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Me−Si Bond Cleavage of Anionic Bis(trimethylsilyl)amide in Scorpionate-Anchored Rare Earth Metal Complexes

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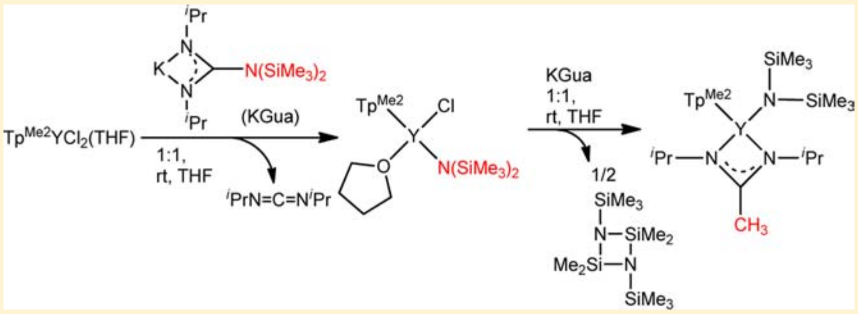
Supporting Information



ABSTRACT: A novel Tp^{Me2}-supported (Tp^{Me2} = tri(3,5-dimethylpyrazolyl)borate) rare earth metal complex promoted Me−Si cleavage of the bis(trimethylsilyl) amide ligand ($[(Me_3Si)_2N]^-$) was observed. Reaction of $Tp^{Me2}LnCl_2$ with 2 equiv of $K[(RN)_2CN(SiMe_3)_2]$ (KGua) gave the methylamidinate complexes $Tp^{Me2}Ln[(RN)_2CMe][N(SiMe_3)_2]$ (R = isopropyl, Ln = Y ($\mathbf{1}^{Y}$), Er ($\mathbf{1}^{Er}$); R = cyclohexyl, Ln = Y ($\mathbf{2}^{Y}$)) in moderate yields. In contrast, $Tp^{Me2}YCl_2(THF)$ reacted with 1 equiv of KGua to afford a C−N cleavage product $Tp^{Me2}Y(Cl)N(SiMe_3)_2(THF)$ (**4**), indicating that this guanidinate ligand is not stable in the yttrium complex with the Tp^{Me2} ligand, and a carbodiimide deinsertion takes place easily. The mechanism for the formation of complexes **1** and **2** was also studied by controlling the substrate stoichiometry and the reaction sequence and revealed that the bis(trimethylsilyl)amine anion $N(SiMe_3)_2^-$ can undergo two routes of γ-methyl deprotonation and Si−Me cleavage for its functionalizations. All these new complexes were characterized by elemental analysis and spectroscopic methods, and their solid-state structures were also confirmed by single-crystal X-ray diffraction.

INTRODUCTION

The unique features of the bis(trimethylsilyl)amide ligand in metal complexes impart many applications in organometallic[1,2] and organic synthesis[3] and material chemistry.[4] The ligand usually acts as an ancillary group in these reaction processes.[1−4] The reactivity on the ligand is rarely observed and mainly focuses on γ-methyl deprotonation due to its lack of a β-hydrogen.[5] Although the strong NSiMe-agostic interactions with metal ions in these complexes have been known for a long time;[6] surprisingly, the transformation involving Me−Si bond cleavage is rarely observed.[7] On the other hand, the cleavage of $C(sp^3)$−Si bonds in organosilicon compounds requires extremely vigorous conditions,[8] but there are some exceptions using a transition metal catalyst.[9] Intramolecular nucleophilic substitution at a silicon center to cleave the $C(sp^3)$−Si bond has also been realized by the use of stoichiometric magnesium or lithium reagents.[10] Recently, Roesky et al. reported a Me−Si bond cleavage of the trimethylsilylamide ligand in a Si(II) center.[11] To our knowledge, examples of $C(sp^3)$−Si bond cleavage mediated by rare earth metal complexes are very rare.[12]

Recently, we have been investigating the structure and reactivity of rare-earth organometallic complexes with the scorpionate Tp^{Me2} ligand[13] and found a γ-methyl deprotonation of the bis(trimethylsilyl)amide ligand without strong base or heating.[13b] To further explore this reacion, we also investigated the reactions of $Tp^{Me2}LnCl_2$ with potassium guanidinate in different molar ratios and found a rare organolanthanide mediated Me−Si bond cleavage of the bis(trimethylsilyl)amide ligand and a carbodiimide deinsertion of the guanidinate ligand. Herein, we would like to report these results.

RESULTS AND DISCUSSION

Treatment of $Tp^{Me2}LnCl_2(THF)$ with 2 equiv of potassium guanidinate $K[(RN)_2CN(SiMe_3)_2]$, prepared by reaction of $KN(SiMe_3)_2$ with carbodiimides (RN═C═NR), in THF at room temperature gave the unexpected methylamidinate lanthanide complexes $Tp^{Me2}Ln[(RN)_2CMe][N(SiMe_3)_2]$ (R = isopropyl, Ln = Y ($\mathbf{1}^{Y}$), Er ($\mathbf{1}^{Er}$); R = cyclohexyl, Ln = Y ($\mathbf{2}^{Y}$)) in moderate yields, as shown in Scheme 1. The

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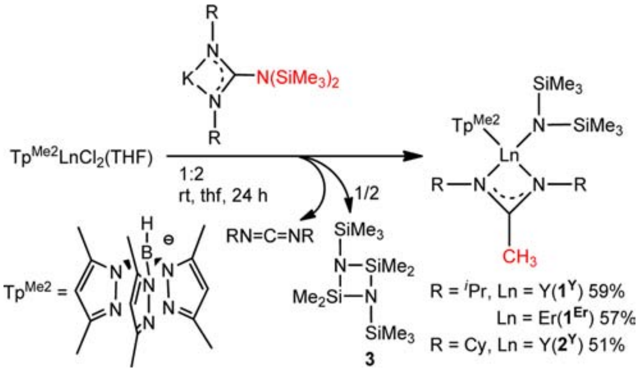
Scheme 1. Synthesis of Lanthanide Methylamidinate Complexes 1 and 2^{Y}



cyclodisilazane byproduct $[Me_3SiN—SiMe_2]_2$ (**3**) was also confirmed by ^1H NMR spectroscopy.[14] These results indicated that a rare Me—Si bond cleavage of the bis(trimethylsilyl)-amide group was observed during these reactions. Single-crystal X-ray analysis indicated that complexes **1** and $\mathbf{2^{Y}}$ are Tp^{Me2}-supported lanthanide silylamide complexes with newly formed methylamidinate ligands. **1** and $\mathbf{2^{Y}}$ were also characterized by elemental analysis and/or ^1H and ^{13}C NMR spectroscopy.

In the ^1H NMR spectra of $\mathbf{1^{Y}}$, a characteristic CH_3 resonance at 1.71 ppm was observed, assignable to the CH_3 group of the newly formed amidine unit $[(^iPrN)_2CCH_3]$. This result was consistent with the observation in the solid-stated structure of $\mathbf{1^{Y}}$. The molecular structures of $\mathbf{1^{Y}}$ and $\mathbf{1^{Er}}$ are displayed in Figure 1. The key structural data show that a methyl-amidinate ligand $[(^iPrN)_2CCH_3]$ is constructed, presumably via a Me—Si bond cleavage and insertion of carbodiimide. The Ln^{3+} ion is bonded to a κ^3-Tp^{Me2} ligand, a η^2-amidinate ligand, and a $N(SiMe_3)_2$ ligand to form a distorted octahedral geometry. In $\mathbf{1^{Y}}$, the equivalent C1—N1 and C1—N1A distances (1.32(1) Å) and Y1—N1 and Y1—N1A distances (2.33(1) Å) indicated that the π-electrons of the C═N double bond in the present structure are completely delocalized in the N—C—N skeleton.[15] The C1—C2 distance is 1.55(2) Å in accordance with a C—C single bond. Figure 2 shows that the molecular structure of $\mathbf{2^{Y}}$ is similar to that of $\mathbf{1^{Y}}$, except the difference of the isopropyl and cyclohexyl groups. In the ^1H NMR spectra of $\mathbf{2^{Y}}$, a single peak at 1.82 ppm is attributed to the CH_3 resonance of the $[(CyN)_2CCH_3]$ moiety. The formation of **1** and $\mathbf{2^{Y}}$ suggests that the $N(SiMe_3)_2$ unit can offer a methyl source via a Me—Si bond cleavage in the present system.[9b]

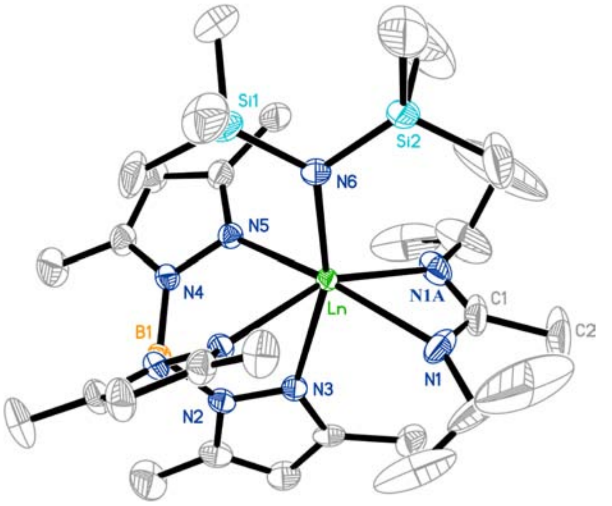


Figure 1. Molecular structures of **1** (Ln = Y($\mathbf{1^{Y}}$), Er($\mathbf{1^{Er}}$)) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (angstroms) and bond angles (deg): For $\mathbf{1^{Y}}$ Y1−N1 2.333(3), Y1−N1A 2.333(6), Y1−N6 2.312(7), N1−C1 1.318(9), N1A−C1 1.318(9), C1−C2 1.546(16); N1−Y1−N1A 57.2(4), Y1−N1−C1 93.5(6), Y1−N1A−C1 93.5(6), N1−C1−N1A 115.8(10), N1−C1−C2 122.1(5), N1A−C1−C2 122.1(5). For $\mathbf{1^{Er}}$ Er1−N1 2.322(5), Er1−N1A 2.322(5), Er1−N6 2.287(7), N1−C1 1.327(9), C1−N1A 1.327(9), C1−C2 1.530(15), N1A−Er1−N1 57.7(4), C1−N1−Er1 93.6(5), N1−Er1−N5A 105.4(2), N1A−C1−N1 115.2(9), N1−C1−C2 122.4(4), N1A−C1−C2 122.4(4). Symmetry transformations used to generate equivalent atoms: x, $-y + 1/2$, z.

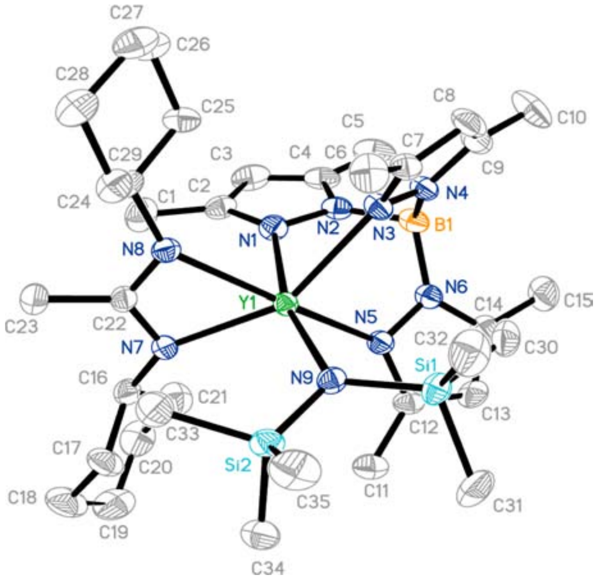
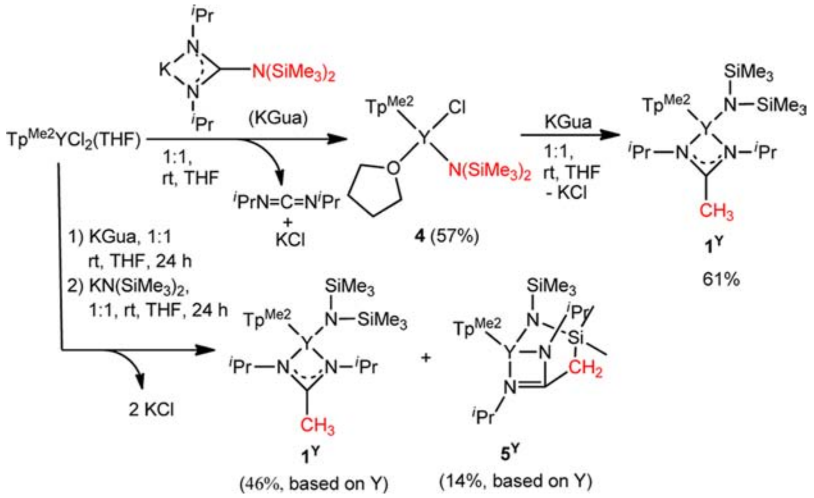


Figure 2. Molecular structures of $\mathbf{2^{Y}}$ with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (angstroms) and bond angles (deg): Y1−N9 2.325(4), Y1−N7 2.334(4), Y1−N8 2.346(5), N7−C22 1.335(7), N8−C22 1.321(7), C22−C23 1.511(8); N7−Y1−N8 57.45(16), N8−C22−N7 115.8(5), C22−N8−Y1 93.3(3), C22−N7−Y1 93.4(3), N7−C22−C23 121.8(5), N8−C22−C23 122.5(5).

To gain more insight into the mechanism for the formation of **1** and $\mathbf{2^{Y}}$, the stepwise reactions of $Tp^{Me2}YCl_2(THF)$ with KGua $(K[(^iPrN)_2CN(SiMe_3)_2])$ were investigated as shown in Scheme 2. Reaction of $Tp^{Me2}YCl_2(THF)$ with 1 equiv of KGua in THF at room temperature yielded $Tp^{Me2}Y(Cl)N(SiMe_3)_2(THF)$ (**4**), a C−N cleavage product, instead of the expected mixed Tp^{Me2}/Gua yttrium chloride $(Tp^{Me2})(Gua)YCl(THF)$. The formation of **4** suggests that the guanidinate ligand is not stable in the metal complexes with the Tp^{Me2} ligand, and a carbodiimide deinsertion easily takes place. To our knowledge, this carbodiimide deinsertion of the tetra-substituted guandinate ligand $[(R'N)_2CNR_2]$ requires drastic conditions in most cases.[16] X-ray diffraction (Figure 3) establishes that **4** is an organoyttrium amido complex without the anionic guanidine ligand. There is an agostic Y···Si bond interaction between the Y^{3+} ion with the silylamide ligand (Y···Si 3.434(4) Å). Complex **4** can also be synthesized by the reaction of $Tp^{Me2}YCl_2(THF)$ with 1 equiv of $KN(SiMe_3)_2$, and **4** further reacts with 1 equiv of KGua in THF at room

Scheme 2. Different Reaction Routes to 1^Y



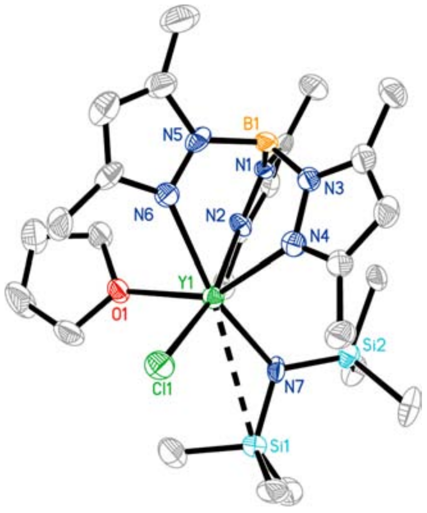


Figure 3. Molecular structures of 4 with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (angstroms) and bond angles (deg): Y1−N7 2.270(8), Y1−O1 2.400(7), Y1−Cl1 2.548(3), Y1−Si1 3.434(4), N7−Si1 1.713(9), N7−Si2 1.741(8); O1−Y1−Cl1 90.75(19), N7−Y1−Cl1 99.8(2), Si1−N7−Si2 115.3(5), Si1−N7−Y1 118.5(4), Si2−N7−Y1 125.7(4), N7−Y1−Si1 26.0(2).

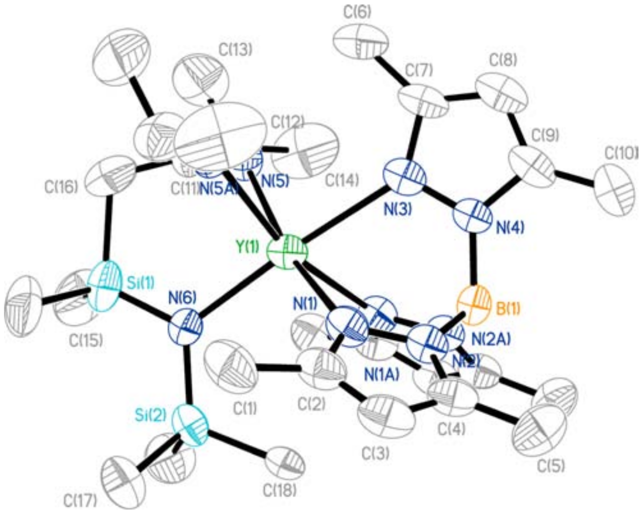
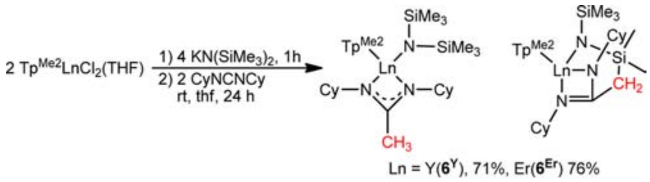


Figure 4. Molecular structures of 5^Y with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (angstroms) and bond angles (deg): Y1−N5A 2.303(6), Y1−N5 2.303(6), Y1−N6 2.316(7), Si1−N6 1.689(8), Si2−N6 1.752(8), Si1−C16 1.975(12), C11−C16 1.499(16), N5−C11 1.386(8), C11−N5A 1.386(8); N5A−Y1−N5 60.7(4), C11−N5−Y1 80.8(6), N5−C11−N5A 114.2(10), N5−C11−C16 121.6(6), N5A−C11−C16 121.6(6), C11−C16−Si1 107.1(8).

temperature to afford 1^Y in 61% isolated yield. However, a one-pot reaction of $Tp^{Me2}YCl_2(THF)_2$ with KGua and $KN(SiMe_3)_2$ in a 1:1:1 molar ratio under the same conditions gave 1^Y and 5^Y ($Tp^{Me2}Y[(^iPrN)_2CCH_2SiMe_2NSiMe_3)]$) in 46% and 14% isolate yields, respectively. ^1H, ^{13}C NMR spectroscopy and X-ray analysis indicated that 5^Y is a γ-methyl deprotonation of the bis(trimethylsilyl)amide anion and carbodiimide insertion product. The molecular structure of 5^Y (Figure 4) is similar to that of the reported compound $Tp^{Me2}Er[(Me_3Si)NSi(Me_2)CH_2C(NCy)_2]$,[13b] except the difference of the isopropyl and cyclohexyl groups. In the ^1H NMR spectrum of 5^Y, a single peak at 2.50 ppm is attributed to the characteristic CH_2 resonance. ^1H NMR monitoring of the reaction of $Tp^{Me2}YCl_2(THF)$ with 2 equiv of KGua in D_8-THF showed the molar ratio of 1^Y and 5^Y is about 4/1. These results indicate that there are two different degradation pathways of the bis(trimethylsilyl)amide ligand, viz. Me−Si cleavage and γ-methyl deprotonation in this system, and the Me−Si cleavage predominates.

The reactions of $Tp^{Me2}LnCl_2(THF)$ with $KN(SiMe_3)_2$ and carbodiimide (CyN=C=NCy) have also been investigated (Scheme 3). $Tp^{Me2}LnCl_2(THF)$ reacted with 2 equiv of $KN(SiMe_3)_2$ in THF at room temperature for 1 h, then subsequently with 1 equiv of CyN=C=NCy to afford

Scheme 3. Synthesis of Complexes 6



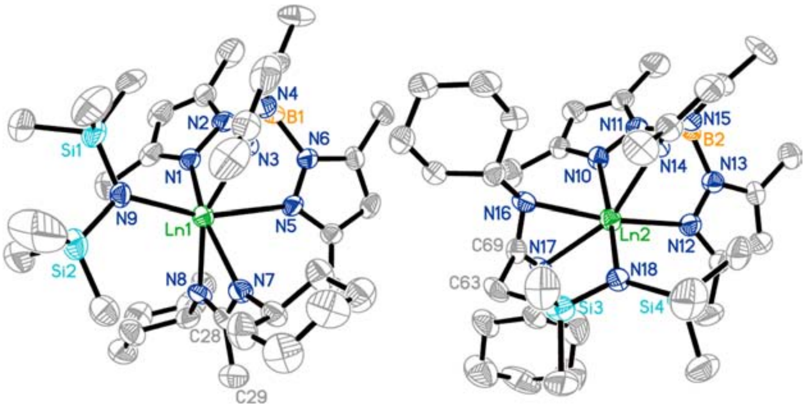
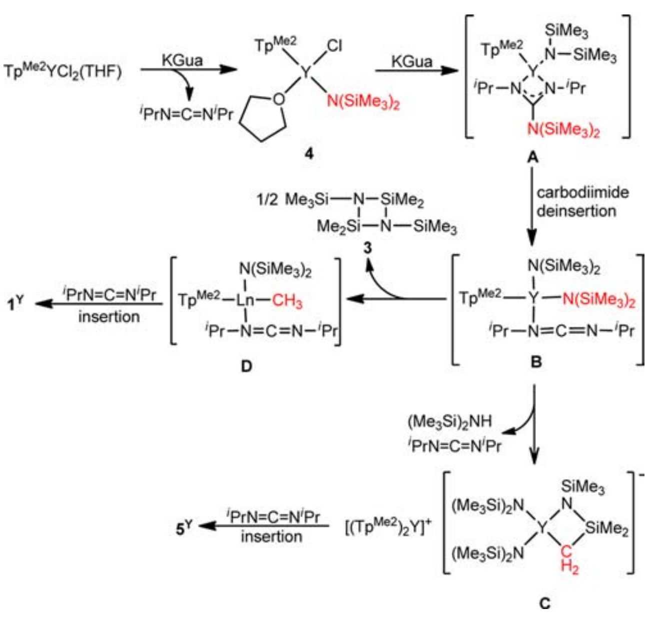


Figure 5. Molecular structures of **6** (Ln = Y($\mathbf{6}^{Y}$), Er($\mathbf{6}^{Er}$)) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (angstroms) and bond angles (deg): For $\mathbf{6}^{Y}$, Y1−N7 2.349(5), Y1−N8 2.345(5), Y1−N9 2.306(5), Y2−N16 2.308(5), Y2−N17 2.326(5), Y2−N18 2.339(4), N7−C28 1.326(8), N8−C28 1.325(8), C29−C28 1.542(8), N16−C69 1.324(7), N17−C69 1.356(7), C63−C69 1.512(8); N7−C28−N8 115.6(6), N7−C28−C29 122.8(7), N8−C28−C29 121.6(7), N16−C69−N17 113.9(5), N16−C69−C63 123.6(6), N17−C69−C63 119.9(6). For $\mathbf{6}^{Er}$, Er1−N7 2.290(16), Er1−N8 2.364(17), Er1−N9 2.306(17), Er2−N16 2.287(18), Er2−N17 2.305(16), Er2−N18 2.335(18), N7−C28 1.31(3), N8−C28 1.33(3), C28−C29 1.47(3), N16−C69 1.31(3), N17 −C69 1.33(3), C63−C69 1.47(3); N7−C28−N8 115(2), N7−C28−C29 119(2), N8−C28−C29 125(2), N16−C69−N17 112(2), N16−C69−C63 123(2), N17−C69−C63 122.8(19).

($\{Tp^{Me2}Ln[(CyN)_2CMe][N(SiMe_3)_2]\}\cdot\{Tp^{Me2}Ln[(CyN)_2CCH_2SiMe_2NSiMe_3)]\}$ Ln = Y($\mathbf{6}^{Y}$), Er($\mathbf{6}^{Er}$)) in 71 and 76% isolated yield, respectively (based on metal). X-ray diffraction shows that **6** consists of an equimolar mixture of the Me—Si bond cleavage product $Tp^{Me2}Ln[(CyN)_2CMe][N(SiMe_3)_2]$ and the γ-methyl deprotonation product $Tp^{Me2}Ln[(CyN)_2CCH_2SiMe_2NSiMe_3)]$, as depicted in Figure 5. The ^{1}H NMR spectra of $\mathbf{6}^{Y}$ also display two resonances at 2.48 and 1.81 ppm assignable to the CH_2 group of the $[(CyN)_2CCH_2SiMe_2NSiMe_3)]$ moiety and the CH_3 group of the $[(CyN)_2C(CH_3)]$ unit.

On the basis of the observations described above, we proposed a possible mechanism for the formation of $\mathbf{1}^{Y}$ and $\mathbf{5}^{Y}$, displayed in Scheme 4. First, the reaction of $Tp^{Me2}LnCl_2(THF)$ with 1 equiv of KGua forms **4**. Complex **4** reacts with another 1 equiv of KGua to give an intermediate **A**. **A** is unstable, and a carbodiimide-deinsertion takes place to produce the intermediate **B**. **B** can undergo two reaction pathways: one is a γ-methyl deprotonation to generate **C** ($[(Tp^{Me2})_2Y]^+\{[(Me_3Si)_2N]_2Y(CH_2SiMe_2NSiMe_3)\}^-$), which transforms to $\mathbf{5}^{Y}$ via an intramolecular insertion of ^{i}PrN═C═N^{i}Pr into a Y—CH$_2$ bond;[13b] another is a Me−Si cleavage of trimethylsilyl group to form the intermediate **D** and **3**. **D** converted to $\mathbf{1}^{Y}$ via an intramolecular insertion of ^{i}PrN═C═N^{i}Pr into Y—CH$_3$ bond.

Scheme 4. Plausible Mechanism for the Formation of $\mathbf{1}^{Y}$ and $\mathbf{5}^{Y}$



In summary, rare earth metal mediated Me—Si cleavage of anionic N(SiMe$_3$)$_2$ was observed for the first time, and offered a straightforward route to construction of the anionic methylamidinate ligands. These results indicate that the Me—Si bond cleavage and γ-methyl deprotonation of anionic N(SiMe$_3$)$_2$ ligand bounded to rare earth metals are competitive under certain conditions.

■ EXPERIMENTAL SECTION

General Procedure. All experiments were performed under a dry nitrogen atmosphere using Schlenk techniques or in a N$_2$-gas glovebox. The solutions such as tetrahydrofuran, toluene, and *n*-hexane were refluxed and distilled over sodium benzophenone ketyl under nitrogen immediately prior to use. Benzene-d_6 and tetrahydrofuran-d_8 were heated to reflux over Na/K alloy and vacuum-transferred. Tp^{Me2}YCl$_2$(THF) was synthesized by a slightly modified literature method.[17] KN(SiMe$_3$)$_2$ (0.5 M in toluene) was purchased from J&K chemical company, and *N*,*N*′-diisopropylcarbodiimide (DIC) and *N*,*N*′-dicyclohexylcarbodiimide (DCC) were purchased from TCI chemical (Shanghai) company and used as received without further purification. Elemental analysis for C, H, and N was carried out on a Rapid CHN-O analyzer. ^{1}H NMR data were obtained on a Jeol ECA-400 NMR spectrometer. Chemical shifts are reported with respect to solvent residual peak, 7.16 ppm (Benzene-d^6) for ^{1}H NMR spectrum, 128.06 ppm (Benzene-d^6) for ^{13}C NMR spectrum.

Synthesis of (Tp^{Me2})Y(N(SiMe$_3$)$_2$)[^{i}PrNC(*CH$_3$*)N^{i}Pr] ($\mathbf{1}^{Y}$). *Method A.* To a 10 mL THF solution of Tp^{Me2}YCl$_2$(THF) (0.265 g, 0.50 mmol) was added slowly the 10 mL THF solution of K[(^{i}PrN)$_2$C-(N(SiMe$_3$)$_2$)] (KGua) (0.326 g, 1.00 mmol). After stirring for 24 h, the solvent was removed under vacuum and the solid residue was extracted with 20 mL toluene. The extract solution was concentrated under reduced pressure to give pale yellow powder. Colorless crystals of $\mathbf{1}^{Y}$ were obtained by slow diffusion of *n*-hexane to the THF solution. Yield: 0.203 g (59%). Anal. calcd for $C_{29}H_{57}BYN_9Si_2$ (687.74): C,

Table 1. Crystal and Data Collection Parameters of Complexes 1^{Y}, 1^{Er}, and 2^{Y}

	1^{Y}	1^{Er}	2^{Y}
formula	$C_{29}H_{57}BN_9Si_2Y$	$C_{29}H_{57}BErN_9Si_2$	$C_{35}H_{65}BN_9Si_2Y$
molecular weight	687.74	766.09	767.86
crystal color	colorless	red	colorless
crystal dimens (mm)	0.20 × 0.12 × 0.08	0.15 × 0.12 × 0.10	0.20 × 0.16 × 0.12
crystal system	monoclinic	monoclinic	orthorhombic
space group	P2(1)/m	P2(1)/m	Pna2(1)
unit cell dimensions			
a (Å)	11.715(8)	11.7039(12)	20.188(7)
b (Å)	14.056(9)	14.0727(14)	12.681(4)
c (Å)	12.208(8)	12.2051(12)	16.605(6)
α (deg)	90.00	90.00	90.00
β (deg)	110.937(8)	110.8400(10)	90.00
γ (deg)	90.00	90.00	90.00
V (Å^3)	1877(2)	1878.7(3)	4251(3)
Z	2	2	4
D_c (g·cm^{-3})	1.217	1.354	1.200
μ (mm^{-1})	1.648	2.328	1.463
F (000)	732	790	1640
radiation (λ = 0.710730 Å)	Mo Kα	Mo Kα	Mo Kα
temperature (K)	293(2)	293(2)	293(2)
scan type	ω-2θ	ω-2θ	ω-2θ
θ range (deg)	1.79−25.00	2.07−25.01	1.90−25.50
h,k,l range	$-13 \le h \le 8$	$-13 \le h \le 13$	$-20 \le h \le 24$
	$-16 \le k \le 16$	$-10 \le k \le 16$	$-15 \le k \le 13$
	$-13 \le l \le 14$	$-14 \le l \le 14$	$-19 \le l \le 20$
no. of reflections measured	7747	7715	20919
no. of unique reflections	3453 [R(int) = 0.0479]	3455 [R(int) = 0.0183]	7889 [R(int) = 0.0785]
completeness to θ	99.9% (25.00)	99.8% (25.01)	100.0% (25.50)
max and min transmission	0.8794 and 0.7340	0.8005 and 0.7215	0.8440 and 0.7585
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	3453/1/231	3455/30/227	7889/1/449
goodness-of-fit on F^2	1.006	1.075	0.919
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0726	R_1 = 0.0374	R_1 = 0.0559
	wR_2 = 0.1677	wR_2 = 0.0991	wR_2 = 0.1269
R indices (all data)	R_1 = 0.0817	R_1 = 0.0388	R_1 = 0.0786
	wR_2 = 0.1720	wR_2 = 0.0998	wR_2 = 0.1336
largest diff. peak and hole (e·Å^{-3})	0.799 and −0.882	0.917 and −1.271	0.679 and −0.440

50.65; H, 8.35; N, 18.33. Found: C, 50.99; H, 8.28; N, 18.57. ^{1}H NMR (400 MHz, C_6D_6), a few drops of THF-d_8 have been added to improve the solubility. δ 5.62 (s, 3H, 4H-Tp^{Me2}), 3.33−3.41 (m, 2H, $CH(CH_3)_2$), 2.68 (s, 6H, CH_3 of Tp^{Me2}), 2.14 (s, 6H, CH_3 of Tp^{Me2}), 2.07 (s, 3H, CH_3 of Tp^{Me2}), 2.02 (s, 3H, CH_3 of Tp^{Me2}), 1.71 (s, 3H, CH_3 of amidinate), 1.32 (d, 6H, $CH(CH_3)_2$, J = 6.4 Hz), 0.95 (d, 6H, $CH(CH_3)_2$, J = 6.8 Hz), 0.62 (s, 9H, $Si(CH_3)_3$), −0.22 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (100 MHz, C_6D_6), a few drops of THF-d_8 have been added to improve the solubility, δ 176.89 (^{i}PrNC(CH_3)N^{i}Pr), 152.40 (C_3N_2H), 150.06 (C_3N_2H), 146.45 (C_3N_2H), 144.04 (C_3N_2H), 106.24 (C_3N_2H), 104.35 (C_3N_2H), 48.62 ($-CH(CH_3)_2$), 27.58 ($-CH(CH_3)_2$), 26.81 ($-CH(CH_3)_2$), 25.95 ($-CH(CH_3)_2$), 25.50 ($-CH(CH_3)_2$), 13.80 (CH_3 of Tp^{Me2}), 13.36 (CH_3 of Tp^{Me2}), 13.08 (CH_3 of Tp^{Me2}), 12.93 (CH_3 of Tp^{Me2}), 9.19 (^{i}PrNC(CH_3)N^{i}Pr), 7.00 ($N(Si(CH_3)_3)_2$), 6.16 ($N(Si(CH_3)_3)_2$). Then the mother liquor was concentrated to dry and washed twice with n-hexane (10 mL). The n-hexane solution was concentrated and cooled at −35 °C to give colorless powder **3** (($Me_3SiNSiMe_2)_2$). Yield: 0.017 g (12%, based on the $N(SiMe_3)_2$ moiety of the KGua ligand). The identify of **3** was confirmed by comparison of its ^{1}H NMR spectrum with literatures values (δ 0.29 ppm, 0.19 ppm).[14]

Synthesis of (Tp^{Me2})Er(N(SiMe$_3$)$_2$)[^{i}PrNC(CH_3)N^{i}Pr] (1^{Er}). To a 10 mL THF solution of Tp^{Me2}Er(μ-Cl)$_3$K(THF)[13b] (0.413 g, 0.50 mmol) was added slowly the 10 mL THF solution of K[(^{i}PrN)$_2$C(N(SiMe$_3$)$_2$)] (KGua) (0.326 g, 1.00 mmol). After stirring for 24 h, the solvent was removed under vacuum, and the solid residue was extracted with 20 mL toluene. The extract solution was concentrated under reduced pressure to give a pale yellow powder. Colorless crystals of 1^{Er} were obtained by slow diffusion of n-hexane to the THF solution. Yield: 0.438 g (57%). Anal. calcd for $C_{29}H_{57}BErN_9Si_2$ (1^{Er}) (766.09): C, 45.47; H, 7.50; N, 16.46. Found: C, 45.65; H, 7.57; N, 16.24.

Synthesis of (Tp^{Me2})Y(N(SiMe$_3$)$_2$)[N(Cy)C(CH$_3$)N(Cy)] (2^{Y}). To a 10 mL THF solution of Tp^{Me2}YCl$_2$(THF) (0.265 g, 0.50 mmol) was slowly added the 15 mL THF solution of K[(CyN)$_2$C(N(SiMe$_3$)$_2$)] (KGua′) (0.812 g, 1.00 mmol) at room temperature. After stirring for 24 h, all volatile substances were removed under vacuum, and the residual solid was extracted with toluene (20 mL). The toluene extract solution was concentrated to dry and was washed with n-hexane (10 mL) to give colorless powder. The colorless powder was dissolved in THF (5 mL) and was diffused by n-hexane to afford 2^{Y} as colorless crystals. Yield: 0.196 g (51%). Anal. calcd for $C_{35}H_{65}BYN_9Si_2$ (767.86): C, 54.75; H, 8.53; N, 16.42. Found: C, 54.53; H, 8.37; N, 16.66. ^{1}H NMR (400 MHz, C_6D_6): δ 5.67 (s, 2H, 4H-Tp^{Me2}), 5.64 (s, 1H, 4H-Tp^{Me2}), 3.05−3.10 (m, 2H, $CH(CH_2)_5$), 2.76 (s, 6H, CH_3 of Tp^{Me2}), 2.14 (s, 6H, CH_3 of Tp^{Me2}), 2.10 (s, 3H, CH_3 of Tp^{Me2}), 2.05 (s, 3H, CH_3 of Tp^{Me2}), 1.82 (s, 3H, CH_3 of amidinate), 1.06−1.77 (m, 20H, $CH(CH_2)_5$), 0.65 (s, 9H, $Si(CH_3)_3$), −0.20 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (100 MHz, C_6D_6): δ 177.20 (CyNC(CH_3)NCy), 149.28 (C_3N_2H), 146.42 (C_3N_2H), 106.66 (C_3N_2H), 57.82 ($-CH(CH_2)_5$), 36.64 ($-CH(CH_2)_5$), 35.21 ($-CH(CH_2)_5$), 26.34 ($-CH(CH_2)_5$), 26.26 (CyNC(CH_3)NCy), 17.17 (CH_3 of Tp^{Me2}), 14.13 (CH_3 of Tp^{Me2}), 14.03 (CH_3 of Tp^{Me2}), 13.24 (CH_3 of Tp^{Me2}), 7.78 ($N(Si(CH_3)_3)_2$), 6.04 ($N(Si(CH_3)_3)_2$).

Synthesis of Tp^{Me2}Y(Cl)N(SiMe$_3$)$_2$(THF) (4). *Method A.* To a 10 mL THF solution of Tp^{Me2}YCl$_2$(THF) (0.265 g, 0.50 mmol) was added slowly the 10 mL THF solution of K[(^{i}PrN)$_2$C(N(SiMe$_3$)$_2$)] (KGua) (0.326 g, 0.50 mmol) at room temperature. After stirring for 24 h, the volatile substances were removed under vacuum, and the residual solid was extracted with toluene (20 mL). Then the toluene extract solution was concentrated to dry, and the residue was dissolved in THF (ca. 8 mL). The THF solution was layered by n-hexane to afford the desired product **4** as colorless crystals. Yield: 0.186 g (57%). Anal. calcd for $C_{25}H_{48}BClYN_7Si_2O$ (654.05): C, 45.91; H, 7.40; N, 14.99. Found: C, 45.65; H, 7.28; N, 15.21. ^{1}H NMR (400 MHz, C_6D_6): δ 5.53 (s, 3H, 4H-Tp^{Me2}), 3.59 (br, 4H, $O(CH_2CH_2)_2$), 2.57(s, 9H, CH_3 of Tp^{Me2}), 2.13 (s, 9H, CH_3 of Tp^{Me2}), 1.37 (br, 4H, $O(CH_2CH_2)_2$), 0.34 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (100 MHz, C_6D_6): δ 150.79 (C_3N_2H), 145.13 (C_3N_2H), 106.54 (C_3N_2H), 70.47 ($O(CH_2CH_2)_2$), 25.29 ($O(CH_2CH_2)_2$), 15.18 (CH_3 of Tp^{Me2}), 13.05 (CH_3 of Tp^{Me2}), 6.55 ($N(Si(CH_3)_3)_2$).

Method B. To a 10 mL THF solution of Tp^{Me2}YCl$_2$(THF) (0.265 g, 0.50 mmol) was slowly added the toluene solution of KN(SiMe$_3$)$_2$ (0.5 M, 1 mL, 0.5 mmol) at room temperature. After workup as described for method A mentioned above, colorless crystals **4** were obtained in 74% (0.242 g) isolated yield.

Synthesis of (Tp^{Me2})Y(N(SiMe$_3$)$_2$)[^{i}PrNC(CH_3)N^{i}Pr] (1^{Y}). *Method B.* To a 10 mL THF solution of Tp^{Me2}Y(Cl)N(SiMe$_3$)$_2$(THF) (**4**) (0.327 g, 0.50 mmol) was added slowly the 10 mL THF solution of K[(^{i}PrN)$_2$C(N(SiMe$_3$)$_2$)] (KGua) (0.163 g, 0.50 mmol) at room temperature. After stirring for 24 h, the volatile substances were removed under vacuum, and the solid was extracted with toluene (20 mL). Then, the toluene solution was concentrated to dry and was dissolved in THF (ca. 5 mL), diffusing of n-hexane to the concentrated

Table 2. Crystal and Data Collection Parameters of Complexes 4, 5^Y, 6^Y, and 6^{Er}

	4	5^Y	6^Y	6^{Er}
formula	$C_{25}H_{48}BClN_7OSi_2Y$	$C_{28}H_{53}BN_9Si_2Y$	$C_{69}H_{126}B_2N_{18}Si_4Y_2$	$C_{69}H_{126}B_2Er_2N_{18}Si_4$
molecular weight	654.05	671.69	1519.68	1676.38
crystal color	colorless	colorless	colorless	pale red
crystal dimens (mm)	0.15 × 0.10 × 0.06	0.20 x0.12 × 0.08	0.12 × 0.10 × 0.06	0.15 × 0.10 × 0.05
crystal system	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$	*Pnma*	*P*2(1)/*c*	*P*2(1)/*c*
unit cell dimensions				
a (Å)	9.478(7)	13.271	16.768(5)	16.770(9)
b (Å)	12.994(10)	14.409	13.323(4)	13.305(8)
c (Å)	15.894(12)	19.625	38.183(11)	38.14(2)
α (deg)	99.137(11)	90.00	90.00	90.00
β (deg)	102.285(10)	90.00	101.087(4)	101.077(8)
γ (deg)	93.141(11)	90.00	90.00	90.00
V (Å^3)	1880(2)	3752.7	8371(4)	8352(8)
Z	2	4	4	4
D_c (g·cm^{-3})	1.155	1.189	1.206	1.333
μ (mm^{-1})	1.712	1.648	1.485	2.101
F (000)	688	1424	3240	3472
radiation (λ = 0.710730 Å)	Mo Kα	Mo Kα	Mo Kα	Mo Kα
temperature (K)	293(2)	293(2)	293(2)	293(2)
scan type	ω-2θ	ω-2θ	ω-2θ	ω-2θ
θ range (deg)	1.33−25.01	1.75−25.01	1.09−25.01	1.09−25.01
h,k,l range	$-10 \le h \le 11$, $-11 \le k \le 15$, $-18 \le l \le 18$	$-15 \le h \le 15$, $-14 \le k \le 17$, $-23 \le l \le 16$	$-19 \le h \le 19$, $-15 \le k \le 15$, $-41 \le l \le 45$	$-19 \le h \le 16$, $-15 \le k \le 15$, $-45 \le l \le 42$
no. of reflections measured	7749	14970	34114	33797
no. of unique reflections	6471 [*R*(int) = 0.0928]	3447 [*R*(int) = 0.1016]	14715 [*R*(int) = 0.1040]	14674 [*R*(int) = 0.0859]
completeness to θ	97.6% (θ = 25.01)	100.0% (θ = 25.01)	99.7% (θ = 25.01)	99.6% (θ = 25.51)
max and min transmission	0.9043 and 0.7833	0.8795 and 0.7341	0.9162 and 0.8419	0.9022 and 0.7434
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/ parameters	6471/1/347	3447/0/219	14715/0/864	14674/19/856
goodness-of-fit on F^2	0.893	0.892	0.869	1.119
final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.1045 wR_2 = 0.2552	R_1 = 0.0680 wR_2 = 0.1762	R_1 = 0.0614 wR_2 = 0.1306	R_1 = 0.1238 wR_2 = 0.3038
R indices (all data)	R_1 = 0.1720 wR_2 = 0.2825	R_1 = 0.1654 wR_2 = 0.2135	R_1 = 0.1661 wR_2 = 0.1659	R_1 = 0.1657 wR_2 = 0.3207
largest diff peak and hole (e·Å^{-3})	1.608 and −0.946	1.395and −0.676	0.456 and −0.676	2.369 and −2.714

solution to afford the desired product **1**^{Y} as colorless crystals. Yield: 0.210 g (61%).

Reaction of Tp^{Me2}YCl$_2$(THF) with KGua and KN(SiMe$_3$)$_2$. To a 10 mL THF solution of Tp^{Me2}YCl$_2$(THF) (0.265 g, 0.50 mmol) was added 5 mL THF solution of K[(^{i}PrN)$_2$C(N(SiMe$_3$)$_2$)] (KGua) (0.163 g, 0.50 mmol) at room temperature. After stirring for 24 h, KN(SiMe$_3$)$_2$ (0.5 M, 1 mL, 0.50 mmol) was added to the solution mixture at room temperature and stirred for 24 h. After workup, **1**^{Y} and **5**^{Y} was obtained in 46% (0.158 g) and 14% (0.047 g) isolated yields, respectively. Anal. calcd for $C_{28}H_{53}BYN_9Si_2$ (671.69) (**5**^{Y}): C, 50.07; H, 7.95; N, 18.77. Found: C, 49.83; H, 7.84; N, 19.03. ^{1}H NMR (400 MHz, C_6D_6): δ 5.69 (s, 1H, 4H-Tp^{Me2}), 5.56 (s, 2H, 4H-Tp^{Me2}), 3.94−4.01 (m, 2H, C*H*(CH$_3$)$_2$), 2.89 (s, 3H, C*H*$_3$ of Tp^{Me2}), 2.51 (s, 6H, C*H*$_3$ of Tp^{Me2}), 2.50(s, 2H, C*H*$_2$), 2.07 (s, 3H, C*H*$_3$ of Tp^{Me2}), 2.05 (s, 6H, C*H*$_3$ of Tp^{Me2}), 1.22 (d, 6H, CH(C*H*$_3$)$_2$, *J* = 6.4 Hz), 1.18 (d, 6H, CH(C*H*$_3$)$_2$, *J* = 6.0 Hz), 0.54 (s, 6H, −Si(C*H*$_3$)$_2$), 0.12 (s, 9H, −Si(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, C_6D_6): δ 176.90 (^{i}PrNC(CH$_2$)N^{i}Pr), 150.07 (C_3N_2H), 146.39 (C_3N_2H), 106.24 (C_3N_2H), 48.63 (−CH(CH$_3$)$_2$), 26.81 (−CH(CH$_3$)$_2$), 25.95 (^{i}PrNC(CH$_2$)N^{i}Pr), 16.16 (CH$_3$ of Tp^{Me2}), 14.22 (CH$_3$ of Tp^{Me2}), 13.35 (CH$_3$ of Tp^{Me2}), 12.93 (CH$_3$ of Tp^{Me2}), 9.19 (−Si(CH$_3$)$_2$), 6.16 (−Si(CH$_3$)$_3$).

Synthesis of (Tp^{Me2})Y(N(SiMe$_3$)$_2$)[CyNC(*CH$_3$*)NCy] (Tp^{Me2})Y-[(Me$_3$Si)NSi(Me$_2$)−*CH$_2$*C(NCy)$_2$] (6^Y). A toluene solution of KN(SiMe$_3$)$_2$ (0.5 M, 4 mL, 2.00 mmol) was added into the 30 mL THF of solution of Tp^{Me2}YCl$_2$(THF) (0.529 g, 1.00 mmol) at room temperature. After stirring for 1 h, *N,N′*-dicyclohexylcarbodiimide (DCC) (0.206 g, 1.00 mmol) was added to the mixture solution. The reaction mixture was continuously stirred for 24 h, the volatile substances were removed under vacuum, and the residual solid was extracted with toluene (30 mL). Then, the toluene extract solution was concentrated to dry and was washed with *n*-hexane (10 mL) to give colorless powder. The colorless powder was dissolved in THF (5 mL) and was diffused by *n*-hexane to afford **6**^{Y} as colorless crystals. Yield: 0.539 g (71%). Anal. calcd for $C_{69}H_{126}B_2Y_2N_{18}Si_4$ (1519.68): C, 54.54; H, 8.36; N, 16.59. Found: C, 54.25; H, 8.27; N, 16.82. ^{1}H NMR (400 MHz, C_6D_6): δ 5.74 (s, 1H, 4H-Tp^{Me2}), 5.67 (s, 2H, 4H-Tp^{Me2}), 5.64 (s, 1H, 4H-Tp^{Me2}), 5.58 (s, 2H, 4H-Tp^{Me2}), 3.66 (m, 2H, C*H*(CH$_2$)$_5$), 3.07 (m, 2H, C*H*(CH$_2$)$_5$), 2.93 (s, 3H, C*H*$_3$ of Tp^{Me2}), 2.77 (s, 6H, C*H*$_3$ of Tp^{Me2}), 2.54 (s, 6H, C*H*$_3$ of Tp^{Me2}), 2.48 (s, 2H, C*H*$_2$), 2.26 (s, 3H, C*H*$_3$ of Tp^{Me2}), 2.13 (s, 6H, CH$_3$ of Tp^{Me2}), 2.07 (s, 3H, C*H*$_3$ of Tp^{Me2}), 2.05 (s, 6H, C*H*$_3$ of Tp^{Me2}), 2.04 (s, 3H, C*H*$_3$ of Tp^{Me2}), 1.81 (s, 3H, C*H*$_3$ of amidinate), 1.09−1.77 (m, 40H, CH(C*H*$_2$)$_5$), 0.65 (s, 9H, Si(CH_3)$_3$), 0.58 (s, 6H, Si(CH_3)$_2$), 0.14 (s, 9H, Si(CH_3)$_3$), −0.20 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (100 MHz, C_6D_6): δ 177.17 (CyNC(CH_3)NCy), 175.93 (CyNC(CH_2)NCy), 150.19 (C_3N_2H), 149.68 (C_3N_2H), 149.45 (C_3N_2H), 146.42 (C_3N_2H), 106.65 (C_3N_2H), 106.39 (C_3N_2H), 57.83 (−CH(CH_2)$_5$), 57.66 (−CH(CH_2)$_5$), 37.23 (−CH(CH_2)$_5$), 36.34 (−CH(CH_2)$_5$), 26.50 (−CH(CH_2)$_5$), 26.33 (−CH(CH_2)$_5$), 26.00 (−CH(CH_2)$_5$), 25.74 (−CH(CH_2)$_5$), 25.47 (CyNC(CH_3)NCy), 23.09 (CyNC(CH_2)NCy), 17.18 (CH_3 of Tp^{Me2}), 16.00 (CH_3 of Tp^{Me2}), 14.40 (CH_3 of Tp^{Me2}), 14.14 (CH_3 of Tp^{Me2}), 13.42 (CH_3 of Tp^{Me2}), 13.26 (CH_3 of Tp^{Me2}), 13.09 (CH_3 of Tp^{Me2}), 12.98 (CH_3 of Tp^{Me2}), 7.79 (−Si(CH_3)$_3$), 6.22 (−Si(CH_3)$_2$), 6.03 (−Si(CH_3)$_3$), 5.89 (−Si(CH_3)$_3$).

Synthesis of (Tp^{Me2})Er(N(SiMe$_3$)$_2$)[CyNC(CH_3)NCy] (Tp^{Me2})Er[(Me$_3$Si)NSi−(Me$_2$)CH_2C(NCy)$_2$] (6Er). Following the procedure described above for **6**^{Y}, the reaction of Tp^{Me2}Er(μ-Cl)$_3$K(THF) (0.826 g, 1.00 mmol) with KN(SiMe$_3$)$_2$ (0.5 M, 4 mL, 2.00 mmol) and DCC (0.206 g, 1.00 mmol) at room temperature gave **6**^{Er} as pink crystals. Yield: 0.637 g (76%). Anal. calcd for $C_{69}H_{126}B_2Er_2N_{18}Si_4$ (1676.38): C, 49.44; H, 7.58; N, 15.04. Found: C, 49.78; H, 7.73; N, 15.17.

X-ray Data Collection, Structure Determination, and Refinement. Suitable single crystals of all complexes **1**−**2** and **4**−**6** were sealed under argon in Lindemann glass capillaries for X-ray structural analysis. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo *Kα* (λ = 0.71073 Å) radiation. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz-polarization effects and empirical absorption with SADABS program.[18] The structures were solved by the direct method using the SHELXL-97 program.[19] All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed using the Bruker Smart program. A summary of the crystallographic data and selected experimental information are given in Tables 1 and 2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data for complexes **1**^{Y}, **1**^{Er}, **2**^{Y}, **4**, **5**^{Y}, **6**^{Y} and **6**^{Er} in CIF format. 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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