# Group 4 Half-Sandwich Tris(trimethylsilylmethyl) Complexes: Thermal Decomposition and Reactivity with *N,N*-Dimethylamine–Borane

Maider Greño, Estefanía del Horno, Miguel Mena, Adrián Pérez-Redondo, Víctor Varela-Izquierdo, and Carlos Yélamos*

Departamento de Química Orgánica y Química Inorgánica, Universidad de Alcalá, 28805 Alcalá de Henares-Madrid, Spain

S *Supporting Information*

ABSTRACT: The thermal decomposition of group 4 trimethylsilylmethyl derivatives $[M(\eta^5\text{-}C_5Me_5)(CH_2SiMe_3)_3]$ (M = Ti (**1**), Zr (**2**), Hf (**3**)) in solution and their reactivity with *N,N*-dimethylamine–borane were investigated. Heating of hydrocarbon solutions of compounds **2** and **3** at 130–200 °C results in the elimination of $SiMe_4$ and the clean formation of the singular alkylidene–alkylidyne zirconium and hafnium compounds $[\{M(\eta^5\text{-}C_5Me_5)\}_3\{(\mu\text{-}CH)_3SiMe\}(\mu_3\text{-}CSiMe_3)]$

(M = Zr (**4**), Hf (**5**)). The reaction of **2** and **3** with $NHMe_2BH_3$ (≥1 equiv) at room temperature affords the dialkyl(dimethylamidoborane) complexes $[M(\eta^5\text{-}C_5Me_5)(CH_2SiMe_3)_2(NMe_2BH_3)]$ (M = Zr (**6**), Hf (**7**)). Compounds **6** and **7** are unstable in solution and decompose with formation of the alkyl(dimethylamino)borane $[B(CH_2SiMe_3)H(NMe_2)]$ (**8**), $SiMe_4$, and other minor byproducts, including the tetranuclear zirconium(III) octahydride complex $[\{Zr(\eta^5\text{-}C_5Me_5)\}_4(\mu\text{-}H)_8]$ (**9**) in the decomposition of **6**. Addition of $NHMe_2BH_3$ to the titanium tris(trimethylsilylmethyl) derivative **1** gives the trinuclear mixed valence Ti(II)/Ti(III) tetrahydride complex $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}H)\}_3(\mu_3\text{-}H)(\mu_3\text{-}NMe_2BH_2)]$ (**10**) at 45–65 °C. While the complete conversion of **1** under argon atmosphere requires excess $NHMe_2BH_3$ (up to 15 equiv), complex **10** is readily prepared with 3 equiv of $NHMe_2BH_3$ under a hydrogen atmosphere indicating that the formation of **10** involves hydrogenolysis of **1** in the presence of $(NMe_2BH_2)_2$. In absence of amine–borane, the reaction of **1** with H_2 leads to the tetranuclear titanium(III) octahydride $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu\text{-}H)_8]$ (**11**), which upon addition of $NHMe_2BH_3$ and subsequent heating at 65 °C affords complex **10**. The X-ray crystal structures of **2**, **4**, **5**, **10**, and **11** were determined.
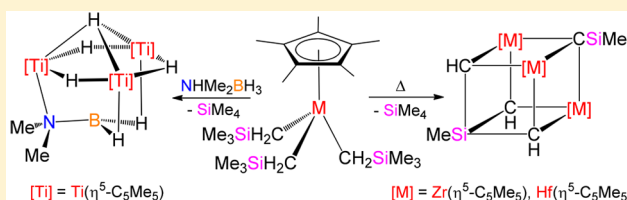
INTRODUCTION

The chemistry of amine–boranes and related base-stabilized borane adducts has seen a rapid resurgence over the past decade.[1−4] The major interest for this intense research arises from the potential application of these systems for chemical hydrogen storage and subsequent H_2 release in a controlled manner. A wide variety of metal complexes from across the whole periodic table has shown to catalyze amine–borane dehydrogenation, and nowadays it is recognized that those transformations are very complicated processes with variable mechanisms depending on the metal center and supporting ligands. In particular, group 4 derivatives have been intensively investigated as highly active homogeneous amine–borane dehydrogenation catalysts. Most of these studies have been performed with metallocene-type sandwich complexes $[M(\eta^5\text{-}C_5R_5)_2X_n]$ with the group 4 metal centers in the +2, +3, and +4 oxidation state,[5−14] but homoleptic amido compounds $[M(NMe_2)_4]$ (M = Ti, Zr)[14] and other zirconium nonmetallocene derivatives were also active toward secondary and primary amine–boranes.[15,16] To isolate key intermediates and to gain mechanistic insight into the catalytic dehydrogenation of amine–boranes several research groups have studied the stoichiometric version of these reactions. In s-block and early

transition-metal systems, the first stage of the reaction appears to involve the formation of amidoborane complexes via N–H bond activation.[1−4,11,15,17−20] The amidoborane NR_2BH_3 ligands bound to the metal centers exhibit M–N and M···H–B interactions, and subsequent hydride transfer from boron to the metal results in aminoboranes $(NR_2BH_2)_n$ and metal hydride species. Consequentially, a potential application of amine–boranes in coordination chemistry is the generation of reactive metal hydride complexes.

Transition-metal hydride compounds are receiving increasing attention in the context of the activation and functionalization of dinitrogen under mild conditions.[21−24] In particular, Hou and co-workers have reported fascinating examples of dinitrogen cleavage and partial hydrogenation by tri- and tetranuclear titanium polyhydride complexes generated by hydrogenolysis of half-sandwich trialkyl derivatives $[Ti(\eta^5\text{-}C_5Me_4SiMe_3)(CH_2SiMe_3)_3]$.[21,25,26] More recently, we have described the cleavage of dinitrogen under ambient conditions by simple exposure of $[Ti(\eta^5\text{-}C_5Me_5)Me_3]$ to commercially available and inexpensive forming gas (H_2/N_2 mixture, 13.5–

16.5% of H_2).[27] As part of a project devoted to the development of reactive group 4 hydride complexes, we became interested in the study of the reactivity of amine–borane adducts with half-sandwich derivatives $[M(\eta^5\text{-}C_5Me_5)\text{-}R_3]$. Thus, our group recently reported several mono-, di-, and trinuclear zirconium hydride species by treatment of amido complexes $[Zr(\eta^5\text{-}C_5Me_5)(NMe_2)_nCl_{3-n}]$ with NHR_2BH_3 (R_2 = Me_2, HtBu).[28] Herein we describe the results obtained in the reaction of tris(trimethylsilylmethyl) derivatives $[M(\eta^5\text{-}C_5Me_5)(CH_2SiMe_3)_3]$ with N,N-dimethylamine–borane. Previously, we decided to evaluate the thermal stability of the half-sandwich trialkyl complexes in solution as a preliminary step in the study of their reactivity.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under argon atmosphere using Schlenk line or glovebox techniques. Toluene, hexane, and pentane were distilled from Na/K alloy just before use. Fluorobenzene was distilled from calcium hydride just prior to use. NMR solvents were dried with Na/K alloy (C_6D_6) or calcium hydride (CDCl$_3$) and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. 1×10^{-3} torr) and subsequently filled with inert gas. Thermolyses in solution at high temperatures were performed by heating flame-sealed NMR or Carius tubes in a Roth autoclave model III. N,N-Dimethylamine–borane (NHMe$_2$BH$_3$) was purchased from Aldrich and used as received. Hydrogen ($\geq$99.9999%, H_2O < 0.5 ppm, O_2 < 0.1 ppm) was purchased from Air Liquide and used as received. $[M(\eta^5\text{-}C_5Me_5)Cl_3]$ (M = Zr, Hf),[29] $[Li(CH_2SiMe_3)]$,[30] and $[Ti(\eta^5\text{-}C_5Me_5)(CH_2SiMe_3)_3]$ (**1**)[31] were prepared according to published procedures.

Samples for infrared spectroscopy were prepared as KBr pellets, and the spectra were obtained using an FT-IR PerkinElmer SPECTRUM 2000 or FT-IR PerkinElmer FRONTIER spectrophotometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Mercury-300 or Unity-500 spectrometers. ^{11}B and ^{1}H–^{29}Si HMBC NMR spectra were obtained using a Bruker AV400 spectrometer. ^{1}H{^{11}B} NMR spectra were recorded on a Bruker AV300 Avance spectrometer. Chemical shifts (δ, ppm) in the ^{1}H and ^{13}C{^{1}H} NMR spectra are given relative to residual protons or to carbon of the solvent. Chemical shifts (δ, ppm) in the ^{29}Si and ^{11}B NMR spectra are given relative to SiMe$_4$ and BF$_3$·OEt$_2$ as external references. Gas chromatography–mass spectrometry (GC-MS) data were obtained on an Agilent GC-MS turbo system (model 5975–7820A) equipped with an HP–5MS capillary column (30 m × 0.25 mm × 0.25 μm) under the following conditions: injector temperature 230 °C, detector temperature 250 °C, 50 °C ramp at 2.5 °C min^{-1} until 75 °C. The effective magnetic moments were determined by the Evans NMR method at 293 K (using a 300 MHz instrument with a field strength of 7.05 T).[32−34] Microanalyses (C, H, N) were performed in a PerkinElmer CHNS/O 2400 or Leco CHNS-932 microanalyzers.

Synthesis of [Zr(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_3$] (2). A 100 mL Schlenk tube was charged with $[Zr(\eta^5\text{-}C_5Me_5)Cl_3]$ (1.00 g, 3.00 mmol), $[Li(CH_2SiMe_3)]$ (0.86 g, 9.13 mmol), and hexane (40 mL). The reaction mixture was stirred at room temperature for 20 h to give a gray solid and a colorless solution. After filtration, the volatile components of the solution were removed under reduced pressure to afford **2** as a white solid (1.21 g, 83%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2951 (vs), 2912 (s), 2893 (s), 2802 (w), 2744 (w), 1496 (w), 1433 (m), 1379 (m), 1292 (w), 1253 (s), 1242 (vs), 1099 (w), 1025 (w), 892 (vs), 847 (vs), 821 (vs), 745 (vs), 724 (s), 706 (vs), 677 (s), 609 (w), 473 (m). ^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ 1.84 (s, 15H; C_5Me_5), 0.34 (s, 6H; CH_2SiMe$_3$), 0.25 (s, 27H; CH_2SiMe$_3$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 20 °C): δ 119.4 (C_5Me_5), 63.8 (CH_2SiMe$_3$), 12.0 (C_5Me_5), 3.2 (CH_2SiMe_3). Anal. Calcd (%) for $C_{22}H_{48}Si_3Zr$ (M_w = 488.10): C 54.14, H 9.91. Found: C 54.12, H 9.60.

Synthesis of [Hf(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_3$] (3). In a fashion similar to the preparation of **2**, the treatment of $[Hf(\eta^5\text{-}C_5Me_5)Cl_3]$ (1.00 g, 2.38 mmol) with $[Li(CH_2SiMe_3)]$ (0.68 g, 7.22 mmol) in hexane (40

mL) gave **3** as a white solid (1.09 g, 80%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2950 (vs), 2913 (vs), 2865 (s), 2811 (w), 2731 (w), 1496 (w), 1437 (m), 1379 (m), 1291 (w), 1256 (s), 1244 (vs), 1100 (w), 1026 (w), 905 (vs), 850 (vs), 823 (vs), 781 (vs), 744 (s), 710 (s), 681 (s), 475 (m). ^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ 1.87 (s, 15H; C_5Me_5), 0.24 (s, 27H; CH_2SiMe$_3$), −0.12 (s, 6H; CH_2SiMe$_3$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 20 °C): δ 118.8 (C_5Me_5), 70.4 (CH_2SiMe$_3$), 11.7 (C_5Me_5), 3.5 (CH_2SiMe$_3$). Anal. Calcd (%) for $C_{22}H_{48}HfSi_3$ (M_w = 575.37): C 45.93, H 8.41. Found: C 45.99, H 8.09.

Synthesis of [{Zr(η^5-C$_5$Me$_5$)}$_3${(μ-CH)$_3$SiMe}(μ_3-CSiMe$_3$)] (4). A 100 mL Carius tube was charged with **2** (0.60 g, 1.23 mmol) and hexane (3 mL). The tube was flame-sealed, and the resultant colorless solution was heated at 140 °C for 5 d. After it cooled at room temperature a brown crystalline solid and a light brown solution were obtained. The tube was opened in the glovebox, and the solid was isolated by filtration onto a glass frit and vacuum-dried to afford **4** as light brown crystals (0.20 g, 57%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2942 (vs), 2908 (vs), 2860 (vs), 2723 (w), 1497 (w), 1440 (s), 1376 (s), 1247 (m), 1229 (m), 1022 (m), 875 (s), 864 (s), 817 (s), 766 (m), 742 (m), 639 (s), 626 (s), 588 (m), 521 (m), 507 (s). ^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ 6.42 (s, 3H; (μ-CH)$_3$SiMe), 2.12 (s, 45H; C_5Me_5), 0.03 (s, 3H; (μ-CH)$_3$SiMe), −0.23 (s, 9H; μ_3-CSiMe_3). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 20 °C): δ 384.2 (μ_3-CSiMe$_3$), 203.4 ((μ-CH)$_3$SiMe), 115.6 (C_5Me$_5$), 11.6 (C_5Me_5), 9.2 (μ_3-CSiMe_3), −16.1 ((μ-CH)$_3$SiMe). ^{29}Si (^{1}H–^{29}Si HMBC) NMR (79.5 MHz, C_6D_6, 20 °C): δ −50.2 (μ_3-CSiMe$_3$), −110.7 ((μ-CH)$_3$$Si$Me). Anal. Calcd (%) for $C_{38}H_{60}Si_2Zr_3$ (M_w = 846.74): C 53.90, H 7.14. Found: C 53.85, H 6.91.

Synthesis of [{Hf(η^5-C$_5$Me$_5$)}$_3${(μ-CH)$_3$SiMe}(μ_3-CSiMe$_3$)] (5). In a fashion similar to the preparation of **4**, a Carius tube with a solution of **3** (0.60 g, 1.04 mmol) in hexane (4 mL) was heated at 180 °C for 7 d to give a light brown solution. The tube was cooled to −30 °C for 3 d to give brown crystals of **5** (0.085 g, 22%), which were isolated by filtration in the glovebox. IR (KBr, cm^{-1}): $\tilde{\nu}$ 2942 (vs), 2906 (vs), 2858 (vs), 2724 (w), 1485 (w), 1435 (m), 1376 (s), 1244 (m), 1229 (s), 1025 (m), 881 (s), 855 (s), 826 (vs), 816 (vs), 792 (s), 742 (s), 648 (vs), 636 (s), 616 (s), 591 (m), 526 (m). ^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ 5.34 (s, 3H; (μ-CH)$_3$SiMe), 2.14 (s, 45H; C_5Me_5), 0.18 (s, 3H; (μ-CH)$_3$SiMe), −0.20 (s, 9H; μ_3-CSiMe_3). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 20 °C): δ 379.4 (μ_3-CSiMe$_3$), 196.4 ((μ-CH)$_3$SiMe), 115.8 (C_5Me$_5$), 11.6 (C_5Me_5), 10.2 (μ_3-CSiMe_3), −18.9 ((μ-CH)$_3$SiMe). ^{29}Si (^{1}H–^{29}Si HMBC) NMR (79.5 MHz, C_6D_6, 20 °C): δ −58.4 (μ_3-CSiMe$_3$), −110.9 ((μ-CH)$_3$$Si$Me). Anal. Calcd (%) for $C_{38}H_{60}Hf_3Si_2$ (M_w = 1108.54): C 41.17, H 5.46. Found: C 41.24, H 4.82.

Synthesis of [Zr(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_2$(NMe$_2$BH$_3$)] (6). *Method A:* A 100 mL Schlenk tube was charged with **2** (0.40 g, 0.82 mmol), NHMe$_2$BH$_3$ (0.14 g, 2.38 mmol), and toluene (30 mL). The reaction mixture was stirred at room temperature for 2 h to give a colorless solution. After filtration, the volatile components of the solution were removed under reduced pressure to afford **6** as a thick colorless oil (0.26 g, 68%). *Method B:* In a mortar, **2** (0.40 g, 0.82 mmol) and NHMe$_2$BH$_3$ (0.057 g, 0.97 mmol) were ground with a pestle for 15 min. The resultant colorless oil was dissolved in pentane (5 mL), and the solution was filtered to a Schlenk tube. The volatile components of the solution were removed under reduced pressure to afford **6** as a thick colorless oil (0.31 g, 82%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2912 (s), 2839 (m), 2791 (w), 2442 (m) (BH$_{term}$), 2100 (m) (BH$_{bridging}$), 1462 (m), 1380 (m), 1243 (vs), 1171 (m), 1045 (w), 1026 (w), 993 (s), 930 (m), 895 (s), 848 (vs), 824 (s), 734 (s), 709 (s), 678 (m), 513 (w), 440 (w), 416 (w). ^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ 2.31 (s, 6H; NMe_2BH$_3$), 1.83 (s, 15H; C_5Me_5), 0.32 (AX system, ^2J(H,H) = 11.0 Hz, 2H; CHHSiMe$_3$), 0.25 (s, 18H; CHHSiMe_3), −0.01 (AX system, ^2J(H,H) = 11.0 Hz, 2H; CHHSiMe$_3$), the NMe$_2$BH_3 resonance signal was not observed. ^{1}H NMR (300 MHz, C_6D_6, 24 °C): δ 2.32 (s, 6H; NMe_2BH$_3$), 1.84 (s, 15H; C_5Me_5), 1.42 (q br, ^1J(H,B) = 91.5 Hz, 3H; NMe$_2$BH_3), 0.33 (AX system, ^2J(H,H) = 11.1 Hz, 2H; CHHSiMe$_3$), 0.25 (s, 18H; CHHSiMe_3), 0.00 (AX system, ^2J(H,H) = 11.1 Hz, 2H; CHHSiMe$_3$). ^{1}H{^{11}B} NMR (300 MHz, C_6D_6, 24 °C): δ 2.34 (s, 6H; NMe_2BH$_3$), 1.86 (s, 15H; C_5Me_5), 1.41 (s, 3H; NMe$_2$BH_3), 0.31 (AX

system, ^2J(H,H) = 11.4 Hz, 2H; C*H*HSiMe$_3$), 0.22 (s, 18H; CHH*SiMe$_3$*), −0.01 (AX system, ^2J(H,H) = 11.4 Hz, 2H; CH*H*SiMe$_3$). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 20 °C): δ 120.2 (*C*$_5$Me$_5$), 54.7 (*C*H$_2$SiMe$_3$), 48.6 (N*Me$_2$*BH$_3$), 12.2 (C$_5$*Me$_5$*), 3.5 (CH$_2$Si*Me$_3$*). ^{11}B NMR (128 MHz, C$_6$D$_6$, 20 °C): δ −3.6 (q, ^1J(B,H) = 90.8 Hz; *B*H$_3$). Anal. Calcd (%) for C$_{20}$H$_{46}$BNSi$_2$Zr (M_w = 458.80): C 52.36, H 10.11, N 3.05. Found: C 51.56, H 9.68, N 4.64. Satisfactory elemental analysis could not be obtained for this oily and unstable compound.

Synthesis of [Hf(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_2$(NMe$_2$BH$_3$)] (7). In a fashion similar to the preparation of **6** (*Method A*), the treatment of **3** (0.40 g, 0.70 mmol) with NHMe$_2$BH$_3$ (0.13 g, 2.21 mmol) in toluene (30 mL) for 24 h afforded **7** as a thick colorless oil (0.29 g, 76%). IR (KBr, cm^{-1}): $\tilde{v}$ 2947 (vs), 2914 (vs), 2880 (s), 2840 (m), 2791 (w), 2450 (m) (BH$_{term}$), 2104 (m) (BH$_{bridging}$), 1463 (m), 1380 (m), 1243 (vs), 1172 (m), 1025 (w), 994 (s), 907 (s), 848 (vs), 820 (s), 781 (m), 735 (s), 711 (m), 678 (m), 518 (w), 441 (w), 415 (w). ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C): δ 2.35 (s, 6H; N*Me$_2$*BH$_3$), 1.89 (s, 15H; C$_5$*Me$_5$*), 0.24 (s, 18H; C*H*HSiMe$_3$), −0.14 (AX system, ^2J(H,H) = 11.4 Hz, 2H; C*H*HSiMe$_3$), −0.40 (AX system, ^2J(H,H) = 11.4 Hz, 2H; CH*H*SiMe$_3$), the NMe$_2$B*H$_3$* resonance signal was not observed. The ^{1}H{^{11}B} NMR (300 MHz, C$_6$D$_6$, 24 °C) spectrum did not allow the assignment of the BH$_3$ resonance signal. ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 20 °C): δ 119.1 (*C*$_5$Me$_5$), 56.4 (*C*H$_2$SiMe$_3$), 48.4 (N*Me$_2$*BH$_3$), 12.1 (C$_5$*Me$_5$*), 3.8 (CH$_2$Si*Me$_3$*). ^{11}B NMR (128 MHz, C$_6$D$_6$, 20 °C): δ −3.9 (q, ^1J(B,H) = 91.3 Hz; *B*H$_3$). Anal. Calcd (%) for C$_{20}$H$_{46}$BHfNSi$_2$ (M_w = 546.06): C 43.99, H 8.49, N 2.57. Found: C 43.54, H 7.80, N 2.70. Satisfactory elemental analysis could not be obtained for this oily and unstable compound.

Thermal Decomposition of [Zr(η^5-C$_5$Me$_5$)-(CH$_2$SiMe$_3$)$_2$(NMe$_2$BH$_3$)] (6) in an NMR Tube-Scale Experiment. A 5 mm valved NMR tube was charged with **6** (0.050 g, 0.11 mmol) and benzene-d_6 (0.60 mL). The resultant colorless solution was heated at 75 °C using a thermostat-controlled oil bath, and the composition of the solution was monitored by ^{1}H NMR spectroscopy. After 4 d, ^{1}H and ^{13}C{^{1}H} NMR spectra showed complete consumption of **6** and revealed new resonances assigned to [B(CH$_2$SiMe$_3$)H(NMe$_2$)] (**8**), SiMe$_4$, and [{Zr(η^5-C$_5$Me$_5$)}$_4$(μ-H)$_8$] (**9**). When it stood at room temperature for 24 h, dark green crystals of **9** were grown at the bottom of the NMR tube. The supernatant solution was decanted and, after dilution with an additional 1.40 mL of benzene-d_6, analyzed by GC-MS to identify the molecular ion M$^+$ for **8** with m/z of 143.1, whereas the base peak of the spectra corresponds to the [{M-Me}]$^+$ ion.

NMR and GC-MS Data for [B(CH$_2$SiMe$_3$)H(NMe$_2$)] (8). ^{1}H NMR (500 MHz, C$_6$D$_6$, 20 °C): δ 2.70 (s, 3H; N*Me*Me), 2.43 (s, 3H; NMe*Me*), 0.37 (d br., ^3J(H,H) = 4.4 Hz, 2H; C*H$_2$*SiMe$_3$), 0.11 (s, 9H; CH$_2$Si*Me$_3$*), the BH resonance signal was not observed. ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 20 °C): δ 45.3 (N*Me*Me), 37.5 (NMe*Me*), 0.8 (CH$_2$Si*Me$_3$*), the B*C*H$_2$SiMe$_3$ resonance signal was not observed. ^{11}B NMR (128 MHz, C$_6$D$_6$, 20 °C): δ 42.1 (d, ^1J(B,H) = 118.6 Hz; BH). GC-MS (retention time of 4.489 min): m/z 143.1 [M$^+$], 128.0 [{M-Me}$^+$].

NMR Data for [{Zr(η^5-C$_5$Me$_5$)}$_4$(μ-H)$_8$][35] (9). ^{1}H NMR (500 MHz, C$_6$D$_6$, 20 °C): δ 2.31 (s, 60H; C$_5$*Me$_5$*), 0.77 (s, 8H; μ-H). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 20 °C): δ 117.4 (*C*$_5$Me$_5$), 12.7 (C$_5$*Me$_5$*).

Synthesis of [{Ti(η^5-C$_5$Me$_5$)(μ-H)}$_3$(μ_3-H)(μ_3-NMe$_2$BH$_2$)] (10). *Method A:* A 100 mL ampule (Teflon stopcock) was charged with [Ti(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_3$] (**1**) (0.30 g, 0.67 mmol), NHMe$_2$BH$_3$ (0.25 g, 4.24 mmol), and toluene (25 mL). The reaction mixture was stirred at 45 °C for 24 h to give a brown solution. After addition of more NHMe$_2$BH$_3$ (0.33 g, 5.60 mmol) to this solution, the mixture was heated at 45 °C for 2 d. The volume of the resultant brown solution was reduced until ca. 4 mL under vacuum. After filtration, the solution was cooled to −35 °C for 7 d to give dark brown crystals of **10** (0.042 g, 32%). *Method B:* A 100 mL ampule (Teflon stopcock) was charged with **1** (0.30 g, 0.67 mmol), NHMe$_2$BH$_3$ (0.12 g, 2.04 mmol), and toluene (25 mL). After it cooled at −78 °C, the argon atmosphere was changed by dihydrogen, and the reaction mixture was stirred at 65 °C for 16 h. The volume of the resultant brown solution

was reduced until ca. 4 mL under vacuum. After filtration, the solution was cooled to −35 °C for 5 d to give dark brown crystals of **10** (0.051 g, 39%). IR (KBr, cm^{-1}): $\tilde{v}$ 2969 (m), 2940 (m), 2901 (vs), 2857 (s), 2819 (m), 2773 (w), 2717 (w), 2037 (m) (BH$_{bridging}$), 1969 (w) (BH$_{bridging}$), 1486 (w), 1439 (m), 1373 (s), 1259 (w), 1197 (m), 1154 (m), 1101 (w), 1065 (w), 1021 (s), 970 (m), 793 (m), 582 (w), 546 (m), 420 (m). ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C): δ 30.38 (s br., $\Delta\nu_{1/2}$ = 415 Hz, 15H; C$_5$*Me$_5$*), 6.32 (s br., $\Delta\nu_{1/2}$ = 25 Hz, 30H; C$_5$*Me$_5$*), the resonance signals for μ_n-H and μ_3-NMe$_2$BH$_2$ ligands were not observed. Anal. Calcd (%) for C$_{32}$H$_{57}$BNTi$_3$ (M_w = 610.23): C 62.98, H 9.42, N 2.30. Found: C 62.65, H 8.94, N 2.39. The effective magnetic moment of **10** was determined to be 1.87 μ_B (based on a unit formula of C$_{32}$H$_{57}$BNTi$_3$) on a C$_6$D$_6$ solution.

Synthesis of [{Ti(η^5-C$_5$Me$_5$)}$_4$(μ-H)$_8$] (11). A 150 mL ampule (Teflon stopcock) was charged with [Ti(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_3$] (**1**) (1.00 g, 2.25 mmol) and hexane (20 mL). After it was cooled at −78 °C, the argon atmosphere was changed by hydrogen. The reaction mixture was allowed to warm to room temperature and was heated at 65 °C for 2 d to give a dark red solution and dark red crystals. The crystals were isolated by filtration onto a glass frit, washed with hexane (3 × 5 mL), and vacuum-dried to afford **11** (0.18 g, 44%). IR (KBr, cm^{-1}): $\tilde{v}$ 2903 (vs), 2855 (s), 2718 (w), 1584 (m), 1491 (w), 1451 (m), 1432 (m), 1372 (s), 1340 (m), 1182 (w), 1123 (w), 1066 (w), 1024 (m), 940 (w), 798 (m), 699 (w), 528 (w), 418 (w). ^{1}H NMR (500 MHz, C$_6$D$_6$, 20 °C): δ 2.24 (s, 60H; C$_5$*Me$_5$*), −1.18 (s, 8H; μ-H). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 20 °C): δ 117.8 (*C*$_5$Me$_5$), 13.6 (C$_5$*Me$_5$*). Anal. Calcd (%) for C$_{40}$H$_{68}$Ti$_4$ (M_w = 740.45): C 64.88, H 9.26. Found: C 64.41, H 9.29.

X-ray Structure Determination of 2, 4, 5, 10, and 11. Colorless crystals of **2** were grown from a hexane solution at −35 °C. Brown crystals of **4** were grown by cooling a fluorobenzene solution at −30 °C. Brown crystals of **5** were obtained by cooling to −30 °C a hexane solution as described above. Dark brown crystals of **10** were grown from a toluene solution at −35 °C. Dark red crystals of **11** were obtained by slow cooling at room temperature of a benzene-d_6 solution of the compound heated at 80 °C in a NMR tube. The crystals were removed from the Schlenks or NMR tube and covered with a layer of a viscous perfluoropolyether (FomblinY). A suitable crystal was selected with the aid of a microscope, mounted on a cryoloop, and immediately placed in the low-temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 150 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit.

Crystallographic data for complexes are presented in Table S1 of the Supporting Information. The structures were solved, using the WINGX package,[36] by direct methods (**2**, **4**, and **5**), Patterson (**10**) (SHELXS-2013),[37] or intrinsic phasing methods (**11**) (SHELXT),[38] and refined by least-squares against F^2 (SHELXL-2014/7).[37] In the crystallographic study of **2**, **4**, and **5**, all non-hydrogen atoms were anisotropically refined, whereas the hydrogen atoms were positioned geometrically and refined by using a riding model.

Crystals of **10** showed disorder for the carbon atoms C(11)−C(20) of the pentamethylcyclopentadienyl group linked to Ti(1). This disorder was treated conventionally by using the PART tool of the SHELXL program and allowing free refinement of the occupancy factor with the FVAR command. The final values of occupancy were 52.9 and 47.1%. All non-hydrogen atoms were anisotropically refined. The hydrogen atoms of the methyl groups were placed geometrically and refined by using a riding model. The rest of the hydrogen atoms (H(1), H(11), H(12), and H(112)) were located in the difference Fourier map and refined isotropically. Moreover the carbon atoms of the disordered pentamethylcyclopentadienyl ligand were restrained with DELU and SIMU instructions.

Finally, all the non-hydrogen atoms were anisotropically refined in the structure determination for complex **11**. The hydrogen atoms of the methyl groups were positioned geometrically and refined by using a riding model. Additionally, XHYDEX tool was employed to locate hydride groups bound to the titanium atoms. Thus, the hydrogen atoms H(12), H(13), H(14), H(23), H(24), H(34), and H(123) were found in the difference Fourier map and refined isotropically. H(124)

was also found in the difference Fourier map with the aid of XHYDEX, but unfortunately the coordinates and the isotropic displacement parameter for this hydrogen atom after the last refinement cycles were not appropriate. Therefore, the coordinates of H(124) were forced to be those found by XHYDEX tool, and refined isotropically. The highest peak found in the Fourier map of 1.82 e Å^{-3} is located close to H(34) (1.93 Å).

■ RESULTS AND DISCUSSION

Synthesis and Thermal Decomposition of [M(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_3$] Complexes. Treatment of the group 4 trichloride complexes [M(η^5-C$_5$Me$_5$)Cl$_3$] with 3 equiv of trimethylsilylmethyllithium [Li(CH$_2$SiMe$_3$)] in hexane at room temperature afforded the trialkyl derivatives [M(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_3$] (M = Ti (**1**), Zr (**2**), Hf (**3**)) in 80−85% yields (Scheme 1). While the synthesis and appropriated

Scheme 1. Synthesis and Thermal Decomposition of 2 and 3
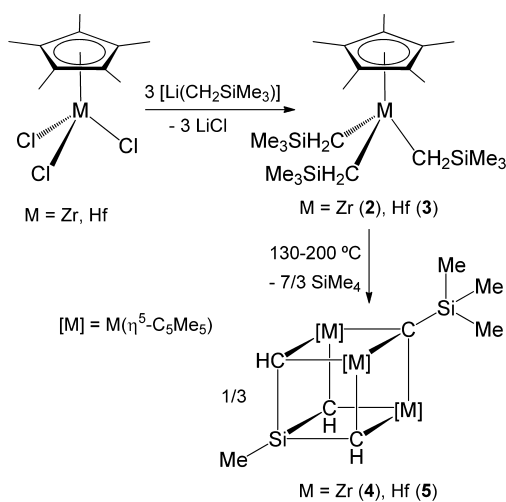

characterization of the titanium complex **1** have been previously reported,[31] the zirconium and hafnium analogues **2** and **3** are poorly described in the literature.[35,39] Trimethylsilylmethyl derivatives **2** and **3** were isolated from the crude reactions as white solids in a pure form according to analytical and spectroscopic techniques. The high solubility of complexes **1**−**3** in hexane leads to lower yields of crystallized samples of the compounds. The X-ray crystal structure of the zirconium derivative **2** reveals the classical three-legged piano-stool geometry for group 4 half-sandwich complexes (Figure S1 in the Supporting Information).

The thermal stability of the trialkyl group 4 derivatives [M(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_3$] in benzene-d_6 solutions was monitored by ^{1}H NMR spectroscopy. The spectra revealed that the titanium complex **1** decomposed slowly at temperatures higher than 45 °C to give SiMe$_4$ and some unidentified species in solution. In contrast, the zirconium analogue **2** is stable up to 110 °C, and at higher temperatures the spectra showed the clean formation of SiMe$_4$ and the alkylidene-alkylidyne complex [{Zr(η^5-C$_5$Me$_5$)}$_3${(μ-CH)$_3$SiMe}(μ_3-CSiMe$_3$)] (**4**) (Scheme 1). Likewise, the hafnium compound **3** decomposed in solution at temperatures higher than 130 °C to give SiMe$_4$ and complex [{Hf(η^5-C$_5$Me$_5$)}$_3${(μ-CH)$_3$SiMe}-(μ_3-CSiMe$_3$)] (**5**). No intermediates or secondary products were detected by NMR spectroscopy in the formation of complexes **4** and **5** at temperatures between 130 and 200 °C.

Despite several attempts, we were not able to isolate any pure compound in the thermal decomposition of the titanium derivative [Ti(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_3$] in hydrocarbon solvents. However, complexes **4** and **5** are readily obtained by thermal treatment of toluene or hexane solutions of the trialkyl precursors **2** and **3** at 130−200 °C. While the compounds can be isolated in good yields as brown solids by simple removing of the volatile components of the reaction mixtures, crystalline samples of complexes **4** and **5** for analytical and spectroscopic techniques were obtained from cooled hexane solutions in 57 and 22% yields, respectively.

Complexes **4** and **5** exhibit a high solubility in hydrocarbon solvents and are extremely air-sensitive both in the solid state and in solution. The ^{1}H and ^{13}C{^{1}H} NMR spectra in benzene-d_6 show resonance signals for three equivalent η^5-C$_5$Me$_5$ ligands and are consistent with C_{3v} symmetry in solution. In addition, the spectra reveal resonances for one (μ-CH)$_3$SiMe ligand per trinuclear unit. The μ-CH alkylidene groups of these ligands appear as singlets at δ = 6.42 and 5.34 in the ^{1}H NMR spectra of **4** and **5**, and the ^{13}C{^{1}H} NMR signals of these moieties occurs at δ = 203.4 and 196.4, respectively. Similar downfield resonances have been reported for other zirconium and hafnium complexes with μ-CHR alkylidene ligands.[40,41] The alkylidyne carbon resonances of the μ_3-CSiMe$_3$ ligands appear at δ = 384.2 and 379.4 in the ^{13}C{^{1}H} NMR spectra of compounds **4** and **5**, respectively. Zirconium and hafnium complexes with μ_3-alkylidyne ligands remain rare in the literature, and the reported examples have been obtained by fortuitous syntheses.[42,43] Nevertheless, our group has reported a number of titanium derivatives with μ_3-alkylidyne groups that show analogous downfield resonance signals such as [{Ti(η^5-C$_5$Me$_5$)}$_4$(μ_3-CH)$_4$] (δ_C = 490.8),[44] [{Ti(η^5-C$_5$Me$_5$)(μ-O)}$_3$(μ_3-CR)] (R = H,[45] Me[46]) (δ_C = 383.8 and 401.7, respectively), and [{Ti(η^5-C$_5$Me$_5$)}$_4$(μ_3-CH)$_2$(μ_3-N)$_2$] (δ_C = 393.7).[27] Finally, the ^{29}Si NMR spectra of compounds **4** and **5** reveal two resonance signals, which can be assigned by HMBC ^{1}H−^{29}Si NMR experiments. Thus, the upfield signals at δ = −110.7 and −110.9 correspond to the (μ-CH)$_3$SiMe ligands, whereas those at δ = −50.2 and −58.4 are due to the μ_3-CSiMe$_3$ moieties.

Single crystals of complexes **4** and **5** for X-ray diffraction studies were obtained from fluorobenzene or hexane solutions, respectively. The molecular structure of the zirconium complex **4** is presented in Figure 1, while selected lengths and angles for both compounds are given in Table 1. The crystal structures show a C_3 axis that crosses the C(4), Si(1), C(2), and Si(2) atoms. The complexes contain distorted [C$_4$M$_3$Si] (M = Zr, Hf) cube-type cores with angles within the cube in the range of 84.5(2)−102.9(2)°. The group 4 atoms form equilateral triangles with Zr···Zr and Hf···Hf separations of 3.251(1) and 3.207(1) Å, respectively. One face of the triangle is capped by a μ_3-CSiMe$_3$ alkylidyne group, while the other face contains a (μ-CH)$_3$SiMe tridentate ligand. Thus, the zirconium and hafnium atoms exhibit three-legged piano-stool arrangements, where two legs are carbon atoms of the μ-alkylidene ligand, and the third is the carbon atom C(2) of the μ_3-CSiMe$_3$ alkylidyne group. The M(1)−C(1) (2.181(5) Å for **4** and 2.166(7) Å for **5**) and M(1)−C(2) (2.212(4) Å for **4** and 2.202(6) Å for **5**) bond lengths are similar to the metal−carbon distances found in related complexes with μ-CHR ligands.[40,41,47−49] The Si(1)−C(1) bond lengths of 1.935(5) and 1.916(7) Å in complexes **4** and **5** are longer than the remaining silicon−carbon distances of the molecules, which are in the range of 1.822(11)−1.878(9) Å.
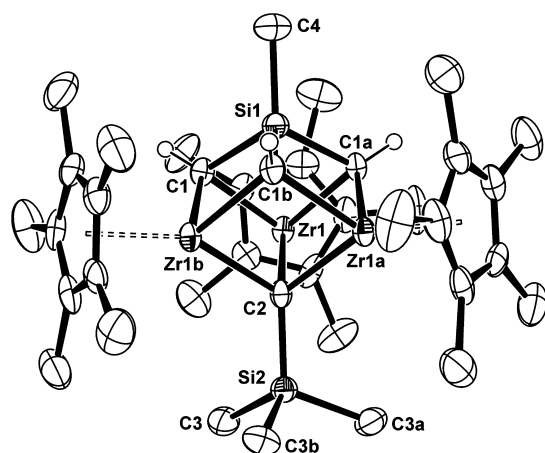
Figure 1. Perspective view of **4** with thermal ellipsoids at the 50% probability level. Hydrogen atoms of the methyl groups are omitted for clarity. Symmetry code: (a) $1 - y, x - y, z$; (b) $1 - x + y, 1 - x, z$.

Table 1. Selected Lengths (Å) and Angles (deg) for 4 and 5

|	M = Zr (4)	M = Hf (5)
M(1)−C(1)	2.181(5)	2.166(7)
M(1)−C(2)	2.212(4)	2.202(6)
C(1)−Si(1)	1.935(5)	1.916(7)
C(2)−Si(2)	1.836(9)	1.822(11)
C(3)−Si(2)	1.877(6)	1.873(7)
C(4)−Si(1)	1.878(9)	1.852(12)
M(1)···M(1)a*	3.251(1)	3.207(1)
M(1)···Si(1)	2.774(2)	2.761(2)
C(1)−M(1)−C(2)	84.5(2)	85.3(2)
C(1)−M(1)−C(1)a*	87.8(3)	87.3(3)
C(1)−Si(1)−C(1)a*	102.9(2)	102.4(3)
M(1)−C(1)−Si(1)	84.5(2)	84.9(3)
M(1)−C(1)−M(1)a*	96.3(2)	95.7(3)
M(1)−C(2)−M(1)a*	94.6(2)	93.4(3)
C(1)−Si(1)−C(4)	115.4(2)	115.8(2)
M(1)−C(2)−Si(2)	121.9(2)	122.8(2)

*Symmetry code: (a) $1 - y, x - y, z$; (b) $1 - x + y, 1 - x, z$.

This lengthening is most likely due to the structural rigidity associated with the coordination of the $(\mu\text{-CH})_3\text{SiMe}$ ligand to the three metal atoms in each molecule.

Reactivity of $[M(\eta^5\text{-}C_5Me_5)(CH_2SiMe_3)_3]$ Complexes with $NHMe_2BH_3$. Treatment of zirconium **2** and hafnium **3** complexes with $NHMe_2BH_3$ (≥1 equiv) in toluene at room temperature resulted in the elimination of 1 equiv of $SiMe_4$ and the formation of the dialkyl(dimethylamidoborane) derivatives $[M(\eta^5\text{-}C_5Me_5)(CH_2SiMe_3)_2(NMe_2BH_3)]$ (M = Zr (**6**), Hf (**7**)) (Scheme 2). These compounds were isolated in 68−76% yields as thick colorless oils that slowly decompose in hydrocarbon solutions at room temperature (vide infra). Despite many attempts, no further substitution of trimethylsilylmethyl ligands in complexes **6** and **7** by dimethylamidoborane groups could be achieved, and the additional $NHMe_2BH_3$ in the reaction mixtures undergoes dehydrogenation to give $(NMe_2BH_2)_2$ and H_2. Noteworthy, the zirconium complex **6** was isolated in 82% yield by grinding in a mortar a solid mixture of **2** and $NHMe_2BH_3$ (1 equiv) with a pestle for 15 min. In contrast, the analogous mechanochemical treatment of the hafnium trialkyl complex **3** and N,N-dimethylamine−borane gave the initial reagents unaltered.

Scheme 2. Reactions of 2 and 3 with NHMe₂BH₃
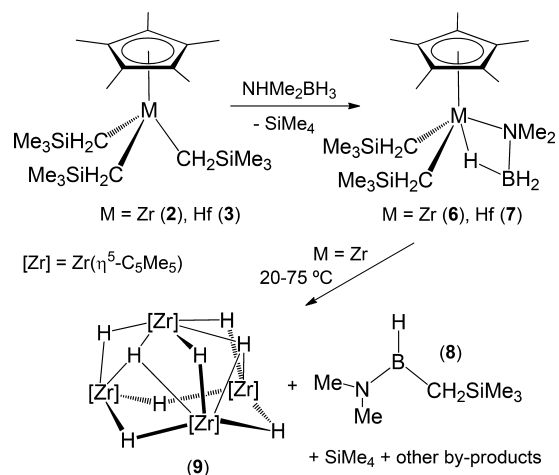
The IR (KBr) spectra of complexes **6** and **7** show one characteristic band at ∼2445 cm⁻¹ for the terminal B−H bonds and one absorption at ∼2100 cm⁻¹ for ν_{BH} vibrations of bridging B−H bonds. These data suggest the existence of M···H−B interactions in the structure of these compounds as those found in other group 4 amidoborane complexes.[11,17−19] However, well-defined quartet resonances (**6**, δ = −3.6, $^1J(B,H)$ = 90.8 Hz; **7**, δ = −3.9, $^1J(B,H)$ = 91.3 Hz) observed in the ^{11}B NMR spectra at room temperature of the complexes in benzene-d_6 could be indicative of monodentate NMe_2BH_3 ligands or a rapid interchange of bridging and terminal B−H bonds in solution. Indeed, ^1H and $^{13}C\{^1H\}$ NMR spectra are consistent with C_s symmetry in the structure of complexes **6** and **7** in benzene-d_6 solution. Thus, the trimethylsilylmethyl ligands are equivalent with the CH_2 moieties giving rise to AX spin systems ($^2J(H,H)$ ≈ 11 Hz) in the ^1H NMR spectra. The methyl groups of the NMe_2BH_3 ligand are also magnetically equivalent in the ^1H NMR spectra and appear as one sharp singlet at room temperature or at low temperatures according to the spectrum taken at −55 °C on a toluene-d_8 solution of complex **7** in a 400 MHz spectrometer. Resonance signals for the BH_3 groups of the NMe_2BH_3 ligands were difficult to locate in the ^1H NMR spectra of complexes **6** and **7** at room temperature. Nevertheless, the ^1H NMR spectrum of **6** at 24 °C showed a broad 1:1:1:1 quartet at δ = 1.42 ($^1J(H,B)$ = 91.5 Hz), which was unambiguously assigned to the BH_3 groups by a $^1H\{^{11}B\}$ NMR experiment. The instability of compounds **6** and **7** in solution hampered a study of the fluxional processes involving the BH_3 groups of the NMe_2BH_3 ligands.

The thermal stability of complexes **6** and **7** in benzene-d_6 was monitored by NMR spectroscopy (Scheme 2). ^1H NMR spectra taken at room temperature and different reaction intervals showed resonances for several new species in solution. After it was heated at 75 °C for 4 d the initial colorless solutions turned to a dark color, and the ^1H NMR spectra showed complete consumption of the dialkyl-(dimethylamidoborane) group 4 precursors. The spectra revealed resonance signals for the alkyl(dimethylamino)borane compound $[B(CH_2SiMe_3)H(NMe_2)]$ (**8**) and $SiMe_4$ as the major products along with multiple resonances for other minor byproducts. However, the ^{11}B NMR spectrum of these dark solutions showed only a doublet resonance at δ = 42.1 ($^1J(B,H)$ = 118.6 Hz), which is consistent with the formation of **8** as a single boron-containing species. The ^1H and $^{13}C\{^1H\}$ NMR

spectra of **8** at room temperature reveal two sharp resonance signals for the magnetically inequivalent methyl groups of the NMe$_2$ moiety, which is indicative of hindered rotation about the B−N bond. The methylene of the BCH$_2$SiMe$_3$ group appears as a broad doublet at δ = 0.37 (^3J(H,H) = 4.4 Hz) in the ^{1}H NMR spectrum, but the corresponding carbon resonance in the ^{13}C{^{1}H} NMR spectrum was not observed due to coupling with ^{11}B. The NMR data of **8** compares well with those reported by Hill and co-workers for the alkyl-(amino)borane compounds [B{CH(SiMe$_3$)$_2$}H(NMe$_2$)] and [B{CH(SiMe$_3$)$_2$}H{N(CH$_2$)$_4$}] characterized in the thermal decomposition of group 2 mixed alkyl(dimethylamidoborane) complexes.[50,51] Compound **8** is stable in benzene-d_6 solution under argon atmosphere, but, in a fashion similar to the behavior observed in those previous studies, we were not able to isolate complex **8** in a pure form because of its decomposition under vacuum. Nevertheless, analysis by GC-MS of a dilute benzene-d_6 solution generated from the decomposition of **6** provided the molecular ion M$^+$ for **8** with m/z of 143.1.

Hill has suggested a mechanism involving an initial β-hydride elimination in the amidoborane ligand, followed by insertion of the generated H$_2$B=NR$_2$ species into the M−C bond, and finally a β-H elimination to produce the alkyl(amino)borane compounds and presumably hydrides MH$_2$.[50,51] Most likely, the formation of **8** from group 4 complexes **6** and **7** occurs via an analogous mechanism. Indeed, resonance signals for the tetranuclear zirconium(III) octahydride compound [{Zr(η^5-C$_5$Me$_5$)}$_4$(μ-H)$_8$] (**9**) were identified in the ^{1}H and ^{13}C{^{1}H} NMR spectra of the dark green solution resulting in the decomposition of **6**. Complex **9** has been structurally characterized by Hou and co-workers through treatment of **2** with H$_2$ (10 atm) at 80 °C, but the isolated yields of **9** are strongly influenced by the reaction conditions.[35] Whereas the presence of the zirconium hydride complex **9** among the multiple minor byproducts of the reaction was clearly observed by NMR spectroscopy, an analogous hafnium octahydride derivative could not be identified in the dark blue benzene-d_6 solution resulting from the decomposition of **7**.

We also studied the treatment of the titanium complex [Ti(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_3$] (**1**) with *N,N*-dimethylamine−borane (Scheme 3). The reaction of **1** with NHMe$_2$BH$_3$ (4 equiv) in benzene-d_6 was monitored by ^{1}H NMR spectroscopy. After 24 h at room temperature, the spectrum showed complete consumption of NHMe$_2$BH$_3$ and revealed resonance signals

Scheme 3. Reactions of 1 with NHMe$_2$BH$_3$ and H$_2$
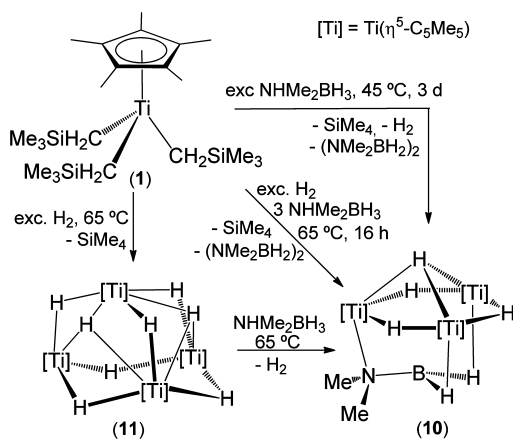
assignable to **1**, the cyclic dimer (NMe$_2$BH$_2$)$_2$, and H$_2$. The ^{1}H NMR spectrum taken after 24 h at 45 °C displayed resonances for (NMe$_2$BH$_2$)$_2$, SiMe$_4$, compound **1**, and two downfield and broad signals centered at δ = 30.38 and 6.32 in a 1:2 ratio. Only after addition of more NHMe$_2$BH$_3$ (4 equiv) to this solution, and subsequent heating at 45 °C for 24 h, the spectrum showed complete conversion of **1** along with an enhanced intensity of the broad resonances. In preparative scale experiments, the complete reaction of **1** required successive additions of NHMe$_2$BH$_3$ (up to 15 equiv) in toluene at 45 °C for 3 d. From the resulting brown solution at −35 °C, suitable crystals for an X-ray crystal-structure determination of the trinuclear titanium tetrahydride complex [{Ti(η^5-C$_5$Me$_5$)(μ-H)}$_3$(μ_3-H)(μ_3-NMe$_2$BH$_2$)] (**10**) were isolated in 32% yield.

The crystal structure of **10** is presented in Figure 2, while selected lengths and angles are given in Table 2. The molecular
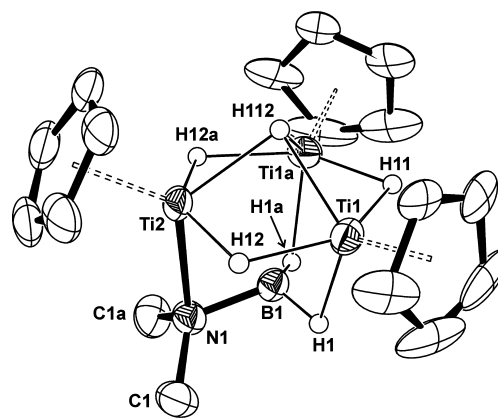

Figure 2. Perspective view of **10** with thermal ellipsoids at the 50% probability level. Methyl groups of the η^5-C$_5$Me$_5$ ligands and hydrogen atoms of the methyl moieties are omitted for clarity. Symmetry code: (a) x, −y, z.

structure of **10** presents a mirror plane bearing the Ti(2), N(1), B(1), H(11), and H(112) atoms. The central core shows three titanium atoms forming an isosceles triangle (Ti(1)−Ti(1)a 2.758(1) Å, Ti(1)−Ti(2) 2.804(1) Å), wherein each edge of the triangle is bridged by one μ-H hydride ligand (Ti(1)−H(11) 1.80(3) Å, Ti(1)−H(12) 1.82(3) Å, and Ti(2)−H(12) 1.82(3) Å). One face of the triangle is capped by a μ_3-H hydride ligand (Ti(1)−H(112) 2.01(3) Å, and Ti(2)−H(112) 2.03(3) Å), whereas the other triangular face contains one μ_3-dimethylaminoborane group. The NMe$_2$BH$_2$ unit is bonded to titanium(2) by the amido nitrogen atom (Ti(2)−N(1) 2.237(3) Å), while the BH$_2$ group binds to each titanium(1) atom through one Ti···H−B interaction (Ti(1)−H(1) 1.98(3) Å). Those Ti−N and Ti−H(B) distances of **10** compare well with those determined in the titanium(III) amidoborane complexes [Ti(η^5-C$_5$H$_5$)$_2$(NH$_2$BH$_3$)] (2.153(3) and 1.95(3) Å, respectively)[18] and [Ti(η^5-C$_5$H$_5$)$_2$(NMe$_2$BH$_3$)] (2.366(3) and 1.92(3) Å, respectively).[11] The B−N bond length of 1.503(5) Å in **10** is slightly shorter than those observed in the mentioned amidoborane complexes (1.534(5) and 1.586(4) Å, respectively) and rules out a significant B−N π-interaction.[52] Compound **10** represents a rare example, where unstable amino-boranes can be trapped within well-defined metal complexes.[52,53]

Compound **10** exhibits a high solubility in toluene, benzene, and hexane resulting in low yields (∼30%) of crystallized

Table 2. Selected Lengths (Å) and Angles (deg) for 10

|			
Ti(2)−N(1)	2.237(3)	B(1)−N(1)	1.503(5)
Ti(1)−H(12)	1.82(3)	Ti(1)−H(11)	1.80(3)
Ti(1)−H(112)	2.01(3)	Ti(1)−H(1)	1.98(3)
Ti(2)−H(12)	1.82(3)	Ti(2)−H(112)	2.03(3)
B(1)−H(1)	1.12(3)	Ti(1)−Ti(2)	2.804(1)
Ti(1)−Ti(1)a*	2.758(1)		
N(1)−Ti(2)−B(1)	37.8(1)	H(11)−Ti(1)−H(12)	140(2)
H(11)−Ti(1)−H(112)	73(1)	H(11)−Ti(1)−H(1)	86(2)
H(12)−Ti(1)−H(112)	76(1)	H(12)−Ti(1)−H(1)	82(2)
H(112)−Ti(1)−H(1)	113(1)	N(1)−Ti(2)−H(12)	84(1)
N(1)−Ti(2)−H(112)	121(1)	H(12)−Ti(2)−H(112)	76(1)
H(12)−Ti(2)−H(12)a*	138(1)	Ti(2)−N(1)−C(1)	118.2(2)
Ti(2)−N(1)−B(1)	76.5(2)	B(1)−N(1)−C(1)	115.5(2)
C(1)−N(1)−C(1)a*	109.7(3)	Ti(2)−B(1)−N(1)	65.8(2)
Ti(2)−B(1)−H(1)	119(2)	N(1)−B(1)−H(1)	114(2)
H(1)−B(1)−H(1)a*	116(2)		

*Symmetry code: (a) $x, -y, z$.

samples, which were used for analytical and spectroscopic techniques. The ^{1}H NMR spectrum in benzene-d_6 at room temperature displays the two downfield and broad resonance signals in a 1:2 ratio described above at δ = 30.38 ($\Delta\nu_{1/2}$ = 415 Hz) and 6.32 ($\Delta\nu_{1/2}$ = 25 Hz) attributable to the η^5-C$_5$Me$_5$ ligands in agreement with a C_s symmetry in solution. The paramagnetic nature of **10** was confirmed by an Evans method determination of its magnetic susceptibility (μ_{eff} = 1.87 μ_B, 293 K, C$_6$D$_6$ solution), which is consistent with the presence of an unpaired electron in the complex. Although resonance signals for the μ_n-hydride and μ_3-NMe$_2$BH$_2$ ligands were not detected in the ^{1}H NMR spectrum of **10**, the IR spectrum (KBr) shows two absorptions at 2037 and 1969 cm^{-1} for ν_{BH} vibrations of bridging B−H bonds. Complex **10** is stable in benzene-d_6 solution under argon or dinitrogen atmosphere at 110 °C and does not react with tetrahydrofuran, pyridine, or triphenylphosphane at that temperature according to NMR experiments.

The unexpected formation of the mixed valence Ti(II)/Ti(III) tetrahydride complex **10** was examined. Since we did not observe resonance signals for SiMe$_4$ in the NMR tube experiment at room temperature, it appears that the titanium trialkyl complex [Ti(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_3$] (**1**) does not react with NHMe$_2$BH$_3$ via N−H activation in contrast to the zirconium and hafnium analogues **2** and **3**. Instead, the experiment showed that the N,N-dimethylamine−borane reagent underwent dehydrogenation to give (NMe$_2$BH$_2$)$_2$ and molecular hydrogen,[54] which did not react with **1** at room temperature. We speculated that H$_2$ produces the hydrogenolysis of **1** at higher temperatures to give a [Ti(η^5-C$_5$Me$_5$)H$_3$] hydride species that subsequently could release hydrogen and capture one dimethylaminoborane unit to give **10**. Indeed, dark brown crystals of compound **10** were isolated in slightly higher yield (39%) by treatment, under a hydrogen atmosphere, a toluene solution of **1** with only 3 equiv of NHMe$_2$BH$_3$ at 65 °C for 16 h (Scheme 3).

Furthermore, an NMR tube experiment showed that complex **1** in benzene-d_6 does not react with hydrogen (1 atm) at room temperature, but the heating of the reaction mixture at 45−65 °C leads to SiMe$_4$ and precipitation of dark red crystals at the bottom of the tube. In preparative scale experiments, exposure of a hexane solution of **1** to 1 atm of H$_2$ at 65 °C resulted in the precipitation of the tetranuclear titanium(III) octahydride compound [{Ti(η^5-C$_5$Me$_5$)}$_4$(μ-H)$_8$]

(**11**) as dark red crystals in 44% yield. The crystal structure of **11** shows a Ti$_4$ tetrahedron, wherein each edge is bridged by one μ-H hydride ligand, and two faces are capped by one μ_3-H hydride ligand (Figure 3 and Table S3 in the Supporting
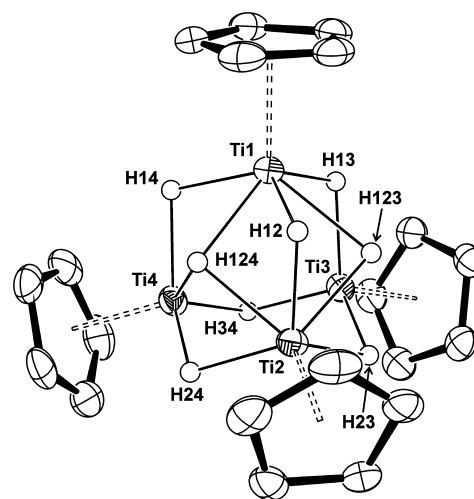
Figure 3. Perspective view of **11** with thermal ellipsoids at the 50% probability level. Methyl groups of the η^5-C$_5$Me$_5$ ligands are omitted for clarity. Selected lengths (Å): Ti(1)−Ti(2) 2.806(1), Ti(1)−Ti(3) 2.828(1), Ti(1)−Ti(4) 2.830(1), Ti(2)−Ti(3) 2.821(1), Ti(2)−Ti(4) 2.803(1), Ti(3)−Ti(4) 2.822(1), Ti−μ-H 1.70(5)−1.83(5), Ti−μ_3-H 1.90−2.13(5).

Information). The Ti−Ti separations fall in a narrow range (2.803(1)−2.830(1) Å, average 2.82(1) Å) and are slightly longer than those found in complex **10**. The Ti−μ-H bond lengths range from 1.70(5) to 1.83(5) Å, whereas the Ti−μ_3-H distances are longer (1.90−2.13(5) Å). The crystal structure of **11** is fully comparable to those reported by Hou and co-workers for complexes [{Ti(η^5-C$_5$Me$_4$SiMe$_3$)}$_4$(μ-H)$_8$],[25] and [{M(η^5-C$_5$Me$_4$R)}$_4$(μ-H)$_8$][35] (M = Zr, Hf; R = SiMe$_3$, Me). Similarly to those examples, the short Ti−Ti distances and the diamagnetic nature in solution of **11** agree with the existence of metal−metal bonding as determined by density functional theory (DFT) calculations for the model compound [{Zr(η^5-C$_5$H$_4$SiH$_3$)}$_4$(μ-H)$_8$].[35]

Compound **11** is poorly soluble in hydrocarbon solvents, pyridine, or tetrahydrofuran and reacts immediately with chloroform-d_1. The ^{1}H NMR spectrum of **11** in benzene-d_6 at room temperature displays two sharp singlets in a 60:8 ratio at δ = 2.24 and −1.18 for the η^5-C$_5$Me$_5$ and μ-H ligands, respectively. These data are consistent with a fluxional behavior of **11** in solution similar to those observed in the analogous group 4 octahydride complexes [{M(η^5-C$_5$Me$_4$R)}$_4$(μ-H)$_8$].[25,35] Interestingly, complex **11** in benzene-d_6 does not react with NHMe$_2$BH$_3$ at room temperature, but its conversion to **10** was observed upon heating the reaction mixture at 65 °C. At that temperature, the ^{1}H NMR spectra showed complete consumption of NHMe$_2$BH$_3$ to give the dehydrogenation products H$_2$ and (NMe$_2$BH$_2$)$_2$, which subsequently might react with **11** to give complex **10**.

■ CONCLUSION

We have presented the clean formation of singular alkylidene-alkylidyne complexes [{M(η^5-C$_5$Me$_5$)}$_3${(μ-CH)$_3$SiMe}(μ_3-CSiMe$_3$)] (M = Zr, Hf) by thermal decomposition of trimethylsilylmethyl derivatives [M(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_3$] at 130−200 °C. The trialkyl zirconium and hafnium complexes [M(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_3$] react with NHMe$_2$BH$_3$ at room temperature to give dialkyl(dimethylamidoborane) compounds [M(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_2$(NMe$_2$BH$_3$)] via N−H activation. These sterically encumbered complexes were found to be unstable at room temperature and decompose with formation of the alkyl(dimethylamino)borane [B(CH$_2$SiMe$_3$)H(NMe$_2$)]. In contrast, NHMe$_2$BH$_3$ in presence of the titanium analogous [Ti(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$)$_3$] undergoes dehydrogenation to give H$_2$ and the cyclic dimer (NMe$_2$BH$_2$)$_2$, and this reaction mixture at 45−65 °C produces the hydride complex [{Ti(η^5-C$_5$Me$_5$)(μ-H)}$_3$(μ_3-H)(μ_3-NMe$_2$BH$_2$)]. The formation of this trinuclear Ti(II)/Ti(III) cluster can be the result of the hydrogenation of the three alkyl groups of the titanium precursor to give a hydride species that subsequently releases H$_2$ and captures a dimethylaminoborane moiety. The trapped NMe$_2$BH$_2$ fragment within a trimetallic [{Ti(η^5-C$_5$Me$_5$)(μ-H)}$_3$(μ_3-H)] system provides a novel bridging aminoborane bonding motif. The isolation of aminoborane complexes is relevant to dehydrogenation mechanisms of amine−boranes, where such compounds are often implicated as elusive intermediates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b01607.

> Experimental crystallographic data of complexes **2**, **4**, **5**, **10**, and **11**; perspective view of the crystal structures of complexes **2** and **5**; tables for selected lengths and angles of the crystal structures of **2** and **11**; ^{1}H and ^{13}C{^{1}H} NMR spectra for complexes **6** and **7**, and those taken after the decomposition of **6** in solution; GC-MS of [B(CH$_2$SiMe$_3$)H(NMe$_2$)] (**8**) (PDF)

Accession Codes

CCDC 1556599−1556603 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: carlos.yelamos@uah.es.

ORCID Ⓘ

Carlos Yélamos: 0000-0003-0425-4799

Notes

The authors declare no competing financial interest.

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