna M. Upton, Arkady Ellern, and Aaron D. Sadow*

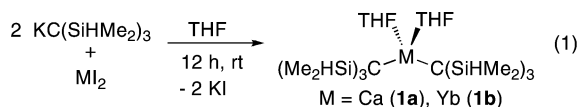
Department of Chemistry and U.S. Department of Energy Ames Laboratory, Iowa State University, Ames, Iowa 50011-3111

Received August 21, 2009; E-mail: sadow@iastate.edu

Transition-metal alkyl compounds containing β -hydrogen and at least one empty orbital in an open cis coordination site are susceptible to elimination. These general rules also apply to elimination reactions in main-group and rare-earth organometallics. While β -eliminations of alkylolithiums tend to require forcing conditions (130–150 °C in hydrocarbon solvent), the heavier congeners react more rapidly.¹ Dialkylmagnesium compounds containing β -hydrogen eliminate olefin upon thermolysis, but very little is known about eliminations of the heavier analogues.² Likewise, coordinatively unsaturated organolanthanides react via β -elimination.³ For example, isobutylene extrusion from $Cp_2ErCMe_3(THF)$ is facilitated by the addition of LiCl, presumably to open a coordination site,^{3c} whereas the lutetium analogue decomposes at 70–80 °C.^{3c} The bridged dimers $[Cp^*OArLu]_2(\mu-H)(\mu-CH_2CH_2R)$ are coordinatively saturated and robust toward elimination.^{3g} Importantly, unsaturated organolanthanides are highly reactive, even mediating C–C bond cleavage through β -Me eliminations.^{3d,f}

In contrast, the tris(alkyl)yttrium compound $Y(C(SiHMe_2)_3)_3$ does not undergo β -elimination, even though it is (at least formally) low-coordinate, contains nine β -SiH groups, and forms labile agostic interactions.⁴ β -Eliminations, as well as other reactivity, might be inhibited by the three large $C(SiHMe_2)_3$ ligands around the Y(III) center (ionic radius 0.9 Å).⁵ To test this idea, we prepared tris(dimethylsilyl)methyl calcium(II) and ytterbium(II) compounds (1.00 and 1.02 Å radii, respectively)⁵ that might be more reactive.

The desired dialkyl compounds $M(C(SiHMe_2)_3)_2THF_2$ [**1**; $M = Ca$ (**1a**), Yb (**1b**)] were prepared in THF from MI_2 and 2 equiv of $KC(SiHMe_2)_3$ ⁴ according to eq 1:



Compounds **1a** and **1b** are essentially isostructural (see Figure 1 for an ORTEP diagram and key structural data for **1b**). The most important structural features are consistent with β -agostic SiH interactions, including short M–Si distances [Ca–Si(2), 3.216(2) Å], small M–C–Si angles [Ca, 90.7(3)°], short M–H distances [Ca–H2s, 2.53(6) Å], and planar M–C–Si–H four-membered rings (the Ca1–C7–Si2–H2s torsion angle is 2.79°). The M–C distances, however, are long [Ca–C7, 2.616(7) Å]. For comparison, the Ca–C bond distances in $Ca(CH(SiMe_3)_2)_2(\text{dioxane})_2$ and $Ca(C(SiMe_3)_2)_2$ are much shorter [2.373(4) and 2.459(9) Å, respectively].^{6,7} Also, the Yb–C distances in the compound $Yb(C(SiMe_3)_3)_2$ [2.490(8) and 2.501(9) Å]⁸ are shorter by ~0.1 Å than those in **1b**.

Three bands assigned to ν_{SiH} in the IR spectra are consistent with three inequivalent SiH groups distinguished by crystallography, including the β -agostic SiH structure (Ca, 1905 cm^{-1} ; Yb, 1890 cm^{-1} ; KBr). The $SiHMe_2$ groups appear to be equivalent as a result of rapid exchange on the 1H NMR time scale, even at 185 K (in toluene- d_8).

Essentially, the IR spectra and structural data suggest that **1a** and **1b** access the configuration required for β -elimination. Additionally, the IR and variable-temperature NMR spectra and the NMR coupling constants suggest that the agostic interactions in **1a** and **1b** are weaker than in $Y(C(SiHMe_2)_3)_3$ (less ground-state stabilization),^{3h} and thus, we expected β -elimination to be more facile.

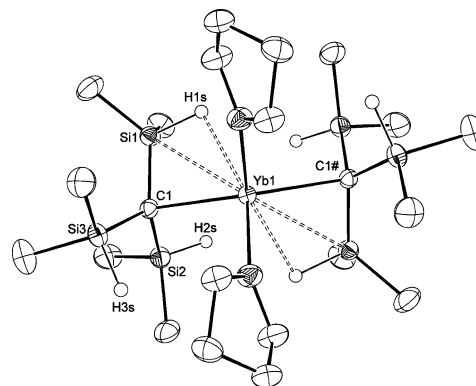
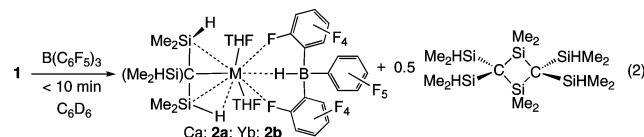


Figure 1. ORTEP diagram of $Yb(C(SiHMe_2)_3)_2THF_2$ (**1b**). Dashed bonds illustrate short Yb1–Si1 and Yb1–H1s distances. Distances (Å): Yb–C1, 2.596(4); Yb–Si1, 3.181(2); Yb–H1s, 2.50(3). Bond angles (deg): Yb–C1–Si1, 90.6(2); C1–Yb–C1, 131.5(2). Torsion angles (deg): Yb1–C1–Si2–H2s, –46.93; Yb1–C1–Si3–H3s, –59.18°.

However, **1a** and **1b** are unchanged after weeks in solution at room temperature under an inert atmosphere. Extended thermolysis (**1a**, >120 h; **1b**, 96 h; 393 K in benzene- d_6) formed $HC(SiHMe_2)_3$ quantitatively (1H NMR spectroscopy); the β -elimination product disilacyclobutane (see below) was not detected. Because **1a** and **1b** possess structural and electronic features consistent with β -elimination but lack that reactivity, we searched for conditions to facilitate eliminations. Cationic species could be more likely to undergo β -elimination, given their enhanced reactivity for insertion (the microscopic reverse of β -elimination).⁹

Alkyl group abstraction by strong Lewis acids is a well-known route to cationic d^0 metal alkyl compounds.^{9c} Reactions of $B(C_6F_5)_3$ and **1a** or **1b** in benzene- d_6 produced a disilacyclobutane (eq 2) previously obtained from $(THF)_2LiC(SiHMe_2)_3$ and $SiCl_4$.¹⁰



The disilacyclobutane is a head-to-tail dimer of the silene $Me_2Si=C(SiHMe_2)_2$, suggesting β -elimination. However, the other products are not consistent with that pathway. The organometallic product shown in eq 2 [$M = Ca$ (**2a**), Yb (**2b**)] contains a $-C(Si-$

HMe₂)₃ ligand and HB(C₆F₅)₃ counterion, revealing that the silene is formed through borane-mediated β -H abstraction rather than β -hydride elimination from a cationic (or zwitterionic) intermediate. SiH abstraction from silanes by strong Lewis acids is known to provide reactive silyl cations,^{11,12} and the selectivity for SiH abstraction rather than carbanion abstraction to give [(Me₂HSi)₃CB(C₆F₅)₃]⁺ may result from steric hindrance.¹³ In contrast, no interaction between HC(SiHMe₂)₃ and B(C₆F₅)₃ could be detected at room temperature in benzene-*d*₆. Likewise, Zn(C(SiHMe₂)₃)₂ and B(C₆F₅)₃ do not react at 65 °C in benzene-*d*₆ over 1 day.

The different ν_{BH} of **2** (**a**, 2329 cm⁻¹; **b**, 2308 cm⁻¹) in the IR spectra suggest a M...HB interaction. For comparison, ν_{BH} in [Cp*₂ZrH][HB(C₆F₅)₃] is 2364 cm⁻¹.¹⁴ Three (**2a**) and two (**2b**) bands are attributed to ν_{SiH} (2077, 2042, and 1957 cm⁻¹ in **2a**; 2074 and 1921 cm⁻¹ in **2b**).

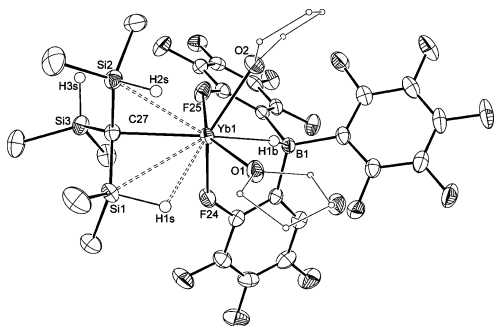
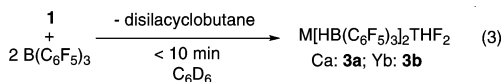


Figure 2. ORTEP diagram of YbC(SiHMe₂)₃THF₂(μ -H)(μ -F-C₆F₄)₂BC₆F₅ (**2b**). THF is drawn using the ball-and-stick representation for clarity. Dashed bonds represent close contacts between Yb and Si or H. Distances (Å): Yb1–C27, 2.593(2); Yb1–Si1, 3.1016(7); Yb1–Si2, 3.0925(7). Angles (deg): Yb1–C27–Si1, 87.42(9); Yb1–C27–Si2, 87.22(9).

The Yb–C bond distances in neutral **1b** and zwitterionic **2b** (Figure 2) are identical within error. In contrast, the Yb–Si distances are shorter in **2b** than in **1b** by 0.08–0.09 Å. As in **1**, only one SiH is oriented directly toward the metal center [Yb1–H1s, 2.41(3) Å; Yb1–C27–Si1–H1s, 0.84°], while the Yb1...H2s distance is longer [2.60(3) Å, Yb1–C27–Si2–H2s, 35.10°]. Regardless, the short Yb–Si distances and small Yb–C–Si angles strongly suggest bonding interactions. Calculation of the solid angles,¹⁵ which describe the percentage of space occupied by ligands around a metal center, show that 20% of the space surrounding the Yb center is open. Thus, interligand steric interactions are not responsible for the short Yb...Si distances.

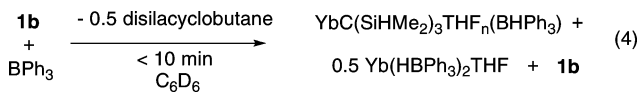
Thermolysis of **2b** (353 K, benzene-*d*₆, 5 days) provided a 4:3 mixture of HC(SiHMe₂)₃ and disilacyclobutane. The metal-containing product could not be identified. Disilacyclobutane again suggests β -elimination; however, we considered a second possible mechanism involving B(C₆F₅)₃ dissociation from **2b** followed by hydride abstraction from another SiH. This pathway was tested by the reaction of 2 equiv of B(C₆F₅)₃ and **1**, which provided M(HB(C₆F₅)₃)₂THF₂ (**3**) and 1 equiv of disilacyclobutane (eq 3):



This experiment clearly shows that B(C₆F₅)₃-mediated H abstraction from zwitterionic **2** is feasible. The product **3** contains two HB(C₆F₅)₃ ligands coordinated in the same κ^3 -H,*F*,*F*-tridentate fashion [see the Supporting Information (SI)].

The SiH groups in **1** and **2** have sufficient hydride character to react with the strong Lewis acid B(C₆F₅)₃. They are also sufficiently

hydridic to react with the much weaker Lewis acid BPh₃. Interestingly, reaction of BPh₃ and **1b** gave a mixture of Yb(C(SiHMe₂)₃)(HBPh₃)(THF)_n (**4**), Yb(HBPh₃)₂THF (**5**), and starting dialkyl **1b** in addition to disilacyclobutane (eq 4):



Reaction of 2 equiv of BPh₃ and **1b** gave **5** and disilacyclobutane (see the SI).

The SiH groups in **1** and **2** are clearly hydridic on the basis of their reactions with Lewis acids. Compounds **1** and **2** contain open coordination sites on Lewis acidic metal centers and accessible β -hydrogens that form agostic interactions. However, these alkyls are clearly deactivated against β -elimination. Most likely, the M...Si interactions and delocalization of charge on the C(SiHMe₂)₃ ligand, as evidenced by X-ray structures and IR spectroscopy, increase the barrier to β -hydride elimination with respect to other pathways.

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Supporting Information Available: Experimental section and X-ray crystallographic data for **1a**, **1b**, **2a**, **2b**, **3a**, **5**, and the 1,3-disilacyclobutane (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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