

γ -Deprotonation of Anionic Bis(trimethylsilyl)amidolanthanide Complexes with a Countered $[(\text{Tp}^{\text{Me}_2})_2\text{Ln}]^+$ Cation

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Received November 19, 2009

$\text{Tp}^{\text{Me}_2}\text{LnCl}_2$ (**1**) reacts with 2 equiv of $\text{KN}(\text{SiMe}_3)_2$ in tetrahydrofuran at room temperature to yield the ligand redistribution/ γ -deprotonation products $[(\text{Tp}^{\text{Me}_2})_2\text{Ln}]^+[(\text{Me}_3\text{Si})_2\text{N})_2\text{Ln}(\text{CH}_2)\text{SiMe}_2\text{N}(\text{SiMe}_3)]^-$ [$\text{Ln} = \text{Er}$ (**2**), Y (**3**)]. Complex **2** can also be obtained by reacting $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{ErCl}$ with KTp^{Me_2} . However, **1** reacts with 1.5 and 1 equiv of $\text{KN}(\text{SiMe}_3)_2$ to yield $[(\text{Tp}^{\text{Me}_2})_2\text{Er}]^+[(\text{Me}_3\text{Si})_2\text{N})_3\text{ErCl}]^-$ (**4**) and $[(\text{Tp}^{\text{Me}_2})_2\text{Er}]^+\{[(\text{Me}_3\text{Si})_2\text{N})\text{Tp}^{\text{Me}_2}\text{ErCl}]_2(\mu\text{-Cl})_2\text{K}\}^-$ (**5**), respectively. Furthermore, it is found that **2** reacts with 2 equiv of $\text{CyN}=\text{C}=\text{NCy}$ ($\text{Cy} = \text{cyclohexyl}$) to give the tandem $\text{HN}(\text{SiMe}_3)_2$ elimination and $\text{Ln}-\text{C}$ insertion product $(\text{Tp}^{\text{Me}_2})\text{Er}[(\text{CyN})_2\text{CCH}_2\text{SiMe}_2\text{N}(\text{SiMe}_3)]$ (**6**) in 71% isolated yield. The results reveal that the γ -deprotonation degree of advancement increases with an increase of the steric hindrance around the central metal ion. All new complexes have been characterized by elemental analysis and spectroscopic properties, and their solid-state structures have also been determined through single-crystal X-ray diffraction analysis.

Introduction

Poly(pyrazolyl)borate anion ligands are currently attracting considerable attention because of both their potential as an alternative to cyclopentadienyl ligands and their outstanding performances in conferring organometallic complexes higher reactivity and new reaction patterns.^{1–4} In

contrast to the ever-growing literature on poly(pyrazolyl)borate complexes of transition metals,^{1,2} examples of lanthanide species incorporating these functionalities remain scarce.^{3–5} There does not appear to be a large effort to expand upon this class of compounds, which is probably due to the lack of viable synthetic methodologies to access these complexes. For example, replacement of the halide (X^-) of $\text{Tp}^{\text{Me}_2}\text{LnX}_2$ or $(\text{Tp}^{\text{Me}_2})_2\text{LnX}$ by other anionic ligands, such as alkyl and amido, remains a significant challenge,^{3a,6} even though it has been established in the past as a very powerful and efficient method for the synthesis of various lanthanocene derivatives.⁷ Most of the $(\text{Tp}^{\text{Me}_2})_2\text{Ln}^{\text{III}}\text{L}$ derivatives were prepared by the oxidation of $(\text{Tp}^{\text{Me}_2})_2\text{Ln}^{\text{II}}$ with organic reagents. Recently, Sella and co-workers reported the synthesis of the first lanthanide(III) amide with the Tp^* ligand $(\text{Tp}^{\text{Me}_2})_2\text{NdNPh}_2$ by prudential control of the reaction conditions of $(\text{Tp}^{\text{Me}_2})_2\text{NdCl}$ with NaNPh_2 .⁸

Bis(trimethylsilyl)amide is a ubiquitous ligand that has been featured in many important discoveries. Its anion lacks

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Table 1. Crystal and Data Collection Parameters of Complexes 2–6

	2	3	4	5	6
formula	C ₄₈ H ₉₇ N ₁₅ B ₂ Si ₆ Er ₂	C ₄₈ H ₉₇ N ₁₅ B ₂ Si ₆ Y ₂	C ₄₈ H ₉₈ N ₁₅ B ₂ Si ₆ ClEr	C ₇₂ H ₁₂₄ N ₂₆ B ₄ Si ₄ Cl ₄ Er ₃ K	C ₃₄ H ₆₁ N ₉ BSi ₂ Er
fw	1409.09	1252.39	1445.54	2192.25	830.17
cryst color	pink	colorless	pink	pink	pink
cryst dimens (mm)	0.12 × 0.10 × 0.06	0.97 × 0.46 × 0.20	0.15 × 0.12 × 0.10	1.40 × 0.51 × 0.24	0.25 × 0.15 × 0.12
cryst syst	triclinic	triclinic	rhombohedral	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>R</i> 3	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>c</i>
unit cell dimens					
<i>a</i> (Å)	13.284(16)	13.262(3)	16.721	12.2692(18)	9.396(6)
<i>b</i> (Å)	14.543(17)	14.478(3)	16.721	14.675(2)	39.59(2)
<i>c</i> (Å)	19.62(2)	19.556(4)	22.056	18.683(3)	10.612(6)
α (deg)	93.049(17)	93.063(3)		112.1090(10)	
β (deg)	95.770(16)	95.874(3)		102.518(2)	102.865(8)
γ (deg)	102.479(16)	102.463(3)	120	92.641(2)	
<i>V</i> (Å ³)	3671(7)	3636.2(12)	5534.8	3012.1(8)	3848(4)
<i>Z</i>	2	2	3	1	4
<i>D</i> _c (g cm ⁻³)	1.275	1.144	1.350	1.209	1.433
μ (mm ⁻¹)	2.407	1.726	2.523	2.276	2.280
<i>F</i> (000)	1440	1324	2214	1105	1716
radiation ($\lambda = 0.71073$ Å)	Mo K α	Mo K α	Mo K α	Mo K α	Mo K α
temperature (K)	293.2	293.2	293.2	293.2	293.2
scan type	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ
θ range (deg)	1.44–25.01	1.05–24.90	1.68–25.01	1.22–25.01	2.03–25.00
<i>h</i> , <i>k</i> , <i>l</i> ranges	-15 ≤ <i>h</i> ≤ 15 -17 ≤ <i>k</i> ≤ 12 -23 ≤ <i>l</i> ≤ 23	-14 ≤ <i>h</i> ≤ 15 -17 ≤ <i>k</i> ≤ 12 -23 ≤ <i>l</i> ≤ 21	-19 ≤ <i>h</i> ≤ 16 -19 ≤ <i>k</i> ≤ 19 -26 ≤ <i>l</i> ≤ 25	-14 ≤ <i>h</i> ≤ 14 -12 ≤ <i>k</i> ≤ 17 -22 ≤ <i>l</i> ≤ 22	-11 ≤ <i>h</i> ≤ 11 -40 ≤ <i>k</i> ≤ 47 -12 ≤ <i>l</i> ≤ 12
no. of reflns measd	15 234	18 189	7409	16 983	15 781
no. of unique reflns	12 654 (<i>R</i> _{int} = 0.0822)	12 468 (<i>R</i> _{int} = 0.0391)	4108 (<i>R</i> _{int} = 0.0973)	10 481 (<i>R</i> _{int} = 0.0240)	6745 (<i>R</i> _{int} = 0.0679)
completeness to θ	97.7% ($\theta = 25.01$)	98.3% ($\theta = 24.90$)	99.8% ($\theta = 25.01$)	98.5% ($\theta = 25.01$)	99.7% ($\theta = 25.00$)
refinement method	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²
data/restraints/param	12 654/2/662	12 468/2/662	4108/3/226	10 481/2/523	6745/1/427
GOF on <i>F</i> ²	0.965	1.036	1.007	1.025	1.153
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0735, w <i>R</i> 2 = 0.1833	<i>R</i> 1 = 0.0747, w <i>R</i> 2 = 0.2194	<i>R</i> 1 = 0.0772, w <i>R</i> 2 = 0.1714	<i>R</i> 1 = 0.0462, w <i>R</i> 2 = 0.1504	<i>R</i> 1 = 0.0814, w <i>R</i> 2 = 0.1850
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1370, w <i>R</i> 2 = 0.2062	<i>R</i> 1 = 0.1500, w <i>R</i> 2 = 0.2653	<i>R</i> 1 = 0.1018, w <i>R</i> 2 = 0.1854	<i>R</i> 1 = 0.0597, w <i>R</i> 2 = 0.1679	<i>R</i> 1 = 0.0996, w <i>R</i> 2 = 0.1938
largest diff peak and hole (e Å ⁻³)	3.051 and -1.511	1.536 and -0.498	5.717 and -0.898	3.458 and -1.700	1.702 and -1.757

β -hydrogen atoms and offers steric protection. Further, the precursor amine is commercially available, as are its alkali-metal complexes. Reliable syntheses of bis(trimethylsilyl)-amide complexes spanning the periodic table exist that function as useful starting materials in organometallic synthesis and catalytic cycles.⁹ So, we are interested in the synthesis of bis(trimethylsilyl)amidelanthanide complexes with the Tp^{Me2} ligands and their reactivity behavior. Here, we report the preparation of the first anionic bis(trimethylsilyl)amidelanthanide complexes featuring a countered [(Tp^{Me2})₂Ln]⁺ cation, wherein a sterically induced γ -deprotonation of the bis(trimethylsilyl)amide ligand has been established.

Experimental Section

General Procedure. All operations involving air- and moisture-sensitive compounds were carried out under an inert atmosphere of purified argon or nitrogen using standard Schlenk techniques. The solvents of tetrahydrofuran (THF) and *n*-hexane were refluxed and distilled over sodium benzophenone ketyl under nitrogen immediately prior to use. Tp^{Me2}LnCl₂ was prepared by the literature method.¹⁰ KN(SiMe₃)₂ and *N,N'*-dicyclohexylcarbodiimide (CyN=C=NCy) were purchased from Aldrich and were used without purification. Elemental analyses for C, H, and N were carried out on a Rapid CHNO

analyzer. IR spectra were obtained on a Nicolet FT-IR 360 spectrometer with samples prepared as Nujol mulls. ¹H NMR data were obtained on a Bruker DMX-400 NMR spectrometer.

Synthesis of [(Tp^{Me2})₂Er]⁺[(Me₃Si)₂N₂Er(CH₂)SiMe₂N(SiMe₃)]⁻ (2). A toluene solution of KN(SiMe₃)₂ (299 mg, 1.50 mmol) was added into the THF solution of Tp^{Me2}Er(*m*-Cl)₃K(THF)₃ (620 mg, 0.75 mmol) at room temperature. After stirring for 24 h, the precipitate was removed by centrifugation, and all volatile substances were removed under vacuum to give a pink powder. Pink crystals of **2** were obtained by the slow diffusion of *n*-hexane to the THF solution. Yield: 357 mg (68%). Elem anal. Calcd for C₄₈H₉₇N₁₅B₂Si₆Er₂: C, 40.91; H, 6.94; N, 14.91. Found: C, 40.77; H, 6.88; N, 15.06. IR (Nujol): 2728s, 2555s, 1590s, 1436s, 1240s, 1185m, 1048s, 961s, 784s, 646m, 609m cm⁻¹. HN(SiMe₃)₂ produced was identified by gas chromatography/mass spectrometry (GC/MS).

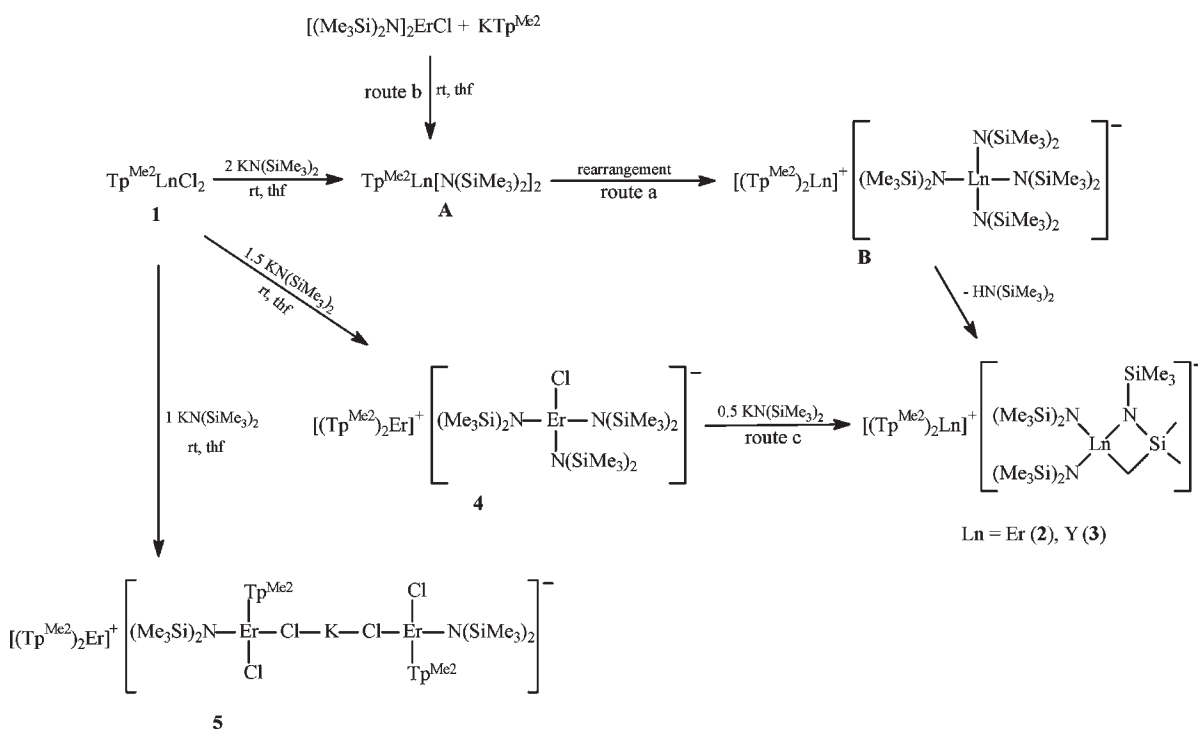
Synthesis of [(Tp^{Me2})₂Y]⁺[(Me₃Si)₂N₂Y(CH₂)SiMe₂N(SiMe₃)]⁻ (3). Following the procedure described for **2**, the reaction of KN(SiMe₃)₂ (340 mg, 1.70 mmol) with Tp^{Me2}YCl₂(THF)₃ (450 mg, 0.85 mmol) gave **3** as colorless crystals. Yield: 410 mg (77%). Elem anal. Calcd for C₄₈H₉₇N₁₅B₂Si₆Y₂: C, 46.04; H, 7.81; N, 16.78. Found: C, 45.87; H, 7.75; N, 16.97. IR (Nujol): 2725s, 2556s, 1588s, 1436s, 1240s, 1185m, 1041s, 960s, 785s, 644m, 610m cm⁻¹. ¹H NMR (C₆D₆, 7.16): δ 5.60 (s, 6H, H-4(Tp^{Me2})), 2.16 (s, 18H, CH₃-Tp^{Me2}), 2.10 (s, 18H, CH₃-Tp^{Me2}), 2.01 (s, 2H, CH₂Si(CH₃)₂), 1.59 (s, 3H, CH₃Si(CH₃)₂), 0.76 (s, 3H, CH₂Si(CH₃)₂), 0.28 (b, 36H + 9H, Si(CH₃)₃).

Synthesis of [(Tp^{Me2})₂Er]⁺[(Me₃Si)₂N₃ErCl]⁻ (4). A toluene solution of KN(SiMe₃)₂ (153 mg, 0.77 mmol) was added to a THF solution of Tp^{Me2}Er(*m*-Cl)₃K(THF)₃ (421 mg, 0.51 mmol)

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Scheme 1. Synthesis of Poly(pyrazolyl)boratelanthanide Bis(trimethylsilyl)amide Complexes 2–5



at room temperature. After stirring for 24 h, the precipitate was removed by centrifugation, and all volatile substances were removed under vacuum to give a pink powder. Pink crystals of **4** were obtained by the slow diffusion of *n*-hexane to a THF solution. Yield: 236 mg (64%). Elem anal. Calcd for $C_{48}H_{98}N_{15}B_2Si_6ClEr_2$: C, 39.88; H, 6.85; N, 14.54. Found: C, 39.67; H, 6.84; N, 14.65. IR (Nujol): 2727s, 2553s, 1537s, 1234s, 1183s, 1000m, 831s, 713m, 691s, 663m, 646m, 593m cm^{-1} .

Synthesis of $[(Tp^{Me_2})_2Er]^+ \{[(Me_3Si)_2N]Tp^{Me_2}LnCl_2(m-Cl)_2K\}^-$ (5**).** A 5 mL toluene solution of $KN(SiMe_3)_2$ (124 mg, 0.62 mmol) was added into a 25 mL THF solution of $Tp^{Me_2}Er(m-Cl)_3-K(THF)_3$ (512 mg, 0.62 mmol) at room temperature. After stirring for 24 h, the precipitate was removed by centrifugation, and all volatile substances were removed under vacuum to give a pink powder. Pink crystals of **5** were obtained by the slow diffusion of *n*-hexane to a THF solution. Yield: 455 mg (67%). Elem anal. Calcd for $C_{72}H_{124}N_{26}B_4Si_4Cl_4Er_3K$: C, 39.44; H, 5.71; N, 16.61. Found: C, 39.21; H, 5.60; N, 16.86. IR (Nujol): 2732s, 2554s, 1578s, 1539s, 1416s, 1239s, 1185m, 1008s, 933s, 843s, 802m, 694s, 646m cm^{-1} .

Synthesis of $(Tp^{Me_2})Er[(CyN)_2CCH_2SiMe_2N(SiMe_3)]$ (6**).** A 5 mL THF solution of $CyN=C=NCy$ (104 mg, 0.50 mmol) was added to a 20 mL THF solution of **2** (352 mg, 0.25 mmol) at room temperature. After stirring for 48 h, all volatile substances were removed under vacuum to give a pink powder. Pink crystals of **6** were obtained by the slow diffusion of *n*-hexane to a THF solution. Yield: 295 mg (71%). Elem anal. Calcd for $C_{34}H_{61}N_9BSi_2Er$: C, 49.19; H, 7.42; N, 15.19. Found: C, 49.05; H, 7.48; N, 15.25. IR (Nujol): 2731s, 2546s, 1661m, 1590m, 1541s, 1289m, 1250s, 1190s, 1039s, 948m, 932s, 838m, 773m, 643m cm^{-1} . $HN(SiMe_3)_2$ produced was identified by GC/MS.

X-ray Data Collection, Structure Determination, and Refinement. Suitable single crystals of complexes **2–6** 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 $Mo K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz and polarization effects and empirical

absorption with the *SADABS* program.¹¹ The structures were solved by direct methods using the *SHELXL-97* program.¹² All non-hydrogen atoms were found from the difference Fourier syntheses. The hydrogen 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 *SHELXL* program. A summary of the crystallographic data and selected experimental information is given in Table 1.

Results and Discussion

In contrast to the simple substitution reaction observed in the treatment of $(Tp^{Me_2})_2NdCl$ with $NaNPh_2$,⁸ the reaction of $Tp^{Me_2}LnCl_2$ (**1**) with 2 equiv of $KN(SiMe_3)_2$ in THF at room temperature did not result in the expected $Tp^{Me_2}Ln[N(SiMe_3)_2]_2$ but instead resulted in the ligand rearrangement/ γ -deprotonation products $[(Tp^{Me_2})_2Ln]^+[(Me_3Si)_2N)_2Ln(CH_2)SiMe_2N(SiMe_3)]^-$ [$Ln = Er$ (**2**), Y (**3**)], as shown in Scheme 1, route a. Complex **2** could be also obtained by the reaction of $((Me_3Si)_2N)_2ErCl$ with 1 equiv of KTp^{Me_2} under the same conditions in a satisfactory yield (Scheme 1, route b), indicating that the present γ -deprotonation is probably driven by the steric effect around the metal ion rather than the base effect of $KN(SiMe_3)_2$ because deprotonation of $N(SiMe_3)_2$ with KTp^{Me_2} would be much less facile.

On the basis of the above results, a plausible mechanism for the formation of **2** and **3** is proposed in Scheme 1. The ligand exchange leads to the formation of $Tp^{Me_2}Ln[N(SiMe_3)_2]_2$ (**A**). Disproportionation of **A** to ionic complex **B**¹⁶ and the subsequent elimination of $HN(SiMe_3)_2$, which

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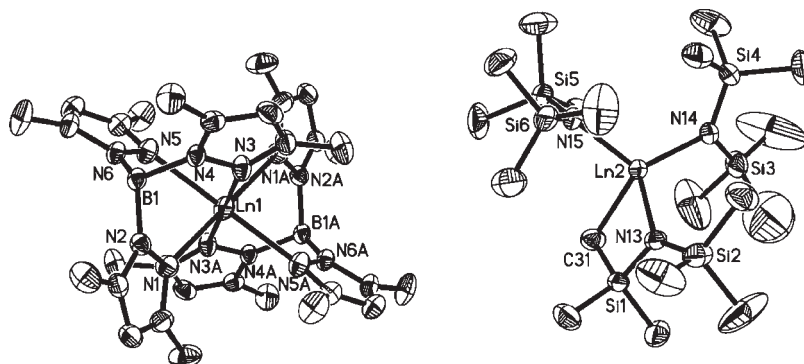


Figure 1. Molecular structures (30% thermal ellipsoids) of **2** (Ln = Er) and **3** (Ln = Y). Selected bond lengths (Å) and angles (deg): Y2–N13 2.224(6), Y2–N15 2.271(6), Y2–N14 2.318(6), Y2–C31 2.428(9), Y2–Si1 2.976(2); Y2–N13–Si1 96.6(3), N13–Si1–C31 102.5(3), Si1–C31–Y2 87.5(3), N13–Y2–C31 73.3(2).

was confirmed by GC/MS, give **2** and **3**.^{13b} Presumably, the driving force for the disproportionation of **A** to **B** most likely arises from the higher stability of bis[poly(pyrazolyl)borate]-lanthanide(III) derivatives compared to the corresponding mono[poly(pyrazolyl)borate]lanthanide(III) complexes, as are often observed in the cyclopentadienyl system.^{7b–d} The presence of anionic $[(\text{Me}_3\text{Si})_2\text{N})_4\text{Ln}]^-$ (Ln = La, Ce, Pr) for the three largest lanthanide metals has been confirmed.¹⁶ However, attempts to isolate the intermediates **A** and **B** were unsuccessful. It is noteworthy that the expansion of such a γ -deprotonation reaction to the larger metals in the lanthanide series such as La^{3+} was unsuccessful. Clearly, this is consistent with the tendency that increased steric hindrance around the Ln^{3+} ion should enhance the γ -deprotonation behavior of the $[(\text{Me}_3\text{Si})_2\text{N})_4\text{Ln}]^-$ moiety.

γ -Deprotonation of the bis(trimethylsilyl)amide ligand is an important strategy to their direct modification. The known γ -deprotonations generally require a strong base and/or heating conditions.^{13,15} In the present system, however, γ -deprotonation readily takes place without the presence of excess $\text{KN}(\text{SiMe}_3)_2$ under very mild conditions. In order to obtain more insight into the formation of **2** and **3**, a variety of experiments for confirming the Tp^{Me_2} redistribution ahead of deprotonation were performed. To our delight, it was found that the rearrangement product **4** could be selectively obtained in 64% isolated yield when **1** reacted with 1.5 equiv of $\text{KN}(\text{SiMe}_3)_2$ (Scheme 1, route c), while the treatment of **1** with 1 equiv of $\text{KN}(\text{SiMe}_3)_2$ gave the Tp^{Me_2} -redistribution product **5**, accompanied with the formation of $(\text{Me}_3\text{Si})_2\text{N}_2\text{ErCl}$ (Scheme 1). These results demonstrate that the mono- Tp^{Me_2} lanthanide complexes containing $\text{N}(\text{SiMe}_3)_2$ ligands are unstable and facily rearrange to the ionic complexes. Furthermore, we found that **4** reacted with 1 equiv of $\text{KN}(\text{SiMe}_3)_2$ to form **2**.

Compounds **2** and **3** were characterized by IR spectroscopic techniques and elemental analysis. The ^1H NMR spectrum of **3** was also determined. A characteristic CH_2

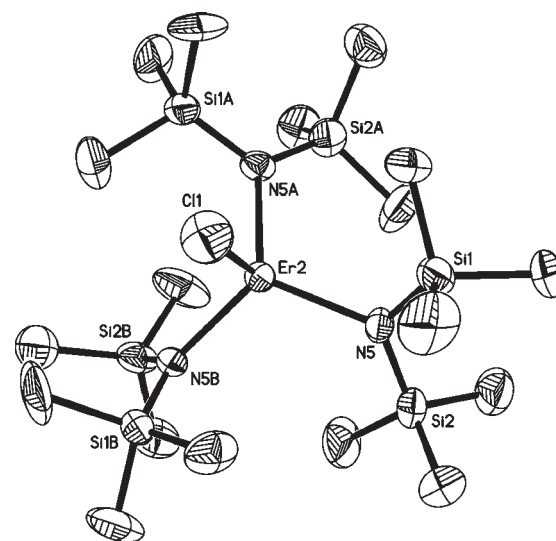


Figure 2. Crystal structure (30% thermal ellipsoids) of the anionic $[(\text{Me}_3\text{Si})_2\text{N})_3\text{ErCl}]^-$ in **4**. Selected bond lengths (Å): Er2–N5 2.267(12), Er2–N5A 2.267(12), Er2–N5B 2.267(12), Er2–C11 2.551(12).

resonance at 2.01 ppm was observed in the ^1H NMR spectrum of **3**. Their crystal structures have been determined by X-ray diffraction analysis. Figure 1 shows that **2** and **3** are isostructural and ionic-type complexes. In the $[(\text{Tp}^{\text{Me}_2})_2\text{Ln}]^+$ cation part, the Ln^{3+} ion carried with it two $\kappa^3\text{-Tp}^{\text{Me}_2}$ ligands to form a sandwich structure. In the $[(\text{Me}_3\text{Si})_2\text{N})_2\text{Ln}(\text{CH}_2\text{SiMe}_2\text{N}(\text{SiMe}_3))]^-$ anion part, the newly formed dianionic $[(\text{CH}_2)\text{SiMe}_2\text{N}(\text{SiMe}_3)]^{2-}$ ligand is coordinated to the Ln^{3+} ion in an η^2 -bonding mode and forms essentially a planar four-membered heterometallacycle. In **3**, the Y2–N13 distance [2.224(6) Å] is shorter than those of Y2–N14 and Y2–N15 [2.318(6) and 2.271(6) Å]. The Y2–C31 distance [2.428(9) Å] is comparable to the corresponding value found for $[(\eta^6\text{-C}_7\text{H}_8)\text{Na}(\text{L})\text{Sm}(\text{CH}_2)\text{SiMe}_2\text{N}(\text{SiMe}_3)]$ [2.464(3) Å],¹³ if the differences in the metal ionic radii are considered.¹⁴

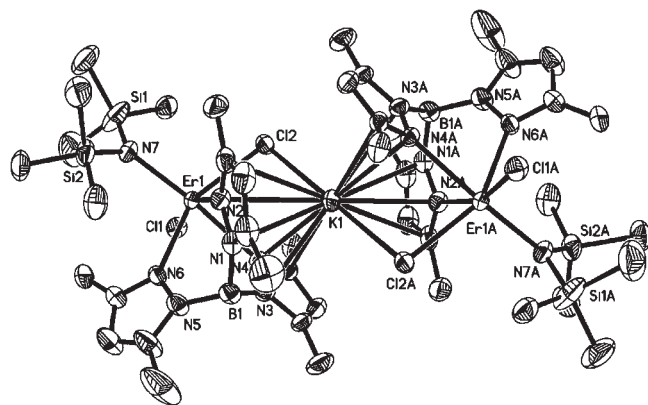
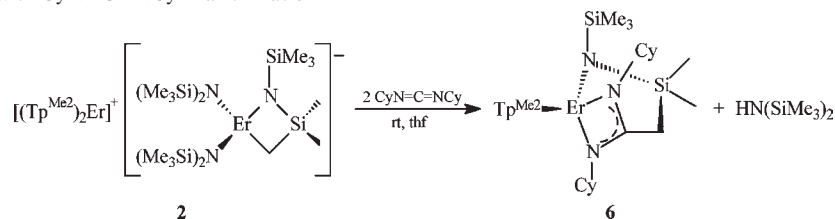
4 is composed of two units: the $[(\text{Tp}^{\text{Me}_2})_2\text{Er}]^+$ cation and the $[(\text{Me}_3\text{Si})_2\text{N})_3\text{ErCl}]^-$ anion. The structure of the cation $[(\text{Tp}^{\text{Me}_2})_2\text{Er}]^+$ in **4** is similar to that of **2**. Figure 2 shows the structure of its anionic part $[(\text{Me}_3\text{Si})_2\text{N})_3\text{ErCl}]^-$; the

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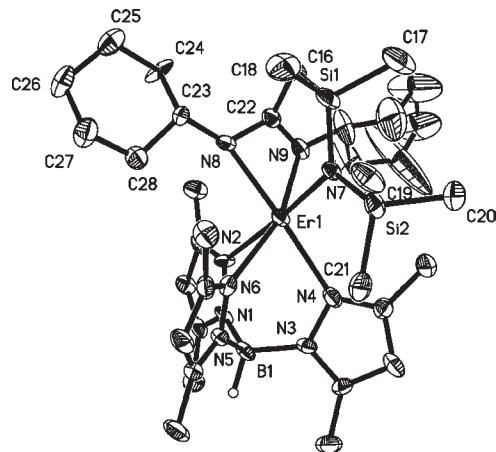
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Scheme 2. Reaction of **2** with CyN=C=NCy in a 1:2 Ratio**Figure 3.** Crystal structure (30% thermal ellipsoids) of the $\{[(\text{Me}_3\text{Si})_2\text{N})\text{Tp}^{\text{Me}_2}\text{LnCl}]_2(\mu\text{-Cl})_2\text{K}\}^-$ anion of **5**. Selected bond lengths (Å): Er1–Cl1 2.575(2), Er1–Cl2 2.6392(19), K1–Cl2 3.1228(19), K1–N4 3.054(6), K1–N2 3.109(7), K1–N3 3.151(6), K1–N1 3.219(7).

erbium ion contacts with three nitrogen atoms from the $\text{N}(\text{SiMe}_3)_2$ groups and one chlorine atom to form a distorted tetrahedral geometry. The overall structure of the anionic $\{[(\text{Me}_3\text{Si})_2\text{N})_3\text{ErCl}]\}^-$ in **4** is similar to that of the neutral compound $\{[(\text{Me}_3\text{Si})_2\text{N})_3\text{CeCl}]\}^-$.¹⁷

X-ray diffraction analysis results show that **5** is also an ionic-type complex. The structure of anionic $\{[(\text{Me}_3\text{Si})_2\text{N})\text{Tp}^{\text{Me}_2}\text{ErCl}]_2(\mu\text{-Cl})_2\text{K}\}^-$ is shown in Figure 3. It is a hetero-trimetallic Er_2K unit, in which each Er^{3+} ion is bonded to one $\kappa^3\text{-Tp}^{\text{Me}_2}$ ligand, one $\text{N}(\text{SiMe}_3)_2$ group, and two chlorine atoms to form a distorted octahedral geometry. The center metal potassium is coordinated by two bridging chlorine atoms and has a weak η^3 interaction with four pyrazolyl rings from two Tp^{Me_2} ligands.¹⁸

Insertions into the M–C bond of the γ -alkylamide chelates have found many synthetic applications.¹⁹ To compare the reactivity of the Ln–C and Ln–N bonds in **2**, we examined its reactivity toward carbodiimide. The reaction of **2** with 2 equiv of CyN=C=NCy in THF at room temperature gave the $\text{HN}(\text{SiMe}_3)_2$ elimination/Ln–C insertion product **6** in 71% isolated yield, without the formation of other metal-containing products as shown in Scheme 2. The result indicates that the Ln–C σ bond is more reactive toward carbodiimide than the Ln–N bonds in **2**, and the treatment

**Figure 4.** Molecular structure (30% thermal ellipsoids) of **6**. Selected bond lengths (Å) and angles (deg): Er1–N8 2.272(9), Er1–N9 2.273(9), Er1–N7 2.308(8), Er1–C22 2.529(11); Er1–N8–C22 85.0(7), Er1–N9–C22 85.1(6), N8–Er1–N9 57.8(3), N8–C22–N9 112.1(10), N8–C22–C16 122.3(11), N9–C22–C16 122.2(10).

of **2** with carbodiimide leads to γ -deprotonation of another $\text{N}(\text{SiMe}_3)_2$ ligand via the elimination of $\text{HN}(\text{SiMe}_3)_2$, probably due to increasing steric hindrance. Consistent with this, the reaction of **2** with 1 equiv of CyN=C=NCy gave a mixture of **2** and **6**, and the eliminated $\text{HN}(\text{SiMe}_3)_2$ was determined by GC/MS. These results further demonstrate that γ -deprotonation of the $\text{N}(\text{SiMe}_3)_2$ ligands might be promoted by the steric factor.

The molecular structure of **6** is shown in Figure 4. The X-ray diffraction analysis results show that the methylene unit of the activated $\text{CH}_2\text{SiMe}_2\text{N}(\text{SiMe}_3)$ group has combined with CyN=C=NCy, forming a four-membered ring. The newly formed amidinate coordinates to the center metal Er^{3+} in a η^3 -bonding mode. The equivalent C22–N8 and C22–N9 distances [1.328(14) and 1.320(15) Å] indicate that the π electrons of the C=N double bond in the present structure are delocalized over the N–C–N unit.²⁰ The Er–N8 and Er–N9 distances [2.272(9) and 2.273(9) Å] are in the range found for other amidinate compounds.²¹

Conclusions

We have synthesized a series of ionic complexes consisting of a $[(\text{Tp}^{\text{Me}_2})_2\text{Ln}]^+$ cation and bis(trimethylsilyl)amidinate derivative anions, **2–5**, and showed that the large steric hindrance around the anionic metal center can promote γ -deprotonation of $\text{N}(\text{SiMe}_3)_2$ ligands. In addition,

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carbodiimide insertion into $[(\text{Tp}^{\text{Me}_2})_2\text{Er}]^+[(\text{Me}_3\text{Si})_2\text{N})_2\text{-Er}(\text{CH}_2\text{SiMe}_2\text{N}(\text{SiMe}_3))]^-$ proceeded, accompanied by γ -deprotonation of complete $\text{N}(\text{SiMe}_3)_2$ ligands, providing insight into the reactivity of these ionic complexes.

Acknowledgment. We thank the National Natural Science Foundation of China, the 973 program (Grant 2009CB825300), the NSF of Shanghai, and the Shanghai

Leading Academic Discipline Project (B108) for financial support.

Supporting Information Available: Tables in CIF format of atomic coordinates and thermal parameters, all bond distances and angles, and experimental data for all structurally characterized complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.