Organometallics **2006,** *25,* 3935−3942

Alkylyttrium Complexes Supported by *N*,*N*′-Dicyclohexyl-*N*″-bis(trimethylsilyl)guanidinate Ligands

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Received March 30, 2006

The reaction of anhydrous YCl_3 with an equimolar amount of lithium *N*,*N*′-dicyclohexyl-*N*″-bis(trimethylsilyl)guanidinate, $Li[(Me_3Si)_2NC(NCy)_2]$, in THF afforded the monoguanidinate dichloro complex $[\{(Me_3Si)_2NC(NCy)_2\}Y\{(\mu\text{-}Cl)_2Li(THF)_2\}(\mu\text{-}Cl)]_2$ (**1**). X-ray diffraction study showed that complex **1** has a bimetallic tetranuclear dimeric core with six μ^2-bridging chloro ligands. Treatment of complex **1** with 4 molar equiv of $LiCH_2SiMe_3$ in hexane at 0 °C yielded the monomeric salt-free dialkyl complex $\{(Me_3Si)_2NC(NCy)_2\}Y(CH_2SiMe_3)_2(THF)_2$ (**2**). The monoguanidinate tetramethyl ate-complex $\{(Me_3Si)_2NC(NCy)_2\}Y[(\mu\text{-}Me)_2Li(TMEDA)]_2$ (**3**) was prepared by the reaction of complex **1** with 8 equiv of MeLi in the presence of excess TMEDA in toluene at 20 °C. The complexes **2** and **3** were structurally characterized. Alkylation of complex **1** with *t*-BuLi (1:4 molar ratio) in hexane resulted in the formation of the bis(guanidinate) alkyl yttrium complex $\{(Me_3Si)_2NC(NCy)_2\}_2Y(t\text{-}Bu)$ (**4**) in 42% yield. The guanidinate ligand redistribution was also observed in the reaction of the mono(guanidinate) dichloro yttrium complex $\{(Me_3Si)_2NC(NCy)_2\}YCl_2(Et_2O)$ (**5**) with 2 molar equiv of $LiCH_2SiMe_3$ in hexane at 0 °C. This reaction afforded ate-complex $\{(Me_3Si)_2NC(NCy)_2\}_2Y(\mu\text{-}CH_2SiMe_3)_2Li$ (**6**) in 34% yield. The X-ray diffraction study has revealed a low formal coordination number of the lithium atom in **6** and its agostic interaction with two methyl carbon atoms of $SiMe_3$ groups.

Introduction

Hydrocarbyl derivatives of the rare earth metals are highly active species that exhibit unique reactivity[1] including hydrocarbon activation[2] and alkane functionalization.[3] Extensive research on the sandwich-type alkyl derivatives of the rare earth metals has demonstrated their high potential in catalysis of a wide range of conversions of unsaturated substrates.[4] On the contrary, the stoichiometric and catalytic performance of half-sandwich bis(hydrocarbyl) complexes still remains poorly explored[5] because accessibility of these compounds was limited by their instability and difficulties of synthesis and isolation. Nevertheless these complexes have recently attracted significant attention as potential precursors to cationic monoalkyl species[6] that were found to be efficient catalysts of homo- and copolymerization of olefins.[7] The fact that reactivity of lanthanide compounds is mainly determined by electrophilicity and coordination unsaturation of the metal center emphasizes the importance of design of new ancillary ligand sets as a means of modification and control of the reactivity of complexes. During the past five years increasing employment of new anionic ancillaries allowed the synthesis and characterization of a noticeable number of rare earth dialkyl derivatives supported by noncyclopentadienyl ligands.[8] Amidinate,[9] triamino-amide,[10] β-diketiminate,[11] anilido-imine,[12] amido diphosphine,[13] and deprotonated aza-18-crown-6[14] ligands were found to form a

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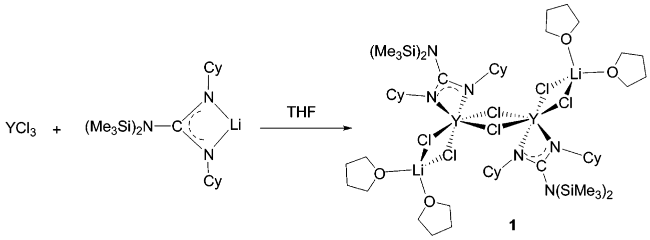
10.1021/om060280c CCC: $33.50

Scheme 1



suitable coordination environment for the synthesis of isolable bis(hydrocarbyl) species. Our recent studies were focused on the tetrasubstituted guanidinate ligand framework,[15] because it is easily available and its electronic and steric properties can be rationally modified by variation of the substituents at the nitrogen atoms. Several examples of alkyl complexes of rare earth metals supported by guanidinate ligands were described recently.[16] We employed the advantages of the $\{(Me_3Si)_2NC(NR)_2\}^-$ (R = *i*-Pr, Cy) coordination environment for the stabilization of lanthanide monoalkyl[17] and hydrido[18] complexes. We report here on the synthesis and structure of novel yttrium neutral and -ate alkyl complexes supported by the bulky *N*,*N*′-dicyclohexyl-*N*″-bis(trimethylsilyl)guanidinate ligand.

Results and Discussion

The σ-bond metathesis reaction of tris(alkyl) complexes of rare earth metals with the appropriate protio ligand precursor is widely used as a synthetic approach to related mono- and dialkyl species.[6b,9,10,14,19] For the preparation of bis(guanidinate) alkylylyttrium species we have successfully employed successive reactions of YCl_3 with sodium (or lithium) guanidinates and alkyllithium reagents.[17] The same synthetic strategy was used for the synthesis of mono(guanidinate) alkylyttrium compounds. The mono(guanidinate) dichloro complex $[\{(Me_3Si)_2NC(NCy)_2\}Y\{(\mu\text{-}Cl)_2Li(THF)_2\}(\mu\text{-}Cl)]_2$ (**1**) was synthesized by reaction of equimolar amounts of YCl_3 and lithium *N*,*N*′-dicyclohexyl-*N*″-bis(trimethylsilyl)guanidinate, $Li[(Me_3Si)_2NC(NCy)_2]$, obtained in situ from $Li(Et_2O)[N(SiMe_3)_2]$ and the 1,3-dicyclohexyl-substituted carbodiimide CyN═C═NCy in THF at 20 °C. Evaporation of THF and recrystallization of the solid residue from toluene allowed isolation of complex **1** in 95% yield (Scheme 1).

Complex **1** was obtained as a colorless crystalline moisture- and air-sensitive solid. It is soluble in THF and toluene and sparingly soluble in hexane. The ^1H and $^{13}C\{^1H\}$ NMR spectra of complex **1** in C_6D_6 at 20 °C show the expected sets of resonances due to the guanidinate part and the coordinated THF molecules. The ^1H NMR signals of the THF methylene protons in **1** appear as broad singlets, reflecting labile coordination.

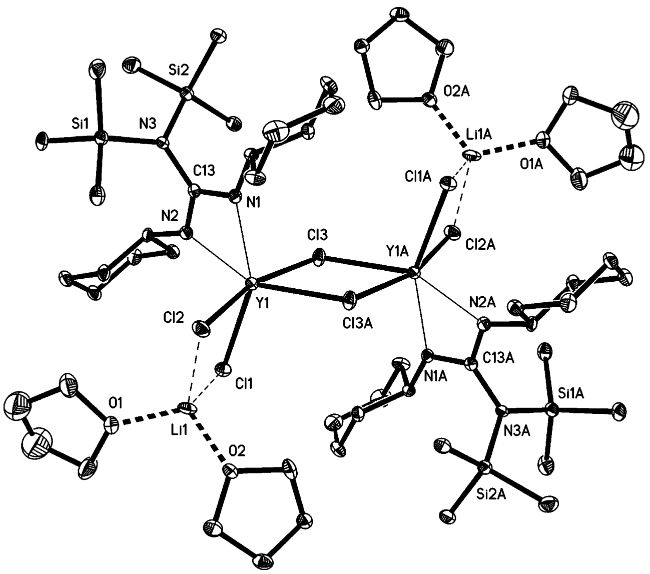


Figure 1. ORTEP diagram (30% probability thermal ellipsoids) of $[\{(Me_3Si)_2NC(NCy)_2\}Y\{(\mu\text{-}Cl)_2Li(THF)_2\}(\mu\text{-}Cl)]_2$ (**1**) showing the non-hydrogen and non-carbon (except C(13)) atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Y(1)−N(2) 2.298(4), Y(1)−N(1) 2.304(5), Y(1)−Cl(2) 2.6227(16), Y(1)−Cl(1) 2.6385(16), Y(1)−Cl(3) 2.7023(15), Y(1)−Cl(3A) 2.7065(15), Y(1)−C(13) 2.738(6), Y(1)−Li(1) 3.540(10), Cl(1)−Li(1) 2.415(11), Cl(2)−Li(1) 2.344(10), Cl(3)−Y(1A) 2.7065(15), Li(1)−O(2) 1.891(11), N(1)−C(13) 1.333(7), N(3)−C(13) 1.438(7), N(2)−C(13) 1.320(7), N(2)−Y(1)−N(1) 57.76(16), Cl(2)−Y(1)−Cl(1) 84.23(5), Cl(3)−Y(1)−Cl(3A) 78.02(5).

Crystals suitable for a single-crystal X-ray diffraction study of **1** were obtained from toluene solution by slow evaporation of the solvent at room temperature. The molecular structure of **1** is depicted in Figure 1; the crystal and structural refinement data are listed in Table 1. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the unit cell. The X-ray diffraction study has revealed that **1** is a dimeric ate-complex containing a bimetallic tetranuclear core, $[Li(\mu\text{-}Cl)_2Y(\mu\text{-}Cl)]_2$ (Figure 1), and its structure is different from those described for related mono(cyclopentadienyl) dichlorides of rare earth metals.[20]

All six chlorine atoms in complex **1** are μ^2-bridging. Two of them form bridges between two yttrium atoms, while four others connect yttrium and lithium atoms. It is noteworthy that Y−Cl bond distances in the Y_2Cl_2 (2.7023(15), 2.7065(15) Å) core are somewhat longer than those in the YCl_2Li fragments (2.6277(16), 2.6385(16) Å). The Y−Cl bond lengths in the planar Y_2Cl_2 fragment are slightly longer than the appropriate distances in the bis(cyclopentadienyl) complexes $[Cp_2Y(\mu\text{-}Cl)]_2$ (2.677(3), 2.693(3) Å),[21] $[(RC_5H_4)_2Y(\mu\text{-}Cl)]_2$ (R = *neo*-menthyl, 2.693(4), 2.696(4), 2.671(4), 2.676(4) Å),[22] and $[(C_5H_4SiMe_3)_2Y(\mu\text{-}Cl)]_2$ (2.684(4), 2.704(1) Å),[23] but slightly shorter than those in the bis(guanidinate) chloride $[\{(Me_3Si)_2NC(N\mathit{i}Pr)_2\}_2Y(\mu\text{-}Cl)]_2$

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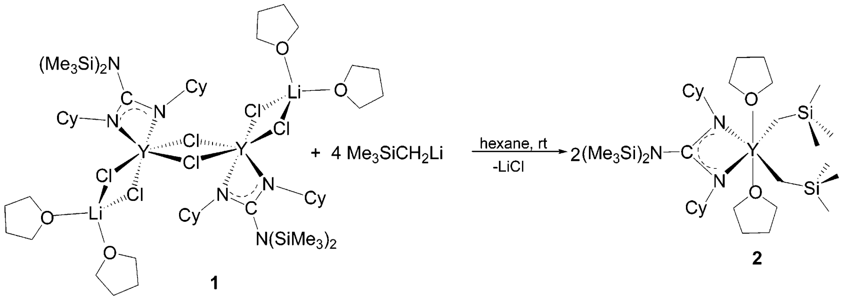
Table 1. Crystallographic Data and Structure Refinement Details for 1, 2, 3, and 6

	1	2	3	6
empirical formula	$C_{54}H_{112}C_{16}Li_2N_6O_4Si_4Y_2$	$C_{35}H_{78}N_3O_2Si_4Y$	$C_{35}H_{84}Li_2N_7Si_2Y$	$C_{48.50}H_{108}LiN_6Si_6Y$
fw	1426.26	774.27	762.06	1039.80
temperature, K	100(2)			
wavelength, Å	0.71073			
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/n$	$C2/c$	$C2/c$
unit cell dimens	$a = 10.7948(17)$ Å	$a = 9.6134(5)$ Å	$a = 13.5835(8)$ Å	$a = 44.657(2)$ Å
	$\alpha = 77.585(4)°$	$\alpha = 90°$	$\alpha = 90°$	$\alpha = 90°$
	$b = 12.651(2)$ Å	$b = 21.0333(11)$ Å	$b = 21.1121(13)$ Å	$b = 13.8992(7)$ Å
	$\beta = 71.865(4)°$	$\beta = 99.5680(10)°$	$\beta = 109.1320(10)°$	$\beta = 114.8090(10)°$
	$c = 14.651(2)$ Å	$c = 22.1719(11)$ Å	$c = 17.6689(11)$ Å	$c = 22.3696(11)$ Å
	$\gamma = 78.358(4)°$	$\gamma = 90°$	$\gamma = 90°$	$\gamma = 90°$
volume, Å^3	1837.2(5)	4420.8(4)	4787.1(5)	12603.3(11)
Z	1	4	4	8
density (calcd), mg/m^3	1.289	1.163	1.057	1.096
absorp coeff, mm^{-1}	1.897	1.458	1.297	1.073
$F(000)$	752	1680	1664	4536
cryst size, mm	0.14× 0.12 × 0.06	0.20× 0.15 × 0.10	0.30× 0.17 × 0.09	0.16× 0.12 × 0.08
θ range	1.48 to 20.50°	1.86 to 26.00°	1.86 to 25.50°	1.55 to 24.00°
index ranges	$-10 \leq h \leq 10$	$-11 \leq h \leq 11$	$-16 \leq h \leq 16$	$-51 \leq h \leq 51$,
	$-12 \leq k \leq 12$	$-25 \leq k \leq 25$	$-25 \leq k \leq 25$	$-15 \leq k \leq 15$
	$-14 \leq l \leq 14$	$-27 \leq l \leq 27$	$-21 \leq l \leq 21$	$-25 \leq l \leq 25$
no. of reflns collected	6470	37 286	19 308	44 507
no. of indep reflns	3645 [$R_{int} = 0.0350$]	8665 [$R_{int} = 0.0319$]	4459 [$R_{int} = 0.0502$]	9877 [$R_{int} = 0.0649$]
completeness to θ	99.1%	99.9%	100.0%	99.8%
absorp corr	SADABS			
max. and min. transmn	0.8947/ 0.7771	0.8679/0.7592	0.8922/0.6971	0.9191/0.8471
refinement method	full-matrix least-squares on F^2			
no. of data/restraints/ params	3645/12/352	8665/0/406	4459/0/382	9877/22/982
goodness-of-fit on F^2	1.010	1.032	0.980	0.952
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0433$,	$R_1 = 0.0303$,	$R_1 = 0.0346$,	$R_1 = 0.0416$,
	$wR_2 = 0.0988$	$wR_2 = 0.0731$	$wR_2 = 0.0746$	$wR_2 = 0.0960$
R indices (all data)	$R_1 = 0.0636$,	$R_1 = 0.0400$,	$R_1 = 0.0505$,	$R_1 = 0.0672$,
	$wR_2 = 0.1052$	$wR_2 = 0.0760$	$wR_2 = 0.0789$	$wR_2 = 0.1040$
largest diff peak and hole, e Å^{-3}	0.772/−0.509	0.494/−0.324	0.488/−0.192	0.803/−0.682

Scheme 2



(2.7173(150, 2.7253(15) Å).[16b] The Y−Cl bond lengths in the YCl_2Li fragment are comparable to the related distances in the bis(cyclopentadienyl) ate-complex $[C_5Me_4(CHCH_2)]_2Y(\mu\text{-}Cl)_2Li(Et_2O)_2$ (2.6289(2), 2.621(2) Å)[24] but expectedly shorter than those in the bis(guanidinate) derivative $[(Me_3Si)_2NC(NCy)_2]_2Y(\mu\text{-}Cl)_2Li(DME)$ (2.6693(3) Å).[17]

Complex **1** in the presence of a 20-fold molar excess of MAO in toluene at 20 °C does not catalyze the polymerization of ethylene and propylene.

Alkylation of **1** with 4 equiv of $LiCH_2SiMe_3$ was performed in hexane at 0 °C. Filtration of the reaction mixture and recrystallization of the solid residue from hexane afforded the mono(guanidinate) dialkyl derivative $\{(Me_3Si)_2NC(NCy)_2\}Y(CH_2SiMe_3)_2(THF)_2$ (**2**) as a colorless crystalline solid in 96% yield (Scheme 2). Complex **2** contains two coordinated THF molecules.

The colorless crystalline compound **2** is moisture- and air-sensitive. The complex is fairly soluble in commonly used organic solvents (THF, toluene, hexane). In an inert atmosphere, it can be stored in the crystalline state at 0 °C without decomposition, while in C_6D_6 solution at 20 °C it slowly decomposes with elimination of Me_4Si. In the ^1H NMR spectrum of complex **2** at 20 °C the hydrogen atoms of methylene groups attached to the yttrium atom appear as a doublet at −0.34 ($^2J_{YH}$ = 3.0 Hz); in the $^{13}C\{^1H\}$ NMR spectrum the appropriate carbons give rise to a doublet at 35.3 ppm ($^2J_{YC}$ = 38.2 Hz). Chemical shifts and coupling constants of the signals of methylene groups YCH_2 in **2** are in a good agreement with the values published for related dialkyl yttrium species supported by monoanionic nitrogen-containing ligands (Table 2). The guanidinate and THF ligands give expected sets of signals in ^1H and ^{13}C NMR spectra.

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Table 2. Chemical Shifts of Signals of Methylene Groups Attached to Yttrium Atom, YCH$_2$, in ^{1}H and ^{13}C Spectra of Complexes (L)Y(CH$_2$SiMe$_3$)$_2$ and Y−C Bond Distances in Complexes (L)Y(CH$_2$SiMe$_3$)$_2$

	^{1}H NMR (YC*H*$_2$)		^{13}C NMR (Y*C*H$_2$)			
complex	δ, ppm	$^2J_{\mathrm{Y-H}}$, Hz	δ, ppm	$^1J_{\mathrm{Y-C}}$, Hz	Y−C bond length, Å	ref
trans-Y(MAC)(CH$_2$SiMe$_3$)$_2$	−1.59	2.5	19.8	32.4	2.461(4)	14
	−0.26	3.3	33.7	36.9	2.476(5)	9b
[*N*,*N*′-*i*Pr$_2$-trac-*N*″-(CH$_2$CH$_2$)N*t*-Bu]Y(CH$_2$SiMe$_3$)$_2$	−0.53	2.1	31.0	38.7	2.421(7)	
	−0.83	3.0				
	−1.00	2.1				
	−0.62	not resolved	29.8	35.4		9b
[*N*,*N*′-Me$_2$-trac-*N*″-(CH$_2$CH$_2$)N*t*-Bu] Y(CH$_2$SiMe$_3$)$_2$	−0.86		28.5	38.9		
	−0.94					
	−1.06					
[Y{η^5:η^1-C$_5$Me$_4$SiMe$_2$(C$_4$H$_3$O-2)}(CH$_2$SiMe$_3$)$_2$ (THF)]	−0.92	2.9	32.1	41.2		6b
[Y{η^5:η^1-C$_5$Me$_4$SiMe$_2$(C$_4$H$_2$MeO-5)-2}(CH$_2$SiMe$_3$)$_2$(THF)]	- 0.91	3.0				6b
[(C$_6$H$_3$*i*-Pr$_2$-2,6)NCH]C$_6$H$_4$(NC$_6$H$_3$*i*-Pr$_2$-2,6)]Y(CH$_2$SiMe$_3$)$_2$(THF)	−0.58	br s	37.5	40.3		12
[(C$_6$H$_3$*i*-Pr$_2$-2,6)NCH]C$_6$H$_4$(NC$_6$H$_3$*i*-Pr$_2$-2,6)]Y(CH$_2$SiMe$_2$Ph)$_2$(THF)	−0.20	9.7	35.1	40.0	2.318(4)	
	−0.46				2.419(4)	
[PhC(NC$_6$H$_3$ *i*-Pr$_2$-2,6)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF)	−0.11	3.0	39.5	40.3	2.374(4)	9b
					2.384(4)	
[PhC(NC$_6$H$_3$*i*-Pr$_2$-2,6)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF)$_2$					2.427(2)	9b
					2.433(2)	
{[Me$_2$N(CH$_2$)$_2$]$_2$N(*t*-Bu)}Y(CH$_2$SiMe$_3$)$_2$	−0.54	not resolved	30.9	36.6	2.463(2)	10b
	−0.81				2.452(2)	

Crystals of **2** suitable for X-ray diffraction studies were obtained by cooling its concentrated hexane solutions to −30 °C. The molecular structure of **2** is shown in Figure 2, and the structure refinement data are listed in Table 1. Complex **2** crystallizes in the monoclinic space group *P*2(1)/*n* with four molecules in the unit cell. X-ray diffraction study has revealed that complex **2** is monomeric. The coordination sphere of the yttrium atom consists of two nitrogen atoms of the bidentate guanidinate ligand, two carbon atoms of the alkyl groups, and two oxygen atoms of two THF molecules, resulting in the formal coordination number 6. The coordination geometry of the yttrium atom can be described as a distorted octahedron with two carbon and two nitrogen atoms in equatorial positions and two oxygen atoms in apical positions. It is noteworthy that the coordination environment of the yttrium atom in complex **2** is very different from that in the related six-coordinated amidinate yttrium derivative [PhC(NC$_6$H$_3$*i*-Pr$_2$-2,6)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF)$_2$. Thus in **2** the planes N(1)Y(1)N(2) and C(24)Y(1)C(20) are nearly coplanar (the value of the dihedral angle between the two planes is 7.7°), while in [PhC(NC$_6$H$_3$*i*-Pr$_2$-2,6)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF)$_2$ they are close to adopting an orthogonal orientation (88.6°).[9b]

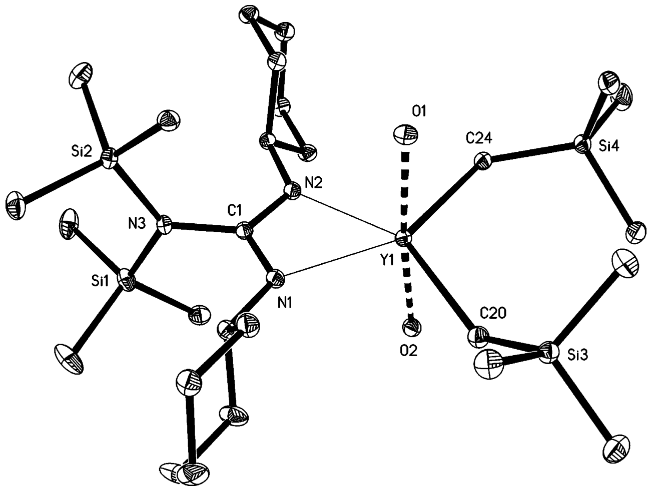
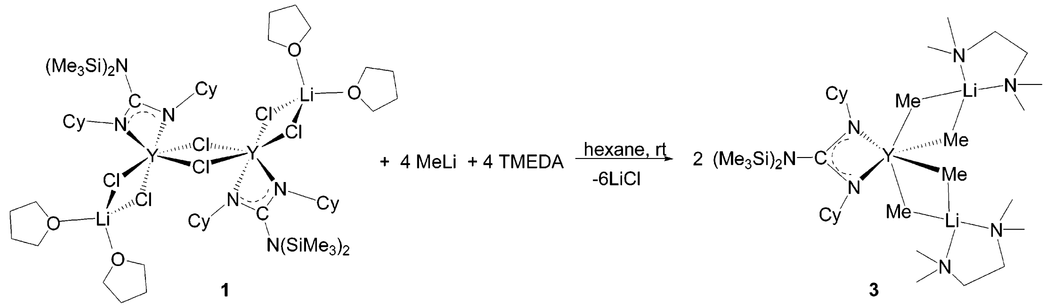


Figure 2. ORTEP diagram (30% probability thermal ellipsoids) of {(Me$_3$Si)$_2$NC(NCy)$_2$}Y(CH$_2$SiMe$_3$)$_2$(THF)$_2$ (**2**) showing the non-hydrogen and non-carbon (except C(1), C(20), and C(24)) atom numbering scheme. Hydrogen atoms and carbon atoms of THF are omitted for clarity. Selected bond distances [Å] and angles [deg]: Y(1)−C(20) 2.462(2), Y(1)−C(24) 2.473(2), Y(1)−N(1) 2.4165(17), Y(1)−N(2) 2.3833(17), Y(1)−O(1) 2.3777(14), Y(1)−O(2) 2.4029(14), Y(1)−C(1) 2.838(2), N(1)−C(1) 1.337(3), C(1)−N(2) 1.328(3), C(20)−Y(1)−C(24) 112.40(7), N(2)−Y(1)−N(1) 55.80(6), O(1)−Y(1)−O(2) 174.50(5).

The Y−C bond lengths in complex **2** are 2.462(2) and 2.473(2) Å, which are comparable to the related distances in dialkyl yttrium complexes (Table 2 and references therein). The distances Y−N(1, 2) (2.3833(17), 2.4165(17) Å) differ only slightly from each other. The C−N(1,2) bond lengths within the guanidinate fragment are also very similar (1.337(3), 1.328(3) Å), thus proving electron delocalization within the anionic NCN units. The considerably longer distance C(1)−N(3) (1.443(3) Å) indicates that the N(SiMe$_3$)$_2$ moiety does not take part in the conjugation. The opposite orientation of the N(SiMe$_3$)$_2$ and the cyclohexyl groups relative to the NCN planes corresponds to the minimization of their mutual steric repulsion. The Y−O bond lengths in **2** (2.3777(14), 2.4029(14) Å) are shorter than those in the related six-coordinated amidinate yttrium complex [PhC(NC$_6$H$_3$*i*-Pr$_2$-2,6)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF)$_2$ (2.427(1), 2.451(1) Å).[9b] Obviously this reflects stronger steric repulsion between THF ligands and bulkier diisopropylphenyl radicals in the amidinate derivative than that in complex **2**.

To generate cationic alkylyttrium species, reactions of complex **2** with both Lewis ((C$_6$H$_5$)$_3$B, (C$_6$F$_5$)$_3$B) and Brönsted ([NHMe$_2$Ph][B(C$_6$F$_5$)$_4$]) acids have been investigated. The reactions have been carried out in THF or toluene at −78 °C in 1:1 molar ratio and afforded oily, viscous products. All attempts to isolate individual organoyttrium compounds from the reaction mixtures failed. Complex **2** has been found to be inactive in ethylene and styrene polymerizations. Complex **2** activated by an equimolar amount of (C$_6$H$_5$)$_3$B or (C$_6$F$_5$)$_3$B in toluene at 20 °C sluggishly oligomerizes ethylene. The catalytic tests with ethylene were carried out under rigorously anaerobic conditions in a sealed glass manometric system (toluene 5 mL, catalyst concentration (1.2−2.6) × 10^{-3} mol/L, 20 °C, ethylene pressure 0.5 atm), which allows monitoring of the polymerization process by absorption of the monomer. For both systems **2**−(C$_6$H$_5$)$_3$B and **2**−(C$_6$F$_5$)$_3$B the monomer absorption did not exceed 4 mol per mol of catalyst (the ethylene solubility in toluene is taken into consideration) and the polymerization process was stopped in 15 min.

Scheme 3



The reaction of **1** with 8 molar equiv of MeLi in the presence of TMEDA was carried out in toluene at 20 °C. Separation of LiCl and recrystallization of the solid residue from diethyl ether resulted in formation of colorless air- and moisture-sensitive crystals of $\{(Me_3Si)_2NC(NCy)_2\}Y[(\mu\text{-}Me)_2Li(TMEDA)]_2$ (**3**) in 44% yield (Scheme 3). Complex **3** is soluble in Et_2O and toluene and insoluble in hexane.

The ^1H NMR spectrum of **3** at room temperature shows a broadened singlet at −0.60 ppm due to the protons of the methyl groups bridging the yttrium and lithium atoms. In the $^{13}C\{^1H\}$ NMR spectrum a broad unresolved resonance at 7.2 ppm is observed for the corresponding carbon atoms. These chemical shifts are consistent with the values previously reported for related complexes.[16b,25,26] The protons of the $(Me_3Si)_2N$ groups give rise in the ^1H NMR spectrum to two singlets (at 0.46 and 0.51 ppm, intensity ratio 1:2), and the appropriate carbon atoms appear in the $^{13}C\{^1H\}$ spectrum also as a set of two signals (2.7 and 2.8 ppm). This obviously points to nonequivalence of the methyl groups due to a restricted rotation of the $(Me_3Si)_2N$ units caused by the environment of the bulky cyclohexyl moieties. The TMEDA and cyclohexyl groups give expected sets of signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra of complex **3**. The presence of lithium in **3** is proved by the ^7Li NMR spectrum, which contains a sole singlet at 4.16 ppm.

The molecular structure of **3** in the solid state was determined by a crystal structure analysis on colorless crystals obtained by slow cooling of its diethyl ether solution to −30 °C. Complex **3** crystallizes in the monoclinic, *C*2/*c* group with four molecules in the unit cell. Crystallographic data are compiled in Table 1. Figure 3 shows that the yttrium atom is coordinated by two nitrogen atoms of the chelating guanidinate ligand, as well as by four methyl carbon atoms, thus resulting in a formal coordination number of 6.

The methyl groups bridge yttrium and lithium atoms. The Y−C bond distances in complex **3** (2.5307(19), 2.5410(16) Å) are slightly longer than those in the related ate-complexes $Cp^*[C_6H_5C(NSiMe_3)_2]Y(\mu\text{-}Me)_2Li(TMEDA)$ (2.480(3), 2.420(6) Å)[27] and $\{(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2\}_2Y(\mu\text{-}Me)_2Li(TMEDA)$ (2.505(4), 2.508(4) Å)[16b] and are comparable to the lengths of the μ-bridging bond in the dimeric complex $[Cp_2Y(\mu\text{-}Me)]_2$ (2.553(10), 2.537(9) Å).[28] The bond angles C(Me)−Y−C(Me) in **3** are in the region of 87.43−107.50°, which is noticeably larger than in the complexes $Cp^*[C_6H_5C(NSiMe_3)_2]Y(\mu\text{-}Me)_2Li(TMEDA)$ (89.67(11)°)[27] and $\{(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2\}_2Y(\mu\text{-}Me)_2Li(TMEDA)$ (91.22(12)°).[16b] The N−C bond lengths within the guanidinate NCN fragment are similar and indicate negative charge delocalization.

Complex **3** has been found to be inactive in ethylene polymerization.

We have attempted the synthesis of the mono(guanidinate) dialkyl derivative $\{(Me_3Si)_2NC(NCy)_2\}Y(\textit{t}\text{-}Bu)_2$ by the reaction of complex **1** with 4 equiv of *t*-BuLi in hexane at 0 °C (Scheme 4). Unexpectedly after separation of LiCl and recrystallization of the resulting off-white solid by cooling of the hexane solution we isolated the bis(guanidinate) monoalkyl complex $\{(Me_3Si)_2NC(NCy)_2\}_2Y(\textit{t}\text{-}Bu)$ (**4**) in 42% yield. Recently we described the synthesis and structure of complex **4**, which was prepared by the metathesis reaction of $[(Me_3Si)_2NC(NCy)_2]_2YCl(THF)$ with *t*-BuLi.

Apparently in the reaction of **1** with *t*-BuLi redistribution of the guanidinate ligands occurs, which results in the formation of **4**. All attempts to isolate other organoyttrium compounds from the reaction mixture failed.

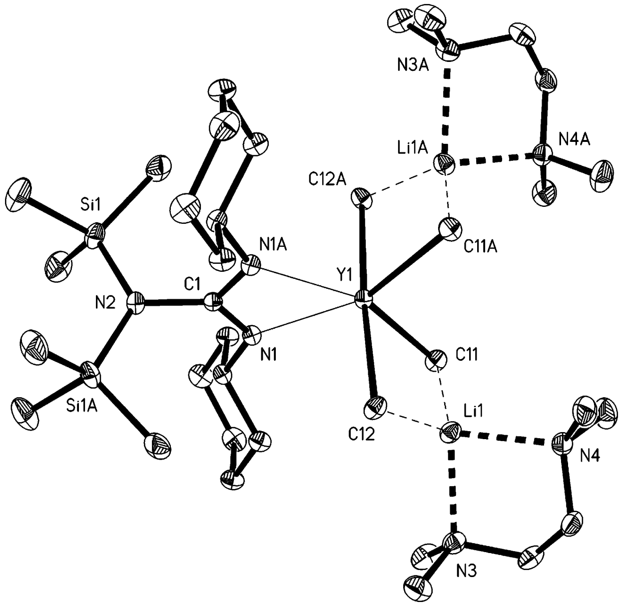


Figure 3. ORTEP diagram (30% probability thermal ellipsoids) of $\{(Me_3Si)_2NC(NCy)_2\}Y[(\mu\text{-}Me)_2Li(TMEDA)]_2$ (**3**) showing the non-hydrogen and non-carbon (except C(1), C(11), C(12), C(11A), and C(12A)) atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Y(1)−N(1A) 2.3934(13), Y(1)−N(1) 2.3934(13), Y(1)−C(11) 2.5307(19), Y(1)−C(11A) 2.5307(19), Y(1)−C(12) 2.5410(16), Y(1)−C(12A) 2.5410(16), Li(1)−C(12) 2.150(3), Li(1)−C(11) 2.211(3), Li(1)−N(4) 2.142(3), Li(1)−N(3) 2.153(3), N(1)−C(1) 1.3284(18), C(1)−N(1A) 1.3284(18), N(1A)−Y(1)−N(1) 55.51(6), C(11)−Y(1)−C(11A) 107.50(9), C(11)−Y(1)−C(12) 90.28(6), C(11A)−Y(1)−C(12) 87.43(6), C(11)−Y(1)−C(12A) 87.43(6), C(11A)−Y(1)−C(12A) 90.28(6), C(12)−Y(1)−C(12A) 176.13(8), C(1)−Y(1)−C(11) 126.3(6), C(1)−Y(1)−C(12) 91.9(6).

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[25] Duchateau, R.; van Wee, C. T.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2279.

[26] Shumann, H. *J. Less-Common Met.* **1985**, *112*, 327.

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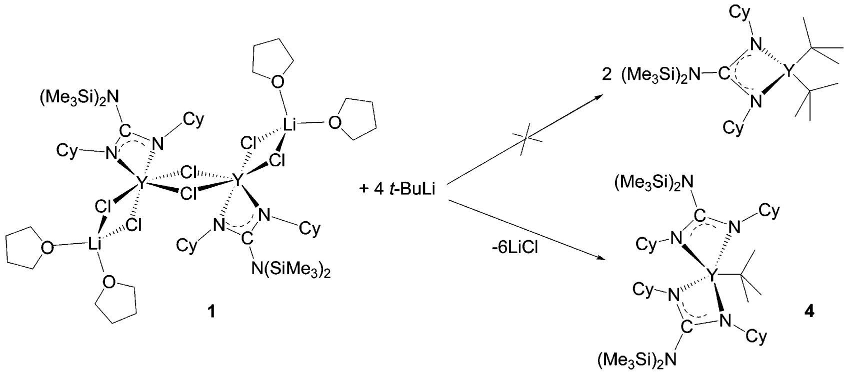
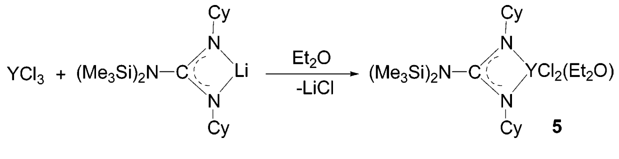
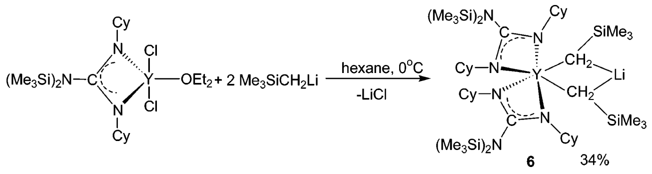
Scheme 4



Scheme 5



Scheme 6



To prepare mono(guanidinate) dialkyl complexes free of Lewis base, we decided to use as a precursor a mono(guanidinate) dichloro yttrium complex containing diethyl ether, which possesses weaker coordination ability. Replacement of THF by diethyl ether in the reaction mixture prevented formation of an ate-complex and allowed isolation of the neutral complex $\{(Me_3Si)_2NC(NCy)_2\}YCl_2(Et_2O)$ (**5**). Reaction of YCl_3 with $Li[(Me_3Si)_2NC(NCy)_2]$ (1:1 molar ratio) obtained in situ from $Li(Et_2O)[N(SiMe_3)_2]$ and the 1,3-dicyclohexyl-substituted carbodiimide has been carried out in diethyl ether at 20 °C. Separation of LiCl by filtration, evaporation of the solvent, and extraction of the residue with hot hexane resulted in isolation of complex **5** as a microcrystalline colorless solid in 71% yield (Scheme 5).

Complex **5** was characterized by spectroscopic methods and microanalysis; unfortunately all our attempts to obtain single crystals of **5** suitable for X-ray investigation failed. Complex **5** is air- and moisture-sensitive; it is soluble in Et_2O and THF and sparingly soluble in hexane and toluene. The ^1H and $^{13}C\{^1H\}$ NMR spectra of complex **5** in C_6D_6 at 20 °C show the expected sets of resonances due to the guanidinate fragment and the coordinated Et_2O molecules and do not exhibit any special features.

Complex **5** was used as a starting material for the preparation of dialkyl species. Reaction of compound **5** with 2 molar equiv of $LiCH_2SiMe_3$ in hexane at 0 °C afforded ate-complex $\{(Me_3Si)_2NC(NCy)_2\}_2Y(\mu\text{-}CH_2SiMe_3)_2Li$ (**6**) instead of the expected neutral dialkyl derivative. Complex **6** was isolated after recrystallization from pentane in 34% yield (Scheme 6) as a colorless, air- and moisture-sensitive crystalline compound, highly soluble in hydrocarbon solvents.

The methylene protons of the alkyl groups bridging the yttrium and lithium atoms appear in the ^1H NMR spectrum of **6** (20 °C) as a broadened singlet at −0.52 ppm, which is high-field shifted compared to the signal of the methylene protons of the terminal alkyl ligands in **2** (−0.25 ppm). The Me_3Si protons of the alkyl radicals give rise to a singlet at 0.29 ppm, while a singlet at 0.36 ppm corresponds to the protons of the $(Me_3Si)_2N$ groups. The presence of a lithium atom in **6** is proved by the ^7Li NMR spectrum, which exhibits a singlet at 5.77 ppm.

Crystallization of **6** by prolonged cooling of the concentrated pentane solutions to −20 °C resulted in single crystals of the solvate containing a half molecule of pentane per one molecule of complex $\{(Me_3Si)_2NC(NCy)_2\}_2Y(\mu\text{-}CH_2SiMe_3)_2Li\cdot(C_5H_{12})_{0.5}$. The molecular structure of **6** is shown in Figure 4, and the crystal and structure refinement data are listed in Table 1. Complex **6** crystallizes in the monoclinic space group *C*2/*c* with eight molecules in the unit cell.

The X-ray diffraction study has revealed that complex **6** is a monomeric ate-complex, where the yttrium atom is coordinated by two nitrogen atoms of two bidentate guanidinate ligands and

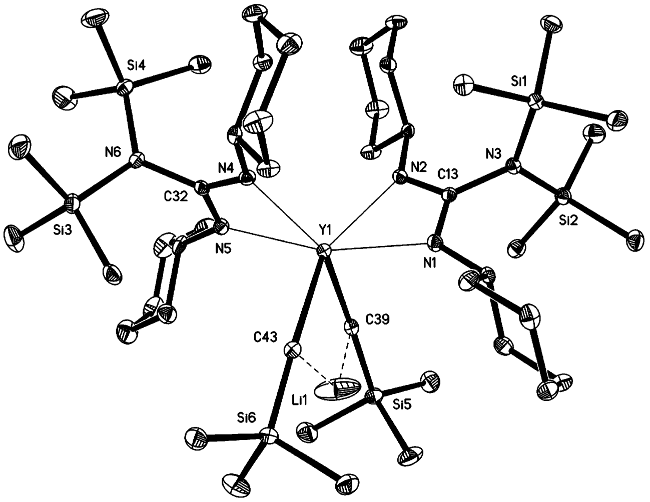


Figure 4. ORTEP diagram (30% probability thermal ellipsoids) of $\{(Me_3Si)_2NC(NCy)_2\}_2Y(\mu\text{-}CH_2SiMe_3)_2Li$ (**6**) showing the non-hydrogen and non-carbon (except C(13), C(32), C(39), and C(43)) atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Y(1)−N(2) 2.3497(14), Y(1)−N(4) 2.3626(15), Y(1)−N(5) 2.3914(13), Y(1)−N(1) 2.3998(14), Y(1)−C(39) 2.543(2), Y(1)−C(43) 2.5460(17), Y(1)−C(13) 2.8118(18), Y(1)−C(32) 2.8167(17), Y(1)−Li(1) 2.882(4), Li(1)−C(43) 2.083(5), Li(1)−C(39) 2.103(5), Li(1)−C(41) 2.514(5), Li(1)−C(45) 2.947(5), Li(1)−C(42) 3.551(5), Li(1)−C(44) 3.482(5), N(1)−C(13) 1.336(2), N(2)−C(13) 1.3274(19), N(4)−C(32) 1.332(2), N(5)−C(32) 1.334(3), N(4)−Y(1)−N(5) 56.25(5), N(2)−Y(1)−N(1) 56.33(4), C(39)−Y(1)−C(43) 88.95(6), C(39)−Li(1)−C(43) 116.78(4), C(39)−Si(5)−C(42) 110.99(9), C(39)−Si(5)−C(41) 108.91(10), C(39)−Si(5)−C(40) 114.59(9), C(43)−Si(6)−C(44) 110.67(9), C(43)−Si(6)−C(45) 109.39(10), C(43)−Si(6)−C(46) 114.82(10).

two carbon atoms of alkyl groups, thus having coordination number 6. Expectedly the bond distances between the yttrium atom and μ-bridging methylene carbons in **6** (2.543(2), 2.5460(17) Å) are noticeably longer than the Y−C bond lengths in compounds with terminal alkyl ligands (**2**: 2.462(2), 2.473(2) Å; for other examples see Table 2) and are comparable to those found in ate-complex **3** (2.5307(19), 2.5410(16) Å). The most interesting feature of this compound is an extremely low formal coordination number of the lithium atom, which is coordinated just by two methylene carbon atoms. Obviously the coordination sphere of the lithium atom is saturated due to agostic interactions with two methyl groups of the trimethylsilyl substituents. Two short contacts between lithium and the methyl carbon atoms are observed: Li(1)−C(41) 2.514(5) and Li(1)−C(45) 2.947(5) Å. However the existence of the agostic interaction in **6** does not effect the bond angles about the silicon atoms in the alkyl fragments; they are rather similar and fall into the range 108.9−114.8°, which is close to the value expected for an sp^3-hybridized silicon atom. The N−C bond lengths within both guanidinate NCN fragments have very close values, reflecting the negative charge delocalization.

Conclusions

The *N*,*N′*-dicyclohexyl-*N″*-bis(trimethylsilyl) guanidinate ligand was found to form a suitable coordination environment for the synthesis of monomeric neutral dialkyl yttrium complexes. Employment of bulky guanidinate ligands also allowed preparation of mono- and bis(guanidinate) alkyl yttrium ate-complexes. Unusually low formal coordination numbers and agostic interactions with the methyl groups of the alkyl ligands have been found for the lithium atom in the complex $\{(Me_3Si)_2NC(NCy)_2\}_2Y(\mu\text{-}CH_2SiMe_3)_2Li$ (**6**) in the solid state.

Experimental Details

All experiments were performed in evacuated tubes, using standard Schlenk-tube techniques, with rigorous exclusion of traces of moisture and air. After drying over KOH, THF was purified by distillation from sodium/benzophenone ketyl, and hexane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl prior to use. C_6D_6 was dried with sodium/benzophenone ketyl and condensed in vacuo prior to use. *N*,*N′*-Dicyclohexylcarbodiimide was purchased from Acros. Anhydrous YCl_3[29] and $[(Me_3Si)_2NLi(Et_2O)]$[30] were prepared according to literature procedures. All other commercially available chemicals were used after the appropriate purification. NMR spectra were recorded on a Bruker DPX 200 spectrometer (^1H, 200 MHz; ^{13}C, 50 MHz; ^7Li, 77.7 MHz) in C_6D_6 at 20 °C, unless otherwise stated. Chemical shifts for ^1H and ^{13}C spectra were referenced internally using the residual solvent resonances and are reported relative to TMS. IR spectra were recorded as Nujol mulls on FSM 1201 and Specord M80 instruments. Lanthanide metal analyses were carried out by complexometric titration. The C, H elemental analysis was made in the microanalytical laboratory of IOMC.

Synthesis of $[\{(Me_3Si)_2NC(NCy)_2\}Y(\mu^2\text{-}Cl)(\mu^2\text{-}Cl)_2Li(THF)_2]_2$ (1). To a solution of $[(Me_3Si)_2NLi(Et_2O)]$ (1.02 g, 4.23 mmol) in THF (30 mL) was added slowly 1,3-dicyclohexylcarbodiimide (0.87 g, 4.23 mmol) at 20 °C, and the reaction mixture was stirred for 45 min. YCl_3 (0.83 g, 4.23 mmol) was added, and the reaction mixture was stirred overnight. The solution was filtered, the solvent evaporated in vacuo, and the solid residue extracted with toluene (2 × 30 mL). The toluene extracts were filtered, and the solution was slowly concentrated at room temperature to a quarter of its volume, cooled to −30 °C, and left overnight. The crystalline precipitate was washed with cold hexane and dried in vacuo at room temperature for 40 min. Complex **1** was obtained as a colorless crystalline solid (2.90 g, 95%). IR (Nujol, KBr, cm^{-1}): 1620 s, 1320 m, 1240 s, 1270 m, 1200 m, 1150 m, 1100 m, 1050 m, 950 s, 930 s, 860 m, 830 s. ^1H NMR (200 MHz, C_6D_6, 20 °C): δ 0.31, 0.37, 0.45 (s, together 36 H, $NSi(CH_3)_3$), 1.43−2.12 (br m, together 56 H, CH_2 Cy, β-CH_2, THF), 3.47 (br m, 4 H, CH Cy), 3.85 (br s, 8 H, α-CH_2, THF). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 20 °C): δ 1.8, 2.3, 2.7 $[N(Si(CH_3)_3)_2]$, 26.4 (β-CH_2, THF), 25.3, 26.1, 35.7, 37.3 (CH_2, Cy), 54.9 (CH, Cy), 70.1 (α-CH_2, THF), 170.9 (CN_3) ppm. Anal. Calcd for $C_{54}H_{112}Cl_6N_6O_4Si_4Y_2$ (1426.26): C, 45.43; H, 7.85; Y, 12.48. Found: C, 45.80; H, 8.02; Y, 12.11.

Synthesis of $[\{(Me_3Si)_2NC(NCy)_2\}Y(CH_2SiMe_3)_2(THF)_2]$ (2). To a solution of **1** (0.95 g, 0.67 mmol) in hexane (20 mL) was added slowly a solution of Me_3SiCH_2Li (0.25 g, 2.67 mmol) in hexane (10 mL) at 0 °C, and the reaction mixture was stirred for 1 h. The pale yellow solution was filtered and concentrated in vacuo to approximately a quarter of its initial volume. The solution was cooled to −30 °C and kept at that temperature for 3 days. The mother liquor was decanted; the solid was washed with cold hexane and dried in vacuo at room temperature for 30 min. **3** was isolated as off-white crystals (0.99 g, 96%). IR (Nujol, KBr, cm^{-1}): 1634 s, 1600 m, 1296 m, 1250 s, 1219 m, 1008 m, 958 s, 942 s, 842 s. ^1H NMR (200 MHz, C_6D_6, 20 °C): δ −0.34 (d, $^2J_{Y-H}$ = 3.0 Hz, 4 H, YCH_2), 0.28 (s, 18 H, $NSi(CH_3)_3$), 0.40 (s, 18 H, $Si(CH_3)_3$), 1.27−2.11 (br m, together 28 H, CH_2 Cy, β-CH_2 THF), 3.31 (br m, 2 H, CH Cy), 3.69 (br s, 8 H, α-THF) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 20 °C): δ 2.4 ($NSi(CH_3)_3)_2$), 4.6, 4.7 ($CH_2Si(CH_3)_3$), 25.9 (β-CH_2, THF), 25.4, 26.2, 37.7 (CH_2, Cy), 35.3 (d, $^1J_{Y-C}$ = 38 Hz, YCH_2), 54.8 (CH, Cy), 68.1 (α-CH_2, THF), 169.0 (CN_3) ppm. Anal. Calcd for $C_{35}H_{76}N_3O_2Si_4Y$ (772.3): C, 54.38; H, 9.84; Y, 11.52. Found: C, 54.73; H, 10.01; Y, 11.38.

Synthesis of $[\{(Me_3Si)_2NC(NCy)_2\}Y\{(\mu^2\text{-}Me)_2Li(TMEDA)\}_2]$ (3). To a solution of **1** (1.12 g, 0.79 mmol) in toluene (20 mL) were slowly added TMEDA (0.37 g, 3.16 mmol) and a solution of MeLi in diethyl ether (4.0 mL, 1.6 M solution, 6.32 mmol) at 0 °C, and the reaction mixture was stirred for 45 min, allowed to warm to room temperature, and stirred for 1.5 h. The brown solution was filtered and the solvent evaporated in vacuo. Complex **3** was isolated by recrystallization from diethyl ether as colorless crystals (0.52 g, 44%). IR (Nujol, KBr, cm^{-1}): 1627 w, 1355 s, 1288 s, 1253 s, 1190 m, 1155 m, 1069 m, 996 m, 954 s, 834 s, 788 m, 638 w cm^{-1}. ^1H NMR (200 MHz, C_6D_6, 20 °C): δ −0.60 (br s, 12 H, Me), 0.46, 0.51 (s, together 18 H, $Si(CH_3)_3$), 1.23−2.20 (br m, 52 H, CH_2 Cy, CH_2, CH_3, TMEDA), 3.58 (br m, 2 H, CH Cy). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 20 °C): δ 2.7, 2.8 ($Si(CH_3)_3$), 7.2 (μ-CH_3), 26.3, 26.5, 26.6, 26.7 (CH_2, Cy), 46.00 ($N(CH_3)$), 54.9 (CH, Cy), 57.0 (NCH_2), 164.6 (CN_3). ^7Li NMR (77.73 MHz, C_6D_6, 20 °C): δ 4.16 ppm. Anal. Calcd for $C_{35}H_{84}Li_2N_7Si_2Y$ (762.1): C, 55.11; H, 11.02; Y, 11.68. Found: C, 54.84; H, 11.40; Y, 11.39.

Reaction of 1 with *t*-BuLi (1:2). Synthesis of $[(Me_3Si)_2NC(NCy)_2]_2Y\textit{t}\text{-}Bu$ (4). To a solution of **1** (1.05 g, 0.74 mmol) in hexane (30 mL) was added a solution of *t*-BuLi (1.97 mL, 1.5 N, 2.96 mmol) at 0 °C. The reaction mixture was stirred for 40 min. The pale yellow solution was filtered and concentrated in vacuo to approximately a quarter of its initial volume. Complex **4** was isolated as colorless crystals (0.55 g, 42%) from hexane under cooling. IR (Nujol, KBr, cm^{-1}): 1620 s, 1330 m, 1220 s, 1260 m, 1205 m, 1150 m, 950 s, 930 s, 830 s. ^1H NMR (200 MHz, C_6D_6, 20 °C): δ 0.28, 0.32, 0.36 (3 s, together 36 H, $Si(CH_3)_3$), 1.48 (s, 9 H, $C(CH_3)_3$), 1.27−2.04 (br m, 40 H, CH_2 Cy), 3.45, 3.63 (2 br m, together 4 H, CH Cy). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 20 °C): δ 2.3, 2.4, 2.8 ($NSiCH_3)_2$), 24.9, 25.9, 26.1, 26.2, 26.4 (CH_2, Cy), 30.6, 30.7 ($C(CH_3)_3$), 37.5 (d, $^1J_{Y-C}$ = 56 Hz, $C(CH_3)_3$), 55.2 (CH, Cy), 168.7 (CN_3) ppm. Anal. Calcd for $C_{42}H_{89}N_6Si_4Y$ (879.4): C, 57.36; H, 10.12; Y, 10.10. Found: C, 56.91; H, 9.77; Y, 9.80.

Synthesis of $[(Me_3Si)_2NC(NCy)_2]YCl_2(Et_2O)$ (5). To a solution of $[(Me_3Si)_2NLi(Et_2O)]$ (0.94 g, 3.90 mmol) in Et_2O (30 mL) was added slowly 1,3-dicyclohexylcarbodiimide (0.80 g, 3.90 mmol) at 20 °C, and the reaction mixture was stirred for 45 min. YCl_3 (0.76 g, 3.90 mmol) was added, and the reaction mixture was stirred overnight. The solution was filtered, the solvent evaporated in vacuo, and the solid residue extracted with hexane (2 × 30 mL). The hexane extracts were filtered, and the solution was slowly concentrated at room temperature to a quarter of its initial volume, cooled to −30 °C, and left overnight. The crystalline precipitate was washed with cold hexane and dried in vacuo at room temperature for 60 min. **2** was isolated as a white microcrystalline solid (1.66 g, 71%). IR (Nujol, KBr, cm^{-1}): 1615 s, 1542 m, 1358 s, 1304 m, 1257 s, 1202 m, 1124 m, 1092 m, 1065 m, 1030 m, 1006 m, 951 s, 842 s, 760 m, 681 m, 638 m. ^1H NMR (200 MHz, C_6D_6, 20 °C): δ 0.43 (s, 18 H, $Si(CH_3)_3$), 1.07 (t, $^3J_{H-H} = 6.8$ Hz, 6 H, CH_3, Et_2O), 1.41−2.01 (br m, 20 H, CH_2 Cy,), 3.23 (q, $^3J_{H-H} = 7.0$ Hz, 4 H, CH_2, Et_2O), 3.44 (br m, 2 H, *CH* Cy). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 20 °C): δ 2.7 ($N(Si(CH_3)_3)_2$), 15.0 (CH_3, Et_2O), 26.1, 26.5, 37.3 (CH_2, Cy), 54.8 (*C*H, Cy), 65.7 (CH_2, Et_2O), 168.8 (CN_3) ppm. Anal. Calcd for $C_{23}H_{50}Cl_2N_3OSi_2Y$ (600.65): C, 45.99; H, 8.38; Y, 14.80. Found: C, 46.40; H, 8.72; Y, 14.48.

Synthesis of $\{(Me_3Si)_2NC(NCy)_2\}_2Y(\mu\text{-}CH_2SiMe_3)_2Li$ (6). To a solution of **2** (0.83 g, 1.38 mmol) in hexane (20 mL) was added a solution of Me_3SiCH_2Li (0.26 g, 2.76 mmol) in hexane (15 mL) at 0 °C, and the reaction mixture was stirred for 30 min. The pale yellow solution was filtered, and hexane was evaporated in vacuo. Complex **4** was isolated upon cooling of a concentrated pentane solution as colorless crystals (0.47 g, 34%). IR (Nujol, KBr, cm^{-1}): 1351 m, 1252 s, 1190 m, 1135 m, 1073 w, 1002 m, 944 s, 858 s, 838 s, 721 m. ^1H NMR (200 MHz, C_6D_6, 20 °C): δ −0.52 (br s, 4 H, μ-CH_2), 0.30 (s, 18 H, $Y(CH_2Si(CH_3)_3)_2$), 0.36 (s, 36 H, $NSi(CH_3)_3$), 1.23−1.96 (br m, 40 H, CH_2 Cy), 3.41 (br m, 4 H, *CH* Cy). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 20 °C): δ 2.3, 3.6 ($CH_2Si(CH_3)_3$), 2.9 ($NSi(CH_3)_3$), 14.6 (d, $^1J_{Y-C} = 63$ Hz, $Y(CH_2SiMe_3)_2$-Li), 26.0, 26.2, 26.3, 37.6, 37.8 (CH_2, Cy), 54.8 (*C*H, Cy), 168.6 (CN_3). Anal. Calcd for $C_{46}H_{102}LiN_6Si_6Y$ (1003.72): C, 55.04; H, 10.24; Y, 8.87. Found: C, 54.72; H, 10.53; Y, 8.46.

X-ray Crystallography. Low-temperature diffraction data of **1**, **2**, **3**, and **6** were collected on a Bruker-AXS Smart Apex diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), performing φ- and ω-scans. All structures were solved by Patterson (**1**) and direct (**2**, **3**, **6**) methods and refined against F^2 on all data by full-matrix least squares with SHELXTL.[31] Absorption correction was applied using SADABS.[32] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms in **1** and **2** were included in idealized positions, and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms ($U_{iso}(H) = 1.5U_{eq}$ for methyl carbons and $1.2U_{eq}$ for other carbons). In **3** and **6** H's (except H atoms in the solvate of pentane) were located from Fourier synthesis and refined isotropically. H atoms in the solvate of pentane (**6**) were placed in idealized positions and refined with $U_{iso}(H) = 1.5U_{eq}$ for methyl carbons and $1.2U_{eq}$ for methylene carbons Crystallographic data and structure refinement details are given in Table 1.

Acknowledgment. This work has been supported by the Russian Foundation for Basic Research (Grant Nos. 05-03-32390, 06-03-32728) and the Grant of President of Russian Federation supporting scientific schools (Nos. 58.2003.3, 1652.2003.3, 8017.2006.3). A.T. thanks the Russian Foundation for Science Support.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM060280C

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