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Homoleptic Divalent Dialkyl Lanthanide-Catalyzed Cross-Dehydrocoupling of Silanes and Amines

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Supporting Information

ABSTRACT: The rare-earth bis(alkyl) compound Sm{(C(SiHMe2)3)2}THF2 (1b) is prepared by the reaction of samarium(II) iodide and 2 equiv of KC(SiHMe2)3. This synthesis is similar to that of previously reported Yb{(C(SiHMe2)3)2}THF2 (1a), and compounds 1a,b are isostructural. Reactions of 1b and 1 or 2 equiv of B(C6F5)3 afford SmC{(SiHMe2)3}HB{(C6F5)3}THF2 (2b) or Sm{(HB{(C6F5)3})2}THF2 (3b), respectively, and 1,3-disilacyclobutane \( \{Me_2Si-C(SiHMe2)2\}\) as a byproduct. Bands from 2300 to 2400 cm\(^{-1}\) assigned to \( \nu_{BH} \) in the IR spectra and highly paramagnetically shifted signals in the \(^{11}B\) NMR spectra of 2b and 3b provided evidence for Sm-coordinated HB{(C6F5)3}. Compounds 1a,b react with the bulky N-heterocyclic carbene (NHC) 1,3-di-tert-butylimidazol-2-ylidene (ImBu) to displace both THF ligands and give three-coordinate monoadducts Ln{(C(SiHMe2)3)ImBu} (Ln = Yb (4a), Sm (4b)). Complexes 4a,b catalyze cross-dehydrocoupling of organosilanes with primary and secondary amines at room temperature to give silazanes and \( H_2 \). whereas 1a,b are not effective catalysts under these conditions. Second-order plots of \( ln([Et_2NH]/[Ph_2SiH_2]) \) vs time for 4a-catalyzed dehydrocoupling are linear and indicate first-order dependence on the silane and amine concentrations. However, changes in the experimental rate law with increased silane concentration or decreased amine concentration reveal inhibition by silane. In addition, excess ImBu or THF inhibit the reaction rate. These data, along with the structures of 4a,b, suggest that the bulky carbene favors low coordination numbers, which is important for accessing the catalytically active species.

INTRODUCTION

Rare-earth-element–carbon bonds react via insertion, \( \sigma \)-bond metathesis, and protonolytic ligand substitution reactions that are important elementary steps in catalytic processes, including olefin polymerization,\(^1\) hydrosilylation,\(^2\) and dehydrocoupling.\(^3\) Trivalent rare-earth alkyls are typical catalysts for these processes, whereas fewer catalytic processes involve divalent rare-earth alkyl compounds.\(^4\) In the few catalytic chemistries involving divalent lanthanides, the metal center is typically a precataltyst that is activated by a one-electron oxidation: for example, in the initiation of acrylate polymerizations.\(^4b,5\) Moreover, while homoleptic tris(alkyl) lanthanide compounds are useful and versatile starting materials for rare-earth organometallic chemistry,\(^6\) fewer homoleptic bis(alkyl) ytterbium(II),\(^7\) europium(II),\(^8\) and samarium(II)\(^4d,9\) compounds are known. Note that, in this series of aqueous lanthanide ions, samarium(II) is the most reducing (−1.55 V vs NHE) followed by ytterbium(II) (−1.15 V) and europium(II) (−0.35 V).\(^10\)

We recently synthesized homoleptic bis(alkyl) ytterbium(II) species Yb{(C(SiHMe2)3)L2 (L2 = THF2, TMEDA), investigated their nonclassical M=H–Si-containing structures, and studied the reactivity of \( \beta \)-SiH groups with electrophiles.\(^11\) Because only a few divalent bis(alkyl) lanthanide compounds have been employed in catalytic processes, we decided to investigate Ln{(C(SiHMe2)3)L2}THF2 (Ln = Yb, Sm) as catalysts for the dehydrocoupling of organosilanes and amines. In this reaction’s initiation, Ln{(C(SiHMe2)3)L2} could undergo protonolysis to give a rare-earth amide. During the cycle, amide transfer to an organosilane through a \( \sigma \)-bond metathesis-like step would provide the silazane product and a rare-earth hydride. Protonolysis of this species would re-form the amide. These steps might be facile with divalent bis(alkyl) rare-earth compounds, or their zwitterionic monoalkyl derivatives, as precatalysts and not require oxidation to initiate the process. This dehydrocoupling pathway, initiated by Sm(II) alkyls, would be in contrast with the aforementioned polymerization initiation as well as the Cp*SmTHF2-catalyzed hydroamination/cyclization of aminoalkenes, which is proposed to first form a samarium(III) amide.\(^14\)

Catalytic cross-dehydrocoupling of silanes with amines is an excellent method for silazane preparation because hydrogen gas is the only byproduct, the degree of amine silylation or silane amination can, in principle, be controlled by the catalyst, and stoichiometric salt byproducts are not formed as is the case in halosilane amination. Silazanes are used extensively as bases,\(^15\) ligands,\(^16\) and silylating agents,\(^17\) including as protecting groups...
in synthesis, F-element, yttrium, and group 2 complexes, along with Lewis acids and Lewis bases, catalyze SiH/NH cross-coupling. In SiH/NH dehydrocoupling reactions catalyzed by bis(disilazido)ytterbium(II) compounds, Cui and coworkers observed that an N-heterocyclic carbene (NHC) ligand is required for efficient conversion. The rate of cross-dehydrocoupling of organosilanes and amines catalyzed by bis(disilazido) ytterbium(II) compounds, Cui and co-workers observed that an N-heterocyclic carbene (NHC) ligand is required for efficient conversion.

Despite the reactivity of carbene-coordinated rare-earth complexes and the importance of NHC ligands in transition-metal-catalyzed processes, the catalytic chemistry of carbene-coordinated rare-earth alkyl compounds is underdeveloped. This limitation in the divalent series may be related to the few available starting organolanthanide(II) materials. In terms of homoleptic rare-earth alkyls, the series of trivalent complexes have been crystallographically characterized. These include the divalent metalloligand adduct C₉⁵-Sm-ImMes₂ (ImMes = 1,3,4,5-tetramethylimidazol-2-ylidene), in which two THF groups from Cp and Sm(ImMe₄) are replaced with C₈H₁₈ (2.64(1) Å) and (C₅Me₅)SmCH(SiMe₃)₂ (2.58 Å) and (C₅Me₅)KTHF₂ (2.64(1) Å), but shorter than in Sm(C(SiMe₃)₂(SiMe₃OMe))₂THF (2.787(5) and 2.845(5) Å). These examples are the only three crystallographically characterized dialkyl samarium(II) compounds found in the Cambridge Structural Database. The second notable feature of 1b is the conformation of C(SiHMe₃)₂ ligands, which each contains one nonclassical Sm–H–Si interaction, giving short Sm–H 1.12 ppm (36 H, 32 Hz at half-height) for the corresponding distance in 1a, as expected on the basis of the larger ionic radii of 7-coordinate Sm²⁺ (1.22 Å) than 7-coordinate Yb²⁺ (1.08 Å). The Sm–C₁ interatomic distance is significantly longer than those in related Sm(II) alkyl compounds, including Sm(C(SiMe₃)₂)₂KTHF₂ (2.58 Å) and (C₅Me₅)SmCH(SiMe₃)₂ (µ-C₅Me₅)KTHF₂ (2.64(1) Å), but shorter than in Sm(C(SiMe₃)₂(SiMe₃OMe))₂THF (2.787(5) and 2.845(5) Å). These examples are the only three crystallographically characterized dialkyl samarium(II) compounds found in the Cambridge Structural Database.

RESULTS AND DISCUSSION

Synthesis of Sm(C(SiHMe₃)₂)₂THF₂. The homoleptic bis(alkyl)samarium compound Sm(C(SiHMe₃)₂)₂THF₂ (1b) is synthesized by the reaction of Sm₂THF₂ and 2 equiv of KC(SiHMe₃)₂, which proceeds in THF over 12 h at room temperature. The solution changes color from blue-green to dark green upon mixing and then to black after 1 h. The diamagnetic isostructural analogues Yb(C(SiHMe₃)₂)₂THF₂ (1a) and Ca(C(SiHMe₃)₂)₂THF₂ (1c) were previously synthesized under similar conditions, but the synthesis of those diamagnetic compounds does not show the dramatic color changes observed for samarium. Sm(C(SiHMe₃)₂)₂THF₂ is isolated as black blocks by crystallization from pentane at −40 °C.

The ²³⁷H NMR spectrum of 1b (all NMR spectra reported were acquired in benzene-d₆ at room temperature unless otherwise specified) contained signals assigned on the basis of their relative integrated ratio, chemical shifts, and line widths. The last two properties are influenced by the nuclei’s interaction with the paramagnetic center. The highly upfield, broad resonance at −66.5 ppm (6 H, 342 Hz at half-height) and the sharp singlet at −1.12 ppm (36 H, 32 Hz at half-height) were assigned to the C(SiHMe₃)₂ ligand. The remaining signals at 11.9 and 2.78 ppm were assigned to THF. The ¹H NMR spectrum of 1b was unchanged after its benzene-d₆ solution was heated at 80 °C for 80 h. The ¹H NMR spectra acquired either through direct or indirect experiments did not contain signals, likely the result of the paramagnetic Sm(II) center.

The single-crystal X-ray diffraction study confirms this idea, showing that the Sm center in 1b adopts a distorted-pseudotetrahedral geometry based on C1/C1# and O1/O1# coordination (Figure 1). The c=01–Sm1–O1# angle of 89.24(7)° is acute, while the c=01–Sm1–C1# angle is larger at 133.96(7)°. The Sm1–C₁ interatomic distance of 2.73(3) Å is ca. 0.14 Å longer than the corresponding distance in 1a, as expected on the basis of the larger ionic radii of 7-coordinate Sm²⁺ (1.22 Å) than 7-coordinate Yb²⁺ (1.08 Å).

The Sm1–C₁ interatomic distance is significantly longer than those in related Sm(II) alkyl compounds, including Sm(C(SiMe₃)₂)₂KTHF₂ (2.58 Å) and (C₅Me₅)SmCH(SiMe₃)₂(µ-C₅Me₅)KTHF₂ (2.64(1) Å), but shorter than in Sm(C(SiMe₃)₂(SiMe₃OMe))₂THF (2.787(5) and 2.845(5) Å). These examples are the only three crystallographically characterized dialkyl samarium(II) compounds found in the Cambridge Structural Database.
stretching modes, while no bands were detected in the region associated with Si–H stretching modes (2100–1800 cm⁻¹).

Direct comparisons of samarium and ytterbium structures by NMR are complicated by paramagnetic effects. Nonetheless, signals in the ¹¹B and ¹³F NMR spectra of 2b and 3b indicate that tris(perfluorophenyl)hydridoborate groups are closely associated with the samarium center. The ¹¹B NMR spectra acquired in bromobenzene-d₄ for 2b and 3b contained paramagnetically shifted broad signals at −88 and −100 ppm, respectively, whereas ¹¹B NMR signals for diamagnetic ytterbium analogues appeared at −20.8 (2a) and −26.4 ppm (3a). Only two signals were observed in the ¹³F NMR spectrum in the ratio of 1:2, assigned to the para and meta fluorines on C₆F₅ groups for compounds 2b and 3b, in comparison to the spectra for the Yb analogues that revealed three fluoride signals.¹¹,a

Reaction with 1,3-Di-tert-butylimidazol-2-ylidene (ImBu). Compounds 1a,b and 1 equiv of 1,3-di-tert-butylimidazol-2-ylidene (ImBu) react almost instantaneously at room temperature in benzene or pentane to displace the THF ligands, affording Ln(C(SiHMe₂)₃)₂ImBu (Ln = Yb (4a), Sm (4b)) quantitatively during in situ reactions (Scheme 2). Recrystallization from pentane at −40 °C affords red crystals of Yb(C(SiHMe₂)₃)₂ImBu (4a) or dark red crystals of Sm(C(SiHMe₂)₃)₂ImBu (4b) in moderate isolated yield.

Scheme 2. Reactions of Ytterbium and Samarium Dialkyls with ImBu

The ¹H NMR spectrum of diamagnetic 4a contained a doublet at 0.45 ppm (JHH = 3.6 Hz, 36 H) and a septet at 4.86 ppm with silicon satellites (JSSF = 144 Hz, 6 H) assigned to the SiHMe₂ moiety, as well as singlets at 1.43 and 6.33 ppm assigned to the coordinated ImBu ligand. These signals remained sharp even in spectra acquired at low temperature (∼200 K) in toluene-d₈. In the ¹³C(¹H) NMR spectrum, a signal at 196.9 ppm for the carbene carbon appeared with a chemical shift similar to that for other lanthanide tris(alkyl) carbene adducts.¹⁶,²⁷ Neither ¹⁵N NMR signals of ImBu nor the ²⁹Si NMR of the SiHMe₂ moieties are changed significantly in 4a in comparison with starting materials.

The SiH regions of the infrared spectra for 4a and 4b were distinct from each other as well as from those of 1a,b. In 4a, a broad signal at 2058 cm⁻¹ was poorly resolved from bands at 2083 and 2114 cm⁻¹, with one low-energy band at 1871 cm⁻¹. In contrast, the spectrum of the samarium analogue contained sharper signals at 2108, 2076, 2064, and 2044 cm⁻¹ as well as two lower energy bands at 1910 and 1796 cm⁻¹. Note that the IR spectra of 1a,b (described above) only contained three νSSF bands, suggesting that compounds 1 and 4 have inequivalent conformations. This idea is supported by single-crystal X-ray diffraction analysis.

X-ray-quality crystals are not yet available for zwitterionic compounds 2b and 3b. The infrared spectra (KBr) of analytically pure 2b, easily isolated after pentane washes, showed bands at 2389, 2306, and 2110 cm⁻¹. In contrast, the IR spectrum of YbC(SiHMe₂)₃HB(C₂F₅)₂THF (2a, KBr) contained bands at 2310 (νSSF), 2074 (νSSF), and 1921 cm⁻¹ (νSSF). The presence of only one SiH band at high energy in 2b suggests that the C(SiHMe₂)₃ group lacks secondary interactions present in 1b and 2a. While the change in IR spectrum is surprising, elemental analysis shows that one C(SiHMe₂)₃ group lacks secondary interactions present in 1b and 2a and the IR band at 2110 cm⁻¹ is not from the hydrocarbon-soluble {Me₂Si–C(SiHMe₂)₂}₂ that is removed during workup. In addition, the IR spectrum of 3b contained bands at 2388 and 2318 cm⁻¹ assigned to B–H
While compounds 4a,b (see Figures 2 and 3) both contain three-coordinate distorted-trigonal-planar metal centers (C1–

\[ \text{Ln–C} > 120^\circ \], the two species crystallize in inequivalent space groups (4a, Pbcn, Z = 8; 4b, P1, Z = 2) with distinctly inequivalent conformations of their alkyl ligands. In 4a, one ligand forms two Yb–H–Si interactions and the other ligand contains only normal Si–H groups. The diagnostic-like ligand in 4a contains two short Yb–H distances (Yb1–H2s, 2.42(3) Å; Yb1–H3s, 2.49(3) Å) and two short Yb–Si distances (Yb1–Si2, 3.118(8) Å; Yb1–Siz3, 3.169(8) Å). In 4b, one alkyl contains one Sm–H–Si interaction, while the other alkyl contains two secondary interactions. The short distances Sm1–H2s (2.54(3) Å), Sm1–Si2 (3.2686(6) Å), Sm1–H4s (2.65(2) Å), and Sm1–Si4 (3.2916(6) Å), acute angles for Sm1–C1–Si2 (88.13(7)°) and Sm1–C8–Si4 (90.27(7)°), and coplanar Sm–C and Si–H vectors (Sm1–C1–Si2–H2s, −3.4(9)°; Sm1–C8–Si4–H4s, 9.9(9)°) are consistent with Sm–H–Si. A second SiH approaches the Sm center (Sm1–H1s, 2.86(2) Å; Sm1–Si1, 3.2973(6) Å; Sm1–C1–Si1, 89.14(7)°), but the Sm1–C1 and Si1–H1s vectors are not coplanar (Sm1–C1–Si1–H1s, −36(1)°). The differences in alkyl ligand conformation may also be reflected in the distinct IR spectra of 4a and 4b, suggesting that the Ln–H–Si close contacts affect the vibrational properties (i.e., Si–H force constants). It is somewhat unexpected that the conformations of 4a and 4b are inequivalent; however, it is also worth noting that the ionic radii for Sm(II) and Yb(II) are different by 0.14 Å.39

Compound 4a is the first reported example of a crystallographically characterized compound with a single alkyl ligand containing two agostic-like SiH groups interacting with a single metal center. Diagnostic features are not generally observed in homoleptic compounds but have been reported for lanthanide-diole disilazide compounds.36 However, the bridging tetramethylsilsilazide ligands in \{La[N(SiHMe2)$_2$]$_3$\}_2 contain close contacts with both La centers.31 In addition, the reaction of Y[N(SiHMe2)$_2$]$_3$THF and ImMe$_2$ (1,3-dimethylimidazolylidine) gives a carbene-coordinated, THF-free compound that also shows Y–H–Si close contacts.32 All three alkyl ligands in Y[C(SiHMe$_2$)$_3$]$_3$ contain two secondary interactions, as characterized by low-temperature NMR studies.33 A solution to X-ray diffraction data was not found. In addition to the unusual diagnostic-like structure in 4a, it is also notable that the other ligand does not contain any other secondary interactions with the Yb center.

As noted above, the central carbons of the C(SiHMe$_2$)$_3$ ligands, the carbene carbon, and the metal center are coplanar in 4a,b. The angles between the alkyl ligands and the carbene group deviate from 120° (C1–Yb1–C25 = 106.25(8)° and C8–Yb1–C25 = 115.03(8)°; C8–Sm1–C15 = 113.99(5)° and C1–Sm1–C15 = 114.29(5)°) suggesting that carbene–alkyl interligand repulsions are less severe than alkyl–alkyl interactions. The Yb1–C1 and Yb1–C8 distances (2.627(3) and 2.611(3) Å, respectively) are slightly longer than in 1a (2.596(4) Å).11a However, the Sm–C distances in 1b (Sm1–C1, 2.733(2) Å and 4b (Sm1–C1, 2.779(2) Å; Sm1–C8, 2.739(2) Å) are similar. This observation may relate to the larger ionic radii of Sm(II) in comparison to Yb(II), which reduces interligand interactions that could affect Ln–C distances in the former complexes.

Crystals of 4a,b persist at room temperature for 2 days under an inert atmosphere. When a solution of 4a in benzene-$d_6$ was heated at 80 °C for 1 day, the alkane HC(SiHMe$_2$)$_3$ was formed at the expense of 4a. The remaining $^1$H NMR signals at 1.60 and 1.75 ppm were attributed to a product resulting from transformation of the ImBu ligand into a new, as yet
unidentified organic species bonded to ytterbium. The crystals of 4a, b also decompose under vacuum to HC(SiMe2)3 and free carbene, and the color of the crystals fades from deep red to pale orange during this decomposition process. Hence, these compounds are used only from freshly recrystallized and isolated material by carefully decanting the pentane solution and briefly evaporating residual solvent under vacuum for short amounts of time.

To better assess the relative stability of carbene vs THF coordination to samarium(II), UV−vis spectra were measured for 1b and 4b. The UV−vis spectrum of 1b in pentane revealed peaks with λmax values of 389 (ε = 556 M−1 cm−1) and 439 nm (ε = 518 M−1 cm−1) shown in Figure 4. The spectrum for compound 4b in pentane contained peaks at 405 nm (ε = 551 M−1 cm−1) and 492 nm (ε = 586 M−1 cm−1), and the lower energy peaks are assigned to f → d transitions. Both compounds have a tail through the visible region, accounting for their dark black color. Upon addition of 2 equiv of THF to 4b, the peak at 492 nm diminishes and intensity of the broad peak of 1b at 439 nm increases. An isosbestic point at 446 nm was apparent in a series of spectra with 2.0, 2.5, 3.0, 3.5, and 4.0 equiv of THF (Figure 4, inset). Thus, the conversion of 4b to 1b upon addition of THF occurs without detectable buildup of intermediates. This process is clearly reversible; however, more than 8 equiv is required for the 4b signals to be overwhelmed by 1b peaks.

Only starting materials were observed in 1H NMR spectra of mixtures containing the zwitterionic compound 2a or 3a and ImBu. In contrast, the reaction of 4a and B(C6F5)3 generates YbC(SiMe2)3{HB(C6F5)3}1ImBu and 0.5 equiv of the 1,3-disilacyclobutane {Me2Si-C(SiMe2)2}2. The 11B NMR spectrum of the reaction mixture contained a doublet at −21 ppm (JHH = 73.6 Hz) and provided good evidence for hydrogen abstraction. The 1H NMR spectrum contained a multiplet at 4.75 ppm (3 JHH = 192 Hz) assigned to the SiH and a singlet at 0.35 ppm (18 H, SiMe2). This large SiH coupling constant suggests that the SiH groups do not interact with the Yb center in this zwitterionic species. The integrated ratio of these signals and the carbene resonances at 6.19 and 1.12 ppm indicate that a 1:1 adduct is formed. Unfortunately, this material has not yet proven isolable.

Cross-Dehydrocoupling of Organosilanes and Amines Catalyzed by Ln(C(SiMe2)3)2ImBu. The divalent compounds 4a,b are efficient precatalysts for cross-dehydrocoupling of Si–H and N–H bonds to give Si–N bonds and H2. Primary and secondary amines effectively couple with primary and secondary silanes to afford the desired silazanes (Tables 1 and 2), which are readily isolated in good yield by distillation. In the absence of 4a,b as a catalyst, only starting materials are observed. Compounds 1a,b, 2a, and 3b, as well as ImBu, were also tested for catalytic activity in the cross-dehydrocoupling of PhMeSiH2 and tBuNH2 but only starting materials were observed in 1H NMR spectra of the reaction mixtures after 1 day at room temperature or 60 °C.

In catalytic reactions, the consumption of organosilane and formation of silazane product were evident from the new downfield-shifted SiH resonances of HSi–NR′2. The 3JHH coupling between SiH and NH provided characteristic splitting patterns for SiH resonances, which appeared as doublets for the silazide RH2SiNHR′ and as triplets in spectra of RHSi(NHR′)2. Although reactions of PhSiH3 and iC3H7NH2 or tBuNH2 in a 1:1 ratio result in a mixture of these silazene and siladiazido products, reactions with excess silane or excess amine provide control over the product identity. For example, the 4a-catalyzed reaction of PhSiH3 and 4 equiv of iC3H7NH2 affords the silyltrimedizido species PhSiH(NiC3H7)2. In addition, the amine’s steric bulk affects the reaction rate in conversions with PhSiH3. Thus, 2 equiv of tBuNH2 and PhSiH3 react to yield the silyldiazido species PhSiH(NiBu)2 after 15 h. The reaction with the secondary amine Et3NH (3 equiv) also requires 15 h to yield the silyldiazido species PhSiH(NEt3)2, but the reaction of phenylsilane and (iC3H7)2NH did not result in any silazane formation after 1 day at room temperature or 60 °C.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Time (h)</th>
<th>% Yield (isolated)</th>
</tr>
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<tbody>
<tr>
<td>PhSiH3 + 4 H2</td>
<td>0.1</td>
<td>63 (62)</td>
</tr>
<tr>
<td>2.2 PhSiH3 + H2N</td>
<td>0.1</td>
<td>72 (71)</td>
</tr>
<tr>
<td>PhSiH3 + 2H2N</td>
<td>15</td>
<td>92 (91)</td>
</tr>
<tr>
<td>2.2 PhSiH3 + H2N</td>
<td>15</td>
<td>75 (73)</td>
</tr>
<tr>
<td>PhSiH3 + 3 HNEt2</td>
<td>15</td>
<td>82 (80)</td>
</tr>
<tr>
<td>PhSiH3 + 5 HNEt2</td>
<td>15</td>
<td>81 (78)</td>
</tr>
</tbody>
</table>

Table 1. Ln(C(SiMe2)3)2ImBu-Catalyzed Dehydrocoupling of PhSiH3 and Amines

Figure 4. UV−vis spectra of Sm(C(SiMe2)3)2THF2 (1b) and Sm(C(SiMe2)3)2ImBu (4b) in pentane (2.0 mM). Inset: titration of 4b with THF.
4a,b-catalyzed reactions of secondary silanes such as PhMeSiH₂ and Ph₂SiH₂ and either primary or secondary amines afford monosilazane products, while the reaction of 2 equiv of silane with primary amines gives disilazanes (Table 2). One such example is illustrated by the 4a-catalyzed reaction of 2 equiv of PhMeSiH₂ and H₂N-iC₃H₇, which gives (PhMeH-Si)₂N-iC₃H₇ as a 1.3:1 mixture of diastereomers after 4 h at room temperature. Similar to the case for primary silanes, only starting materials are observed in mixtures of the bulky secondary amine (iC₃H₇)₂NH and secondary silanes. Additionally, only starting materials are observed in mixtures of tertiary silanes such as BnMe₂SiH (Bn = CH₂Ph), Et₃SiH, and (CH₂==CH)SiMe₂H with primary or secondary amines after 1 day at room temperature or at 60 °C.

The reaction of Ph₂SiH₂ and Et₂NH catalyzed by 4a yields Ph₂HSiNEt₂ as the sole coupling product when a range of silane to amine ratios (1:1 to 1:25) were used. Therefore, this transformation was used as a representative conversion for mechanistic studies. Concentration vs time profiles of Ph₂SiH₂ and Et₂NH were measured by ¹H NMR spectroscopy and quantified by integration relative to a standard of known concentration. Upon addition of catalyst 4a to mixtures of Ph₂SiH₂ and Et₂NH, free ImBu and the alkane HC(SiHMe₂)₃, resulting from protonolysis, were detected by ¹H NMR spectroscopy. The active catalytic species is part of this mixture, and dehydrocoupling ensues. Four concentration regimes were investigated, namely combinations of high and low [Et₂NH] and [Ph₂SiH₂]. Under conditions of low \([\text{Ph}_2\text{SiH}_2]_{\text{ini}}\) (81 mM) and high \([\text{Et}_2\text{NH}]_{\text{ini}}\) (673 mM), with \([4a]\) equal to 8–16 mM, second-order plots suggest first-order dependence on each reagent. The data analysis is limited by the faster initial consumption of ca. 5 mM of Et₂NH during catalyst initiation in comparison to that during dehydrocoupling. In spite of this limitation, second-order rate constants increase in a series of experiments in which \([4a]\) is increased.

A plot of observed second-order rate constants vs catalyst concentration (i.e., \([4a]\)) reveals a linear dependence, giving the ternary rate law of eq 2

\[
-d[\text{Ph}_2\text{SiH}_2]/dt = k'_{\text{obs}}[\text{Ph}_2\text{SiH}_2][\text{Et}_2\text{NH}]
\]

with \(k'_{\text{obs}} = (1.04 \pm 0.07) \times 10^{-7} \text{mM}^{-2} \text{s}^{-1}\) (Figure 5). The nonzero intercept indicates that a portion of the ytterbium species is not active for catalysis, and given the formation of noncoordinated NHC, at least one of the inactive species is likely carbene-free. On the basis of this and the observation of free NHC during the reaction, we hypothesized that additional NHC might increase catalytic activity by disfavoring dissociation. Instead, excess ImBu or excess THF inhibits the rate of catalytic conversion. This inhibition likely results from the ytterbium amide or ytterbium hydride catalytic intermediates coordinating either THF or excess ImBu, since 4a and excess ImBu do not afford detectable quantities of Yb(C-SiHMe₂)₃(ImBu)₂. An additional and unexpected inhibition process was also observed in the decrease in the second-order rate constant with increasing \([\text{Ph}_2\text{SiH}_2]\) (Figure 6).

At low concentrations of amine, the concentration profiles show rapid initial conversion followed by a slower second phase as the reaction approaches completion. Thus, the experimental ternary rate law is likely only valid for given concentration regimes (and not valid at high \([\text{Ph}_2\text{SiH}_2]\) or low \([\text{Et}_2\text{NH}]\)). Within the conditions of Figure 5, and taking into account the qualitative observations under the other conditions, a few conclusions are apparent. First, the ternary rate law suggests that interaction of one of the reagents (silane or amine) with catalytic intermediates is reversible and precedes the turnover-limiting step. Because higher concentrations of Ph₂SiH₂ inhibit the catalytic reaction, possibly by formation of a Yb–Ph₂SiH₂ adduct as an off-cycle species, the reversible interaction of catalyst and Ph₂SiH₂ is unlikely to be part of the catalytic cycle.
Instead, reversible ytterbium(II)—amine coordination is proposed as a key step for the conversion. This ytterbium amine compound is unlikely to be a hydride, which would rapidly react to give ytterbium amide and H₂. The alternative is therefore suggested in which the turnover-limiting step would involve the interaction of a ytterbium amido amine compound (e.g., A in Scheme 3) and Ph₂SiH₂. Second, formation of deactivation by Ph₂SiH₂ is reversible, because greater than 3 half-lives of conversion were observed under several conditions, and an irreversible catalyst decomposition reaction would likely be noticed with severely nonlinear kinetic plots. This coordinatively unsaturated intermediate could be a ytterbium hydride (e.g., B), which might form a [Yb]H(H-SiH₂Et₂) species related to those proposed for Ru³⁵ but could also be a ytterbium amide, such as C in Scheme 3. We favor the latter, because if B or its inhibited forms were the catalyst resting state, then second-order dependence on [Et₂NH] would be expected.

CONCLUSION

The structure and non-redox-based chemistry of ytterbium and samarium compounds Ln(C(SiHMe₂)₃)₁₂THF₂ are very similar in terms of structure and reactivity toward the Lewis acid B(C₆F₅)₃ and substitution of THF ligands by ImBu. In addition, the carbene adducts of both dialkyl rare-earth compounds are similarly reactive in dehydrocoupling of amines and organosilanes. However, there are a few notable differences between the samarium and ytterbium compounds, which appear in the IR spectra of Ln(C(SiHMe₂)₃)₁₂HB(C₆F₅)₃THF₂ and the X-ray crystal structures of Ln(C(SiHMe₂)₃)₁₂ImBu. Notably, the ytterbium compound 4a contains one diagnostic-like alkyl ligand and one alkyl ligand lacking secondary interactions, whereas both alkyl ligands in the samarium analogue contain 3c-2e Sm—H—Si structures.

The Ln(C(SiHMe₂)₃)₁₂HB(C₆F₅)₃THF₂ compounds do not react with ImBu under the accessible conditions, and apparently the substitution of THF in the zwitterionic compounds is more difficult than in the neutral 1a,b. An NHC ligand coordinates to ytterbium in Yb(C(SiHMe₂)₃)₁₂HB-(C₆F₅)₃ImBu, which is formed from the reaction of 4a and B(C₆F₅)₃. Even so, the ImBu ligand dissociates from 4a,b upon addition of small amounts of THF or amines, as suggested by the UV—vis titration, by the observation of free ImBu in catalytic reaction mixtures, or even under vacuum. The coordination and substitution chemistry of Yb and Sm in these alkyl compounds affects catalytic dehydrocoupling of amines and silanes. Coordination of substrates and exogenous ligands, including THF and ImBu, inhibit catalysis, and not all of the ytterbium precatalyst gives active catalytic sites, as shown by kinetic studies. The free ImBu present during catalysis suggests that irreversible catalyst deactivation involves its dissociation from the rare-earth center. On the basis of these observations, we are currently investigating bidentate hemilabile carbene ligands to access coordinative unsaturation but stabilize lanthanide(II)—ligand interactions in these alkyl compounds.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox unless otherwise indicated. Water and oxygen were removed from benzene and pentane solvents using an IT PureSolv system. Benzene-d₆ was heated to reflux over Na/K alloy and vacuum-transferred. The compounds Yb₁₂, Sm₁₂THF₂, KC(SiHMe₂)₁₂, B(C₆F₅)₃, and Yb(C(SiHMe₂)₃)₁₂THF₂ were prepared following literature procedures. 1,3-Di-tert-butylimidazol-2-ylidene (ImBu) was purchased from Sigma-Aldrich and used as received. NMR spectroscopic data for (Me₂SiC(SiHMe₂)₃)₃³⁶ and the catalytic products PhSi(NHPr)₃, (PhSiH₂)₃NiPr, PhSiH(NH₂Bu₃, (PhSiH₂)₃NtBu, (PhMeSiH)₂NiPr, PhMeSiH(NH₂Bu), PhMeSiH(NEt₂), Ph₂SiH(NHPr), Ph₂SiH-

Figure 6. Plot of observed second-order rate constant versus [Ph₂SiH₂] at 298 K in benzene-d₆. The curve is drawn to merely guide the eye and does not represent the results of a least-squares regression analysis.

Scheme 3. Proposed Catalytic Cycle Consistent with Experimental Kinetic Observations

HC(SiHMe₂)₃ presumably as part of catalyst initiation, implies that a ytterbium amido species is an intermediate. Note that independent reactions of 4a and Et₂NH also give HC(SiHMe₂)₃, although ytterbium amido products were not isolable. Third, deactivation by excess ImBu, THF, or even Ph₂SiH₂ but not Et₂NH suggests that catalysis involves a coordinatively unsaturated species, which must interact with Et₂NH for the reaction to proceed. We propose that
(NHBu), PhH3SiN(CH3)2, and PhSiH(NeTS)2 match those previously reported.

1H, 13C(CH3)2, 11B-, H-15N HMBC, 19F, and H-29Si HMBC NMR spectra were collected on a Bruker DRX-400 spectrometer, a Bruker Avance III-600 spectrometer, or an Agilent MR 400 spectrometer. 1H NMR spectra were referenced to an external standard of BF3·Et2O. 13C chemical shifts were originally referenced to CDCl3 and recalculated to the CH3NO2 chemical shift by adding ~381.9 ppm. Infrared spectra were measured on a Bruker Vertex 80 instrument. Elemental analyses were performed using a PerkinElmer 2400 Series II CHN/S instrument. X-ray diffraction data were collected on a Bruker AXS APEX II diffractometer. UV–vis spectra were measured on an Agilent 8453 Diode Array UV–vis instrument.

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**General Procedure for NMR Kinetics Measurements.** The reaction progress was monitored by single-scan acquisition of a series of 1H NMR spectra at regular intervals on a Bruker DRX-400 spectrometer. Hexamethylbenzene was used as a standard of accurately known and constant concentration (0.010 M in benzene-d5). The temperature in the NMR probe was preset for each experiment at 25 °C (verified for each experiment with a thermocouple placed in an NMR tube in toluene in the probe). A range of silane to amine ratios (1:1 to 1:2.5) was used to study the catalytic reaction of Ph3SiH and.
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Et₃NH in benzene-d₆. Kinetic measurements were studied at low concentration of Ph₃SiH₂ (0.081 M) and high concentration of Et₃NH (0.673 M).

Representative Example. The catalytic reaction of Ph₃SiH₂ and Et₃NH using 10 mol % of Yb{C(SiHMe₂)₃}₂ImBu as catalyst is described. A 5 mL stock solution of C₂Me₆ internal standard (0.0081 g, 0.0499 mmol, 10.0 mM) in benzene-d₆ was prepared using a 5 mL volumetric flask. The stock solution (0.50 mL) was added by a 1 mL glass syringe to a known amount of 4a (0.0052 g, 0.0071 mmol). The resulting solution was transferred to a NMR tube and capped with a rubber septum, and a 1H NMR spectrum was acquired. Neat glass syringe was added Ph₂SiH₂ (0.013 g, 0.071 mmol) and Et₂NH (0.052 g, 0.711 mmol) were added to the NMR tube by injecting through the rubber septum. Then, the NMR tube was quickly placed in the NMR probe. Single-scan spectra were acquired automatically at preset time intervals at 25 °C. The concentration of silane and product at any given time was determined by the integration of silane and product resonances relative to the integration of the internal standard. Second-order rate constants (kobs) were obtained by nonweighted linear least-squares fits of the data to the second-order rate law: ln[(Et₂NH)/[Ph₃SiH₂]] = −kobs[Ph₃SiH₂]. The experimental third-order rate constant kobs was determined by measuring kobs for several catalyst concentrations. A plot of second-order rate constants vs catalyst concentrations gave a first-order dependence on catalyst concentration with the overall rate law −d[Ph₃SiH₂]/dt = kobs[Catalyst][Ph₃SiH₂][Et₃NH].

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00138.

Spectra of new compounds, synthetic procedures, ¹H NMR spectra of catalysis products, and kinetics plots (PDF)

Crystallographic information files for Sm{C(SiMe₂)₃}₂THF (1b), Yb{C(SiMe₂)₃}₂ImBu (4a), and Sm{C(SiMe₂)₃}₂ImBu (4b) (CIF)

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Notes

The authors declare no competing financial interest.

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