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Novel Bis((trimethylsilyl)benzamidinato)titanium(III) Complexes. Preparation and Crystal Structures of $\{PhC[(Me_3Si)N]_2\}_2Ti(\mu\text{-}Cl)_2Li(TMEDA)$, $\{PhC[(Me_3Si)N]_2\}_2Ti(BH_4)$, and $\{PhC[(Me_3Si)N]_2\}_2Ti(\eta^3\text{-allyl})$

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The reactions of both $TiCl_2(TMEDA)_2$ and $TiCl_3(THF)_3$ with 2 equiv of $PhC[(Me_3Si)N]_2Li(TMEDA)$ in THF formed forest green crystals of $\{PhC[(Me_3Si)N]_2\}_2Ti(\mu\text{-}Cl)_2Li(TMEDA)$ (**1**) in good yields. Further reaction of **1** in toluene with $LiBH_4$ formed light brown crystals of $\{PhC[(Me_3Si)N]_2\}_2Ti(BH_4)$ (**2**). While the reactions of **1** with several organolithium and -magnesium reagents invariably gave intractable residues, a thermally stable Ti(III)–allyl derivative, $\{PhC[(Me_3Si)N]_2\}_2Ti(\eta^3\text{-allyl})$ (**4**), was obtained in crystalline form from the reaction of **1** with (allyl)MgBr in THF. Crystal data for **1**, **2**, and **4** are as follows. **1**: $C_{32}H_{62}N_6Si_4Cl_2TiLi$, $M = 768.97$, triclinic $P\bar{1}$, $a = 13.999(9)$ Å, $b = 15.32(1)$ Å, $c = 11.279(7)$ Å, $\alpha = 106.65(5)°$, $\beta = 96.87(6)°$, $\gamma = 80.43(6)°$, $V = 2278(3)$ Å^3, $Z = 2$, $R = 0.072$, $R_w = 0.058$, GOF = 4.03, for 366 parameters and 3217 out of 6379 unique reflections. **2**: $C_{26}H_{50}N_4Si_4TiB$, $M = 589.76$, triclinic, $P\bar{1}$, $a = 12.957(6)$ Å, $b = 13.252(5)$ Å, $c = 11.468(4)$ Å, $\alpha = 102.24(3)°$, $\beta = 107.53(3)°$, $\gamma = 69.71(3)°$, $V = 1748(1)$ Å^3, $Z = 2$, $R = 0.040$, $R_w = 0.046$, GOF = 1.53, for 326 parameters and 4604 out of 6156 unique reflections. **4**: $C_{29}H_{51}Si_4TiN_4$, $M = 615.99$, triclinic, $P\bar{1}$, $a = 11.894(3)$ Å, $b = 15.316(5)$ Å, $c = 10.928(2)$ Å, $\alpha = 101.59(2)°$, $\beta = 93.51(2)°$, $\gamma = 67.16(2)°$, $V = 1796.8(9)$ Å^3, $Z = 2$, $R = 0.043$, $R_w = 0.056$, GOF = 2.35.

Introduction

Interest in the chemistry of transition metal borohydrides has been stimulated by several attractive features including a variety of possible modes of bonding to the transition metals (mono–,[1] bi–,[2] and tridentate[3]), relevance for methane activation modeling studies,[4] their possible utilization as precursors for the preparation of transition metal hydrides[5] and solid metal borides,[6] and reactivity with organic substrates.[7]

We are interested in the synthesis, characterization, and utilization of trivalent titanium borohydrides as a synthetic tool for the preparation of new Ti(III) compounds. Although these compounds show considerable potential for the preparation of highly reactive titanium(III) hydrides,[8] only two borohydride Ti(III) complexes have been reported[9] on non-cyclopentadienyl systems. Since this paucity of the literature might be ascribed to an apparent instability of these derivatives,[10] we have employed in this work a sterically demanding anionic, bidentate (trimethylsilyl)benzamidinate ligand[11] with the aim of synthesizing sterically protected titanium(III) borohydrides. The bis((trimethylsilyl)benzamidinate ligand possesses, in fact, several characteristics (large steric hindrance, presence of an extensively delocalized π-electron system, anionic nature, and little possibility for involvement into the reactivity of the metal center) which might impart to the transition metal the type of stability found in the bis(cyclopentadienyl) systems.[11] Furthermore, the chelating nature of this ligand might engage the transition metal into partial dissociation equilibria which, by making available additional coordination sites, can be important for catalytic performances. Finally, bis(benzamidinato)titanium(III) complexes may serve as starting materials for the preparation of novel and stable Ti(III)–alkyls, whose chemistry remains largely unexploited.

We report in this paper the preparation and structural characterization of the first bis(benzamidinato)titanium(III) chloride and its transformation into the corresponding borohydride and allyl derivatives.

Experimental Section

All operations were performed under the inert atmosphere of a nitrogen-filled drybox (Vacuum Atmospheres) or by the use of standard Schlenk

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Table I. Crystal Data and Structural Analysis Results

complex	**1**	**2**	**4**
formula	$C_{32}H_{62}N_6Si_4Cl_2TiLi$	$C_{26}H_{50}N_4Si_4TiB$	$C_{29}H_{51}Si_4TiN_4$
fw	768.97	589.76	615.99
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.999(Å)	12.957(6)	11.894(3)
b (Å)	15.32(1)	13.252(5)	15.316(5)
c (Å)	11.279(7)	11.468(4)	10.928(2)
α (deg)	106.65(5)	102.24(3)	101.59(2)
β (deg)	96.87(6)	107.53(3)	93.51(2)
γ (deg)	80.43(6)	69.71(3)	67.16(2)
V (Å^3)	2278(3)	1748(1)	1796.8(9)
Z	2	2	2
radiation (Mo Kα; Å)	0.710 69	0.710 69	0.710 69
T (°C)	25	−161	−160
D_{calcd} (g cm^{-3})	1.121	1.120	1.138
μ_{calcd} (cm^{-1})	4.33	3.95	3.88
R, R_w, GOF	0.072, 0.058, 4.03	0.040, 0.046, 1.53	0.043, 0.056, 2.35

techniques. $TiCl_2(TMEDA)_2$ (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine)[12] and $TiCl_3(THF)_3$ were prepared according to published procedures.[13] TMEDA was chromatographed over Al_2O_3 and distilled over molten potassium after refluxing; PhCN was distilled in vacuo; $(Me_3Si)_2NLi$ was prepared by treating the corresponding amine with *n*-BuLi in hexane; allylbromide (Aldrich) was used as received. Infrared spectra were recorded on a Perkin-Elmer 283 instrument from Nujol mulls prepared in a drybox. NMR spectra were recorded on a Varian Gemini 200-MHz spectrometer. Elemental analyses were carried out at the Microanalytical Department of the Chemistry Department at the Rijksuniversiteit Groningen and at Galbraith Laboratories. Samples for magnetic susceptibility measurements were sealed in calibrated tubes inside a drybox and measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated following standard methods,[14] and corrections for underlying diamagnetism were applied to the data.[15]

Preparation of $PhC(NSiMe_3)_2Li(TMEDA)$. A solution of $(Me_3Si)_2NLi$ (43.0 g, 0.26 mol) in hexane (500 mL) was reacted at −10 °C with freshly distilled PhCN (26.5 g, 0.26 mol). The solution was stirred for approximately 4 hs at room temperature and then slowly warmed up to 50 °C. The mixture was then cooled to room temperature and treated with neat TMEDA (40.0 g, 0.34 mol). Colorless crystals of $PhC(NSiMe_3)_2Li(TMEDA)$ began to precipitate at room temperature. The mixture was allowed to stand for 4 h at room temperature and overnight at −50 °C. The crystalline product (67.6 g, 0.17 mol, 65%) was filtered under nitrogen, dried in vacuo, and used without further purification. ^{1}H-NMR (C_6D_6, 200 MHz, 25 °C), δ: 7.19 (m, 5H, phenyl), 2.00 (s, 12H, Me-TMEDA), 1.84 (s, 4H, CH_2-TMEDA), −0.02 (s, 18H, Me_3Si).

Preparation of ($\{PhC[(Me_3Si)N]_2\}_2Ti(\mu\text{-}Cl)_2Li(TMEDA)$ (1). Method A. Freshly prepared $PhC(NSiMe_3)_2Li(TMEDA)$ (2.3 g, 5.9 mmol) was added at room temperature to a THF solution (100 mL) of $TiCl_3(THF)_3$ (1.1 g, 3.0 mmol) containing an excess of TMEDA (2.5 mL). The color turned dark green upon mixing, and stirring was continued for 3 h. The solvent was removed in vacuo, and the residual solid redissolved in ether (50 mL). The suspension was filtered and forest green crystals of **1** (1.2 g, 1.5 mmol, 53%) separated from the resulting solution upon standing at −30 °C. Anal. Calcd (found) for $C_{32}H_{62}N_6TiCl_2Si_4Li$: C, 49.98 (49.87); H, 8.13 (8.11); N, 10.93 (10.55); Ti, 6.23 (6.19); Cl, 9.22 (9.01). IR [Nujol mull, KBr, cm^{-1}]: 1295 (w), 1260 (sh), 1245 (s), 1170 (w), 1160 (w), 1130 (w), 1070 (w), 1010 (w), 985 (s), 950 (w), 920 (w), 845 (vs), 790 (m), 760 (s), 720 (m), 700 (m), 595 (w), 500 (s). μ_{eff} = 1.75 μ_B.

Method B. Freshly prepared $PhC(NSiMe_3)_2Li(TMEDA)$ (3.5 g, 9.0 mmol) was added at low temperature (−60 °C) to a toluene suspension (100 mL) of $TiCl_2(TMEDA)_2$ (1.6 g, 4.5 mmol) containing a small excess of TMEDA (1.5 mL). The color turned deep orange-brown, and stirring was continued during the warming up to room temperature. The solvent was removed in vacuo, the residual solid redissolved in ether (50 mL), and the solution filtered. Forest-green crystals of **1** (1.3 g, 1.7 mmol, 38%) separated upon standing at −30 °C.

Method C. A red THF solution (50 mL) of **3** (vide infra) (10.0 g, 15 mmol) was stirred for 24 h at room temperature with lithium foil (0.1 g, 15 mmol) in the presence of excess TMEDA (4 mL). The resulting brown-greenish solution was evaporated to dryness, the residual solid was redissolved in ether (100 mL), and the insoluble residue was eliminated by filtration. The remaining solution was concentrated and allowed to stand at −30 °C overnight, yielding forest-green microcrystals of **1** (3.5 g, 4.5 mmol, 30%).

Preparation of $\{PhC[(Me_3Si)N]_2\}_2Ti(BH_4)$ (2). A toluene solution (50 mL) of **1** (1.0 g, 1.3 mmol) was stirred in the presence of an excess of $LiBH_4$ (0.15 g, 7.0 mmol). The initial green color slowly turned orange-brown during the 12 h of stirring at room temperature. The solvent was removed in vacuo and the residual solid redissolved in hexane (50 mL). After filtration, the resulting clear solution was allowed to stand overnight at −30 °C, during which time light-brown crystals of **2** separated (0.54 g, 0.91 mmol, 70%). Anal. Calcd (found) for $C_{26}H_{50}N_4Si_4BTi$: C, 52.95 (52.33); H, 8.55 (8.23); N, 9.50 (9.47), Ti, 8.12 (8.07). IR (Nujol mull, KBr, cm^{-1};: 2420 (m), 2395 (m), 2110 (m), 1370 (vs), 1240 (s), 1170 (w), 1125 (w), 980 (s), 920 (w), 840 (vs), 780 (m), 758 (s), 700 (m), 520 (s). μ_{eff} = 1.70 μ_B.

Preparation of $\{PhC[(Me_3Si)N]_2\}_2TiCl_2$ (3). A solution of $TiCl_4(TMEDA)$ (30 g, 9.8 mmol) in THF (500 mL) was stirred overnight at room temperature in the presence of $PhC(NSiMe_3)_2Li(TMEDA)$ (75.8 g, 19.6 mmol). The solvent was evaporated in vacuo from the resulting red solution, and the solid red residue was redissolved in Et_2O (600 mL). After filtration, concentration, and cooling overnight at −30 °C, orange-red crystals of **3** (40.0 g, 6.2 mmol, 63%) formed. Anal. Calcd (found) for $C_{26}H_{46}N_4Si_4TiCl_2$: C, 48.11 (48.36); H, 7.07 (7.18); N, 8.55 (8.68); Ti, 7.31 (7.41). IR [Nujol mull, KBr, cm^{-1}]: 1330 (vs), 1195 (sh), 1120 (w), 950 (m), 935 (s), 810 (vs), 740 (s), 710 (s), 690 (s), 660 (s), 640 (br), 555 (w), 470 (s), 400 (w), 330 (w). ^{1}H-NMR (C_6D_6, 200 MHz, 25 °C), δ: 7.35, 7.11 (m, 5H, phenyl), 0.45 (s, 18H, Me_3Si).

Preparation of $\{PhC[(Me_3Si)N]_2\}_2Ti(\eta^3\text{-allyl})$ (4). The addition of an ether solution of allyl–MgBr (8.2 mL, 1.4 M) to a solution of **1** (8.7 g, 11.3 mmol) in THF (200 mL) at −20 °C turned dark red-brown. The solution was stirred for 3 h at room temperature, whereupon the solvent was removed in vacuo and the solid residue was redissolved in ether (200 mL). The resulting suspension was filtered and the solvent evaporated in vacuo. The residual solid was suspended in hexane (200 mL) and the solution filtered. Upon concentration and overnight cooling at −50 °C, yellow-green crystals of **4** (2.1 g, 3.4 mmol, 30%) were separated from the hexane solution. Anal. Calcd (found) for $C_{29}H_{51}N_4Si_4Ti$: C, 56.15 (56.55); H, 8.17 (8.35); N, 9.00 (9.10). IR [Nujol mull, KBr, cm^{-1}]: 3060 (w), 1450 (vs), 1260 (sh), 1240 (s), 1170 (w), 1070 (w), 1030 (w), 1005 (m), 980 (s), 920 (m), 830 (vs), 800 (s), 780 (s), 740 (s), 720 (m), 700 (s), 690 (sh), 510 (vs), 440 (w), 370 (w). μ_{eff} = 1.63 μ_B.

X-ray Characterization. Data were collected at room temperature for complex **1** and at a temperature of −160 °C for **2** and **4**. The ω–2θ scan technique to a maximum 2θ value of 50.0° was used for suitable air-sensitive crystals sealed in a glass capillary, for the crystal measured at room temperature, or mounted on glass fibers, for samples measured at low temperature. Cell constants and the orientation matrix were obtained from the least-squares refinement of 25 carefully centered reflections in a maximum range of 25.0° < 2θ < 29.5°, 21.5° < 2θ < 25.4°, and 48.2° < 2θ < 49.7° for **1**, **2**, and **4** respectively. The intensities of three representative reflections were measured after every 150 reflections to probe crystal and instrument stability. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically. The hydrogen atom positions of complex **1** were calculated but not refined. Although all the hydrogen positions of both **2** and **4** were located in difference Fourier maps, a successful isotropic refinement was possible only in the case of **4**. In the case of complex **2**, only the hydrogen atoms of the BH_4 group were isotropically refined due to an unfavorble observation/parameter ratio. The final cycles of full-matrix least-squares refinement were based on the number of observed reflections with $I > 2.5\sigma(I)$ and corresponding parameters. Neutral atomic scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in F_{calc}. All calculations were performed using the TEXSAN package on a Digital VAX station. Details on data collections and structure refinements are reported in Table I and in the supplementary material. The final atomic coordinates are given in the supplementary material. Selected bond distances and angles are given in Table II.

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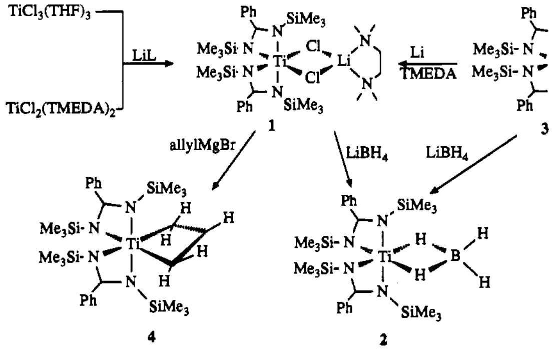
Table II. Selected Bond Distances (Å) and Angles (deg)

1	2	4
Ti1–Cl1 = 2.495(4)	Ti1–N1 = 2.059(3)	Ti1–N1 = 2.111(2)
Ti1–Cl2 = 2.460(4)	Ti1–N2 = 2.108(2)	Ti1–N2 = 2.153(2)
Li1–Cl1 = 2.35(2)	Ti1–H47 = 1.92	Ti1–N3 = 2.116(2)
Li1–Cl2 = 2.32(2)	Ti1–H48 = 1.92	Ti1–N4 = 2.198(2)
Ti1–N1 = 2.135(7)	Ti1–N3 = 2.064(2)	Ti1..C1 = 2.505(3)
Ti1–N2 = 2.128(7)	Ti1–N4 = 2.173(2)	Ti1–C27 = 2.297(4)
Ti1–N5 = 2.152(7)	Ti1–B1 = 2.426(4)	Ti1–C28 = 2.263(4)
Ti1–N6 = 2.163(8)	B1–H47 = 1.14	Ti1–C29 = 2.368(5)
N5–Si1 = 1.734(8)	N1–Si1 = 1.749(2)	N1–Si1 = 1.747(2)
Li1–N3 = 2.10(2)	Ti1–N1–C1 = 90.6(2)	C1–N1 = 1.340(3)
Li1–N4 = 2.16(2)	Ti1–N2–C1 = 88.7(2)	C27–C28 = 1.333(8)
Ti1–Cl1–Li1 = 90.6(4)	N1–C1–N2 = 115.1(2)	C28–C29 = 1.160(7)
Cl1–Ti1–Cl2 = 85.1(1)	N1–Ti1–N2 = 65.42(9)	N2–Ti1–N3 = 104.92(9)
Cl1–Li1–Cl2 = 91.7(6)	H47–Ti1–H48 = 55.5	Ti1–N1–C1 = 90.3(2)
N1–Ti1–N2 = 63.4(3)	Ti1–H47–B1 = 101.63	Ti1–N2–C1 = 88.9(2)
N5–Ti1–N6 = 62.8(3)	H47–B1–H48 = 104.4	N1–C1–N2 = 116.5(2)
N5–Ti1–Cl1 = 90.7(2)	Ti1–N1–C1–N2 = 3.5(2)	Ti1–N3–C14 = 132.1(2)
N6–Ti1–Cl1 = 91.9(2)	Ti1–N4–C15–N3 = 2.8(2)	Ti1–N4–C14 = 88.2(2)
N3–Li1–N4 = 85.2(7)	H47–Ti1–H48–B1 = 7.0	N3–C14–N4 = 117.0(3)
Cl1–Ti1–Cl2–Li1 = 5.6(5)		C27–C28–C29 = 149.3(7)
Ti1–N1–C1–N2 = 3.5(2)		C27–Ti1–C29 = 62.0(2)
Ti1–N4–C15–N3 = 2.8(2)		N1–Ti1–N2= 64.22(9)
		N3–Ti1–N4 = 63.51(9)
		Ti1–N2–C1–N1 = 2.8(2)

Scheme I



L = trimethylsilylbenzamidate
TMEDA = N,N,N',N'-tetramethylethylenediamine

Results and Discussion

The reaction of $TiCl_3(THF)_3$ with 2 equiv of the bis((trimethylsilyl)benzamidinato)lithium–TMEDA complex $PhC[(Me_3Si)N]_2Li(TMEDA)$ [TMEDA = *N,N,N′,N′*-tetramethylethylenediamine] in the presence of a light excess of TMEDA proceeded at room temperature in THF, forming an emerald-green solution from which forest-green octahedral crystals of $\{PhC[(Me_3Si)N]_2\}_2Ti(\mu\text{-}Cl)_2Li(TMEDA)$ (**1**) could be isolated in good yield and analytically pure from (Scheme I). Complex **1** was also obtained, although in lower yield, by reaction of $TiCl_2(TMEDA)_2$ with 2 equiv of lithium benzamidinate. In spite of the fact that other titanium-containing products are likely to be formed, the reaction (probably a disproportionation) produces by far the best quality product in terms of crystallinity and purity. Reduction of the corresponding bis(benzamidinato)titanium(IV) dichloride, $\{PhC[(Me_3Si)N]_2\}_2TiCl_2$ (**3**), with a stoichiometric amount of metallic lithium and in the presence of a little excess of TMEDA also produced **1**. Further reaction of **1** at room temperature with $LiBH_4$ in toluene led to the formation of the corresponding borohydride derivative (**2**), which could be isolated in high yield as light brown crystals. In analogy to the case of the bis(cyclopentadienyl)borohydride derivatives,[16] attempts to prepare a bis(borohydrido)titanium(IV) bis(benzamidinate), by reacting **3** with either a stoichiometric amount or an excess of $LiBH_4$, formed complex **2** in low yield, contaminated by a variable amount of intractable material. The IR spectrum of **2** showed three medium intensity absorptions at 2420, 2395, and 2110 cm^{-1}, which are characteristic of bidentate BH_4.[16]

A preliminary test on the ability of the benzamidinate ligand to stabilize trivalent titanium alkyl derivatives has been carried out with several organolithium and -magnesium RM reagents [R = Me, *n*-Bu, *t*-Bu, CH_2Ph; M = Li, MgBr]. While the utilization of 2 equiv of alkylating agent was necessary to obtain complete disappearance of the starting material, oily and intractable residues were invariably formed. Only in the case of (allyl)MgBr, albeit in poor yield, was it possible to isolate thermally stable, yellow-green crystals of the corresponding Ti(III) allyl derivative **4**. The absence of absorption bands in the region 1650–1500 cm^{-1} of the IR spectrum suggests that the allyl moiety is η^3-bonded to the metal.

Complexes **1**, **2**, and **4** are paramagnetic and showed magnetic moments as expected for a d^1 electronic configuration (μ_{eff} = 1.75, 1.70 and 1.63 μ_B for **1**, **2**, and **4** respectively).

The crystal structures of the three complexes have been determined by X-ray analysis. Complex **1** is formed by one octahedral titanium atom chelated by two benzamidinate ligands and connected to one Li(TMEDA) moiety via two chlorine bridges, forming an almost planar $TiCl_2Li$ core [Ti1–Cl1–Li1–Cl2 = 5.6(5)°] (Figure 1). The distorted coordination octahedron centered on titanium is defined by the four nitrogen atoms [N1–Ti1–N2 = 63.4(3)°; N5–Ti1–N6 = 62.8(3)°] of two benzamidinate ligands and the two bridging chlorine atoms [Cl1–Ti1–Cl2 = 85.1(1)°]. The two benzamidinate ligands form four-membered rings almost coplanar with the titanium atom [torsion angles Ti1–N2–C2–N1 = 7.9(9)°, Ti1–N5–C1–N6 = 6.7(9)°]. The Ti–Cl distances [Ti1–Cl1 = 2.495(4) Å, Ti1–Cl2 = 2.460(4) Å] are significantly elongated with respect to complex **3**[17] in contrast to the Ti–N distances [ranging from 2.128(7) to 2.163(7) Å], which are rather comparable. The considerable steric hindrance in the molecule might be responsible for preventing dimerization, otherwise commonly found in bis(cyclopentadienyl)titanium(III) halides,[18] and for the formation of the unusual MCl_2-Li core which, although very common in lanthanide chemistry,[19] is unprecedented in the chemistry of titanium(III).

The crystal structure of complex **2** was of sufficient quality to allow to locate all the hydrogen atoms although unfortunate high

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(16) (a) Melmed, K. M.; Coucouvanis, D.; Lippard, S. *Inorg. Chem.* **1973**, *12*, 232. (b) Semenenko, K. N.; Lobkovskii, E. B.; Shumakov, A. I. *J. Struct. Chem. USSR (Engl. Transl.)* **1976**, *17*, 912.

(17) Roesky, H. W.; Meller, B.; Noltemeyer, M.; Schmidt, H. G.; Scholz, U.; Sheldrick, G. M. *Chem. Ber.* **1988**, *121*, 1403.

(18) See, for example: Jungst, R.; Sekutowski, J. D.; Luly, M.; Stucky, G. *Inorg. Chem.* **1977**, *16*, 1645.

(19) See, for example: Lappert, M. F.; Singh, A.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1981**, 1191.

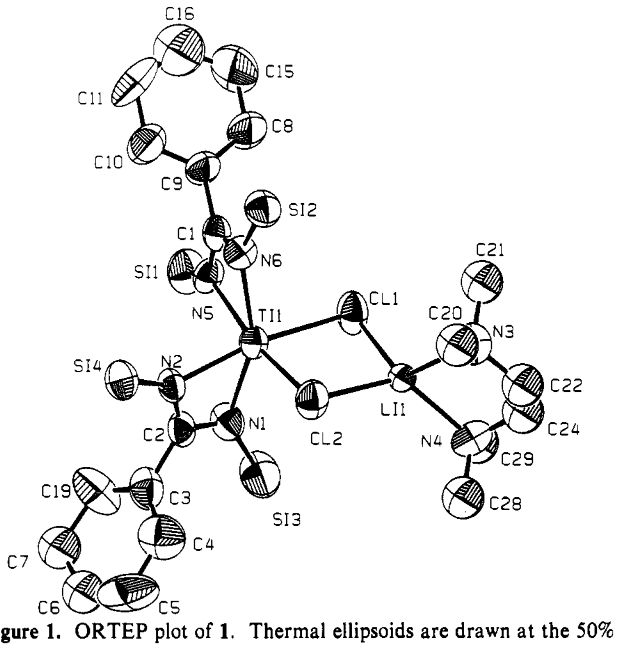

Figure 1. ORTEP plot of **1**. Thermal ellipsoids are drawn at the 50% probability level.

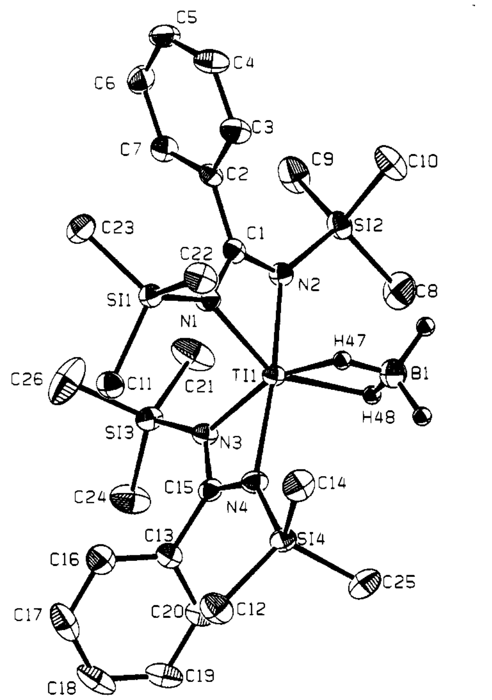

Figure 2. ORTEP plot of **2**. Thermal ellipsoids are drawn at the 50% probability level.

parameter-to-observation ratio allowed to refine only the hydrogen atom positions of the BH_4 group. In analogy with complex **1**, the titanium atom is placed in the center of a slightly distorted octahedron with the coordination polyhedron defined by four nitrogen atoms of two benzamidinate ligands [N1-Ti1-N2 = 65.42(9)°; N3-Ti1-N4 = 64.45(9)°] and two hydrogen atoms of one borohydride group [H47-Ti1-H48 = 56.0°] (Figure 2). The two benzamidinate ligands form planar four-membered rings with the titanium atom [torsion angles Ti1-N1-C1-N2 = 3.5(2)°; Ti1-N4-C15-N3 = 2.8(2)°]. The TiH_2B core is slightly folded [Ti1-H47-B1-H48 = 7.0°] with a relatively short Ti-B distance [Ti1-B1 = 2.421(4) Å]. The angles subtended by boron and titanium at the bridging hydrogen atoms [Ti1-H47-B1 = 102.0°; Ti1-H48-B1 = 101.0°] are rather narrow. The Ti-H distances [Ti1-H47 = 1.92 Å; Ti1-H48 = 1.92 Å] are normal and compare well with those of the other two titanium(III) borohydride complexes $(BH_4)_3Ti(CH_3OCH_2CH_2OCH_3)$[9c] and $(BH_4)_3Ti(PMe_3)_2$.[9d]

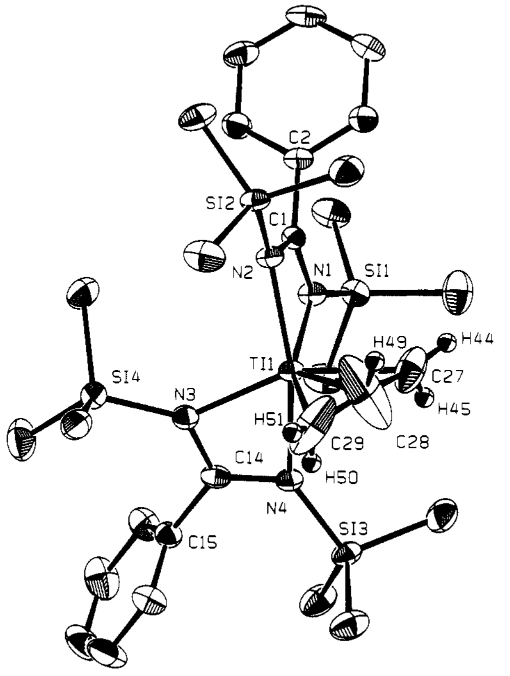

Figure 3. ORTEP plot of **4**. Thermal ellipsoids are drawn at the 50% probability level.

The structure of complex **4** (Figure 3) shows the same disposition of the two benzamidinate ligands rotated with respect to each other, already observed in complexes **1** and **2**, with comparable Ti-N distances [ranging from 2.111(2) to 2.198(2) Å] and N-Ti-N angles [N1-Ti1-N2 = 64.22(9)°]. Even in this case, the two benzamidinate ligands are coplanar with the titanium atom [torsion angles Ti1-N2-C1-N1 = 2.8(2)°; Ti1-N3-C14-N4 = 2.9(2)°]. The allyl fragment adopts a rather curious asymmetric conformation. The two C-C bond distances are significantly different [C27-C28 = 1.333(8) Å; C28-C29 = 1.160(7) Å], therefore suggesting different bond orders. This unusual structural feature, together with a rather wide angle subtended at the central carbon atom [C27-C28-C29 = 149.3(7)°], might be ascribed to the considerable steric hindrance provided by the two benzamidinate ligands. In spite of the marked difference between the two C-C distances, the Ti-C distances are comparable. The shortest Ti-C contact, which is formed with the central carbon atom [Ti1-C28 = 2.263(4) Å], is very similar to one of the two formed with the two terminal carbon atoms [Ti1-C27 = 2.297(4) Å]. The third Ti-C distance [Ti1-C29 = 2.368(5) Å] is slightly longer. Similar to the case of the $Cp_2Ti(\eta^3\text{-allyl})$ derivatives,[20] the plane defined by the three allylic carbon atoms is skewed with respect to the titanium-centroid axis.

In summary, these preliminary results indicate that the *N,N'*-bis(trimethylsilyl)benzamidinate ligand may function as a versatile tool in the preparation and stabilization of organometallic and inorganic complexes of trivalent titanium. A point of genuine interest lies in the ligand ability to stabilize the Ti-allyl function, otherwise unknown besides the cyclopentadienyl systems, which will be a key area of any future study.

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Supplementary Material Available: Tables listing atomic positional parameters, anisotropic thermal parameters, complete bond distances and angles, and least-squares planes for **1**, **2**, and **4** (81 pages). Ordering information is given on any current masthead page.

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