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Yttrium Alkyl and Benzyl Complexes with Amino−Amidinate Monoanionic Ancillary Ligands[†]

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The sequential reaction of YCl$_3$(THF)$_{3.5}$ with [*t*-BuC(N*i*-Pr)$_2$]Li (Li[**A**]) and 2 equiv of LiCH(SiMe$_3$)$_2$ gave the mono(amidinate) dialkyl yttrium complex [*t*-BuC(N*i*-Pr)$_2$]Y[CH(SiMe$_3$)$_2$]$_2$(μ-Cl)Li(THF)$_3$ (**1**), which was structurally characterized. Use of the potentially tridentate amidinate−amine ligands [PhC(NSiMe$_3$)N(CH$_2$)$_n$NMe$_2$]$^-$ ($n = 2$, **B**; 3, **C**) yielded the salt-free dialkyl complexes [PhC(NSiMe$_3$)N(CH$_2$)$_n$NMe$_2$]Y[CH(SiMe$_3$)$_2$]$_2$ ($n = 2$, **2a**; 3, **2b**). A structure determination of **2a** showed the tridentate ligand to adopt an approximately meridional geometry. Attempts to prepare analogous benzyl or trimethysilylmethyl complexes with ligand **B** yielded the ate-complexes Li[PhC(NSiMe$_3$)N(CH$_2$)$_2$NMe$_2$]$_2$Y(R)$_2$ (R = CH$_2$Ph, **3a**; CH$_2$SiMe$_3$, **3b**). A crystal structure of **3a** showed that the Li ion is encapsulated by two amidinate and two amine nitrogens. The increased spacer length between the amidinate and amine functionalities in ligand **C** prevented encapsulation of the Li ion, but still produced a bis(amidinate) yttrium benzyl complex, [PhC(NSiMe$_3$)N(CH$_2$)$_3$NMe$_2$]$_2$YCH$_2$Ph (**4**). In this compound only one of the two dimethylamino functionalities is coordinated to the metal center.

Introduction

Neutral alkyl complexes of the group 3 metals and lanthanides are highly reactive species that exhibit interesting catalytic properties. Extensive research on the bis(pentamethylcyclopentadienyl) hydrocarbyl and hydride complexes of these metals has revealed their ability to perform catalytic olefin polymerization,[1] hydrogenation,[2] hydroamination/cyclization,[3] C−H activation,[1,4] and a range of other catalytic conversions.[5] Group 3 metal and lanthanide mono(cyclopentadienyl) dialkyl species were found to be much less easily obtained than the corresponding metallocene monoalkyl derivatives.[6] In particular, the ease of ligand redistribution reactions makes it difficult to obtain these species in pure form. Dialkyl complexes are of interest as potential precursors to cationic group 3 metal and lanthanide alkyls, of which little has been reported as yet and which are expected to be highly reactive.[7]

Non-cyclopentadienyl ancillary ligands for group 3 metal and lanthanide complexes are receiving increasing attention. Recent examples include mono- and diamide diphosphines,[8] deprotonated mono- and diazacrown ethers,[7b,9] β-diketiminates,[7a,10] and aminotroponiminates.[11] In our group, monoanionic benzamidinate

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[†] Netherlands Institute for Catalysis Research (NIOK) Publication No. RUG-00-4-1.

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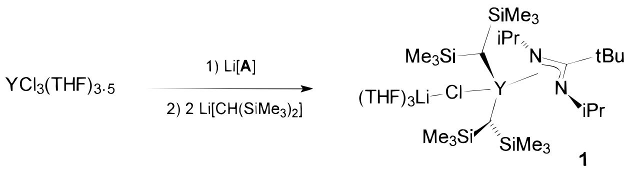
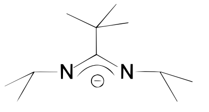
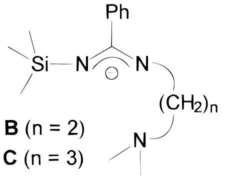
Scheme 1



and alkoxysilylamide ligands were used to explore the chemistry of bis(benzamidinate)[12] and bis(alkoxysilylamide)[13] yttrium alkyls and hydrides. Preliminary attempts to prepare mono(amidinate) yttrium dialkyls using the *N*,*N*′-bis(trimethylsilyl)benzamidinate ligand led to complex product mixtures.[14] To obtain these species, either a more sterically hindered amidinate is required or amidinates that can give additional electronic stabilization to the highly electronically unsaturated metal center are required. In this contribution we describe efforts to prepare mono(amidinate) yttrium dialkyl species using the sterically hindered amidinate $[t\text{-BuC}(Ni\text{-Pr})_2]^-$ (**A**)[15] and the *N*(dimethylaminoalkyl),*N*′(trimethylsilyl)benzamidinates $[\text{PhC}(\text{NSiMe}_3)\text{N}(\text{CH}_2)_n\text{NMe}_2]^-$ ($n = 2$, **B**;[16] 3, **C**). These efforts were successful for the sterically demanding alkyl group $\text{CH(SiMe}_3)_2$, whereas for less bulky alkyls (CH_2SiMe_3, CH_2Ph) ligand redistribution reactions occur to give various bis(amidinate) yttrium alkyl derivatives.



A



B (n = 2)
C (n = 3)

Results

The lithium salt of the amino−amidinate ligand $[\text{PhC}(\text{NSiMe}_3)\text{N}(\text{CH}_2)_2\text{NMe}_2]^-$ (**B**) is obtained by reaction of the lithium silylamide $\text{Li}[\text{Me}_2\text{N}(\text{CH}_2)_2\text{NSiMe}_3]$ with benzonitrile, as was reported previously by our group.[16] The analogue with the $(\text{CH}_2)_3$ spacer between the amidinate and the amine can be obtained similarly from the appropriate silylamide. The use of potassium metal or potassium reagents to deprotonate the silylamines followed by reaction with benzonitrile leads to the analogous potassium salts K[**B**] and K[**C**]. It was reported by Roesky et al. that 1 equiv of a potassium aminotroponiminate reacts readily with yttrium trichloride to yield a dimeric mono(aminotroponiminato)yttrium dichloride complex.[11a,b] We initially attempted to prepare well-defined mono(amidinate) yttrium dichloride starting materials by analogous 1:1 reactions of the lithium or potassium amidinate salts of **A**, **B**, and **C** with $\text{YCl}_3(\text{THF})_{3.5}$. These reactions generally yielded noncrystalline products with poorly defined stoichiometries. For the preparation of mono(amidinate)yttrium dialkyls we therefore made use of a reaction sequence in which initially $\text{YCl}_3(\text{THF})_{3.5}$ is reacted in THF with 1 equiv of the appropriate amidinate salt, followed by subsequent additon of 2 equiv of the alkylating agent.

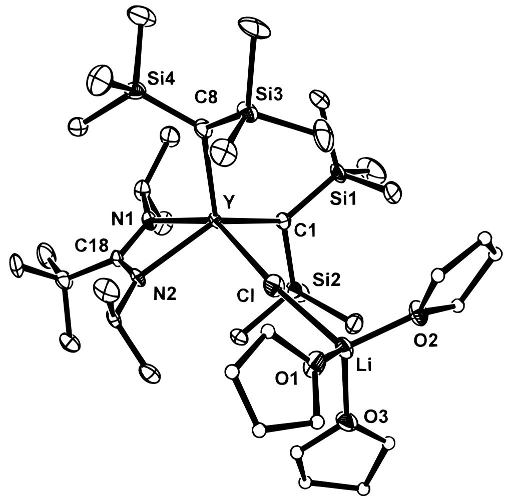


Figure 1. Molecular structure of $[t\text{-BuC}(Ni\text{-Pr})_2]\text{Y}[\text{CH}(\text{SiMe}_3)_2]_2(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (**1**).

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for Compound 1

Y−Cl	2.639(2)	Li−O(1)	1.921(13)
Y−N(1)	2.339(6)	Li−O(2)	1.905(12)
Y−N(2)	2.353(4)	Li−O(3)	1.926(13)
Y−C(1)	2.460(7)	N(1)−C(18)	1.340(9)
Y−C(8)	2.454(7)	N(2)−C(18)	1.335(9)
Li−Cl	2.362(12)		
N(1)−Y−N(2)	55.9(2)	Y−Cl−Li	167.2(3)
C(1)−Y−C(8)	116.3(2)	Y−C(1)−Si(1)	123.4(3)
Cl−Y−N(1)	145.33(16)	Y−C(1)−Si(2)	110.4(3)
Cl−Y−N(2)	94.92(14)	Si(1)−C(1)−Si(2)	117.9(4)
Cl−Y−C(1)	93.14(16)	Y−C(8)−Si(3)	118.0(3)
Cl−Y−C(8)	103.71(17)	Y−C(8)−Si(4)	122.8(3)
		Si(3)−C(8)−Si(4)	112.5(4)

Such a sequential reaction of $\text{YCl}_3(\text{THF})_{3.5}$ with $[t\text{-BuC}(Ni\text{-Pr})_2]\text{Li}$ (Li[**A**])[15] and 2 equiv of $\text{Li}[\text{CH}(\text{SiMe}_3)_2]$ in THF afforded, after pentane extraction and crystallization, large crystals of the mono(amidinate)−dialkyl complex $[t\text{-BuC}(Ni\text{-Pr})_2]\text{Y}[\text{CH}(\text{SiMe}_3)_2]_2(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (**1**, Scheme 1) in 83% isolated yield. An X-ray structure determination of **1** (Figure 1, selected interatomic distances and angles in Table 1) shows the practically linear coordination of LiCl to the yttrium center, with three (disordered) THF molecules completing the coordination sphere of Li. The linear bonding of an alkali-metal halide to a metal center has been observed on several occasions in lanthanide hydrocarbyl complexes where the steric bulk of the ligands is insufficient to shield the lanthanide metal coordination sphere.[17] As in the bis(amidinate) yttrium complexes,[12] the bite angle of the $N,N'\text{-}\sigma^2$ amidinate ligand is very small ($\text{N}(1)-\text{Y}-\text{N}(2) = 55.9(2)°$). The Y−C(alkyl) distances are close to those observed in other $\text{Y}-\text{CH}(\text{SiMe}_3)_2$ complexes.[12,13,18,19] In the solid state the alkyl groups are rotated relative to each other (dihedral angles C(1)−Y−C(8)−

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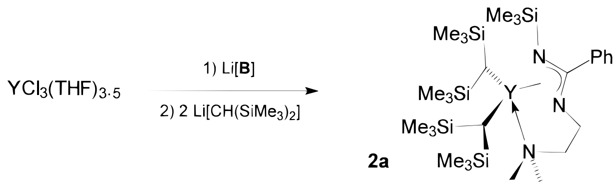
Scheme 2



Si(3) = −86.2(4)°, C(8)−Y−C(1)−Si(1) = 22.3(5)°) to minimize the steric repulsion between the two bulky groups. This is also observed in the ate-complex [(THF)-Li(μ-Ot-Bu)$_2$]Y[CH(SiMe$_3$)$_2$]$_2$, in which the yttrium is four-coordinate.[19] In some yttrium and lanthanide −CH(SiMe$_3$)$_2$ complexes (e.g., Cp*$_2$LnCH(SiMe$_3$)$_2$[1c,18] and Cp*La[CH(SiMe$_3$)$_2$]$_2$[6b−d]) a strong distortion of the alkyl Y−C−Si angles is observed that stems from an interaction of the β-Si−C bond with the metal center.[20] In complex **1** no such distortion of the Y−C−Si angles is present. This interaction was also absent from the bis(amidinate) and bisalkoxysilylamido yttrium−CH-(SiMe$_3$)$_2$ complexes.[12,13] Solution NMR spectra of **1** at ambient temperature show equivalent alkyl SiMe$_3$ and *i*-Pr methyl groups, implying fluxional behavior. Cooling a toluene-d_8 solution of **1** leads to broadening of the resonances, but at −90 °C the slow exchange limit had not yet been reached. The ^{1}H and ^{13}C NMR characteristics of the Y−alkyl CH-moiety are close to those of the bis(amidinate) complex [PhC(NSiMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$[12] and differ from those in Cp*$_2$YCH(SiMe$_3$)$_2$,[18] in which the ^{13}C NMR resonance is found considerably more upfield (δ 25.2 ppm, compared to 44.1 ppm in **1**).

The coordination of 1 equiv of LiCl to the yttrium center of **1** suggests that the amidinate employed provides insufficient protection to the metal center. To prevent incorporation of alkalimetal halide, a similar synthesis was performed with the lithium salts of the potentially tridentate amino−amidinates [PhC(NSiMe$_3$)N(CH$_2$)$_n$NMe$_2$]$^-$ (n = 2, **B**; 3, **C**). After recrystallization from pentane, these reactions afforded the salt-free mono(amidinate)−dialkyls [PhC(NSiMe$_3$)N(CH$_2$)$_n$-NMe$_2$]Y[CH(SiMe$_3$)$_2$]$_2$ (n = 2, **2a**; 3, **2b**) in modest isolated yield (Scheme 2). The derivative with n = 2 (**2a**) was characterized by single-crystal X-ray diffraction. The structure (Figure 2, selected interatomic distances and angles in Table 2) shows that the amino−amidinate ligand is indeed tridentate, with the ligand adopting an approximately meridional coordination mode. This contrasts with the facial tridentate coordination mode that was observed for this ligand in the vanadium(III) complex [PhC(NSiMe$_3$)N(CH$_2$)$_2$NMe$_2$]VCl$_2$(THF).[16] The coordination sphere of Y in **2a** is directly related to that in **1**, with the main difference that the N(3)−Y−N(2) angle in **2a** (66.6(2)°) is considerably smaller than the Cl−Y−N(2) angle of 94.9(2)° in **1**. The NMR spectral features of the Y−alkyl moieties in **2** are very similar to those of **1**, but showing varying degrees of fluxionality at ambient temperature. For **2a** there are clearly two separate alkyl SiMe$_3$ resonances, whereas for **2b** one broad alkyl SiMe$_3$ resonance is observed. Warming the sample of **2a** leads to coalescence of the two alkyl SiMe$_3$ resonances around 50 °C. The increase in amidinate−amine spacer length on going from **2a** to **2b** leads only to slight downfield shifts of the Y−CH ^{1}H and ^{13}C NMR resonances.

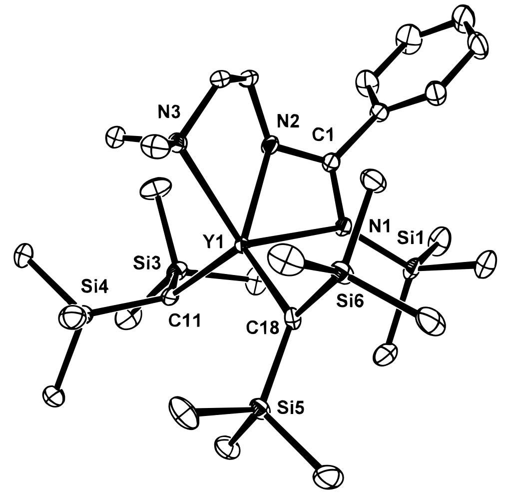


Figure 2. Molecular structure of [PhC(NSiMe$_3$)N(CH$_2$)$_2$-NMe$_2$]Y[CH(SiMe$_3$)$_2$]$_2$ (**2a**).

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Compound 2

Y−N(1)	2.366(3)	N(1)−C(1)	1.345(6)
Y−N(2)	2.284(4)	N(2)−C(1)	1.327(5)
Y−N(3)	2.576(4)		
Y−C(11)	2.425(5)		
Y−C(18)	2.471(4)		
N(1)−Y−N(2)	57.75(12)	Y−C(11)−Si(3)	119.2(2)
N(2)−Y−N(3)	66.57(12)	Y−C(11)−Si(4)	114.4(2)
N(1)−Y−N(3)	119.76(12)	Si(3)−C(11)−Si(4)	115.2(2)
C(11)−Y−C(18)	118.17(15)	Y−C(18)−Si(5)	122.9(2)
N(3)−Y−C(11)	108.46(13)	Y−C(18)−Si(6)	116.9(2)
N(3)−Y−C(18)	108.37(13)	Si(5)−C(18)−Si(6)	115.8(2)

The successful synthesis of compounds **2** has shown that the use of the tridentate amino−amidinate monoanionic ligand enables the isolation of monomeric, salt-free mono(amidinate)−dialkyl yttrium species. The bulky alkyl group employed, bis(trimethylsilyl)methyl, is very suitable for obtaining stable, highly electron-deficient alkyl species, but rather disadvantageous for further reactivity studies. We therefore applied the same synthesis strategy to try and isolate dialkyl species with less sterically encumbered alkyl groups, viz., trimethylsilylmethyl and benzyl. The sequential reactions of YCl$_3$(THF)$_{3.5}$ with 1 equiv of Li[PhC(NSiMe$_3$)N-(CH$_2$)$_2$NMe$_2$] (Li[**B**]) and 2 equiv of Me$_3$SiCH$_2$Li or PhCH$_2$K resulted in relatively low yields of products with an amino−amidinate-to-alkyl ratio of 1:1 (as seen by NMR). A crystal structure determination of the benzyl derivative (vide infra) showed that these products are in fact bis(amino−amidinate) yttrium ate-complexes of the type Li[PhC(NSiMe$_3$)N(CH$_2$)$_2$NMe$_2$]$_2$Y-(R)$_2$ (R = CH$_2$Ph, **3a**; CH$_2$SiMe$_3$, **3b**). They are obtained in significantly higher yields when the appropriate amino−amidinate-to-yttrium ratio of 2:1 is used in the synthesis (Scheme 3).

A crystal structure determination of Li[PhC(NSiMe$_3$)N(CH$_2$)$_2$NMe$_2$]$_2$Y(CH$_2$Ph)$_2$ (**3a**) showed two independent molecules of **3a** in the unit cell that differ mainly by the orientation of the benzyl groups (rotation

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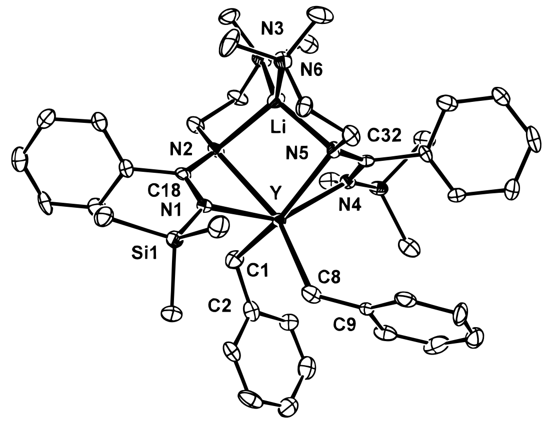


Figure 3. Molecular structure of Li[PhC(NSiMe$_3$)N(CH$_2$)$_2$NMe$_2$]$_2$Y(CH$_2$Ph)$_2$ (**3a**). Only one of the two independent molecules is shown.

Scheme 3

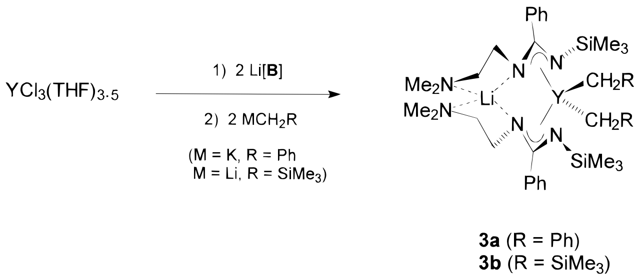


Table 3. Selected Interatomic Distances (Å) and Angles (deg) for Compound 3 (molecule 1 of the asymmetric unit only)

Y(1)−N(1)	2.431(5)	Li(1)−N(2)	2.109(13)
Y(1)−N(2)	2.450(7)	Li(1)−N(3)	2.039(14)
Y(1)−N(4)	2.403(7)	Li(1)−N(5)	2.036(14)
Y(1)−N(5)	2.476(6)	Li(1)−N(6)	2.045(13)
Y(1)−C(1)	2.490(8)	Y(1)−C(8)	2.463(6)
N(1)−C(18)	1.349(10)	N(4)−C(32)	1.346(10)
N(2)−C(18)	1.333(10)	N(5)−C(32)	1.283(10)
C(1)−Y(1)−C(8)	105.1(3)	N(1)−Y(1)−N(2)	55.5(2)
Y(1)−C(1)−C(2)	109.1(5)	N(1)−Y(1)−N(4)	145.4(2)
Y(1)−C(8)−C(9)	119.7(5)	N(1)−Y(1)−N(5)	95.3(2)
N(1)−Y(1)−C(1)	100.2(2)	N(2)−Li(1)−N(3)	87.3(5)
N(1)−Y(1)−C(8)	91.3(2)	N(2)−Li(1)−N(5)	104.1(6)
N(2)−Y(1)−C(1)	86.6(2)	N(3)−Li(1)−N(5)	134.5(6)
N(2)−Y(1)−C(8)	146.6(2)	N(5)−Li(1)−N(6)	88.9(5)

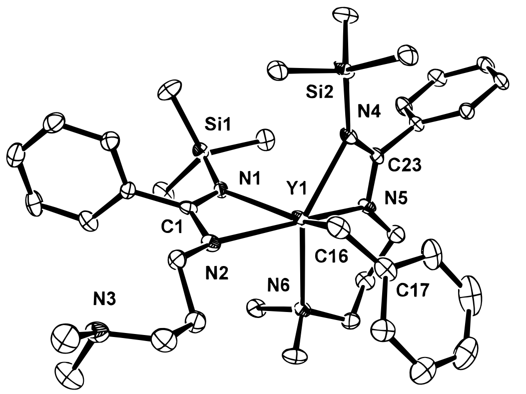
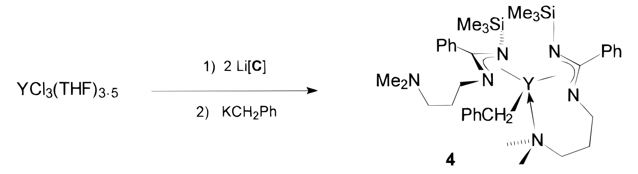


Figure 4. Molecular structure of [PhC(NSiMe$_3$)N(CH$_2$)$_3$NMe$_2$]$_2$YCH$_2$Ph (**4**).

Scheme 4



around the Y−CH$_2$ axis). In Figure 3 only one of the two independent molecules is shown (molecule 1, selected interatomic distances and angles in Table 3). Molecule 2 is somewhat more "regular" in that it approaches (noncrystallographic) C_2 symmetry. In **3a** two amino−amidinate ligands are bound to yttrium, but the ligand dimethylamino functionalities are coordinated to a Li$^+$ ion that is further ligated by the alkyl-substituted amidinate nitrogens. These nitrogen atoms, N(2) and N(5) in Figure 3, are thus bound to both yttrium and lithium and create, together with the dimethylamino nitrogens, a distorted tetrahedral site for the lithium ion. Two benzyl ligands are bound to yttrium, and the complex can be described as a zwitterion with a Li cation and a bis(amidinate) yttrium dibenzyl anion. The two benzyl groups are essentially η^1-bound, and neither the crystal structure nor the NMR spectra (benzyl methylene $^1J_{\mathrm{CH}} = 117.1$ Hz) present evidence for additional interaction of the benzyl groups with the metal center. The Li site is distorted tetrahedral, with the smallest N−Li−N angles (around 88°) for the pairs of chelating nitrogens, N(2)/N(3) and N(5)/N(6). The solution NMR spectra indicate effective C_2 symmetry, showing an ABX pattern for the benzyl methylene protons in **3a**, whereas the alkyl methylene proton resonances in **3b** appear to be accidentally degenerate.

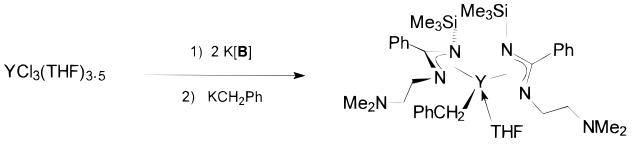
It is thus observed that a reduction of alkyl group size from bis(trimethylsilyl)methyl to trimethylsilylmethyl or benzyl leads to the formation of bis(amino−amidinate) yttrium complexes through ligand redistribution. It is difficult to say a priori if this is an effect intrinsic to the size reduction of the alkyl group or that this is induced by the "incarceration" of the lithium ion in the four-coordinate site that is created by the two amino−amidinate ligands and that seems particularly suitable to bind lithium. To test this, we performed two experiments in which the binding of the alkali metal ion should be disfavored: (a) an increase in spacer length in the amino−amidinate from (CH$_2$)$_2$ to (CH$_2$)$_3$, to increase the size of the cage, and (b) the use of the (CH$_2$)$_2$ spacer with a larger alkali metal ion, potassium.

The reaction of YCl$_3$(THF)$_{3.5}$ with 1 equiv of Li[PhC(NSiMe$_3$)N(CH$_2$)$_3$NMe$_2$] (Li[**C**]) and 2 equiv of PhCH$_2$K resulted in a relatively low yield of the salt-free bis(amino−amidinate) yttrium benzyl complex [PhC(NSiMe$_3$)N(CH$_2$)$_3$NMe$_2$]$_2$YCH$_2$Ph (**4**). Again, this compound could be obtained in a higher isolated yield when the appropriate amidinate-to-yttrium-to-benzyl ratio of 2:1:1 was employed (Scheme 4). Slow crystallization from pentane yielded single crystals of stoichiometry **4**·(pentane)$_{0.5}$ suitable for X-ray diffraction. The structure of **4** (Figure 4, selected interatomic distances and angles in Table 4) shows that two amino−amidinates are bound to yttrium, but that the dimethylamino group of only one of the ligands is coordinated to the metal center. This tridentate ligand adopts a meridional coordination mode. The benzyl group in the 12-electron complex **4** exhibits a more acute Y−CH$_2$−C$_{\mathrm{ipso}}$ angle (96.3(3)°) than the benzyl groups in **3a**, but still not as

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for Compound 4

Y−N(1)	2.367(4)	N(1)−C(1)	1.339(6)
Y−N(2)	2.394(4)	N(2)−C(1)	1.315(6)
Y−N(4)	2.363(4)	N(4)−C(23)	1.326(6)
Y−N(5)	2.358(4)	N(5)−C(23)	1.327(6)
Y−N(6)	2.539(4)		
Y−C(16)	2.487(6)		
N(1)−Y−N(4)	94.41(13)	N(4)−Y−N(5)	57.05(13)
N(1)−Y−N(5)	104.72(14)	N(5)−Y−N(6)	76.78(13)
N(1)−Y−N(6)	94.51(13)	N(4)−Y−N(6)	133.73(13)
N(1)−Y−C(16)	133.20(18)	N(6)−Y−C(16)	115.03(17)
N(2)−Y−N(5)	157.17(15)	Y−C(16)−C(17)	96.3(3)

Scheme 5



5

pronounced as in, for example, $Cp^*_2CeCH_2Ph$ (86°).[21] The benzyl methylene CH coupling constant of 121.9 Hz is somewhat larger that that observed for **3a**.

The above result clearly suggests that encapsulation of the alkali metal ion is not the driving force for the formation of bis(amino−amidinate) yttrium alkyl complexes when relatively small alkyl groups are employed. In addition we performed the reaction of $YCl_3(THF)_{3.5}$ with 1 equiv of $K[PhC(NSiMe_3)N(CH_2)_2NMe_2]$ (K[**B**]) and 2 equiv of $PhCH_2K$. This resulted in a relatively low yield of a compound that, based on ^1H and ^{13}C NMR data, was identified as the THF adduct of the bis(amino−amidinate) yttrium benzyl complex, $[PhC(NSiMe_3)N(CH_2)_2NMe_2]_2YCH_2Ph(THF)$ (**5**, Scheme 5). It thus appears that in the bis(amino−amidinate) complexes the $(CH_2)_2$ spacer renders intramolecular coordination of the dimethylamino functionality less favorable; in this case coordination of one molecule of THF is preferred. Again, this compound is obtained more conveniently (with an isolated yield of 60%) when the correct stoichiometry of the reagents is used.

Discussion

Using the amidinate anionic functionality, it proved possible to prepare highly electron-deficient (10-electron) yttrium dialkyl species of the type (amidinate)Y(L)$[CH(SiMe_3)_2]_2$, where L is a Lewis base (either $(THF)_3LiCl$ in **1** or a tethered dimethylamino group in **2**). In these complexes the amidinate and L functionalities are arranged in an approximately meridional geometry. Interestingly, for yttrium and the small lanthanide lutetium the isoelectronic dialkyls $Cp^*M[CH(SiMe_3)_2]_2$ could not be obtained, although they are available for the larger lanthanides La and Ce.[6b−d] The meridional arrangement of the ancillary ligands in **1** and **2** allows a different orientation of the two large alkyl groups relative to each other than in the Cp* complexes, thus relieving steric hindrance around the metal center.

Although bis(amidinate)$YCH(SiMe_3)_2$ complexes are known,[12] formation of bis(amidinate)complexes was not found to pose difficulties in the synthesis of the mono(amidinate) $CH(SiMe_3)_2$ complexes **1** and **2**. This did occur in attempts to prepare mono(amidinate) complexes with smaller metal-bound alkyl groups. It remains to be seen if such compounds themselves are inherently unstable or if disproportionation is brought about by the presence of alkalimetal halide. There is precedent for the promotion of ligand scrambling by alkalimetal halides.[22]

In the first transition metal complex of the amino−amidinate ligand **B**, the V(III) complex $[PhC(NSiMe_3)N(CH_2)_2NMe_2]VCl_2(THF)$,[16] a facial η^3-coordination mode was observed. This was surprising, as it necessitated strong nonplanarity of the dimethylaminoethyl-substituted amidinate nitrogen (the sum of the angles around this nitrogen atom is 336.4°). The structure of the yttrium complex **2** shows that this amino−amidinate ligand can also readily adopt a meridional η^3-coordination mode when the metal center is larger and less specific for an octahedral complex geometry. But even in these compounds it is seen that the alkyl-substituted amidinate nitrogen is not as rigorously planar as the $SiMe_3$-substituted amidinate nitrogen is. The sums of the angles around the alkyl-substituted amidinate nitrogens are 349.3° in **2** and 359.3° and 352.6° in **4**. It was seen in the structure of the ate-complex **3a** that the ligand can also support the formation of bimetallic complexes (in this case with one amidinate nitrogen bound to Y, the other one bridging between Y and Li, and with the amine nitrogen bound to Li). It thus appears that the amino−amidinate ancillary ligand is quite versatile in its coordination modes, and we expect interesting results from the chemistry of this ligand with other transition metals and lanthanides.

Conclusions

Mono(amidinate) yttrium dialkyls (amidinate)YR_2(L) (L = Lewis base) are accessible via salt methathesis for $R = CH(SiMe_3)_2$. An amine Lewis base can be incorporated into the ancillary ligand to give salt- and solvent-free dialkyls (amidinate−amine)YR_2. Use of alkyl groups smaller than bis(trimethylsilyl) leads to ligand redistribution to give bis(amidinate) yttrium complexes. In the case of the amidinate−amine ancillary ligands, a fitting match between the spacer linking the amidinate and amine functionalities and the alkalimetal ion can lead to ate-complexes of the type (alkalimetal)(amidinate−amine)$_2YR_2$.

Experimental Section

All experiments were performed under nitrogen atmosphere using standard glovebox and Schlenk techniques. Deuterated solvents (Aldrich) were dried over Na/K alloy and vacuum transferred before use (C_6D_6, THF-d_8). Toluene, THF, diethyl ether, and pentane were distilled from Na or Na/K alloy before use. The compounds $[t\text{-BuC}(Ni\text{-Pr})_2]Li$[15] and Li[**B**],[16] $YCl_3(THF)_{3.5}$,[23] $Me_2N(CH_2)_2N(H)SiMe_3$,[16] $PhCH_2K$,[24] Me_3SiCH_2Li,[25]

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[21] Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 3246.

[22] For examples in cyclopentadienyl lanthanide chemistry see references cited in: Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865.

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[24] Lochmann, L.; Trekoval, J. *J. Organomet. Chem.* **1987**, *326*, 1.

[25] Negishi, E.; Swanson, D. R.; Rousset, C. J. *J. Org. Chem.* **1990**, *55*, 5406.

and $\mathrm{(Me_3Si)_2CHLi}$[26] were prepared according to literature procedures. Benzonitrile (Aldrich) was degassed and dried over molecular sieves (4 Å) before use. The diamines $\mathrm{Me_2N(CH_2)_{\mathit{n}}NH_2}$ ($n = 2, 3$; Aldrich) were used as purchased.

NMR spectra were run at ambient temperature on a Varian VXR-300 spectrometer unless mentioned otherwise. Elemental analyses were performed by the Microanalytical Department of the University of Groningen. Every value is the average of at least two independent determinations. In many of the complexes the carbon contents found are consistently and reproducibly too low relative to the calculated values (by 0.5% to up to 1.8% absolute), whereas for the other elements correct values are obtained. It is possible that formation of inert carbides (especially of Si) is responsible for this.

[*t*-BuC(N*i*-Pr)₂]Y[CH(SiMe₃)₂]₂LiCl(THF)₃ (1). Solid Li[**A**] (0.23 g, 1.21 mmol) was added to a suspension of $\mathrm{YCl_3(THF)_{3.5}}$ (0.53 g, 1.20 mmol) in THF (20 mL) at −40 °C. The mixture was allowed to warm to room temperature and was stirred overnight. The resulting solution was cooled to −40 °C, and solid $\mathrm{LiCH(SiMe_3)_2}$ (0.39 g, 2.40 mmol) was added. After stirring for 5 h at −10 °C the solvent was removed in vacuo, and the residue was stripped of remaining THF by stirring with pentane (2 × 5 mL), which was subsequently pumped off. Extraction with pentane (3 × 30 mL), concentrating, and cooling to −20 °C yielded **1** (0.85 g, 0.98 mmol, 83%) as white crystals. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 4.01 (sept, $^3J_{\mathrm{HH}} = 6.3$ Hz, 2 H, $\mathrm{C\mathit{H}Me_2}$), 3.57 (m, 12 H, THF), 1.43 (m, 12 H, THF), 1.20 (d, $^3J_{\mathrm{HH}} = 6.3$ Hz, 12 H, $\mathrm{CH\mathit{Me}_2}$), 1.14 (s, 9 H, $\mathrm{C\mathit{Me}_3}$) 0.35 (s, 36 H, $\mathrm{CH(Si\mathit{Me}_3)_2}$), −0.87 (d, $^2J_{\mathrm{YH}} = 2.1$ Hz, 2 H, $\mathrm{C\mathit{H}SiMe_3}$). ^{13}C{^{1}H} NMR (75.4 MHz, $\mathrm{C_6D_6}$): δ 178.3 ($\mathrm{\mathit{C}CMe_3}$), 68.2 (THF), 46.8 ($\mathrm{\mathit{C}HMe_2}$), 44.1 (d, $^1J_{\mathrm{YC}} = 31.7$ Hz, $\mathrm{\mathit{C}HSiMe_3}$) 31.4 ($\mathrm{\mathit{C}Me_3}$), 27.5, ($\mathrm{CH\mathit{Me}_2}$), 5.8 ($\mathrm{CHSi\mathit{Me}_3}$). Anal. Calcd for $\mathrm{C_{37}H_{85}O_3N_2YLiClSi_4}$ (848.45): C, 52.30; H, 10.08; N, 3.30; Y, 10.46. Found: C, 51.18; H, 10.03; N, 2.86; Y, 10.43.

Me₂N(CH₂)₃NHSiMe₃. This diamine was prepared according to the procedure described for the $\mathrm{(CH_2)_2}$-bridged analogue.[16] To a solution of $\mathrm{Me_2N(CH_2)_2NH_2}$ (8 g, 80.0 mmol) and $\mathrm{Et_3N}$ (38 mL, 270 mmol) in dioxane (50 mL) was added $\mathrm{Me_3SiCl}$ (11.6 mL, 80 mmol). The resulting white suspension was then warmed to 95 °C and stirred overnight at this temperature. After filtration and extraction of the remaining white solid with ether (2 × 100 mL) the solvents were removed in vacuo from the combined filtrate and extracts. A distillation of the remaining liquid under reduced pressure (80 mmHg, 70−75 °C) gave $\mathrm{Me_2N(CH_2)_3NHSiMe_3}$ as a colorless liquid (11.7 g, 66.4 mmol, 83%). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 2.72 (t, $^3J_{\mathrm{HH}} = 3.9$ Hz, 2 H, $\mathrm{NC\mathit{H}_2(CH_2)_2NMe_2}$), 2.18 (t, $^3J_{\mathrm{HH}} = 3.9$ Hz, 2 H, $\mathrm{NCH_2CH_2C\mathit{H}_2NMe_2}$), 2.08 (s, 6 H, $\mathrm{N\mathit{Me}_2}$), 1.45 (m, 2 H, $\mathrm{NCH_2C\mathit{H}_2CH_2NMe_2}$), 0.07 (s, 9 H, $\mathrm{NSi\mathit{Me}_3}$).

Li[PhC(N(CH₂)₃NMe₂)(NSiMe₃)] (Li[C]). A solution of $\mathrm{Me_2N(CH_2)_3NHSiMe_3}$ (11.7 g, 66.4 mmol) in ether (50 mL) was cooled to 0 °C, and 26.5 mL of 2.5 M BuLi/hexane was added dropwise. After stirring for 3 h, the mixture was warmed to ambient temperature, and benzonitrile (6.7 mL, 66.0 mmol) was added. The yellow reaction mixture was stirred overnight, after which the solvent was removed in vacuo to give an orange oil, which slowly solidified. Washing with pentane gives Li[**C**] (13.0 g, 53.4 mmol, 81.0%) as a yellow solid. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 7.05 (m, 5 H, Ar), 2.89 (t, $^3J_{\mathrm{HH}} = 5.1$ Hz, 2 H, $\mathrm{NC\mathit{H}_2(CH_2)_2NMe_2}$), 2.17 (br t, 2 H, $\mathrm{NCH_2CH_2C\mathit{H}_2NMe_2}$), 1.98 (s, 6 H, $\mathrm{N\mathit{Me}_2}$), 1.25 (qui, $^3J_{\mathrm{HH}} = 5.4$ Hz, 2 H, $\mathrm{NCH_2C\mathit{H}_2CH_2NMe_2}$), 0.10 (s, 9 H, $\mathrm{NSi\mathit{Me}_3}$). ^{13}C NMR (75.4 MHz, $\mathrm{C_6D_6}$): δ 177.5 ($\mathrm{\mathit{C}Ph}$), 143.7 (Ph C_{ipso}), 129.2 (d, $J = 158.6$ Hz, *o*-Ph), 126.6 (d, $J = 159$ Hz, *p*-Ph and *m*-Ph), 60.4 (t, $J = 131.7$ Hz, $\mathrm{N\mathit{C}H_2(CH_2)_2NMe_2}$), 50.0 (t, $J = 130.6$ Hz, $\mathrm{N(CH_2)_2\mathit{C}H_2NMe_2}$), 46.2 (q, $J = 134.2$ Hz, $\mathrm{N\mathit{Me}_2}$), 29.0 (t, $J = 124.4$ Hz, $\mathrm{NCH_2\mathit{C}H_2CH_2NMe_2}$), 3.2 (q, $J = 117.2$ Hz, $\mathrm{NSi\mathit{Me}_3}$). Anal. Calcd for $\mathrm{C_{15}H_{26}N_3SiLi}$ (283.41): C, 63.57; H, 9.25; N, 14.83; Li, 2.45. Found: C, 63.57; H, 9.30; N, 14.56; Li, 2.34.

[PhC(N(CH₂)₂NMe₂)(NSiMe₃)]Y[CH(SiMe₃)₂]₂ (2a). Solid Li[**B**] (0.33 g, 1.2 mmol) was added to a suspension of $\mathrm{YCl_3(THF)_{3.5}}$ (0.53 g, 1.2 mmol) in THF (30 mL) at −40 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The resulting solution was cooled to −40 °C and treated with $\mathrm{LiCH(SiMe_3)_2}$ (0.40 g, 2.4 mmol). After stirring for 3 additional hours at −10 °C, the solvent was removed in vacuo. The residue was stripped of remaining THF by stirring with pentane (2 × 5 mL), which was subsequently removed in vacuo. Extraction with pentane (3 × 30 mL) and cooling to −20 °C yielded **2a** (0.23 g, 0.34 mmol, 29%) as white crystals. The low isolated yield appears to be due to the high solubility of the product. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 7.16 (m, 2 H, Ar), 7.06 (m, 3 H, Ar), 2.71 (t, $^3J_{\mathrm{HH}} = 5.8$ Hz, 2 H, $\mathrm{NC\mathit{H}_2CH_2NMe_2}$), 2.14 (s, 6 H $\mathrm{N\mathit{Me}_2}$), 2.02 (t, $^3J_{\mathrm{HH}} = 5.8$ Hz, 2 H, $\mathrm{NCH_2C\mathit{H}_2NMe_2}$), 0.41 (s, 18 H, $\mathrm{YCH(Si\mathit{Me}_3)_2}$), 0.38 (s, 18 H, $\mathrm{YCH(Si\mathit{Me}_3)_2}$), 0.17 (s, 9 H, $\mathrm{NSi\mathit{Me}_3}$), −1.00 (d, 9 H, $^2J_{\mathrm{YH}} = 2.2$ Hz, $\mathrm{YC\mathit{H}(SiMe_3)_2}$). ^{13}C NMR (75.4 MHz, $\mathrm{C_6D_6}$): δ 179.7 (s, $\mathrm{NN'\mathit{C}Ph}$), 137.5 (s, Ph $\mathrm{C_{ipso}}$), 129.3 (d, $J = 153.7$ Hz, *o*-Ph), 128.5 (d, $J = 147.3$ Hz, *m*-Ph), 126.8 (d, $J = 158.6$ Hz, *p*-Ph), 62.6 (t, $J = 135.4$ Hz, $\mathrm{N\mathit{C}H_2CH_2NMe_2}$), 45.8 (q, $J = 135.4$ Hz, $\mathrm{N\mathit{Me}_2}$), 44.2 (t, $J = 135.4$ Hz, $\mathrm{NCH_2\mathit{C}H_2NMe_2}$), 41.4 (dd, $^1J_{\mathrm{YC}} = 32.9$, $^1J_{\mathrm{CH}} = 89.0$ Hz, $\mathrm{Y\mathit{C}H(SiMe_3)_2}$), 5.9 (q, $J = 117.0$ Hz, $\mathrm{YCH(Si\mathit{Me}_3)_2}$), 6.0 (q, $J = 117.1$ Hz, $\mathrm{YCH(Si\mathit{Me}_3)_2}$), 3.3 (q, $J = 118.3$ Hz, $\mathrm{NSi\mathit{Me}_3}$). Anal. Calcd for $\mathrm{C_{28}H_{62}N_3Si_5Y}$ (669.28): C, 50.20; H, 9.34; N, 6.28; Y, 13.28. Found: C, 49.91; H, 9.43; N, 5.86; Y, 12.95.

[PhC(N(CH₂)₃NMe₂)(NSiMe₃)]Y[CH(SiMe₃)₂]₂ (2b). A procedure analogous to the one described for **2a** above, using Li[**C**] (0.18 g, 0.62 mmol) and $\mathrm{YCl_3(THF)_{3.5}}$ (0.28 g, 0.62 mmol) in 30 mL of THF, yielded 0.12 g (0.17 mmol, 29%) of **2b** as white crystals. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 7.17 (m, 2 H, Ph), 7.04 (m, 3 H, Ph), 2.60 (t, $^3J_{\mathrm{HH}} = 5.8$ Hz, 2 H, $\mathrm{NC\mathit{H}_2(CH_2)_2NMe_2}$), 2.18 (s, 6 H $\mathrm{N\mathit{Me}_2}$), 2.01 (t, $^3J_{\mathrm{HH}} = 5.1$ Hz, 2 H, $\mathrm{N(CH_2)_2C\mathit{H}_2NMe_2}$), 1.15 (br p, 2 H, $\mathrm{NCH_2C\mathit{H}_2CH_2NMe_2}$) 0.40 (br, 36 H, $\mathrm{YCH(Si\mathit{Me}_3)_2}$), 0.17 (s, 9 H, $\mathrm{NSi\mathit{Me}_3}$), −0.89 (d, 9 H, ${}_2J_{\mathrm{YH}} = 2.2$ Hz, $\mathrm{YC\mathit{H}(Si\mathit{Me}_3)_2}$). ^{13}C NMR (75.4 MHz, $\mathrm{C_6D_6}$): δ 181.4 (s, $\mathrm{\mathit{C}Ph}$), 137.5 (s, Ph $\mathrm{C_{ipso}}$), 128.6 (d, $J = 161.0$ Hz, *o*-Ph), 127.9 (*m*-Ph, partially overlapped), 125.9 (d, $J = 159.7$ Hz, *p*-Ph), 62.7 (t, $J = 128.1$ Hz, $\mathrm{NC\mathit{H}_2(CH_2)_2NMe_2}$), 47.0 (t, $J = 134.2$ Hz, $\mathrm{N(CH_2)_2\mathit{C}H_2NMe_2}$), 46.5 (q, $J = 136.7$ Hz, $\mathrm{N\mathit{Me}_2}$), 43.4 (dd, $^1J_{\mathrm{YC}} = 32.9$ Hz, $^1J_{\mathrm{CH}} = 87.9$ Hz, $\mathrm{Y\mathit{C}H}$), 26.0 (t, $J = 125.6$ Hz, $\mathrm{NCH_2\mathit{C}H_2CH_2NMe_2}$), 6.5 and 6.2 (br q each, $J = 117$ Hz, $\mathrm{YCH(Si\mathit{Me}_3)_2}$), 3.3 (t, $J = 118.3$ Hz, $\mathrm{NSi\mathit{Me}_3}$).

Li[PhC(NSiMe₃)N(CH₂)₂NMe₂]₂Y(CH₂Ph)₂ (3a). Solid Li[**B**] (0.10 g, 0.4 mmol) was added to a suspension of $\mathrm{YCl_3(THF)_{3.5}}$ (0.09 g, 0.2 mmol) in THF (20 mL) at ambient temperature. After stirring for 2 h the resulting solution was cooled to −40 °C and $\mathrm{KCH_2Ph}$ (0.6 g, 0.4 mmol) was added. The orange mixture was stirred for 2 h, then warmed to ambient temperature. The solvent was removed in vacuo, and the resulting orange oil was rinsed with pentane (10 mL). Extraction with toluene (3 × 30 mL), concentration of the extracts, and cooling to −20 °C gave **3a** (0.12 g, 0.15 mmol, 74%) as a yellow microcrystalline material. A reaction of $\mathrm{YCl_3(THF)_{3.5}}$ (0.13 g, 0.3 mmol) and Li[**B**] (0.08 g, 0.3 mmol) with 2 equiv of $\mathrm{KCH_2Ph}$ (0.08 g, 0.6 mmol) under otherwise similar conditions yielded 0.07 g of **3a** (28%). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 7.3 (m, 8 H, Ph), 7.21 (br t, 2 H, Ph), 7.08 (m, 4 H, Ph), 6.88 (m, 2 H, Ph), 6.76 (m, 4 H, Ph), 2.8 (m, 6 H, $\mathrm{NC\mathit{H}_2C\mathit{H}HNMe_2}$), 2.42 (dd, $^2J_{\mathrm{HH}} = 8.6$ Hz, $^2J_{\mathrm{YH}} = 3.3$ Hz, 2 H, $\mathrm{YC\mathit{H}_2Ph}$), 2.31 (dd, $^2J_{\mathrm{HH}} = 8.6$ Hz, $^2J_{\mathrm{YH}} = 2.7$ Hz, 2 H, $\mathrm{YC\mathit{H}_2Ph}$), 1.92 (s, 6 H $\mathrm{N\mathit{Me}_2}$), 1.57 (m, 2 H, $\mathrm{NCH_2CH\mathit{H}NMe_2}$), 1.48 (s, 6 H, $\mathrm{N\mathit{Me}_2}$), 0.06 (s, 18 H, $\mathrm{NSi\mathit{Me}_3}$). ^{13}C NMR (75.4 MHz, $\mathrm{C_6D_6}$): δ 181.9 (s, $\mathrm{NN'\mathit{C}Ph}$), 155.0 (s, Ph $\mathrm{C_{ipso}}$), 138.7(s, Ph $\mathrm{C_{ipso}}$), 129.8 (d, $J = 161.1$ Hz, Ph CH), 129.0 (d, $J = 153.8$ Hz, Ph CH), 128.7 (d, $J = 155.0$ Hz, Ph CH), 124.7 (d, $J = 154.9$ Hz, Ph CH), 124.3 (d, $J = 150.1$ Hz, Ph CH), 116.4 (d, $J = 157.3$ Hz, Ph CH), 60.4 (t, $J = 131.9$ Hz, $\mathrm{N\mathit{C}H_2CH_2NMe_2}$), 53.9 (d, $^1J_{\mathrm{YC}} = 32.9$ Hz, t, $^1J_{\mathrm{CH}} = 117.1$ Hz, $\mathrm{Y\mathit{C}H_2Ph}$), 45.9 (t, $J = 136.7$ Hz, $\mathrm{NCH_2\mathit{C}H_2NMe_2}$) 45.9 (q, $J = 137.9$ Hz, $\mathrm{N\mathit{Me}_2}$), 42.1

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(q, J = 131.7 Hz, NMe_2), 3.1 (q, J = 118.4 Hz, NSiMe_3). Anal. Calcd for $C_{42}H_{62}N_6Si_2YLi$ (803.01): C, 62.82; H, 7.78; N, 10.47; Y, 11.07; Li, 0.86. Found: C, 60.91; H, 8.14; N, 10.30; Y, 10.90; Li, 0.79

Li[PhC(NSiMe$_3$)N(CH$_2$)$_2$NMe$_2$]$_2$Y(CH$_2$SiMe$_3$)$_2$ (3b). A suspension of $YCl_3(THF)_{3.5}$ (0.13 g, 0.3 mmol) in THF (20 mL, −40 °C) was treated with Li[**B**] (0.08 g, 0.3 mmol). The resulting pale yellow solution was allowed to warm to room temperature and was stirred overnight. Subsequently the mixture was cooled to −40 °C, and $LiCH_2SiMe_3$ (0.03 g, 0.3 mmol) was added. After warming to room temperature, the solution was stirred for 2 h. The solvent was removed in vacuo, and the residual THF removed by stirring twice with pentane (5 mL), which was then pumped off. The mixture was extracted with pentane (2 × 30 mL). Concentration and cooling to −20 °C afforded **3b** (0.09 g, 0.1 mmol, 37%) as white crystals. ^1H NMR (300 MHz, C_6D_6): δ 7.78 (d, 2 H, $^3J_{HH}$ = 7.3 Hz, *o*-Ph), 7.21 (t, 2 H, $^3J_{HH}$ = 7.3 Hz, *m*-Ph), 7.12 (t, 2 H, $^3J_{HH}$ = 7.6 Hz, *m*-Ph), 7.07 (t, 2 H, $^3J_{HH}$ = 7.3 Hz, *p*-Ph), 6.87 (d, $^3J_{HH}$ = 6.9 Hz, 2 H, *o*-Ph), 2.8 (m, 6 H, NCH_2CHHNMe$_2$), 1.94 (s, 6 H NMe_2), 1.53 (m, 2 H, NCH$_2$CHHNMe$_2$), 1.48 (s, 6 H, NMe_2), 0.61 (s, 18 H, CH$_2$SiMe_3), 0.21 (s, 18 H, NSiMe_3), −0.32 (d, 4 H, $^2J_{YH}$ = 2.5 Hz).^{13}C NMR (75.4 MHz, C_6D_6): δ 180.9 (s, NN′CPh), 139.5 (s, Ph C_{ipso}), 129.5 (d, J = 153.7 Hz), 128.5 (d, J = 153.7 Hz), 127.8 (d, J = 158.6 Hz), 127.7 (d, J = 161.1 Hz), 125.3 (d, J = 158.7 Hz, all Ph CH), 60.9 (t, J = 133.0 Hz, NCH$_2$CH$_2$NMe$_2$), 46.3 (t, J = 134.2 Hz, NCH$_2$$CH_2NMe_2$), 45.9 (q, J = 133.0 Hz, NMe_2), 42.1 (q, J = 135.4 Hz, NMe_2), 31.3 (d, $^1J_{YC}$ = 36.6 Hz, t, $^1J_{CH}$ = 95.1 Hz, YCH$_2$), 5.4 (q, J = 118.3 Hz, CH$_2$SiMe_3), 3.4 (q, J = 118.3 Hz, NSiMe_3). Anal. Calcd for $C_{36}H_{70}N_6Si_2YLi$ (794.18): C, 54.38; H, 8.87; N, 10.57. Found: C, 53.60; H, 9.03; N, 10.27.

[PhC(N(CH$_2$)$_3$NMe$_2$)(NSiMe$_3$)]$_2$YCH$_2$Ph (4). To a suspension of $YCl_3(THF)_{3.5}$ (0.45 g, 1.0 mmol) in THF (40 mL) was added solid Li[PhC(N(CH$_2$)$_3$NMe$_2$)(NSiMe$_3$)] Li[**C**] (0.57 g, 2.0 mmol). The reaction mixture was stirred overnight and then cooled to −40 °C, after which KCH_2Ph (0.13 g 1.0 mmol) was added. The mixture was allowed to warm to ambient temperature and stirred for an additional hour. The solvent was removed in vacuo and the residue extracted with pentane (3 × 50 mL). Concentration and cooling to −20 °C yielded **4**(pentane)$_{0.5}$ (0.42 g, 0.57 mmol, 57%) as yellow crystals. The reaction of equimolar amounts of $YCl_3(THF)_{3.5}$ (0.34 g, 0.76 mmol) and Li[**C**] (0.22 g, 0.76 mmol) with 2 equiv of KCH_2Ph (0.2 g, 1.5 mmol) yielded 0.15 g of **4**(pentane)$_{0.5}$ (0.2 mmol, 26%). ^1H NMR (300 MHz, C_6D_6): δ 7.25 (m, 8 H, Ph), 7.17 (m, 4 H, Ph), 7.07 (m, 2 H, Ph), 6.75 (t, $^3J_{HH}$ = 6.6 Hz, 1 H, Bz *p*-H), 2.99 (t, 4 H, $^3J_{HH}$ = 6.9 Hz, NCH_2(CH$_2$)$_2$NMe$_2$), 2.31 (br, 2 H, CH_2Ph), 2.08 (overlap, 16 H CH_2NMe$_2$ and NMe_2), 1.49 (br m, 4 H, −CH_2−), 0.15 (s, 18 H, NSiMe_3). ^{13}C NMR (75.4 MHz, C_6D_6): δ 179.9 (s, NN′CPh), 154.7(s, Ph C_{ipso}), 138.5(s, Ph C_{ipso}), 128.9 (d, J = 153.7 Hz), 128.4 (d, J = 153.5 Hz), 128.1 (d, J = 159.8 Hz), 126.4 (d, J = 154.3 Hz), 123.4 (d, J = 151.3 Hz), 116.0 (d, J = 158.5 Hz, all Ph CH), 60.0 (t, d, J = 133.0 Hz, NCH$_2$(CH$_2$)$_2$NMe$_2$), 52.5 (d, $^1J_{YC}$ = 29.3 Hz, t, $^1J_{CH}$ = 121.9 Hz, YCH$_2$Ph), 47.2 (t, J = 133.0 Hz, N(CH$_2$)$_2$$CH_2NMe_2$), 45.8 (q, J = 134.2 Hz, NMe_2), 29.2 (t, J = 124.4 Hz, NCH$_2$$CH_2CH_2NMe_2$), 2.6 (q, J = 117.0 Hz, NSiMe_3). Anal. Calcd for $C_{37}H_{59}N_6YSi.(C_5H_{12})_{0.5}$ (732.99 + 36.07): C, 61.96; H, 8.52; N, 10.93; Y, 11.56. Found: C, 61.66; H, 8.51; N, 10.45; Y, 10.72.

K[Me$_2$N(CH$_2$)$_2$NSiMe$_3$]. A solution of $Me_2N(CH_2)_2NHSiMe_3$ (7.0 g, 43.2 mmol) and styrene (2.3 g, 21.9 mmol) in ether (60 mL) was stirred with potassium (1.7 g, 43.0 mmol) for 24 h, after which almost all the potassium had reacted. The volatiles were removed in vacuo, and the powdery residue was extracted with ether (3 × 100 mL). Concentration and cooling to −20 °C yielded K[Me$_2$N(CH$_2$)$_2$NSiMe$_3$] (1.67 g, 8.35 mmol, 20%) as an off-white powder. ^1H NMR (300 MHz, C_6D_6): δ 3.40 (br, 2 H, NCH_2CH$_2$NMe$_2$), 2.26 (t, $^3J_{HH}$ = 5.1 Hz, 2 H, NCH$_2$CH_2NMe$_2$), 2.00 (s, 6 H NMe_2), 0.19 (s, 9 H, NSiMe_3).

Table 5. Crystallographic Data for 1 and 2a

	1	2a
formula	$C_{37}H_{85}ClLiN_2O_3Si_4Y$	$C_{28}H_{62}N_3Si_5Y$
mol wt	849.74	670.15
cryst syst	momoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	13.422(1)	9.350(5)
b, Å	17.781(1)	10.724(1)
c, Å	21.269(1)	20.363(5)
α, deg		88.71(4)
β, deg	91.62(1)	81.68(3)
γ, deg		75.09(2)
V, Å^3	5074.0(5)	1952.0(12)
Z	4	2
D_{calc}, g cm^{-3}	1.112	1.140
F(000)	1840	720
μ(Mo K$\bar{\alpha}$), cm^{-1}	13.3	16.67
cryst size, mm	0.10 × 0.25 × 0.50	0.25 × 0.30 × 0.33
	Data Collection	
radiation	Mo K$\bar{\alpha}$	Mo K$\bar{\alpha}$
λ (Mo Kα)	0.71073	0.71073
T, K	130	130
θ range, deg	1.15, 25.5	1.01, 27.0
scan type	$\omega/2\theta$	$\omega/2\theta$
$\Delta\omega$	$0.90 + 0.34 \tan\theta$	$1.15 + 0.34 \tan\theta$
data set	−16:16, 0:21, 0:25	−11:11, −13:13, −25:0
horz, vert aperture, mm	$3.2 + \tan\theta$; 4.0	$3.2 + \tan\theta$; 4.0
ref reflns	024, 2.1	−114, 2.2
rms dev in %	1−33, 0.23 3−12, 0.61	0−2−4, 0.8 −2−10, 3.1
drift correction	1.000−1.037	0.984−1.000
X-ray exposure time, h	132.0	181.0
total data	10 010	8709
unique data	9392	8465
data with criterion: ($F_o \geq 4.0\sigma(F_o)$)	4912	6480
	Refinement	
number of reflns ($F_o^2 \geq 0$)	9386	8465
no. of refined params	461	582
$wR(F^2)$[a]	0.2060	0.1441
weighting scheme:[b] a, b	0.1077, 0.0	0.0782, 2.57
$R(F)$[c]	0.0793	0.0488
goodness of fit	0.975	1.058
min, max resid density, e/Å^3	−0.55, 0.99(10)	−1.76, 1.08(12)
$(\Delta/\sigma)_{max}$ final cycle	<0.001	<0.001

[a] $wR(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ for $F_o^2 > 0$. [b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $R(F) = \sum(||F_o| - |F_c||)/\sum|F_o|$ for $F_o > 4.0\sigma(F_o)$.

K[PhC(N(CH$_2$)$_2$NMe$_2$)(NSiMe$_3$)] (K[B]). A procedure was followed similar to that for Li[**B**] starting from K[Me$_2$N(CH$_2$)$_2$NSiMe$_3$] (1.5 g, 5.5 mmol) and benzonitrile (0.5 mL, 5.5 mmol), yielding 1.9 g of K[**B**] (6.2 mmol, 83%). ^1H NMR (300 MHz, C_6D_6): δ 7.23 (m, 5 H, Ar), 3.10 (t, 2 H, $^3J_{HH}$ = 5.4 Hz, NCH_2CH$_2$NMe$_2$), 2.22 (br, 2 H, NCH$_2$CH_2NMe$_2$), 1.86 (s, 6 H NMe_2), 0.09 (s, 9 H, NSiMe_3). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 173.5 (NN′CPh), 145.1 (Ph C_{ipso}), 128.7 (o-Ph), 126.8 (m-Ph), 125.8 (p-Ph), 63.4 (NCH$_2$CH$_2$NMe$_2$) 48.5 (NCH$_2$$CH_2NMe_2$), 45.19 (N$Me_2$), 4.0 (NSi$Me_3$).

[PhC(N(CH$_2$)$_2$NMe$_2$)(NSiMe$_3$)]$_2$YCH$_2$Ph(THF) (5). To a slurry of 0.23 g of $YCl_3(THF)_{3.5}$ (0.50 mmol) in 30 mL of THF was added 0.30 g of K[**B**] (1.0 mmol). The mixture was stirred overnight, then cooled to − 40 °C, and 0.07 g (0.50 mmol) of KCH_2Ph was added. The mixture was allowed to warm to ambient temperature and was stirred for an additional 2 h. The solvent was removed in vacuo, and the residue was stripped of remaining THF by stirring with pentane, which was subsequently pumped off. Extraction with pentane (2 × 40 mL), concentrating, and cooling the extract to −20 °C

Table 6. Crystallographic Data for 3a and 4

	3a	**4**
formula	$C_{42}H_{62}LiN_6Si_2Y$	$C_{37}H_{56}N_6Si_2Y.(C_5H_{12})_{0.5}$
mol wt	803.01	769.07
cryst syst	momoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	19.695(3)	8.762(3)
b, Å	19.968(3)	11.350(2)
c, Å	23.502(3)	22.234(4)
α, deg		80.56(1)
β, deg	101.37(1)	89.39(2)
γ, deg		79.39(2)
V, $Å^3$	9061(2)	2145.3(9)
Z	8	2
D_{calc}, g cm^{-3}	1.177	1.196
F(000)	3408	822
μ(Mo K$\bar{\alpha}$), cm^{-1}	13.71	14.5
cryst size, mm	0.15 × 0.19 × 0.28	0.20 × 0.25 × 0.50
	Data Collection	
radiation	Mo K$\bar{\alpha}$	Mo K$\bar{\alpha}$
λ(Mo Kα), Å	0.71073	0.71073
T, K	130	130
θ range, deg	1.02, 25.0	1.85, 25.0
scan type	$\omega/2\theta$	$\omega/2\theta$
$\Delta\omega$	$1.15 + 0.34 \tan \theta$	$0.80 + 0.34 \tan \theta$
data set	0:23, 0:23, −27:27	0:10, −13:13, −26:26
horz, vert aperture, mm	3.2 + tan θ; 4.0	3.2 + tan θ; 4.0
ref reflns	3−33, 1.3	11−5, 1.7
rms dev in %	33−3, 0.8	222, 7.8
	−333, 1.1	201, 7.5
drift correction	0.992−1.007	1.000−1.058
X-ray exposure time, h	202.9	107.6
total data	17 183	8100
unique data	15 918	7554
data with criterion: ($F_o \geq 4.0\ \sigma(F_o)$)	7483	5784
	Refinement	
number of reflns ($F_o^2 \geq 0$)	15 914	7554
no. of refined params	957	449
$wR(F^2)$[a]	0.1998	0.1761
weighting scheme:[b] a, b	0.0907, 0.0	0.1105, 0.1840
$R(F)$[c]	0.0840	0.0586
goodness of fit	0.949	1.115
min, max resid density, e/$Å^3$	−1.34, 0.82(11)	−1.18, 1.25(11)
$(\Delta/\sigma)_{max}$ final cycle	<0.001	<0.001

[a] $wR(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ for $F_o^2 > 0$. [b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $R(F) = \sum(||F_o| - |F_c||)/\sum|F_o|$ for $F_o > 4.0\sigma(F_o)$.

yielded **5** (0.23 g, 0.31 mmol, 60%) as a yellow microcrystalline solid. ^{1} H NMR (300 MHz, C_6D_6): δ 7.25−7.05 (m, 14 H, Ph), 6.66 (br t, 1 H, Bz *p*-H), 3.77 (m, 4 H, THF), 3.04 (t, 4H, $^3J_{HH}$ = 6.6 Hz, $NCH_2CH_2NMe_2$), 2.26 (d, $^2J_{YH}$ = 2.7 Hz, 2 H YCH_2-Ph), 2.20 (t, $^3J_{HH}$ = 6.6 Hz, 4 H, $NCH_2CH_2NMe_2$), 2.10 (s, 12 H N*Me*$_2$), 1.47 (m, 4 H, THF), 0.13 (s, 18 H, NSi*Me*$_3$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 178.9 (s, NN′*C*Ph), 155.2 (s, Ph C_{ipso}), 138.9 (s, Ph C_{ipso}), 129.4 (d, J = 153.8 Hz, *o*-Ph), 128.3 (d, J = 161 Hz, 2 × Ph CH), 126.9 (d, J = 152.5 Hz, *m*-Ph), 122.9 (d, J = 152.5 Hz, Ph CH), 115.9 (d, J = 158.6 Hz, *p*-Ph), 68.8 (t, J = 145.2 Hz, THF), 62.1 (t, J = 133.0 Hz, $NCH_2CH_2NMe_2$), 52.4 (d, $^1J_{YH}$ = 28.0 Hz, t, $^1J_{CH}$ = 123.7 Hz, YCH_2Ph), 45.9 (t, J = 134.0 Hz, $NCH_2CH_2NMe_2$), 45.5 (q, J = 133.0 Hz, N*Me*$_2$), 25.6 (t, J = 131.8 Hz, THF), 3.0 (q, J = 118.4 Hz, NSi*Me*$_3$).

Crystal Structure Determinations. Suitable crystals of **1**, **2a**, **3a**, and **4**·(pentane)$_{0.5}$ were mounted on a glass needle in a drybox and transferred under inert atmosphere into the cold nitrogen stream of an Enraf-Nonius CAD4-F diffractometer (monochromated Mo Kα). Accurate cell parameters and an orientation matrix were determined from the setting of 22 reflections in the ranges 15.00° < θ < 20.33° (**1**), 16.79° < θ < 21.62° (**2a**), 14.85° < θ < 18.96° (**3b**), and 16.52° < θ < 20.42° (**4**). Reduced cell calculations did not indicate any higher lattice symmetry.[27] Crystal data and details on data collection and refinement are presented in Tables 5 and 6. Intensity data were corrected for Lorentz and polarization effects, but not for absorption. The structures were solved using Patterson methods, and the models were extended by direct methods applied to difference structure factors (*DIRDIF*[28]). All calculations were performed on a HP9000/735 computer with the program packages *SHELXL*[29] (least-squares refinement) and *PLATON*[30] (calculation of geometric data and the ORTEP illustrations). For **1**, **3a**, and **4** the hydrogen atoms were refined riding on their carrier atoms, and the methyl groups were refined as rigid groups that were allowed to rotate freely. For **2a** all hydrogen atom positional and isotropic thermal parameters were refined. In **1** the THF molecules bound to Li show significant disorder, which was difficult to treat with disorder models. Ultimately, restraints were used in the final refinement (in which the disorder is compensated by the large thermal displacement parameters). In **4** the *n*-pentane solvent molecule is disordered, with the central carbon atom located at the inversion center. A 50:50 disorder model for C(38) was used in the refinement.

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Supporting Information Available: Full crystallographic details, positional and thermal parameters, and distances and angles for **1**, **2a**, **3a**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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