Lanthanide Silanimines

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Dehydrosilylation of $ArNHSiH_3$ with Ytterbium(II) Amide: Formation of a Dimeric Ytterbium(II) Silanimine Complex**

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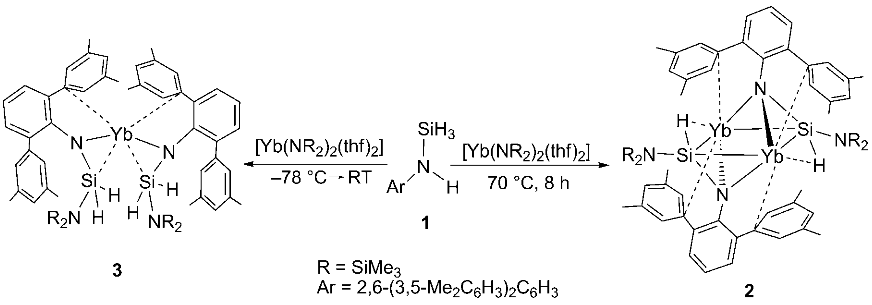
Si–H bond activation with lanthanide alkyl and hydride compounds is known to yield hydrides or silyl complexes by σ-bond metathesis, which is a fundamental step for several important catalytic processes, such as dehydropolymerization of silanes and hydrosilylation of unsaturated organic compounds.[1] Although a few reports on hydrosilylation of alkenes and imines and dehydrogenative silylation of amines with lanthanide amides have appeared,[2] studies on reactions of amides with hydrosilanes are still very scant. It has been shown that silanolysis of a Ln–N bond can give the lanthanide hydride with the formation of a new Si–N bond.[3] The related approaches on the isolation and structural characterization of lanthanide complexes with hydrosilylamido ligands revealed the existence of interesting agostic β-(Si–H)···Ln interactions, which can be viewed as modes for understanding the nature of the initial Si–H coordination to the metal centers.[4]

Although several types of agostic lanthanide hydrosilylamido complexes have been obtained by the employment of $[N(SiMe_2H)_2]^-$ and $[tBuN(SiMe_2H)]^-$ ligands, their reactivity has been virtually unexplored.[5] A few metal hydrosilylamido complexes can be converted into the corresponding silanimine complexes by either Si–H σ-bond metathesis or oxidative addition to the metal centers.[6a,f] These unsaturated silicon complexes, although very rare in number, have been shown to display interesting structural features and reactivity.[6] Inspired by these findings, we became interested in the investigation of primary aminosilanes with an $HN{-}SiH_3$ linkage in lanthanide chemistry, as the elimination of hydrogen may take place to give lanthanide silanimine complexes. In addition, primary silanes are normally much more reactive and may undergo multiple reactions involving the Si–H bonds, which may allow us to study the unexplored fate of agostic complexes. In this vein, the novel bulky primary aminosilane $ArNHSiH_3$ (**1**, Ar = 2,6-$(3,5\text{-}Me_2C_6H_3)_2C_6H_3$) was prepared, in which the bulky terphenyl group would render the formation of well-defined low-coordinate complexes.[7] Herein we report on the preparation and isolation of the first lanthanide silanimine complex $[\{ArNSiH[N(SiMe_3)_2]\}_2Yb_2]$ (**2**) with a Yb_2Si_2 core and the monomeric homoleptic lanthanide(II) amide $\{ArNSiH_2[N(SiMe_3)_2]\}_2Yb$ (**3**) with significant Si(H)–Yb agostic interactions by reactions of **1** with $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$ (Scheme 1).



Scheme 1. Synthesis of complexes **2** and **3**.

The primary aminosilane **1** was prepared in 83 % yield by the reaction of ArNHLi with $SiCl_4$ followed by reduction with $LiAlH_4$ in refluxing diethyl ether. Treatment of **1** with one equivalent of $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$ in toluene at 70 °C for 8 h resulted in the formation of the dimeric ytterbium silanimine complex **2** as dark green crystals in 72 % yield. The analogous reaction of the ytterbium amide with two equivalents of **1** in toluene at −78 °C, however, yielded the monomeric homoleptic ytterbium amide **3** in 31 % yield as dark purple crystals after crystallization from *n*-hexane. Complexes **2** and **3** were fully characterized by ^1H, ^{13}C, ^{29}Si, and ^{171}Yb NMR and IR spectroscopy, elemental analysis, and single-crystal X-ray analysis.

The X-ray single-crystal analysis of **2** disclosed a dimeric structure (Figure 1) with $ArNSiH[N(SiMe_3)_2]$ being coordinated to the two Yb atoms in $\mu{:}\eta^2$ fashion. The structure contains a planar Yb_2Si_2 ring with the two nitrogen atoms residing on the two sides of the plane, respectively, leading to an almost central-symmetric structure. The Yb–Si bond lengths (3.0644–3.0831(14) Å) are similar to those in $[Cp^*YbSi(SiMe_3)_3(thf)_2]$ (3.032(3) Å),[8a] $K[YbSi(SiMe_3)_3\{N(SiMe_3)_2\}_2]$ (3.0387(10) Å),[8b] and the polymeric complex $[\{Cp^*_2Yb(SiH_3)K(thf)\}_n]$ (3.091(3) Å, $Cp^* = C_5Me_5$).[8c] The Yb–N bond lengths (2.444 and 2.470(4) Å) are comparable to known bridging Yb–N distances, for example, in the ate

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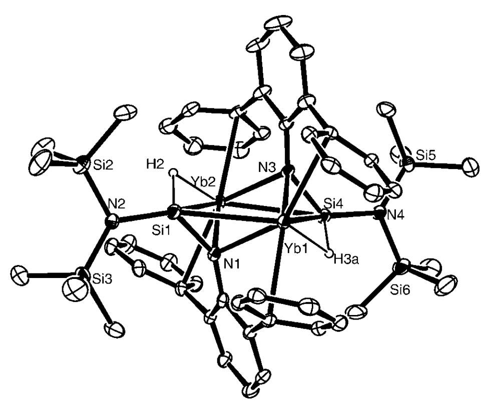


Figure 1. ORTEP drawing of **2** with 30% probability ellipsoids. Hydrogen atoms, with the exception of the two atoms bonded to Si, and the methyl groups on the phenyl ring are omitted for clarity. Selected bond lengths [Å] and angles [°]: Yb1–Si1 3.0831(14), Yb1–Si4 3.0760(14), Yb2–Si1 3.0780(14), Yb2–Si4 3.0644(14), Yb1–N1 2.444(4), Yb1–N3 2.470(4), Yb1–H3A 2.23(5), Si4–H3A 1.63(5), Yb2–H2 2.31(4), Si1–H2 1.53(4), Si1–N1 1.810(4), Si4–N3 1.839(4); N1-Yb1-N3 82.22(13), N3-Yb2-N1 81.90(13), Yb2-N3-Yb1 97.86(14), Yb1-N1-Yb2 98.01(14), Yb1-N1-Yb2 98.01(14), Si4-Yb1-Si1 105.50(4), Si4-Yb2-Si1 105.91(4), Yb2-Si1-Yb1 74.10(3), Yb2-Si4-Yb1 74.39(3), N3-Si4-Yb1 53.40(13), Si4-N3-Yb1 89.89(15), N3-Yb1-Si4 36.71(9), N1-Si1-Yb2 53.51(12), Si1-N1-Yb2 90.47(16), N1-Yb2-Si1 36.02(9).

complex $[NaYb\{N(SiMe_3)_2\}_3]$[9a] (2.46(2) Å) and the dimeric complex $[Yb_2\{N(SiMe_3)_2\}_4]$[9b,c] (2.502(3) Å). Notably, the Si–N bonds of the bridging silanimine ligand (1.810(4) and 1.839(4) Å) are much longer than that observed in the monomeric zirconium silanimine complex $[Cp_2Zr(\eta^2\text{-}Me_2SiN\mathit{t}Bu)(PMe_3)]$[6a] (1.654(1) Å), and even longer than a normal Si–N single bond in aminosilyl complexes (1.70–1.78 Å),[10] probably because of the hypervalent silicon atoms and the bridging nitrogen atoms. Silanimine complexes, in principle, may exhibit bonding modes represented by the extreme resonance forms of π and metallacyclic structures. Therefore, the bonding in **2** can be best considered as metallacyclic bonding owing to the long Si–N bond.

The most striking feature in **2** is the existence of the three-centered, two-electron (3c-2e) α-Si–H–Yb agostic bonding. The long Si–H distances (1.53(4) and 1.63(5) Å) and the close Yb–H contacts (2.23(5) and 2.31(4) Å) are diagnostic for this bonding. Furthermore, the Yb–H distances are very close to those in the known divalent ytterbium hydrides (2.22(4)–2.26(3) Å).[3] The ^{1}H NMR spectrum of **2** contains the resonance for the SiH group at $\delta = 4.58$ ppm ($^1J_{SiH} = 65$ Hz), which is low-field shifted relative to the value for the aminosilane **1** ($\delta = 4.16$ ppm ($^1J_{SiH} = 214$ Hz). The significantly decreased $^1J_{SiH}$ coupling constant observed in **2** and the red-shifted band at 1539 cm^{-1} for the Si–H stretching vibration in the IR spectrum of **2** indicate significant weakening of the Si–H bond,[4] owing to the high Lewis acidity of the low-coordinate ytterbium atoms. A similar significant weakening of a Si–H bond was observed in a cationic hafnium silyl complex.[11] The ^{171}Yb NMR spectrum of **2** exhibits a sharp resonance at $\delta = -285.3$ ppm, indicating that the two Yb atoms are equivalent on the NMR time scale. Complex **2** is the first example of a dinuclear lanthanide silyl complex with a Ln_2Si_2 core. Only two examples of well-characterized dinuclear complexes with bridging silanimine ligands are known.[6d] Complex **2** features two Yb–Si bonds in the strained metallacyclic motif. Most lanthanide complexes with Ln–Si bonds are stabilized by cyclopentadienyl ligands, which have been shown to be highly reactive toward unsaturated molecules, and in some cases even toward a C–H bond.[8,12]

The most notable structural features of **3** (Figure 2) include the wide N1-Yb1-N3 angle of 160.27(14)°, the hypervalent Si1 and Si4 atoms with the close Yb⋯Si contacts of 3.1391(16) and 3.1372(17) Å, as well as the Yb–arene interactions as indicated by the short Yb1–C37 and Yb1–C7 separations of 2.772(5) and 2.813(5) Å.[13] The short Yb–Si contacts are even very similar to the Yb–Si single bonds observed in the Yb^{II} complex $[Yb(SiPh_3)_2(thf)_4]$[8d] (3.158(2) Å). Furthermore, the two Yb-N-Si angles (99.11(2) and 98.13(2)°) are remarkably contracted. Unfortunately, the hydrogen atoms on the silicon atoms cannot be located by the X-ray single-crystal analysis, which hampers analysis of the detail bonding situation. The Yb–N bond lengths (2.397(4) and 2.419(4) Å) are within the reported range for ytterbium amides.[9] Complex **3** appears to be the first example of monomeric homoleptic divalent lanthanide amides. The wide N-Yb-N angle in **3** is remarkable in comparison with the considerable bent X-Ln-X (137.0(4)–142.73(8)°, X = C, S) units observed in the few structurally characterized quasi-two-coordinate lanthanide species, namely $[Yb\{C(SiMe_3)_3\}_2]$ and $[Ln(SAr^*)_2]$ (Ln = Yb, Eu, Sm; Ar* = 2,6-Trip$_2$C$_6$H$_3$; Trip = 2,4,6-iPr$_3$C$_6$H$_2$).[14] This unusual feature may result from the significant intramolecular β-Si⋯Yb interaction as well as the Yb⋯π-arene interaction.

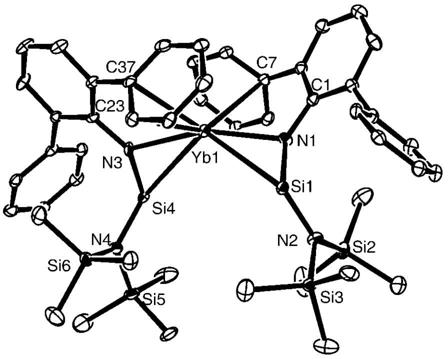
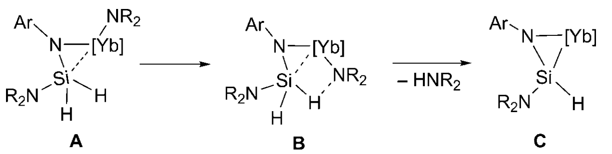


Figure 2. ORTEP drawing of **3** with 30% probability ellipsoids. Hydrogen atoms and the methyl groups on the phenyl ring are omitted for clarity. Selected bond lengths [Å] and angles [°]: Yb1–N1 2.397(4), Yb1–N3 2.419(4), Yb1–Si1 3.1391(16), Yb1–Si4 3.1372(17), Yb1–C7 2.813(5), Yb1–C37 2.772(5); N1-Yb1-N3 160.27(14), N1-Yb1-Si1 31.96(10), N1-Si1-Yb1 48.95(14), N1-Si1-N2 122.9(2), N3-Yb1-Si4 32.14(10), N3-Si4-Yb1 49.76(13).

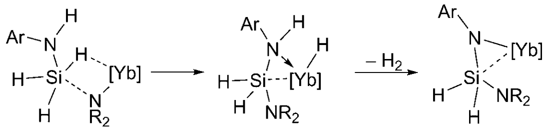
The ^{1}H NMR spectrum of **3** exhibits only one broad singlet at $\delta = 4.31$ ppm for the hydrosilyl groups at room temperature, indicating its fluxional behavior. As the temperature was lowered to 193 K, two doublets for the hydrosilyl groups were observed in the ^{1}H NMR spectrum: The doublet at $\delta = 4.17$ and 4.30 ppm ($^1J_{\mathrm{SiH}} = 257$ Hz) corresponds to the terminal SiH group, while the other at $\delta = 4.19$ and 4.27 ppm ($^1J_{\mathrm{SiH}} = 104$ Hz) can be assigned to the β-agostic Yb···(H–Si) hydrogen atoms owing to the small coupling constant.[4a] The ^{171}Yb NMR spectrum of **3** displays a triplet at $\delta = 960.3$ ppm ($J_{\mathrm{YbH}} = 64$ Hz), which falls in the range for Yb$^{\mathrm{II}}$ amides.[15] Furthermore, the IR spectrum of **3** exhibits red-shifted bands with peaks at 1782 and 1749 cm^{-1} for the agostic Si–H absorptions and one band at 2159 cm^{-1} for the terminal Si–H vibration. These spectroscopic data indicate that only one of the two β-hydrogen atoms on each of the silicon atoms is involved in the interaction with the ytterbium atom.

Heating a solution of **3** in C_7D_8 at 80 °C for 24 h did not lead to the formation of **2**, indicating that **2** was not formed from **3** under the conditions for the preparation of **2**. However, when a solution of **3** in C_7D_8 was heated to 120 °C and then maintained at this temperature for 16 h, approximately two thirds of **3** were converted into **2** alone with the formation of $ArNHSiH_2NR_2$ and a small amount of unidentified products as indicated by the ^{1}H NMR analysis. It is evident that **2** was formed from **3** through intramolecular protolysis of one of the amido ligands. Therefore, it seems reasonable to propose the monosubstituted complex **A** (Scheme 2; R = $SiMe_3$) as the intermediate for the formation of **2** by Yb–N σ-bond metathesis via four-center transition state **B** to give **C** similar to the thermolysis of **3** at 120 °C. The relatively low temperature for the conversion of **A** into **2** may be due to the relatively small steric effect of the $[(Me_3Si)_2N]^-$ group relative to that of $[ArNSiH_2(NR_2)]^-$.



Scheme 2. Proposed intramolecular Yb–N σ-bond metathesis.

Reaction of **1** with $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$ was conducted under various conditions with the expectation to isolate the intermediate **A**. Mixing of **1** with $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$ in the molar ratio 1:1 in toluene at −78 °C for 48 h with stirring resulted in the formation of **2** and a new species in the ratio 2:3 as indicated by proton NMR analysis in C_6D_6. Heating the mixture in toluene at 70 °C for 8 h led to a color change from dark brown to dark green with an almost complete conversion (yield of 95 % according to NMR spectroscopy) into **2**. Attempts to isolate the new species were unsuccessful to date probably because of its instability and easy transformation to **2** under the experimental conditions. It is quite possible that the new dark brown species could be the intermediate **A**. Complex **3** was not detected under these conditions. Similar experiments with 2 equivalents of **1** at low temperature yielded exclusively **3** (yield of 85 % according to NMR spectroscopy) alone with small amounts of unidentified products, and **2** was not observed by NMR analysis. The low yield for **3** isolated in the preparative-scale reaction may result from the high solubility of **3** even in *n*-hexane. The reaction sequences for the formation of **3** with the elimination of hydrogen are noteworthy since the elimination of hydrogen from the aminosilane H_2NSiH_3 has been predicted to be quite endothermic and unlikely under normal conditions.[16] Indeed, the decomposition of **1** was not observed in C_7D_8 at 100 °C within 2 h. These experiments suggest that Si–N coupling and hydrogen transfer from the Si atom to the Yb atom by Yb–N bond metathesis should be the initial step, which is followed by the deprotonation of the N–H group with the elimination of hydrogen as shown in Scheme 3. Furthermore, the results indicate that Si–H bond metathesis is preferred to N–H bond elimination under the optimized synthetic conditions.



Scheme 3. Proposed hydrogen elimination mechanism.

In summary, the first lanthanide silanimine complex and the first monomeric homoleptic lanthanide amide have been obtained by the reaction of the aminosilane $ArNHSiH_3$ with $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$. Silanimine complex **2** has an unprecedented dimeric structure with an $Yb_2Si_2N_2$ cluster core, in which α-SiH···Yb agostic interactions are observed. The homoleptic amide **3** is remarkable in that the wide N-Yb-N angle is distinct from the known quasi-two-coordinate lanthanide alkyls and thiolates. Reactivity studies of **2** and **3**, as well as of reactions of $ArNHSiH_3$ with other lanthanide amides are currently in progress.

Experimental Section

2: $ArNHSiH_3$ (0.66 g, 2.0 mmol) in toluene (5 mL) was added to a stirred solution of $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$ (1.34 g, 2.1 mmol) in toluene (5 mL) at room temperature. The mixture was maintained at 70 °C for 8 h. Dark green crystals of **2** (0.96 g, 72.6 %) were obtained after workup. ^{1}H NMR (C_6D_6, 400 MHz): $\delta = 0.44$ (s, 18 H, $SiMe_3$), 2.01, 2.11, 2.25, 2.26 (s, 12 H, $m\text{-}C_6H_3(CH_3)_2$), 4.58 (br s, 1 H, $^1J_{\mathrm{SiH}} = 65$ Hz, SiH), 6.34 (s, 2 H, Ar-H), 6.65 (m, 1 H, Ar-H), 7.04 (m, 4 H, Ar-H), 7.74 ppm (m, 2 H, Ar-H); ^{13}C NMR (C_7D_8, 75 MHz): $\delta =$ 6.2, 22.0, 22.4, 115.4, 126.9, 127.9, 130.3, 130.8, 139.0, 141.1, 144.5, 158.0 ppm; ^{29}Si NMR (C_7D_8, 59.6 MHz): $\delta = -0.3$ ($SiMe_3$), −158.9 ppm (ArNSiH); ^{171}Yb NMR ([D_8]toluene, 70.1 MHz): $\delta =$ −285.3 (s, $\omega_{1/2} = 15$ Hz); IR (KBr, cm^{-1}): $\tilde{\nu}$(Si–H) = 1539 cm^{-1}.

3: $ArNHSiH_3$ (1.32 g, 4.0 mmol) in toluene (10 mL) was added to a stirred solution of $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$ (1.24 g, 1.94 mmol) in toluene (5 mL) at −78 °C. Complex **3** was obtained as dark purple crystals (0.73 g, 32 %). ^{1}H NMR (C_6D_6, 400 MHz): $\delta = 0.124$ (s, 36 H, $SiMe_3$), 2.16 (s, 24 H, $m\text{-}C_6H_3(CH_3)_2$), 4.20 (s, 4 H, SiH_2), 6.65 (s, 2 H, Ar-H), 6.96 (s, 4 H, Ar-H), 7.34 (m, 2 H, Ar-H), 7.79 ppm (s, 1 H, Ar-H); ^{13}C NMR (C_6D_6, 75 MHz): $\delta =$ 4.8, 21.6, 114.9, 125.7, 126.4, 126.8, 129.3, 138.3, 141.9, 142.7, 152.3 ppm; ^{29}Si NMR (C_6D_6, 59.6 MHz): $\delta =$ 3.2 ($SiMe_3$), −57.1 ppm ($ArNSiH_2$); ^{171}Yb NMR ([D_8]toluene, 70.1 MHz): $\delta = 960.3$ ppm (s, $\omega_{1/2} = 120$ Hz, $J_{\mathrm{YbH}} = 64$ Hz); IR (KBr, cm^{-1}): $\tilde{\nu}$(Si–H) = 2159, 1782, 1749 cm^{-2}.

Further details of the synthesis and characterization of **1**–**3** are given in the Supporting Information. CCDC 779169 (**2**) and 779170

(**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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