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The First *β*-Diketiminato Complex of Terbium Containing Two Alkyl Groups: A Model Compound for $LLnR_2$ (Ln = Lanthanide, R = Alkyl) Systems[†]

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Reaction of a new *β*-diketiminato derivative of terbium, $LTbBr_2$ (L = [*N*,*N''*-(1,3-dimethyl-1,3-propanediylidene)bis[*N'*,*N'*-diethyl-1,2-ethanediamine]]), in the molar ratio 1:2 with $LiCH_2SiMe_3$ gives the terbium complex $LTb(CH_2SiMe_3)_2$, whose structure was established by elemental and X-ray analyses.

Introduction

Neutral non-cyclopentadienyl bis-hydrocarbyl complexes of the 4f elements with the general formula $LLnR_2$, of which very little has been reported yet,[1] may be of general interest as catalysts or precursors for catalytically active cationic monoalkyl species.[2−4] These systems allow greater flexibility in their reactivity, for example toward simple alkenes, as was already shown by similar complexes of early transition metals.[3,5,6] The importance of the cationic monoalkyl species has been earlier documented for the d^0 complexes of group 4 transition metals.[7]

As suggested by Piers et al. in their timely review,[8] the bulky amidinate donor,[9,10] the bis-oxazoline ancillary ligand,[11] the *β*-diketiminato chelate,[12] and the linked amido-triazacyclononane ligand[13] show great potential in this respect. Nevertheless as far as *β*-diketiminato-containing derivatives of lanthanides are concerned, the known compounds are rare: only one complex of cerium[1] and a few complexes of scandium were reported.[3,5] The explanation behind it resides in the difficulties (salt occlusion, dimerization, THF ligation) encountered when attempting to prepare such compounds. Additionally, the tendency toward ligand redistribution and elimination reactions of the desired targets makes it difficult to obtain these species in a pure form.[9]

As previously enumerated, there are generally three major pathways to prepare organometallic compounds of early transition metals and lanthanides, namely, salt, alkane, and amine elimination, respectively.[2a,8] Although, there are many disadvantages when salt elimination is applied, caused by, for instance, the scarcity of difunctional base-free precursors of the general formula $LLnX_2$ (X = halogen), it still remains the method of choice owing to its easy handling and accessibility of starting materials. Therefore a major task prior to obtaining any bis-hydrocarbyl complexes of the early transition metals or the lanthanides via the salt elimination protocol is the availability of the bifunctional precursors $LLnX_2$ (X = Cl, Br, I), ideally salt- (i.e., LiCl) and solvent-free in order not to dampen further metathesis reaction. Taking into account all these difficulties we have tailored previously a *β*-diketiminato ligand (L = [*N*,*N''*-(1,3-dimethyl-1,3-propanediylidene)-bis[*N'*,*N'*-diethyl-1,2-ethanediamine]])[14] that contains two dangling arms with hard neutral donors incorporated that proved to satisfy all the requirements and to be entirely inert and nonlabile. Thus salt- and base-free

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[†] Dedicated to Professor Michel Pouchard on the occasion of his 65th birthday.

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dihalogeno lanthanide complexes could be obtained.[14−17] By comparison by using another type of substituent on the β-diketiminato ligand core only one salt- and base-free complex of this sort was obtained, namely, [Sc{(N(C_6H_3*i*Pr_2-2,6)C(*t*Bu))$_2$CH}Cl_2].[5]

Herein, we report the results of our recent investigations in this field, namely, the synthesis of both the new bis-hydrocarbyl terbium complex, LTb(CH_2SiMe_3)$_2$ (**3**), and its base- and salt-free precursor, LTbBr_2 (**2**). Furthermore the isolation and characterization of the lithium salt **1**, used to prepare LTbBr_2, is also presented.

Results and Discussion

1.1. Synthesis of LLi (1). As previously shown by us,[14] the lithium salt can be easily prepared by reaction of (2-diethylaminoethyl)-[3-(2-diethylaminoethylimino)-1-methylbut-1-enyl]amine (LH) with MeLi in ether at −78 °C, followed by subsequent solvent removal, which afforded an oily product which further crystallizes as LLi (**1**) almost quantitatively (eq 1).

$$\mathrm{LH} + \mathrm{MeLi} \xrightarrow[-\mathrm{CH_4}]{\text{ether, } -78\ ^\circ\mathrm{C}} \underset{\mathbf{1}}{\mathrm{LLi}} \tag{1}$$

The complex **1** has been characterized by multinuclear NMR spectroscopy, EI-MS, and elemental analysis and shows that no extra molecule of solvent is required to stabilize the product, as in the case of the lithium salt of a stericallly encumbered β-diketiminato ligand, [Li{(N(C_6H_3*i*Pr_2-2,6)C(Me))$_2$CH}(OEt_2)].[18] A downfield shift of the resonance corresponding to the hydrogen atom in the γ position referred to lithium in the ligand core was observed for **3** when compared with **2** in the ^1H NMR spectra (C_6D_6, 0.2 ppm).

The salt crystallizes in the triclinic $P\bar{1}$ space group, with two molecules of LLi in the asymmetric unit, which are independent crystallographically but chemically equivalent (only one is displayed in Figure 1 for simplicity). The differences of the bond lengths and angles between the two molecules **1a** and **1b** are small.

The ligand L acts as a tetradentate ligand; thus the Li atom has the coordination number four. The lithium lies on both the backbone (NC_3N and N(1)N(2)N(3)N(4)) planes with slightly distorted planar geometries. The lithium atom is involved in two five- and one six-membered ring. The Li−N bond lengths have two different values corresponding to the two singular bonding modes in which the Li cation is involved (see Table 1). Although the Li(1)−N(1) and Li(1)−N(2) bond lengths are somewhat longer than in the case of [Li{(N(C_6H_3*i*Pr_2-2,6)C(Me))$_2$CH}(OEt_2)] (av 1.91 Å),[18] this does not affect the delocalized π-system which can be deduced from the C−N and C−C bond lengths of the backbone. As far as the Li(1)−N(3) or Li−N(4) distances are concerned, slightly longer bonds are observed by comparison to similar Li−N distances found in [($Me_2NCH_2CH_2$)$_2$NLi]$_2$[19] (e.g., 2.08 Å).

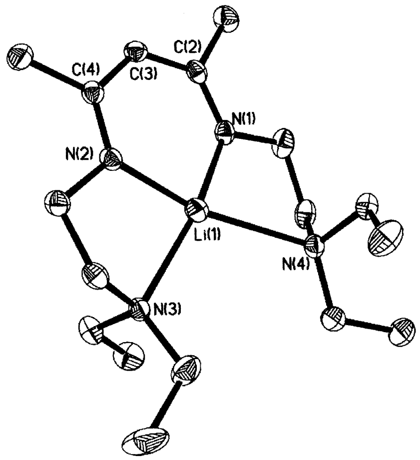

Figure 1. Molecular structure of **1** showing 50% probability ellipsoids (one molecule is drawn for simplicity, and the hydrogen atoms are omitted for clarity).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for LLi (1)

bond lengths		bond angles	
	Molecule **1a**		
Li(1)−N(1)	1.968(3)	N(2)−Li(1)−N(1)	93.55(13)
Li(1)−N(2)	1.974(3)	N(1)−Li(1)−N(4)	79.86(10)
Li(1)−N(3)	2.265(3)	N(2)−Li(1)−N(3)	82.71(10)
Li(1)−N(4)	2.450(3)	N(4)−Li(1)−N(3)	107.02(11)
N(2)−C(4)	1.3143(19)	N(1)−C(2)−C(3)	123.79(13)
N(1)−C(2)	1.315(2)	C(2)−C(3)−C(4)	127.81(14)
C(2)−C(3)	1.409(2)	N(2)−C(4)−C(3)	122.99(14)
C(4)−C(3)	1.414(2)		
	Molecule **1b**		
Li(2)−N(6)	1.965(3)	N(6)−Li(2)−N(5)	93.54(12)
Li(2)−N(5)	1.969(3)	N(8)−Li(2)−N(6)	82.33(11)
Li(2)−N(7)	2.275(3)	N(7)−Li(2)−N(5)	82.03(11)
Li(2)−N(8)	2.300(3)	N(8)−Li(2)−N(7)	108.96(12)
N(6)−C(21)	1.319(2)	N(5)−C(19)−C(20)	123.07(15)
N(5)−C(19)	1.317(2)	N(6)−C(21)−C(20)	123.63(15)
C(19)−C(20)	1.409(3)	C(21)−C(20)−C(19)	127.99(15)
C(21)−C(20)	1.405(3)		

1.2. Synthesis of LTbBr$_2$ (2). Treatment of LLi with an equivalent amount of anhydrous TbBr_3 in toluene at refluxing temperature afforded LTbBr_2, in good yield (eq 2).

$$\underset{\mathbf{1}}{\mathrm{LLi}} + \mathrm{TbBr_3} \xrightarrow[-\mathrm{LiBr}]{\text{refluxing toluene}} \underset{\mathbf{2}}{\mathrm{LTbBr_2}} \tag{2}$$

Compound **2** is very soluble in aromatic solvents, dichloromethane, and THF, and it is thermally very robust, with a melting point of 216 °C. Mass spectrometry and elemental analysis showed that compound **2** is monomeric and base-free and contains no lithium bromide. Important is that complex **2** was prepared using the anhydrous salt rather than the THF adduct. The monomeric structure was confirmed by single-crystal X-ray structural analysis. A ^1H NMR resonance spectrum that spanned over 330 ppm, due to the paramagnetic nature of the terbium atom, was observed showing broad but distinct resonances.

Single crystals suitable for X-ray studies were obtained by slow evaporation of the solvent followed by

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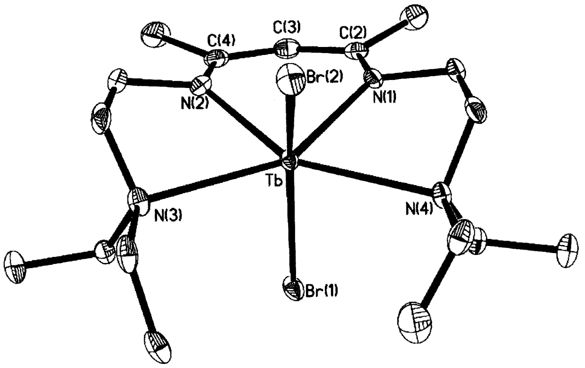

Figure 2. Molecular structure of **2** showing 50% probability ellipsoids (the hydrogen atoms are omitted for clarity). (The structure presents additional disorder of one ethyl group, which is not shown.)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for LTbBr$_2$ (2)

bond lengths		bond angles	
Tb(1)−N(1)	2.353(3)	N(1)−Tb(1)−N(2)	79.28(13)
Tb(1)−N(2)	2.341(4)	N(1)−Tb(1)−N(4)	69.90(12)
Tb(1)−N(3)	2.605(4)	N(4)−Tb(1)−N(3)	141.06(12)
Tb(1)−N(4)	2.610(3)	N(2)−Tb(1)−N(3)	69.74(13)
Tb(1)−X(1)	2.743(1)	Tb(1)−N(1)−C(1)	126.1(3)
Tb(1)−X(2)	2.801(1)	N(1)−C(2)−C(3)	124.5(4)
N(1)−C(2)	1.333(7)	C(2)−C(3)−C(4)	129.8(4)
N(2)−C(4)	1.338(7)	C(3)−C(4)−N(2)	124.2(4)
C(2)−C(3)	1.407(8)	C(4)−N(2)−Tb(1)	125.8(3)
C(3)−C(4)	1.398(8)	X(1)−Tb(1)−X(2)	149.611(16)

refrigeration for several hours at −26 °C. Complex **2** (Figure 2) crystallizes in the orthorhombic *Pca*2$_1$ space group. A local distortion is observed due to the different orientation of one of the ethyl groups from one of the arms of the ligand. Selected bond distances and angles for **2** are listed in Table 2. Both pendant arms of the ligand are coordinated to the metal center, and all four nitrogen atoms and the metal atom are in the same plane. The coordination number at the metal is six, and the geometry around the metal atom is pseudooctahedral (the Br−Tb−Br angles significantly differ from 180°), which led, as a direct consequence, to the unequal Tb−Br bond lengths. This arrangement can be compared with that of MX$_2$ (M = heavier group 2 or a divalent group 3 element and X = halogen or cyclopentadienyl).[20] The Tb−N bond lengths of the pendant arms are longer than those of the backbone, due to the coordinative and covalent character involved in different bonding modes. The expected delocalization of the electrons on the ligand framework is clearly shown by the C−C and C−N bond lengths.

1.3. Synthesis of LTb(CH$_2$SiMe$_3$)$_2$ (3). The reaction of LTbBr$_2$ with 2 equiv of LiCH$_2$SiMe$_3$ was carried out in diethyl ether (the reaction failed in toluene, THF, and benzene, respectively) at −78 °C, and the mixture was left to reach room temperature overnight (eq 3).

$$\underset{\mathbf{2}}{\mathrm{LTbBr_2}} + 2\mathrm{LiCH_2SiMe_3} \xrightarrow[\substack{\text{2. hexane} \\ -2\text{LiBr}}]{\text{1. ether, } -78\ ^\circ\text{C}} \underset{\mathbf{3}}{\mathrm{LTb(CH_2SiMe_3)_2}} \qquad (3)$$

Finally the solvent was removed and the desired compound was extracted with hexane from the crude product and crystallized at −26 °C. The reactions attempted in toluene and benzene occurred not under expected precipitation of LiBr (no solid substance was observed during the reaction) probably due to salt occlusion. The reaction in THF did not lead after workup similar to the reaction in ether to crystallization, and subsequent removal of solvent yielded, in contrast to ether, an oil. Complex **3** is highly air and moisture sensitive. The ^{29}Si NMR spectrum of **3** showed one resonance at −0.091 ppm (C$_6$D$_6$), and interestingly it has almost the same chemical shift as that of LiCH$_2$SiMe$_3$ (−0.06 ppm, C$_6$D$_6$). The ^{1}H NMR spectrum spans over 200 ppm but proved difficult to interpret due to the broad resonances observed. Surprisingly no decomposition was observed for **3** in a deuterated benzene solution at room temperature.

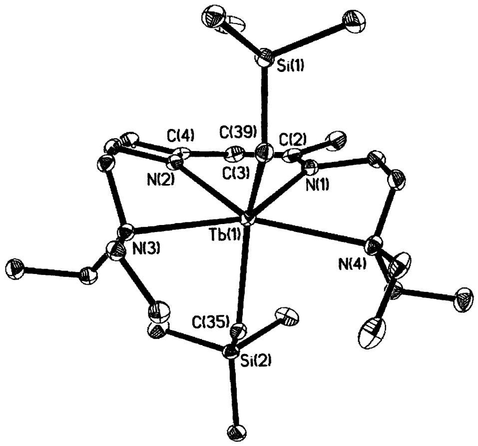

Figure 3. Molecular structure of **3** showing 50% probability ellipsoids (one molecule is drawn for simplicity, and the hydrogen atoms are omitted for clarity).

The X-ray structure of **3** is shown in Figure 3. Complex **3** crystallizes in the monoclinic *P*2$_1$/*c* space group and contains two crystallographically independent but chemically similar molecules in the unit cell. For **3**, there are insignificant differences between the bond lengths and angles of the two independent molecules (Table 3). In **3** both pendant arms of the ligand are coordinated to the Tb atom, which was expected due to the electrophilicity of the metal. The coordination number at the metal is the same as that in **2** (six), and the geometry around the metal atom is pseudooctahedral, showing that the ligand is indeed tetradentate. The Tb−C bond lengths (av 2.507 Å) are shorter than Tb−Me (2.57 Å) in [(tBuC$_5$H$_4$)$_2$Tb(μ-Me)]$_2$,[21] indicating the σ bond character (Table 3). The C−Tb−C angle substantially deviates from 180°. By comparison the Tb−N bond lengths of **3** are a bit longer than those of **2** regardless of the bonding mode. The C−C and C−N bond lengths within the ligand framework in compound **3** do not significantly diverge from the corresponding bond lengths in **1** and **2**.

In several studies, it has been shown that a β-diketiminato ligand can act either as a donor of four σ electrons or as a donor of six (2σ−π) electrons.[22] An indication

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for $LTb(CH_2SiMe_3)_2$ (3)

bonds lengths		bond angles	
Molecule **3a**			
Tb(1)−N(1)	2.383(2)	N(2)−Tb(1)−N(1)	77.91(7)
Tb(1)−N(2)	2.3771(19)	N(1)−Tb(1)−N(4)	68.82(7)
Tb(1)−N(3)	2.6902(19)	N(2)−Tb(1)−N(3)	68.64(6)
Tb(1)−N(4)	2.6954(19)	N(3)−Tb(1)−N(4)	144.32(6)
Tb(1)−C(39)	2.492(2)	N(1)−C(2)−C(3)	124.4(2)
Tb(1)−C(35)	2.508(2)	N(2)−C(4)−C(3)	124.5(2)
N(1)−C(2)	1.329(3)	C(4)−C(3)−C(2)	129.9(2)
C(2)−C(3)	1.403(4)	C(39)−Tb(1)−C(35)	135.47(8)
C(3)−C(4)	1.401(3)		
N(2)−C(4)	1.326(3)		
Molecule **3b**			
Tb(2)−N(6)	2.3754(19)	N(6)−Tb(2)−N(5)	78.93(7)
Tb(2)−N(5)	2.3867(19)	N(7)−Tb(2)−N(8)	141.60(6)
Tb(2)−N(7)	2.694(2)	N(6)−Tb(2)−N(7)	69.74(7)
Tb(2)−N(8)	2.703(2)	N(5)−Tb(2)−N(8)	69.72(6)
Tb(2)−C(43)	2.508(2)	N(5)−C(21)−C(20)	125.0(2)
Tb(2)−C(47)	2.518(3)	N(6)−C(19)−C(20)	125.0(2)
N(6)−C(19)	1.338(3)	C(21)−C(20)−C(19)	130.6(2)
N(5)−C(21)	1.330(3)	C(43)−Tb(2)−C(47)	141.80(8)
C(21)−C(20)	1.396(3)		
C(19)−C(20)	1.400(4)		

whether there is predominantly 2σ or $2\sigma-\pi$ bonding between the ligand and the metal can be deduced from the deviation of the metal from the NC_3N backbone. Interestingly, the mean deviation of the Tb atom from the NC_3N plane (0.80 Å for **2**; 0.73 and 0.90 Å for **3**) defines the binding mode of the ligand as a four-electron donor, which is, however, rare in the lanthanide chemistry for β-diketiminato ligands.[14] Comparing the mean deviation for $[(C(H)(C(Ph)NSiMe_3)_2)Ce(CH(SiMe_3)_2)_2]$[1] (1.839 Å) with those of **2** and **3** clearly shows that in the latter species the ligand acts as a six-electron donor. However this is a reasonable consequence of the nature of the ligand. Due to the very high electrophilicity of the lanthanide ions and their less demanding stereochemical environment, the lanthanide ions tend to adopt the stereochemistry that confers them the highest electron density. Hence, complexes with a β-diketiminato ligand, which have bulky aromatic or aliphatic substituents bonded to the N atoms, will coordinate mainly in a Cp-like manner. Unlike those ligands, the $Et_2NCH_2CH_2NC(Me)CHC(Me)NCH_2CH_2NEt_2$ ligand possesses two Lewis basic sites, which will confer a higher electron density to the metal center (8 electrons), if the cation would be arranged on the backbone plane.

Conclusion

The lithium salt, **3**, that contains two additional hard donors enables obtaining the first salt- and solvent-free difunctional lanthanide complexes, such as $LPrCl_2$,[14] $LPrBr_2$,[14] $LHoI_2$,[17] and $LTbBr_2$, **3**.

However, the metathesis reactions of the dihalides proved to be very difficult depending very much on the reaction conditions. Hence, only $LTb(CH_2SiMe_3)_2$ (**3**) has been prepared by salt elimination, isolated, and fully characterized. Even so, it has been shown that by general reactions the area of Cp-free bis-hydrocarbyl derivatives can be extended and confirmed that incorporating donors within the pendant arms is an interesting strategy for preparing this kind of complex. This approach has also been used for ligands, such as amidinates.[9,23]

Experimental Section

General Methods. All manipulations were performed on a dual-manifold line or in a glovebox under a purified N_2 atmosphere, using Schlenk techniques with rigorous exclusion of moisture and air. The samples for spectral measurements were prepared inside an MBraun MB 150-GI glovebox, where the O_2 and H_2O levels were normally maintained below 1 ppm. Commercial grade solvents were purified and freshly distilled following usual procedures prior to their use.[24] Melting points of all new compounds were measured in sealed capillaries on a Bühler SPA-1 instrument and are reported uncorrected. ^1H, ^{13}C, ^{29}Si, and ^7Li NMR spectra (C_6D_6) were recorded on Bruker MSL-400, AM-250, and AM-200 instruments. The chemical shifts are reported in ppm with reference to external standards, more explicitly, $SiMe_4$ for ^1H and ^{13}C nuclei, and LiCl/D_2O for ^7Li nucleus. The heteroatom NMR spectra were measured in the ^1H-decoupled mode. The downfield shifts from the reference are quoted positive and the upfield shifts are reported as negative values. The solvents for NMR measurements were dried over K or CaH_2 and trap-to-trap distilled prior to use. Mass spectra were obtained on a Finnigan MAT 8230 instrument by EI technique. Elemental analyses were performed at the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. The following compounds were prepared according to the literature protocols: LH,[14] $LiCH_2SiMe_3$,[25] and $TbBr_3$.[26]

LLi (1). Diethyl ether (50 mL) was added to (2.85 g, 9.6 mmol) LH in a 100 mL Schlenk flask. The mixture was cooled to −78 °C, and a solution of MeLi (6 mL) in diethyl ether (1.6 M, 9.6 mmol) was added dropwise. The reaction was stirred for 2 h at −78 °C and then stirred overnight at room temperature until the methane evolution had ceased. Then the solvent was removed to give a yellowish oil that further crystallizes quantitatively. Yield: 2.90 g (>99%). Mp: 81 °C. Anal. Calcd for **3**, $C_{17}H_{35}LiN_4$: C, 67.51; H, 11.66; N, 18.53. Found: C, 67.32; H, 11.74; N, 18.43. ^1H NMR (200.13 MHz, C_6D_6): δ 4.78 (s, 1 H, C*H*), 3.38 (t, 4 H, NCH_2CH_2N, $J = 5.93$ Hz), 2.44 (m, 12 H, $CH_2N(CH_2)_2$), 2.05 (s, 6 H, CCH_3), 0.77 (t, 12 H, CH_2CH_3, $J = 7.11$). ^{13}C NMR (125.75 MHz, C_6D_6): δ 164.24 (*C*CH*C*), 93.24 (*C*H), 53.89 ($CNCH_2$), 46.84 (NCH_2CH_2), 45.23 (NCH_2CH_3), 21.68 ($CHCCH_3$), 10.85 (NCH_2CH_3). ^7Li NMR (300.13 MHz, C_6D_6): δ 1.79. EI-MS: *m/z* (rel int %) 302 [M^+, 8], 216 [$M^+ - C_5H_{12}N$, 70], 86 [$C_5H_{12}N$, 100].

$LTbBr_2$ (2). A solution of **1**, freshly prepared (2.20 g, 7.3 mmol) in toluene (30 mL), was added dropwise to a suspension of $TbBr_3$ (2.91 g, 7.3 mmol) in toluene (30 mL) in a 100 mL Schlenk flask. Then, the reaction mixture was refluxed overnight. The suspension was filtered and concentrated until crystals formed. Finally, the resulting solution was warmed, and it was left undisturbed several hours at room temperature. The large yellow crystals that formed were separated by filtration, washed with pentane (50 mL), and dried in vacuo. Yield: 3.85 g (86%). Mp: 216 °C. Anal. Calcd for $C_{17}H_{35}Br_2N_4Tb$: C, 33.24; H, 5.74; N, 9.12. Found: C, 33.35; H, 5.75; N, 9.09. ^1H NMR (200.13 MHz, C_6D_6): δ 187.23, 165.29, 76.05, 1.40, −15.53, −118.57. EI-MS: *m/z* (rel int %) 614 [M^+, 14], 528 [$M^+ - C_5H_{12}N$, 66], 86 [$C_5H_{12}N$, 100].

$LTb(CH_2SiMe_3)_2$ (3). To a mixture of $LTbBr_2$ (0.7 g, 1.13 mmol) and $LiCH_2SiMe_3$ (0.214 g, 2.27 mmol) was added ether (30 mL) at −78 °C. The mixture was left to react overnight until it reached room temperature. The removal of the solvent, extraction with hexane (25 mL), and concentration under

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Table 4. Crystal Data and Summary of X-ray Data Collection for 1−3

	1	**2**	**3**
empirical formula	$C_{34}H_{40}Li_2N_8$	$C_{17}H_{35}Br_2N_4Tb$	$C_{25}H_{57}N_4Si_2Tb$
fw	604.86	614.23	628.85
temperature	173(2) K	133(2) K	100(2) K
λ	0.71073 Å	0.71073 Å	1.54178 Å
cryst syst	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$Pca2_1$	$P2_1/c$
unit cell dimens	$a = 9.3657(9)$ Å $b = 10.6804(11)$ Å $c = 19.804(2)$ Å $\alpha = 95.689(2)°$ $\beta = 90.317(2)°$ $\gamma = 101.314(2)°$	$a = 19.891(3)$ Å $b = 8.213(2)$ Å $c = 13.806(2)$ Å	$a = 21.073(3)$ Å $b = 16.359(2)$ Å $c = 18.641(2)$ Å $\beta = 101.06(2)°$
volume, Z	1932.3(3)Å^3, 2	2255.4(7) Å^3, 4	6306.8(14) Å^3, 8
density (calcd)	1.040 g/cm^3	1.809 g/cm^3	1.325 g/cm^3
abs coeff	0.062 mm^{-1}	6.685 mm^{-1}	11.875 mm^{-1}
F(000)	672	1200	2624
cryst size	0.5 × 0.3 × 0.2 mm^3	0.5 × 0.4 × 0.4 mm^3	0.20 × 0.10 × 0.10 mm^3
θ range for data collect.	1.95 to 28.28°	2.05 to 24.71°	2.14 to 57.95°
index ranges	$-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $0 \leq l \leq 26$	$-23 \leq h \leq 23$, $-9 \leq k \leq 9$, $-16 \leq l \leq 16$	$-23 \leq h \leq 21$, $-17 \leq k \leq 16$, $-20 \leq l \leq 18$
reflns collected	30 056	30 036	26 169
ind reflns	8821 [$R_{int} = 0.0330$]	3831 [$R_{int} = 0.0774$]	8602 [$R_{int} = 0.0242$]
completeness to $\theta = \theta_{max}$	91.8%	99.9%	98.0%
refinement method	full-matrix least-squares on F^2		
data/restraints/params	8821/0/409	3831/40/243	8602/0/601
goodness-of-fit on F^2	1.051	1.051	1.034
final R indices [$I>2\sigma(I)$]	$R_1 = 0.0599$, $wR_2 = 0.1343$	$R_1 = 0.0206$, $wR_2 = 0.0546$	$R_1 = 0.0209$, $wR_2 = 0.0524$
R indices (all data)	$R_1 = 0.0802$, $wR_2 = 0.1447$	$R_1 = 0.0209$, $wR_2 = 0.0547$	$R_1 = 0.0232$, $wR_2 = 0.0536$
largest diff peak and hole	0.236 and −0.248 e Å^{-3}	1.224 and −0.999 e Å^{-3}	0.685 and −0.356 e Å^{-3}

reduced pressure (10 mL) gave upon cooling (−26 °C) 0.88 g (81%) of **3**, which were filtered off. Mp: 86 °C. Anal. Calcd for $[C_{25}H_{57}N_4Si_2Tb]_2$: C, 47.75; H, 9.14; N, 8.91. Found: C, 47.42; H, 9.30; N, 8.81. ^{29}Si NMR (99.36 MHz, C_6D_6): δ −0.09. EI-MS: m/z (rel int %) 542 [$M^+ - C_5H_{12}N$, 4], 86 [$C_5H_{12}N$, 100].

X-ray Structure Determination and Details of Refinement. X-ray quality crystals of **1**−**3** were mounted on glass fibers in rapidly cooled perfluoropolyether.[27] Data for crystal structure of **1** were collected on a Bruker Smart Apex CCD diffractometer; for **2** on a Stoe Image Plate IPDS II-System; and for **3** on a SMART 6000 diffractometer. The data for all compounds were collected at low temperature (the temperatures for individual compounds are mentioned in Table 4) using graphite Mo Kα or Cu Kα radiations. Relevant crystal data are given in Table 4. The data reduction and space group determination were carried out using Siemens SHELXTL family of programs.[28] The structures were solved by direct methods, SHELXS-97,[29] and refined against F^2 using SHELXL-97.[30] The various advanced features (e.g., restraints and constraints) of the SHELXL program were used to treat the disordered ethyl group in complex **2**. The heavy atoms were refined anisotropically. Hydrogen atoms were included using the riding model with U_{iso} tied to U_{iso} of the parent atoms.

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Supporting Information Available: Tables listing details of the crystal data collection, atom coordinates, anisotropic thermal parameters, calculated positional parameters for the hydrogen atoms, and bond distances and angles. This material is available free of charge via Internet at http://pubs.acs.org.

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