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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*

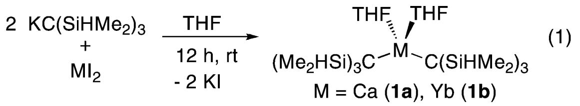
Department of Chemistry and U.S. Department of Energy Ames Laboratory, Iowa State University, Ames, Iowa 50011-3111

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 alkyllithiums 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 faciliated by the addition of LiCl, presumably to open a coordination site,[3e] whereas the lutetium analogue decomposes at 70−80 °C.[3c] The bridged dimers $[Cp^*OArLu]_2(\mu\text{-}H)(\mu\text{-}CH_2CH_2R)$ 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:



$$2\ KC(SiHMe_2)_3 + MI_2 \xrightarrow[12\text{ h, rt}\ -2\ KI]{THF} (Me_2HSi)_3C{-}M(THF)_2{-}C(SiHMe_2)_3 \qquad (1)$$

M = Ca (**1a**), Yb (**1b**)

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 $Ca(CH(SiMe_3)_2)_2(dioxane)_2$ 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.

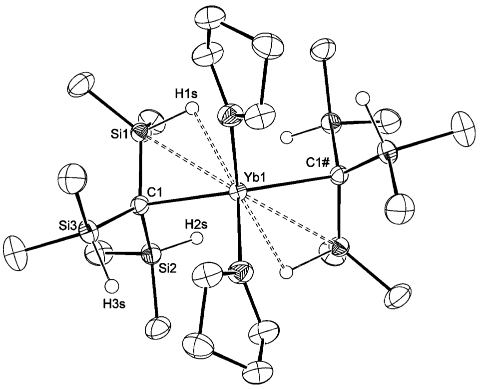
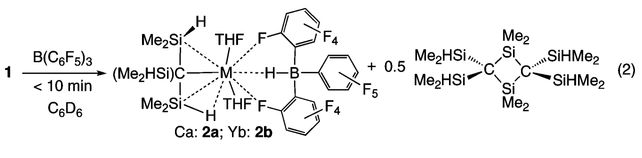


Figure 1. ORTEP diagram of $Yb(C(SiHMe_2)_3)_2THF_2$ (**1b**). Dashed bonds illustrate short Yb1−Si1 and Yb1−H1s distances. Distances (Å): Yb−C1, 2.596(4); Yb−Si1, 3.181(2); Yb−H1s, 2.50(3). Bond angles (deg): Yb−C1−Si1, 90.6(2); C1−Yb−C1, 131.5(2). Torsion angles (deg): Yb1−C1−Si2−H2s, −46.93; Yb1−C1−Si3−H3s,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

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$HMe_2)_3$ ligand and $HB(C_6F_5)_3$ 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 $[(Me_2HSi)_3CB(C_6F_5)_3]^-$ may result from steric hindrance.[13] In contrast, no interaction between $HC(SiHMe_2)_3$ and $B(C_6F_5)_3$ could be detected at room temperature in benzene-d_6. Likewise, $Zn(C(SiHMe_2)_3)_2$ and $B(C_6F_5)_3$ 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 $[Cp^*{}_2ZrH][HB(C_6F_5)_3]$ 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**).

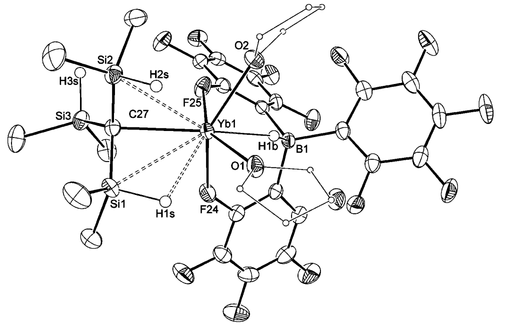

Figure 2. ORTEP diagram of $YbC(SiHMe_2)_3THF_2(\mu\text{-}H)(\mu\text{-}F\text{-}C_6F_4)_2BC_6F_5$ (**2b**). THF is drawn using the ball-and-stick representation for clarity. Dashed bonds represent close contacts between Yb and Si or H. Distances (Å): Yb1−C27, 2.593(2); Yb1−Si1, 3.1016(7); Yb1−Si2, 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 $HC(SiHMe_2)_3$ and disilacyclobutane. The metal-containing product could not be identified. Disilacyclobutane again suggests β-elimination; however, we considered a second possible mechanism involving $B(C_6F_5)_3$ dissociation from **2b** followed by hydride abstraction from another SiH. This pathway was tested by the reaction of 2 equiv of $B(C_6F_5)_3$ and **1**, which provided $M(HB(C_6F_5)_3)_2THF_2$ (**3**) and 1 equiv of disilacyclobutane (eq 3):

$$\begin{matrix}\mathbf{1}\\ +\\ 2\,B(C_6F_5)_3\end{matrix} \xrightarrow[\substack{<10\text{ min}\\ C_6D_6}]{-\text{ disilacyclobutane}} \begin{matrix}M[HB(C_6F_5)_3]_2THF_2\\ \text{Ca: }\mathbf{3a}\text{; Yb: }\mathbf{3b}\end{matrix} \qquad (3)$$

This experiment clearly shows that $B(C_6F_5)_3$-mediated H abstraction from zwitterionic **2** is feasible. The product **3** contains two $HB(C_6F_5)_3$ 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 $B(C_6F_5)_3$. They are also sufficiently hydridic to react with the much weaker Lewis acid BPh_3. Interestingly, reaction of BPh_3 and **1b** gave a mixture of $Yb(C(SiHMe_2)_3)(HBPh_3)(THF)_n$ (**4**), $Yb(HBPh_3)_2THF$ (**5**), and starting dialkyl **1b** in addition to silacyclobutane (eq 4):

$$\begin{matrix}\mathbf{1b}\\ +\\ BPh_3\end{matrix} \xrightarrow[\substack{<10\text{ min}\\ C_6D_6}]{-\ 0.5\text{ disilacyclobutane}} \begin{matrix}YbC(SiHMe_2)_3THF_n(BHPh_3)\ +\\ 0.5\ Yb(HBPh_3)_2THF\ +\ \mathbf{1b}\end{matrix} \qquad (4)$$

Reaction of 2 equiv of BPh_3 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 $C(SiHMe_2)_3$ 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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