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Article

N,*N*′-Diisopropyl-*N*″-bis(trimethylsilyl)guanidinate Ligand as a Supporting Coordination Environment in Yttrium Chemistry. Synthesis, Structure, and Properties of Complexes $[(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2]YCl_2(THF)_2$, $[(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2]Y(CH_2SiMe_3)_2(THF)_2$, and $[(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2]Y[(\mu\text{-}H)(\mu\text{-}Et)_2BEt]_2(THF)$[†]

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The reaction of anhydrous YCl_3 with an equimolar amount of lithium *N*,*N*′-diisopropyl-*N*″-bis(trimethylsilyl)guanidinate, $Li[(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2]$, in tetrahydrofuran (THF) afforded the monomeric monoguanidinate dichloro complex $\{(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2\}YCl_2(THF)_2$ (**1**). Alkylation of complex **1** with 2 equiv of $LiCH_2SiMe_3$ in hexane at 0 °C yielded the monomeric salt-free dialkyl complex $\{(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2\}Y(CH_2SiMe_3)_2(THF)_2$ (**2**). The bis(triethylborohydride) complex $[(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2]Y[(\mu\text{-}H)(\mu\text{-}Et)_2BEt]_2(THF)$ (**5**) was prepared by the reaction of complex **1** with 2 equiv of $LiBEt_3H$ in a toluene–THF mixture at 0 °C. The complexes **1**, **2**, and **5** were structurally characterized. Complex **2** as well as the systems **2**–Ph_3B, **2**–Ph_3B–MAO, and **1**–MAO (MAO = methylaluminoxanes) in toluene were inactive in ethylene polymerization, while the product obtained in situ from the reaction of complex **2** with a 2-fold molar excess of $PhSiH_3$ in toluene polymerized ethylene with moderate activity.

Introduction

Chelating monoanionic guanidinate ligands have attracted considerable attention as ancillary coordination environments in the coordination and organometallic chemistry of main-group and d-transition metals due to their flexibility of coordination and their easily modifiable electronic and steric properties.[1] Tetrasubstituted guanidinate anions, which are isoelectronic to cyclopentadienyl ligands and are hard Lewis bases, can serve as a promising alternative supporting ligation system capable of making a significant impact in the development of new lanthanide compounds. The related amidinate ligands have been successfully employed in the synthesis of a wide range of organolanthanide compounds,[2] among which the cationic alkyl complexes present a particular interest as efficient catalysts for olefin polymerization.[3] Guanidiante ligands have only been introduced into the field of lanthanide chemistry very recently, but they have already been shown to be a suitable coordination environment providing for the stabilization of mono-[4] and dialkyl,[5] hydride,[6] and borohydride[7] complexes and the synthesis of isolable low-valent lanthanide species.[8]

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[†] Dedicated to Prof. W. J. Evans on the occasion of his 60th birthday.

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Half-sandwich dialkyl lanthanide complexes[9] have attracted significant attention as potential precursors to cationic monoalkyl species[10] that were found to be efficient catalysts of homo- and copolymerization of olefins.[11] The idea to modify and to control the reactivity of complexes by the rational design of the coordination sphere of a metal atom has provided increasing interest in ligand "tailoring" and the employment of new anionic ancillaries in organolanthanide chemistry. As a result of this, a noticeable number of rare-earth dialkyl derivatives supported by non-cyclopentadienyl ligands have been synthesized and characterized. Amidinate,[2e,3] triamino-amide,[12] β-diketiminate,[13] anilido-imine,[14] amido diphosphine,[15] and deprotonated aza-18-crown-6[16] ligands have been successfully employed.

Metallocene-type lanthanide borohydride complexes have been known for three decades;[17] nevertheless, this class of compounds still attracts considerable attention due to their structural diversity and high catalytic activity.[18] A new rise of interest in lanthanide borohydrido complexes has been initiated by communications on their catalytic activity in lactone,[19] lactide,[20] and methyl methacrylate[21] polymerizations. The lanthanide sandwich and half-sandwich borohydrides have been used as precatalysts in two-component systems for ethylene,[22] styrene,[23] and isoprene[22,23] polymerizations. The lanthanide compounds containing the tris(alkyl)borohydride ligand $[R_3BH]^-$ as well as their chemical properties still remain virtually unexplored.[24]

Previously, we reported on the synthesis of mono-,[4d] dialkyl[5] and borohydrido[7d] lanthanide complexes supported by bulky $\{(Me_3Si)_2NC(NCy)_2\}^-$ ligands. We report here on the synthesis, structure, and properties of new yttrium dichloro, dialkyl, and bis(triethylborohydride) complexes coordinated by the less sterically demanding *N*,*N*′-diisopropyl-*N*″-bis(trimethylsilyl)guanidinate ligand.

Experimental Details

All experiments were performed in evacuated tubes, using standard Schlenk-tube techniques, with the rigorous exclusion of traces of moisture and air. After drying over KOH, tetrahydrofuran (THF) was purified by distillation from sodium/benzophenone ketyl, hexane, and toluene 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*′-diisopropylcarbodiimide was purchased from Acros. $LiBHEt_3$ was purchased from Aldrich. Anhydrous YCl_3,[25] $[(Me_3Si)_2NLi(Et_2O)]$,[26] and Me_3SiCH_2Li[27] were prepared according to literature procedures. All other commercially available chemicals were used after the appropriate purifications. NMR spectra were recorded on a Bruker DPX 200 spectrometer (^{1}H, 200 MHz; ^{13}C, 50 MHz; ^{11}B, 64.2 MHz) in C_6D_6 at 20 °C, unless otherwise stated. Chemical shifts for ^{1}H 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 instruments. Lanthanide metal analyses were carried out by complexometric titration. The C, H elemental analysis was made in the microanalytical laboratory of the G. A. Razuvaev Institute of Organometallic Chemistry.

Synthesis of $[\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}YCl_2(THF)_2$ (1). To a solution of $[(Me_3Si)_2NLi(Et_2O)]$ (1.15 g, 4.77 mmol) in THF (30 mL) 1,3-diisopropylcarbodiimide (0.6 g, 0.74 mL, 4.77 mmol) was added slowly at 20 °C, and the reaction mixture was stirred for 45 min. YCl_3 (0.93 g, 4.77 mmol) was added, and the reaction mixture was stirred overnight. The solution was filtered, the solvent was evaporated in vacuo, and the solid residue was 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 (2.81 g, 91%). ^{1}H NMR (200 MHz, C_6D_6, 20 °C): δ 4.08 (sept, $^3J_{H-H} = 6.4$ Hz, 2 H, C*H*(CH_3)$_2$), 3.85 (br s, 8 H, α-C*H*$_2$, THF), 1.47, 1.27, 1.10 (d, $^3J_{H-H} = 6.4$ Hz, 12 H, CH-(C*H*$_3$)$_2$), 1.41 (br s, 8 H, β-C*H*$_2$ THF), 0.29, 0.18 (s, 18 H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 20 °C): δ 169.0 (*C*N_3), 69.2 (α-*C*H_2, THF), 45.8 (*C*H(CH_3)$_2$), 26.4 (β-*C*H_2, THF), 25.2 (CH-

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Table 1. Crystallographic Data and Structure Refinement Details for **1**, **2**, and **5**

	1	**2**	**5**
empirical formula	$C_{21}H_{48}Cl_2N_3O_2Si_2Y$	$C_{29}H_{70}N_3O_2Si_4Y$	$C_{29}H_{72}B_2N_3OSi_2Y$
fw	590.61	694.15	645.61
T, K	100(2)	100(2)	100(2)
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P2(1)/n$
unit cell dimens			
a, Å	9.132(3)	12.8551(9)	16.5541(11)
b, Å	11.807(4)	22.9931(16)	11.8514(8)
c, Å	15.195(5)	13.4924(9)	19.2605(13)
α, deg	89.010(7)	90	90
β, deg	89.645(8)	91.3940(1)	93.440(1)
γ, deg	67.755(6)	90	90
V, Å^3	1516.1(8)	3986.9(5)	3771.9(4)
Z	2	4	4
D (calculated), g/cm^3	1.294	1.156	1.137
abs coeff, mm^{-1}	2.199	1.609	1.633
F(000)	624	1504	1408
crystal size, mm	0.10 × 0.08 × 0.05	0.20 × 0.15 × 0.08	0.40 × 0.35 × 0.30
θ range for data collection, deg	23.00	25.00	26.00
index ranges			
	$-10 \leq h \leq 10$	$-15 \leq h \leq 15$	$-20 \leq h \leq 20$
	$-12 \leq k \leq 12$	$-27 \leq k \leq 27$	$-14 \leq k \leq 14$
	$-8 \leq l \leq 16$	$-16 \leq l \leq 16$	$-23 \leq l \leq 23$
reflns collected	6788	15 431	31 865
independent reflns	4133	3521	7417
R_{int}	0.0548	0.0375	0.0291
completeness to θ	98.4	100.0	99.9
data/restraints/params	4133/6/280	3521/0/318	7417/0/351
GOF on F^2	1.065	1.066	1.016
final R indices [$I > 2\sigma(I)$]			
R_1	0.1345	0.0277	0.0473
R_2	0.3430	0.0666	0.1278
R indices (all data)			
R_1	0.1597	0.0349	0.0575
R_2	0.3530	0.0685	0.1334
largest diff peak and hole, e•Å^3	3.687/−1.647	0.512/−0.292	0.984/−0.475

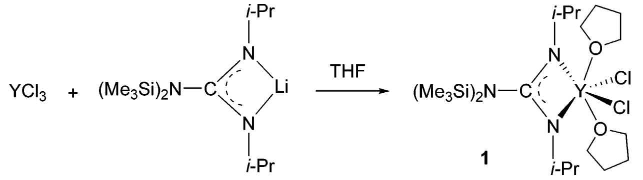
(CH_3)$_2$), 2.2, 1.7 [(N(Si(CH_3)$_3$)$_2$] ppm. Anal. Calcd for $C_{21}H_{48}Cl_2N_3O_2Si_2Y$: C, 42.71; H, 8.19; Y, 15.05. Found: C, 42.23; H, 8.04, Y, 14.82. IR (Nujol, KBr, cm^{-1}): 1638 s, 1613 m, 1245 s, 1212 m, 1170 m, 1140 w, 1120 w, 1079 m, 1049 s, 1004 w, 840 m, 756 m, 680 w.

Synthesis of [{$(Me_3Si)_2NC(N\textit{i}Pr)_2$}$Y(CH_2SiMe_3)_2(THF)_2$] (2). To a solution of **1** (0.82 g, 1.39 mmol) in hexane (20 mL) a solution of Me_3SiCH_2Li (0.26 g, 2.78 mmol) in hexane (10 mL) was slowly added at 0 °C, and the reaction mixture was stirred for 1 h. The pale-yellow solution was filtered and concentrated in vacuo to approximately one-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, and the solid was washed with cold hexane and dried in vacuo at room temperature for 30 min. Complex **3** was isolated as off-white crystals (0.81 g, 84%). ^{1}H NMR (200 MHz, C_6D_6, 20 °C): δ 3.77 (br m, together 10 H, α-CH_2, THF, C*H*(CH$_3$)$_2$), 1.36 (br s, 8 H, β-CH_2, THF), 1.20 (d, $^3J_{H-H}$ = 6.4 Hz, 12 H, C*H*(CH$_3$)$_2$), 0.39 (s, 18 H, Si(CH_3)$_3$), 0.25 (s, 18 H, NSi(CH_3)$_3$), −0.38 (d, $^2J_{Y-H}$ = 3.0 Hz, 4 H, YCH_2) ppm. ^{13}C{^{1}H} NMR (50 MHz, C_6D_6, 20 °C): δ 168.5 (*C*N$_3$),69.3 (α-*C*H$_2$, THF), 45.6 (*C*H(CH$_3$)$_2$), 35.1 (d, $^1J_{Y-C}$ = 38.0 Hz, Y*C*H$_2$), 26.9 (CH(*C*H$_3$)$_2$), 25.1 (β-*C*H$_2$, THF), 4.5 (CH$_2$Si(*C*H$_3$)$_3$), 2.2 (NSi(*C*H$_3$)$_3$)$_2$) ppm. Anal. Calcd for $C_{29}H_{70}N_3O_2Si_4Y$: C, 50.18; H, 10.16; Y, 12.81. Found : C, 50.73; H, 10.311; Y, 12.56. IR (Nujol, KBr, cm^{-1}): 1638 s, 1600 w, 1324 m, 1250 s, 1200 m, 1167 w, 1140 w, 1120 w, 1052 s, 950 s, 840 s, 760 w, 690 m.

Synthesis of [{$(Me_3Si)_2NC(N\textit{i}Pr)_2$}Y*t*-Bu$_2$(THF)] (4). Complex **1** (1.39 g, 2.36 mmol) and *t*-BuLi (3.15 mL, 1.5 M solution in pantane, 4.72 mmol) were mixed in hexane (15 mL) at 0 °C. The reaction mixture was stirred 1 h. The solution was filtered and concentrated in vacuo to approximately one-quarter of its' initial volume then cooled to −18 °C overnight. The mother liquid was decanted, and the off-white solid was washed with cold hexane and dried in vacuo 30 min. Complex **5** was isolated as a colorless microcrystalline product (1.17 g, 78%).^{1}H NMR (200 MHz, C_6D_6, 20 °C): δ 3.90 (sept, 2 H, $^2J_{HH}$ = 6.6 Hz, C*H*Me$_2$), 3.71 (br m, 4 H, α-CH_2, THF), 1.37 (s, 18 H, C(CH_3)$_3$), 1.32 (br m, 4 H, β-CH_2, THF), 1.19 (d, 12 H, $^2J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 0.27 (s, 18 H, Si(CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (50 MHz, C_6D_6, 20 °C): δ 141.7 (*C*N$_3$), 68,1 (α-*C*H$_2$, THF), 29.8 (d, $^1J_{YC}$ = 60 Hz, Y*C*Me$_3$), 27.1 (β-*C*H$_2$, THF), 24.6 (CH(*C*H$_3$)$_2$), 14.0 (C(*C*H$_3$)$_3$), 2.4 (Si(*C*H$_3$)$_3$) ppm.

Synthesis of [$(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2$]Y[($\mu$-H)($\mu$-Et)$_2$BEt]$_2$(THF) (5). To a solution of **1** (0.72 g, 1.22 mmol) in toluene (20 mL) a solution of LiBHEt$_3$ in THF (2.44 mL, 1.0 M solution, 2.44 mmol) was slowly added at 0 °C. The reaction mixture was stirred for 45 min, allowed to warm to room temperature, and stirred for 1.5 h. The solution was filtered, the volatiles were evaporated in vacuo, and the solid residue was extracted with hexane (2 × 30 mL). Complex **5** was isolated after recrystallization from hexane as colorless crystals (0.51 g, 65%). ^{1}H NMR (200 MHz, C_6D_6, 20 °C): δ 3.76 (m, 2 H, C*H*(CH$_3$)$_2$), 3.61 (br s 4 H, α-CH_2, THF), 1.29 (br s, 4 H, β-CH_2, THF), 1.24, 1.06 (d, $^3J_{H-H}$ = 6.4 Hz, together 12 H, CH(CH_3)$_2$), 0.99 (br s, 18 H, B(CH$_2$CH_3)$_3$), 0.68 (br m, 12 H, B(CH_2CH$_3$)$_3$), 0.20, 0.14 (s together 18 H, Si(CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (50 MHz, C_6D_6, 20 °C): δ 169.2 (*C*N$_3$), 69.4 (α-*C*H$_2$, THF), 46.1 (*C*H(CH$_3$)$_2$), 26.9, 26.1 (CH(*C*H$_3$)$_2$), 24.9 (β-*C*H$_2$, THF), 18.6 (B(CH$_2$*C*H$_3$)$_3$) 8.5 (B(*C*H$_2$CH$_3$)$_3$) 2.0 (NSi(*C*H$_3$)$_3$)$_2$) ppm. ^{11}B NMR (64.2 MHz, C_6D_6, 20 °C): δ −9.3 (br s) ppm. Anal. Calcd for $C_{29}H_{72}B_2N_3OSi_2Y$: C, 53.95; H, 11.24; Y, 13.77. Found: C,

Scheme 1



1

54.16; H, 11.40; Y, 13.69. IR (Nujol, KBr, cm^{-1}): 2280 s, 1637 s, 1572 m, 1252 s, 1180 m, 1103 w, 1051 m, 955 m, 918 m, 828 m, 812, 496 s.

X-ray Crystallography. Low-temperature diffraction data of **1**, **2**, and **5** were collected on a Bruker-AXS Smart Apex diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). All structures were solved by direct methods and refined against F^2 on all data by full-matrix least squares with *SHELXTL*.[28] Absorption correction was applied using *SADABS*.[29] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms in **1** and **5** (except hydride H atoms in Et_3BH groups) 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). The H atoms in **2** and the hydride H atoms in Et_3BH groups in **5** were located from Fourier synthesis and refined isotropically. Crystallographic data and structure refinement details are given in Table 1.

Results and Discussion

Mono(guanidinate) dichloro complex $\{(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2\}YCl_2(THF)_2$ (**1**) was synthesized by the reaction of YCl_3 with an equimolar amount of lithium *N*,*N*′-diisopropyl-*N*″-bis(trimethylsilyl)guanidinate, $Li[(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2]$, obtained in situ from $Li(Et_2O)[N(SiMe_3)_2]$ and the 1,3-diisopropyl-substituted carbodiimide $\textit{i}\text{-}PrN{=}C{=}N\textit{i}\text{-}Pr$ in THF at 20 °C. The evaporation of THF, extraction of the solid residue with toluene, and the filtration and cooling of the toluene solution to −30 °C allowed the isolation of complex **1** in 91% yield (Scheme 1). Surprisingly, unlike the related dichloro yttrium derivative containing the dicyclohexyl-substituted guanidinate ligand which was isolated as a dimeric ate-complex $[\{(Me_3Si)_2NC(NCy)_2\}Y\{(\mu\text{-}Cl)_2Li(THF)_2\}(\mu\text{-}Cl)]_2$[5] compound **1** was obtained as a monomeric salt-free complex.

Complex **1** was obtained as colorless crystalline moisture- and air-sensitive solid. It is soluble in THF and toluene and slightly 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 ligand and the coordinated THF molecules. The ^1H NMR signals of the THF methylene protons in **1** appear as broad singlets reflecting labile coordination. Crystals of **1** were obtained from toluene solution by the 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** was analyzed by X-ray crystallography and was found to crystallize in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. Although the connectivity of the atoms was established, the poor quality of crystals did not allow accurate information to be obtained on bond distances and angles.

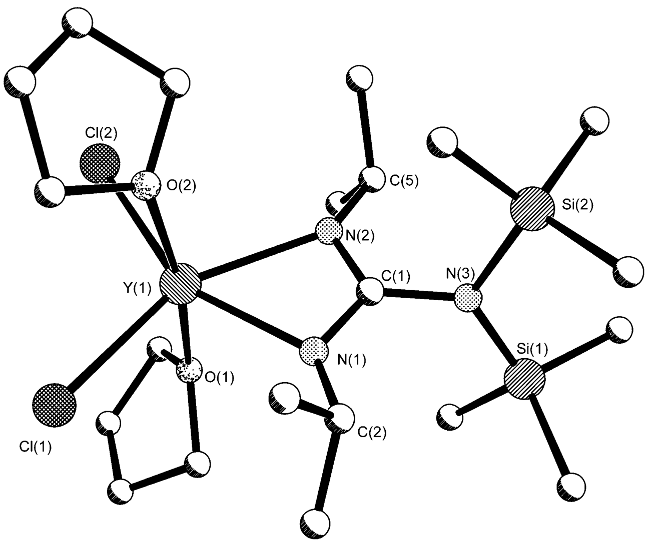
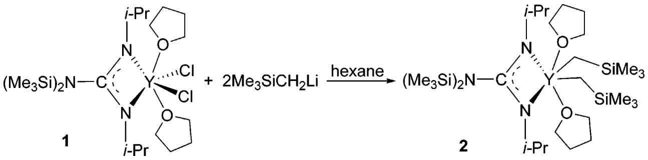


Figure 1. Ball-and-stick plot of crystallographically characterized **1**.

Scheme 2



1 **2**

The coordination sphere of the yttrium atom consists of two nitrogen atoms from the bidentate guanidinate ligand, two chlorine atoms, and two oxygen atoms from the two THF molecules. This results in a formal coordination number of 6. The coordination geometry of the yttrium atom can be described as that of a distorted octahedron.

The system **1**−MAO (MAO = methylaluminoxanes) in toluene was found to be inactive in ethylene polymerization (20 °C, 0.5 bar).

Recently we reported synthesis, structure, and properties of a dialkyl yttrium complex supported by the dicyclohexylguanidinate ligand $\{(Me_3Si)_2NC(NCy)_2\}Y(CH_2SiMe_3)_2(THF)_2$ (**3**).[5] Here, we describe the synthesis and properties of the dialkyl yttrium complex coordinated by the less sterically demanding diisopropylguanidinate ligand.

The alkylation of **1** with 2 equiv of $LiCH_2SiMe_3$ was carried out in hexane at 0 °C. Filtration, concentration, and cooling of the reaction mixture to −30 °C afforded the mono(guanidinate) dialkyl compound $\{(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2\}Y(CH_2SiMe_3)_2(THF)_2$ (**2**) as a colorless crystalline solid in 84% yield (Scheme 2). Complex **2** contains two coordinated THF molecules.

The off-white crystalline compound **2** is moisture- and air-sensitive. The complex is fairly soluble in commonly used organic solvents (THF, toluene, hexane), that hamper its isolation. Complex **2** is rather stable in an inert atmosphere; at −18 °C it can be kept without decomposition for 3 months. In a C_6D_6 solution at 20 °C it slowly decomposes with the elimination of Me_4Si and unidentified products. Complete

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(28) Sheldrick G. M. *SHELXTL*, *Structure Determination Software Suite*, version 6.12; Bruker AXS: Madison, WI, 2000.

(29) Sheldrick G. M. *SADABS*, *Area Detector Absorption Correction Program*, version 2.01; Bruker AXS: Madison, WI, 1998a.

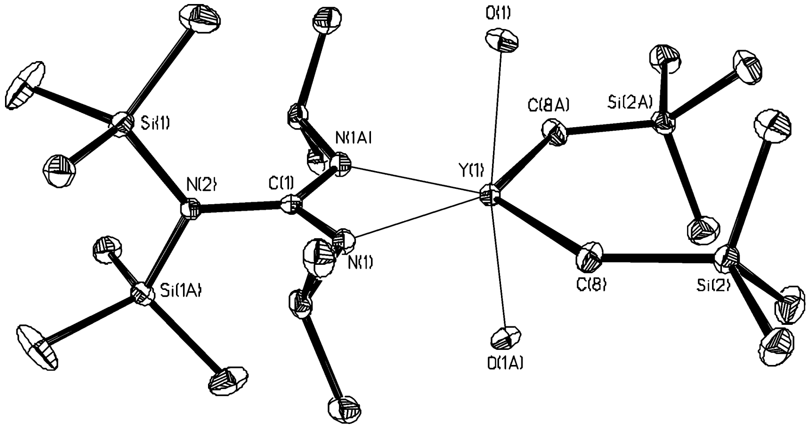
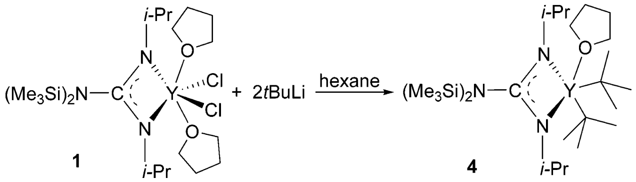


Figure 2. ORTEP diagram (30% probability thermal ellipsoids) of **2**. Hydrogen atoms and carbon atoms of THF are omitted for clarity. Selected bond distances (Å) and angles (deg): Y(1)−C(8) 2.466(2), Y(1)−N(1) 2.406(1), Y(1)−O(1) 2.362(1), N(1)−C(1) 1.330(2), C(8)−Y(1)−C(8A) 123.4(1), N(1A)−Y(1)−N(1) 55.25(7), O(1)−Y(1)−O(1A) 170.18(5).

decomposition under these conditions took ~20 days. According to the ^{1}H NMR data, no activation of C−H bonds within the guanidinate ligands occurs. In the ^{1}H NMR spectrum of complex **2** at 20 °C, the hydrogen atoms of the methylene groups attached to the yttrium atom appear as a doublet at −0.38 ppm ($^2J_{YH}$ = 3.0 Hz); in the ^{13}C{^{1}H} NMR spectrum, the appropriate carbons give rise to a doublet at 35.1 ppm ($^2J_{YC}$ = 38.0 Hz). The guanidinate and THF ligands give the expected sets of signals in the ^{1}H and ^{13}C NMR spectra.

Colorless crystals of complex **2** suitable for X-ray diffraction studies were obtained by storing its concentrated hexane solutions at −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 *C*2/*c* with four molecules in the unit cell. X-ray diffraction study has revealed that **2** is a monomeric salt-free complex. The coordination sphere of the yttrium atom is made up of two nitrogen atoms of the bidentate guanidinate ligand, two carbon atoms from the alkyl groups, and two oxygen atoms from the two THF molecules. This results in the formal coordination number of six. The coordination geometry of the yttrium atom can be described as that of a distorted octahedron. The coordination environments of the yttrium atoms in complexes **2** and **3** seem to be very similar; nevertheless, it is worth noting that the C−Y−C bond angle in **2** (123.4(1)°) is much bigger compared with the corresponding value in **3** (112.40(7)°),[5] thus reflecting stronger steric repulsion between the CH_2SiMe_3 ligands and bulkier cyclohexyl groups. The yttrium atom geometries in complexes **2** and **3** noticeably differ from that in the related six-coordinate amidinate yttrium derivative $[PhC(NC_6H_3i\text{-}Pr_2\text{-}2,6)_2]Y(CH_2SiMe_3)_2(THF)_2$.[3a] Thus, in **2** and **3** the planes defined by the atoms N−Y−N and C−Y−C are nearly coplanar (the values of the dihedral angles between the two planes in **2** and **3** are 5.1° and 7.7°, respectively) while in the $[PhC(NC_6H_3i\text{-}Pr_2\text{-}2,6)_2]Y(CH_2SiMe_3)_2(THF)_2$ complex they adopt a close to orthogonal orientation (88.6°).[3a] Obviously, such a difference is caused by the tendency to minimize mutual steric repulsion of the ligands in the case of the bulkier amidinate ligand.

Scheme 3



The Y−C bond lengths in complex **2** are 2.466(2) Å which are comparable to the related distances in the dialkyl yttrium complexes.[3a,5,12b,16] The distances Y−N(1,1A) (2.406(1) Å) are slightly longer than those in complex **1**. The equal C−N bond lengths within the guanidinate fragment (1.330(2) Å) prove electron delocalization within the anionic NCN units. The Y−O bond lengths in **2** (2.362(1) Å) are somewhat shorter than those in the related complex **3** (2.378(1) and 2.403(1) Å).[5]

In order to generate cationic alkylyttrium species supported by the diisopropylguanidinate ligands, reactions of the complex **2** with both Lewis ($(C_6H_5)_3B$, $(C_6F_5)_3B$) and Brønsted ($[NHMe_2Ph][B(C_6F_5)_4]$) acids have been carried out in THF or toluene at −78 °C in a 1:1 molar ratio. Unfortunately, all the reactions afforded intractable mixtures of products and all attempts to isolate individual organoyttrium compounds from the reaction mixtures failed. Complex **2** is inactive in ethylene and styrene polymerizations. The systems **2**−Ph_3B and **2**−Ph_3B−MAO in toluene do not catalyze ethylene polymerization (20 °C, 0.5 bar).

We carried out the reaction of complex **1** with a 2-fold molar excess of *t*BuLi in hexane solution at 0 °C (Scheme 3).

Separation of the precipitate of LiCl and cooling of the concentrated hexane solution at −20 °C resulted in the formation of an off-white microcrystalline solid. According to the ^{1}H and ^{13}C NMR spectra and yttrium metal microanalysis, this complex can be formulated as $\{(Me_3Si)_2NC(Ni\text{-}Pr)_2\}Y(t\text{Bu})_2(THF)$ (**4**). Unfortunately, all our attempts to obtain crystals suitable for X-ray diffraction study as well as reproducible C, H microanalysis data failed. Obviously, this is related to the low stability of this complex, which decomposes completely over the course of 1 day in C_6D_6 at room temperature. Slow decomposition of complex **4** takes place even when it is kept at −20 °C. The reaction of complex **2** with Ph_2CHK in THF did not afford isolable alkyl yttrium complexes.

The synthesis of the first rare-earth polyhydrido complexes composed of "$(C_5Me_4SiMe_3)LnH_2$" units was realized recently and demonstrated very rich reactivity.[30] Lanthanide dihydride compounds supported by non-cyclopentadienyl ancillary ligands still remains a challenge. The most common synthetic route to lanthanide hydrido complexes is the σ-bond metathesis reaction of parent alkyls under treatment with dihydrogen[31] or phenylsilane.[32,6b] We attempted the preparation of dihydride species coordinated by diisopropylguanidinate ligands using the reaction of complex **2** with 2 equiv of $PhSiH_3$ or with H_2 (1 barr) in hexane. The reaction occurs at 20 °C and affords a colorless crystalline precipitate which has very low solubility in hexane, cyclohexane, benzene, or toluene. When the precipitate was treated with THF, the evolution of a gas (supposedly H_2) was observed. Unfortunately, all attempts to grow crystals suitable for X-ray diffraction study were unsuccessful. Further work on this subject is being actively pursued at the moment.

In order to evaluate catalytic activity of the species formed in the system complex **2**−$PhSiH_3$ in ethylene polymerization, we carried out the reaction in the presence of the monomer (molar ratio **2**/$PhSiH_3$ = 1:2, toluene, 20 °C, ethylene pressure = 0.5 bar). The catalytic tests with ethylene were carried out under rigorously anaerobic conditions in a sealed glass manometric system (toluene 5 mL, catalyst concentration 4.33×10^{-3} mol/L), which allowed the monitoring of the polymerization process by consumption of the monomer ($mol_{ethylene}/mol_{Cat.}$). The species formed after treatment of complex **2** with $PhSiH_3$ catalyzed the slow polymerization of ethylene, and after 3 h the absorption of ethylene was 27 mol per mol of yttrium metal (Figure 3).

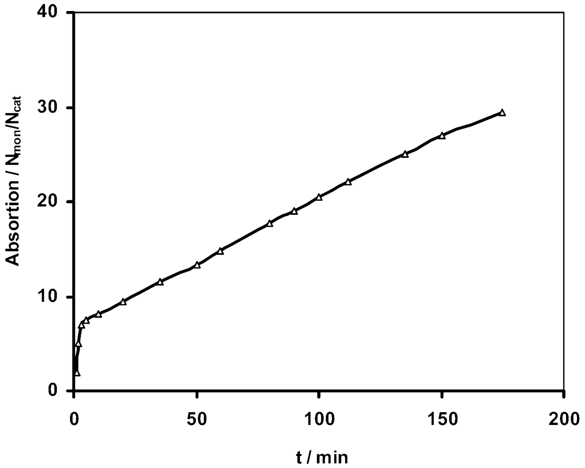
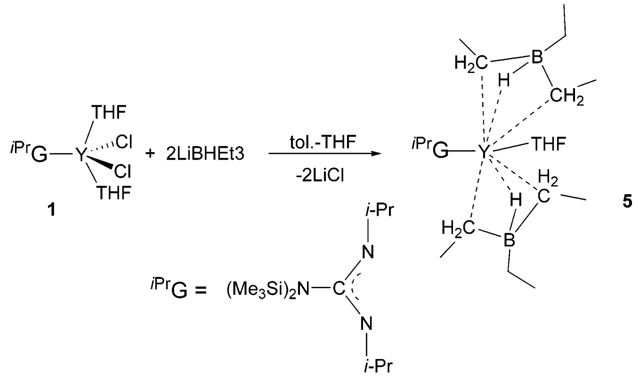


Figure 3. Polymerization of ethylene catalyzed by system complex **2**−$PhSiH_3$ (1:2 molar ratio, toluene 5 mL, catalyst concentration 4.33×10^{-3} mol/L, 20 °C, ethylene pressure = 0.5 atm).

Scheme 4



Evans and co-workers have reported the formation of triethylborohydride lanthanum complexes $(C_5Me_5)_2La[(\mu\text{-}H)(\mu\text{-}Et)_2BEt]$ and $(C_5Me_5)_2La(THF)[(\mu\text{-}H)(\mu\text{-}Et)_2BEt]$ in the reactions of metallocene-type hydride $[(C_5Me_5)_2LaH]_x$ with Et_3B.[24a] A scandium triethylborohydride complex containing β-diketiminate and anilido ligands $\{[(2,6\text{-}i\text{-}Pr_2C_6H_3)NC(Me)]_2CH\}[NH(2,6\text{-}i\text{-}Pr_2C_6H_3)]Sc(HBEt_3)$ was obtained by the metathesis reaction of the corresponding chloride $\{[(2,6\text{-}i\text{-}Pr_2C_6H_3)NC(Me)]_2CH\}[NH(2,6\text{-}i\text{-}Pr_2C_6H_3)]ScCl(THF)$ with $NaBHEt_3$ and was found to promote carbon−oxygen bond cleavage of Et_2O.[24b] Sandwich triethylborohydride complexes of Nd and Sm were synthesized using the same synthetic approach.[24c,d] A bis(triethylborohydride) yttrium complex coordinated by a guanidinate ligand was prepared by a metathesis reaction of compound **1** with 2 equiv of $LiBHEt_3$ in a toluene−THF mixture at 0 °C (Scheme 4).

Filtration of the reaction mixture, evaporation of the solvent in vacuo, and recrystallization of the solid residue from hexane afforded complex $[(Me_3Si)_2NC(N\text{-}i\text{-}Pr)_2]Y[(\mu\text{-}H)(\mu\text{-}Et)_2BEt]_2(THF)$ (**5**) as colorless crystals in 65% yield. Complex **5** is well soluble in toluene and sparingly soluble in hexane and is thermally stable in both C_6D_6 solution and the crystalline state. The ^1H NMR spectrum of complex **5** at 20 °C shows that the ethyl fragments are equivalent in this compound. The hydride signal was not located in the ^1H NMR spectrum of **5** presumably due to broadening resulting from coupling of the hydride to both ^{89}Y and ^{11}B nuclei. Unlike the ^{11}B NMR spectra of mono(triethylborohydride) complexes $[(C_5Me_5)_2La[(\mu\text{-}H)(\mu\text{-}Et)_2BEt]$[24a] and $\{[(2,6\text{-}i\text{-}Pr_2C_6H_3)NC(Me)]_2CH\}[NH(2,6\text{-}i\text{-}Pr_2C_6H_3)]Sc(HBEt_3)$[24b] that contained doublets corresponding to boron atoms coupled to the hydrido ligand, the spectrum of complex **5** at room temperature displays a broad singlet at −9.3 ppm.

Colorless crystals of complex **5** suitable for X-ray diffraction studies were obtained by storing its concentrated hexane solutions at −30 °C. The molecular structure of **5** is shown in Figure 4, and the structure refinement data are listed in Table 1. Complex **5** crystallizes in the monoclinic space group, *P*2(1)/*n* with four molecules in the unit cell.

X-ray diffraction study has revealed that **5** is a monomeric complex. The molecular structure shows that the yttrium

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(30) (a) Tardiff, O.; Nishiura, M.; Hou, Z. *Organometallics* **2003**, *22*, 1171−1173. (b) Cui, D.; Tardiff, O.; Hou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 1312−1313. (c) Li, X.; Baldamus, J.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2006**, *45*, 8184−8188.

(31) (a) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091−8103. (b) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103−8110.

(32) Voskoboinikov, A. Z.; Parshina, I. N.; Shestakova, A. K.; Butin, K. P.; Beletskaya, I. P.; Kuz'mina, L. G.; Howard, J. A. K. *Organometallics* **1997**, *16*, 4690−4700.

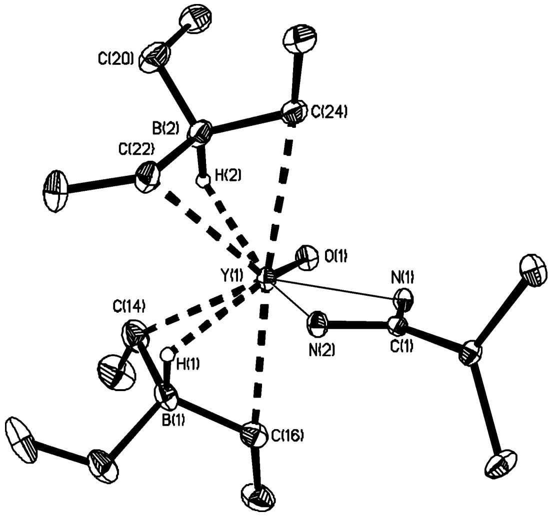

Figure 4. ORTEP diagram (30% probability thermal ellipsoids) of **5**. Methylene groups of THF, methyl radicals of $SiMe_3$ groups, and isopropyl fragments of guanidinate ligands are omitted for clarity. Selected bond distances (Å) and angles (deg): Y(1)−C(16) 2.761(3), Y(1)−C(24) 2.850(3), Y(1)−C(22) 2.886(3), Y(1)−C(14) 3.002(4), Y(1)−N(1) 2.332(2), Y(1)−N(2) 2.337(2), Y(1)−O(1) 2.448(2), Y(1)−B(1) 2.658(4), Y(1)−B(2) 2.671(4), N(1)−C(1) 1.333(4), C(1)−N(2) 1.331(3), N(1)−Y(1)−N(2) 56.98(8), B(1)−Y(1)−B(2) 114.9(1), C(24)−Y(1)−C(22) 56.67(9), C(16)−Y(1)−C(14) 59.0(1).

aatom in **5** is coordinated by a chelating guanidinate ligand, two triethylborohydride anions, and one THF molecule. Each of the triethylborohydride groups in **5** is bound to the yttrium atom by two μ^2-ethyl ligands and one μ^2-hydrido ligand in the coordination fashion similar to that previously reported for complexes $(C_5Me_5)_2La[(\mu\text{-H})(\mu\text{-Et})_2BEt]$, $(C_5Me_5)_2La(THF)[(\mu\text{-H})(\mu\text{-Et})_2BEt]$,[24a] and $\{[(2,6\text{-}i\text{-}Pr_2C_6H_3)NC(Me)]_2CH\}[NH(2,6\text{-}i\text{-}Pr_2C_6H_3)]Sc(HBEt_3)$.[24b] The third ethyl group of the $BHEt_3^-$ anion remains terminal and does not participate in the metal−ligand bonding. The Y−B distances are 2.658(4) and 2.671(4) Å. In each of the μ^2-bridging CH_2 fragments of the ethyl groups, one hydrogen atom is oriented toward the yttrium atom, thus reflecting its participation in bonding.

Conclusions

The *N*,*N′*-diisopropyl-*N″*-bis(trimethylsilyl)guanidinate ligand allows the synthesis and isolation of new monomeric salt-free yttrium complexes $[(Me_3Si)_2NC(N\textit{i}\text{-Pr})_2]YCl_2(THF)_2$, $[(Me_3Si)_2NC(N\textit{i}\text{-Pr})_2]Y(CH_2SiMe_3)_2(THF)_2$, and $[(Me_3Si)_2NC(N\textit{i}\text{-Pr})_2]Y[(\mu\text{-H})(\mu\text{-Et})_2BEt]_2(THF)$. Unlike **2**, a related derivative $\{(Me_3Si)_2NC(N\textit{i}\text{-Pr})_2\}Y(\textit{t}Bu)_2(THF)$ easily decomposes even at low temperature. The system $[(Me_3Si)_2NC(N\textit{i}\text{-Pr})_2]Y(CH_2SiMe_3)_2(THF)_2$−$PhSiH_3$ (1:2 molar ratio) in toluene polymerizes ethylene with moderate activity.

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