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Monomeric, Four-Coordinate Group 4 Metal Complexes with Chelating Bis(*tert*-butylamido)cyclodisilazane Ligands: Syntheses and Molecular Structures of $\{(MeSiN^tBu)_2(N^tBu)_2\}MCl_2$ and $\{(MeSiN^tBu)_2(N^tBu)_2\}MMe_2$, M = Zr, Hf

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The interaction of $(MeSiN^tBu)_2(N^tBuLi)_2$ with MCl_4 in hot toluene produces $\{(MeSiN^tBu)_2(N^tBu)_2\}MCl_2$, M = Zr (**1**), Hf (**2**), in good yields. The light-yellow and colorless solids are isostructural and crystallize in the monoclinic crystal system, space group $P2_1/n$, with four molecules in the unit cell. The unit cell dimensions for **1** (293 K) are $a = 9.174(6)$ Å, $b = 18.027(13)$ Å, $c = 16.515$ Å, $\beta = 98.81(6)°$, and those for **2** (213 K) are $a = 9.1871(1)$ Å, $b = 17.8553(2)$ Å, $c = 16.4770(3)$ Å, $\beta = 99.339(1)°$. The metal atoms are pseudotetrahedrally coordinated by cyclodisilazane and chloride ligands but have one additional weak bonding interaction with a cyclodisilazane ring-nitrogen atom. Treatment of **1** or **2** with 2 equiv of MeMgCl in ether affords the corresponding dimethyl species $\{(MeSiN^tBu)_2(N^tBu)_2\}MMe_2$, M = Zr (**3**), Hf (**4**). These isostructural, colorless organometallic compounds are remarkably stable to atmospheric oxygen and moisture. They crystallize in the monoclinic space group $C2/c$, $Z = 4$. The cell parameters for **3** (298 K) are $a = 18.867(2)$ Å, $b = 9.361(1)$ Å, $c = 18.059(3)$ Å, $\beta = 119.49(1)°$, and those for **4** (212 K) are $a = 18.8066(4)$ Å, $b = 9.3208(2)$ Å, $c = 17.8725(3)$ Å, $\beta = 119.508(1)°$. The dimethyl species are structurally very similar to the dichloro complexes **1** and **2**, with the notable exception that the metal centers in these organometallic compounds are truly four-coordinate.

Due to the economic importance of the Ziegler−Natta polymerization of olefins there is currently considerable research interest in transition metal compounds that can catalyze this reaction.[2] Although the Ziegler−Natta process was initially run with rather ill-defined heterogeneous catalyst mixtures,[3] it is now increasingly practiced homogeneously with modified mono- or dicyclopentadienyl group 4 metal complexes and various cocatalysts.[2c] Among the most active and selective compounds for these polymerization reactions are cationic species derived from *ansa*-metallocenes[4] and the so-called constrained-geometry catalysts (CGC), *viz.*, $[\{(\eta^5\text{-}C_5Me_4)SiMe_2(N^tBu)\}MCl_2]$[5] (see Figure 1).

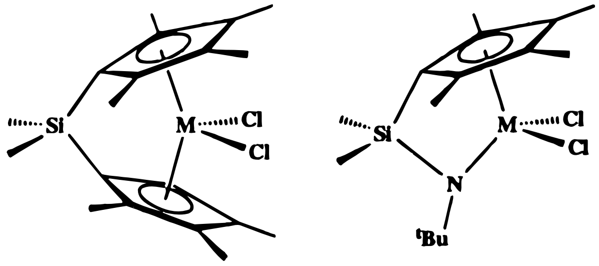

Figure 1. Structural comparison of an *ansa*-metallocene (left) and a constrained-geometry catalyst (right), two of the best homogeneous Ziegler−Natta precatalysts.

The impressive catalytic activity of constrained-geometry catalysts—hybrid compounds of organometallic and classical coordination chemistry—has caused renewed interest in the well-established group 4 metal−amide chemistry.[6] Despite a flurry of research activity in this area, however, many of the recent attempts to synthesize amide-based catalysts using tri-[7] and tetradentate[8] amides have failed to provide truly four-coordinate molecules, a structural feature considered important for polyolefin catalysts. Very recent examples of group 4 compounds with chelating diamide ligands have yielded species whose structures more closely resemble those of organometallic

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(2) For some recent reviews, see: (a) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1. (b) Kaminsky, W. *Catal. Today* **1994**, *20*, 257. (c) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(3) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980,** *18*, 99.

(4) (a) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (b) Wochner, F.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 69. (c) Hortmann, K.; Brintzinger, H. H. *New J. Chem.* **1992**, *16*, 52. (d) Wild, F. R. W. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63. (e) Yang, X.; Stern, C. L.; Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1375.

(5) (a) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. European Patent Application EP-416-815-A2. (b) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867. (c) Devore, D. D.; Timmers, F. J.; Hasha, D. L.; Rosen, R. K.; Marks, T. J.; Deck, P. A.; Stern, C. L. *Organometallics* **1995**, *14*, 3132. 36. (d) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, *2*, 74. (e) For a complex closely related to CGCs, see: du Plooy, K. E.; Moll, U.; Wocadlo, S.; Massa, W.; Okuda, J. *Organometallics* **1995**, *14*, 3129.

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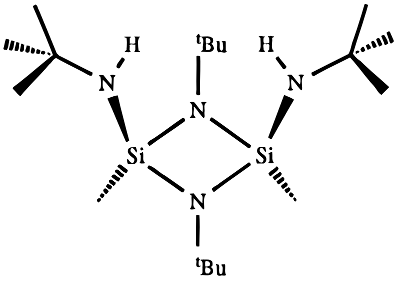
precatalysts, but even in these complexes the metal atoms are often in five- or six-coordinate environments, due to dimerization or solvent coordination.[9]

Active polyolefin catalysts are pseudotetrahedral, but nitrogen-donor ligands based on ethylene and ortho-disubstituted arenes tend to have bite angles that are too small for tetrahedral coordination. Longer alkyl or disilyl chains, by contrast, introduce too much flexibility into the ligand backbone, causing coordinative lability. Because the two amide groups should ideally be separated by about 3.8 Å,[10] the large and rigid cyclodisilazanes would seem well-suited as ligands for early transition metals. These ligands also offer the possibility of electron donation through the cyclodisilazane ring, and this should provide an additional stabilizing feature for electron-deficient metal centers. On the basis of these general structural and electronic considerations, we set out to synthesize group 4 metal complexes of *cis*-2,4-bis(*tert*-butylamino)-1,3-di(*tert*-butyl-2,4-dimethylcyclodisilazane, $\{(MeSiN^tBu)_2(N^tBuH)_2\}$, **A**, a molecule with a long record as a stabilizing ligand in main-group metal chemistry.[11]



A

Experimental Section

General Considerations. All operations described herein were performed under an atmosphere of purified nitrogen or argon in standard Schlenk-type glassware. The solvents were dried and freed of dissolved molecular oxygen by distillation from sodium or potassium benzophenone ketyl immediately before use. Mass spectra were recorded in the chemical ionization mode on a VG Micromass 7070E-HF double-focusing spectrometer, using methane as the ion source. Except for the molecular ions, peaks are quoted only if their relative intensities exceeded 10%. NMR spectra were recorded on a Varian VXR-300 spectrometer. ^{1}H NMR spectra are referenced relative to C_6D_5H (7.15 ppm), and ^{13}C NMR spectra are referenced relative to C_6D_6 (128.0 ppm). Melting points were obtained on a Mel-Temp apparatus; they are uncorrected. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ, and Robertson Microlit Laboratories, Madison, NJ.

The tetrachlorides of zirconium and hafnium were purchased from Aldrich and Aesar, respectively, and were used as received. The THF adducts $ZrCl_4(THF)_2$ and $HfCl_4(THF)_2$ were synthesized by published procedures.[12] Methylmagnesium chloride was obtained from Aldrich and used as received or diluted to the desired concentration. The cyclodisilazane *cis*-$\{(MeSiN^tBu)_2(N^tBuH)_2\}$ and its dilithium salt were prepared using improved versions of published procedures.[11b,13] They can also be prepared according to the original literature reference.[11b] $\{(MeSiN^tBu)_2(N^tBuLi)_2{\cdot}2THF\}$ was prepared by an unpublished method.[13]

Synthesis of $\{(MeSiN^tBu)_2(N^tBu)_2\}ZrCl_2$, 1. In a 100-mL, three-neck flask equipped with an inert gas inlet, a reflux condenser, and a magnetic stirring bar, 0.245 g (1.05 mmol) of $ZrCl_4$ and 0.400 g (1.05 mmol) of $\{(MeSiN^tBu)_2(N^tBuLi)_2\}$ were heated in 25 mL of toluene at 80 °C for 24 h. Removal of LiCl by filtration on a medium-porosity frit and concentration of the light-yellow solution to 15 mL, followed by cooling to −12 °C for 3 days, yielded 0.304 g of a light-yellow crystalline solid. The supernatant was concentrated to 7 mL and stored at −12 °C for 2 days to give an additional 0.121 g of product for an overall yield of 79.9%. Note: If $\{(MeSiN^tBu)_2(N^tBuLi)_2{\cdot}2THF\}$, $ZrCl_4(THF)_2$, or both are used as source materials, the reaction mixture must be filtered cold (0 °C) in order to remove unreacted $ZrCl_4(THF)_2$, which is somewhat soluble in toluene at room temperature.

Mp: 254 °C dec. ^{1}H NMR (300 MHz, benzene-d_6, 21 °C): δ = 1.46 (s, 18H, N^{t}Bu), 1.21 (s, 18H, N^{t}Bu), 0.46 (s, 6H, SiMe). ^{1}H NMR (300 MHz, toluene-d$_8$, −80 °C): δ = 1.45 (s, 18H, N^{t}Bu), 1.15 (s, 18H, N^{t}Bu), 0.27 (s, 6H, SiMe). ^{13}C NMR (75 MHz, benzene-d_6, 21 °C): δ = 57.8 (s), 52.6 (s), 34.1 (q, J_{HC} = 125 Hz), 33.5 (q, J_{HC} = 125 Hz), 4.9 (q, J_{HC} = 122 Hz). Mass Spectrum (PCI, methane): *m/z* (%) 494.99 (100.0), 495.99 (53.2), 496.98 (83.6), 497.99 (32.2), 498.99 (54.2), 499.99 (16.3), 500.97 (21.6), 514.94 (63.1), 515.93 (32.70), 516.94 (72.9), 517.94 (29.9), 518.94 (50.5), 519.95 (15.8), 520.95 (24.1), 530.97 (26.9), 531.97 (16.7), 532.96 (27.9), 533.96 (13.8), 534.96 (18.3). Anal. Calcd for $C_{18}H_{42}N_4Cl_2Si_2Zr$: C, 40.60; H, 7.95; N, 10.52. Found: C, 40.56; H, 8.24; N, 10.20.

Synthesis of $\{(MeSiN^tBu)_2(N^tBu)_2\}HfCl_2$, 2. This compound was prepared in a manner analogous to that used for the synthesis of **1**. In a 100-mL, three-neck flask, 0.584 g (1.82 mmol) of $HfCl_4$ was heated (100 °C) with 0.700 g of $(MeSi)_2(N^tBu)_2(N^tBuLi)_2$ in 25 mL of toluene for 2 days. Overall yield: 0.754 g (66.7%). Note: If $\{(MeSiN^tBu)_2(N^tBuLi)_2{\cdot}2THF\}$, $HfCl_4(THF)_2$, or both are used as source materials, the reaction mixture must be filtered cold (0 °C) in order to remove unreacted $HfCl_4(THF)_2$, which is somewhat soluble in toluene at room temperature.

Mp: 256 °C dec. ^{1}H NMR (300 MHz, benzene-d_6, 21 °C): δ = 1.45 (s, 18H, N^{t}Bu), 1.22 (s, 18H, N^{t}Bu), 0.47 (s, 6H, SiMe). ^{13}C NMR (75 MHz, benzene-d_6, 21 °C): δ = 56.4 (s), 52.7 (s), 34.8 (q, J_{HC} = 125 Hz), 33.4 (q, J_{HC} = 125 Hz), 5.6 (q, J_{HC} = 122 Hz). MS (PCI, methane): m/z (%) 581.97 (37.9), 582.97 (67.7), 583.98 (58.6), 584.99 (100), 586.00 (40.3), 587.01 (34.05), 601.97 (21.1), 602.96 (37.4), 603.96 (37.7), 604.95 (65.0), 605.95 (31.0), 606.94 (35.0), 607.94 (11.8), 617.99 (13.4), 618.99 (21.2), 620.00 (19.3), 621.01 (25.1), 622.02 (12.9), 623.03 (12.5). Anal. Calcd for $C_{18}H_{42}N_4Cl_2$ Hf Si_2: C, 34.86; H, 6.83; N, 9.03. Found: C, 34.90; H, 7.13; N, 8.89.

Synthesis of $\{(MeSiN^tBu)_2(N^tBu)_2\}ZrMe_2$, 3. To a cooled (0 °C) solution of 0.201 g (0.377 mmol) of $\{(MeSiN^tBu)_2(N^tBu)_2\}ZrCl_2$ in 20 mL of ether was added 0.3 mL of a 3.0 M ethereal MeMgCl solution.

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(6) (a) Bürger, H.; Wannagat, U. *Monatsh. Chem.* **1963**, *94*, 761. (b) Arioldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Abdul Malik, K. M.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2010. (c) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 2928. (d) Planalp, R. P.; Andersen, R. A.; Zalkin, A. *Organometallics* **1983**, *2*, 16. (e) Cummins, C. C.; Van Duyne, G. D.; Schaller, C. P.; Wolczanski, P. T. *Organometallics* **1991**, *10*, 164. (f) Fryzuk, M. D.; Williams, H. D.; Rettig, S. J. *Inorg. Chem.* **1983**, *22*, 863. (g) Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030.

(7) (a) Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B. *J. Chem. Soc., Dalton Trans.* **1995**, 25. (b) Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Wainwright, A. P. *J. Organomet. Chem.* **1995**, *501*, 333. (c) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672. (d) Memmler, H.; Walsh, K.; Gade, L. H.; Lauher, J. W. *Inorg. Chem.* **1995**, *34*, 4062. (e) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1992**, *11*, 1452. (f) Friedrich, S.; Gade, L. H. *Organometallics* **1995**, *14*, 5344. (g) Reger, D. L.; Tarquini, M. E. *Inorg. Chem.* **1983**, *22*, 1064. (h) Reger, D. L.; Tarquini, M. E. *Inorg. Chem.* **1982**, *21*, 840.

(8) (a) Floriani, C.; Ciurli, S.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 70. (b) De Angelis, S.; Solari, E.; Gallo, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1992**, *31*, 2520. (c) Brand, H.; Arnold, J. *J. Am.Chem. Soc.* **1992**, *114*, 2266. (d) Uhrhammer, R.; Black, D. G.; Gardner, T. G.; Olsen, J. D.; Jordan, R. F. *J. Am. Chem. Soc.* **1993**, *115*, 8493.

(9) (a) Aoyagi, K.; Gantzel, P. K.; Kalai, K.; Tilley, T. D. *Organometallics* **1996**, *15*, 923. (b) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1996**, *15*, 562. (c) Dias, H. V. R.; Jin, W.; Wang, Z. *Inorg. Chem.* **1996**, *35*, 6074. (d) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 5478.

(10) This number is based on metal−nitrogen distances of 2.10 Å and an N−M−N angle of 130°.

(11) (a) Veith, M.; Goffing, F.; Becker, S.; Huch, V. *J. Organomet. Chem.* **1991**, *406*, 105. (b) Veith, M.; Goffing, F.; Huch, V. *Chem. Ber.* **1988**, *121*, 943. (c) Veith, M.; Becker, S.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1237. (d) Veith, M.; Goffing, F.; Huch, V. *Z. Naturforsch.* **1988**, *43b*, 846.

(12) Manzer, L. *Inorg. Chem.* **1977**, *16*, 525.

(13) Grocholl, L.; Stahl, L. Manuscript in preparation.

On warming, the initially turbid solution became cloudy. It was then stirred at room temperature for an additional 12 h and filtered on a medium-porosity frit. The clear, colorless solution was concentrated to 3 mL and stored in a freezer for 5 days. This procedure afforded 0.141 g of colorless, thin plates corresponding to a 76% yield based on **1**.

Mp: 235 °C dec. ^{1}H NMR (300 MHz, benzene-d_6, 21 °C): δ = 1.53 (s, 18H; N^{t}Bu), 1.19 (s, 18H, N^{t}Bu), 0.69 (s, 6H, ZrMe), 0.53 (s, 6H, SiMe). ^{13}C NMR (75 MHz, benzene-d_6, 21 °C): δ = 56.2 (s), 51.5 (s), 43.5 (q, J_{HC} = 110 Hz), 34.7 (q, J_{HC} = 125 Hz), 34.0 (q, J_{HC} = 125 Hz), 5.3 (q, J_{HC} = 122 Hz). MS (PCI, methane): m/z (%) 68.99 (37.6), 118.99 (10.5), 130.05 (11.0), 130.99 (17.4), 131.05 (19.2), 132.04 (15.4), 171.13 (14.4), 180.99 (10.5), 228.14 (16.7), 284.20 (17.4), 285.20 (11.3), 300.23 (17.9), 358.29 (100.0), 359.29 (36.8), 372.30 (24.5), 490.25 (1.0), 491.25 (1.1). Anal. Calcd for $C_{20}H_{48}N_4Si_2Zr$: C, 48.84; H, 9.83; N, 11.38. Found: C, 48.53; H, 9.53; N, 11.09.

Synthesis of $\{(\mathrm{MeSiN^tBu})_2(\mathrm{N^tBu})_2\}\mathrm{HfMe}_2$, 4. To a solution of 0.197 g (0.317 mmol) of $\{(\mathrm{MeSiN^tBu})_2(\mathrm{N^tBu})_2\}\mathrm{HfCl}_2$ in 20 mL of ether was added 0.740 mmol of MeMgCl in 10 mL of ether. After a few drops of the Grignard reagent had been added, the initially clear solution became cloudy. It was stirred for an additional 12 h and then filtered on a medium-porosity frit. The clear, colorless filtrate was concentrated to 5 mL and stored at −12 °C for 7 days. This procedure afforded 0.095 g of colorless, thin plates (52% yield based on **2**).

Mp: 242 °C dec. ^{1}H NMR (300 MHz, benzene-d_6, 21 °C): δ = 1.47 (s, 18H, N^{t}Bu), 1.20 (s, 18H, N^{t}Bu), 0.54 (s, 6H, HfMe), 0.52 (s, 6H, SiMe). ^{13}C NMR (75 MHz, benzene-d_6, 21 °C): δ = 56.8 (q, J_{HC} = 110 Hz), 55.3 (s), 51.6 (s), 35.1 (q, J_{HC} = 128 Hz), 33.9 (q, J_{HC} = 129 Hz), 6.0 (q, J_{HC} = 120 Hz). MS (PCI, methane): m/z (%) 68.99 (119.3), 99.99 (13.2), 118.99 (33.0), 130.99 (56.1), 168.99 (19.3), 180.99 (31.63), 230.99 (14.1), 357.29 (100.0), 358.29 (30.2), 359.29 (10.7), 372.31 (12.2), 578.27 (0.6), 581.28 (0.8). Anal. Calcd for $C_{20}H_{48}N_4HfSi_2$: C, 41.47; H, 8.35; N, 9.67. Found: C, 41.52; H, 8.41; N, 9.26.

X-ray Diffraction Studies. $\{(\mathrm{MeSiN^tBu})_2(\mathrm{N^tBu})_2\}\mathrm{ZrCl}_2$, 1. Diffraction intensities on a light yellow bar-shaped crystal were collected at 293 K on a Siemens-Stoe AED2 four-circle diffractometer, using graphite-monochromated Mo Kα (λ = 0.7107 Å) radiation. Of 4749 unique data collected in the 3.3−50.1° 2Θ range (index ranges: $-10 \le h \le 10$, $0 \le k \le 21$, $0 \le l \le 19$), 3836 were observed ($I > 2\sigma(I)$) and used in the refinement. Lorentz and polarization corrections and a semiempirical absorption correction (ψ-scans) were applied to the data set. The structure was solved in the unambiguous space group $P2_1/n$ (No. 14) with the direct methods option of the SHELXS-86[14] program package. The positions of the zirconium atom and the atoms comprising the four-membered ring were taken from the initial *E*-map. Iterative difference Fourier maps yielded the positions of all remaining heavy atoms and of some of the hydrogen atoms. A final difference map showed no peaks greater than 0.351 e Å^{-3}. The atomic scattering factors were provided by the program and their sources are referenced therein. All 249 parameters were refined (non-hydrogen atoms anisotropically and hydrogen atoms isotropically in calculated positions) by using full-matrix least-squares methods on F_o^2 in the SHELXL-93[15] program package.

$\{(\mathrm{MeSiN^tBu})_2(\mathrm{N^tBu})_2\}\mathrm{HfCl}_2$, 2. Data were collected using a Siemens SMART CCD (charge coupled device) diffractometer equipped with an LT-2 low-temperature apparatus operating at 213 K. A colorless cube of dimensions 0.15 × 0.15 × 0.15 mm was chosen and mounted on a glass capillary with silicone grease. Intensities were measured using ω scans of 0.3°/frame for 10 s, until a complete hemisphere was collected. A total of 1271 frames and 10 688 reflections were collected with a final resolution of 0.84 Å. The index ranges were $-10 \le h \le 11$, $-20 \le k \le 23$, $-21 \le l \le 20$. These data were merged (R_{int} = 0.0258) to provide 4637 unique observed data. The first 50 frames were re-collected at the end of data acquisition to monitor for decay, which was less than 1%. Cell parameters were retrieved using SMART[16] software and refined using SAINT[17] on all observed reflections. Data reduction was performed with the SAINT software which corrects for Lp and decay. An absorption correction was applied using SADABS,[18] which was supplied with the program. The structure was solved in the uniquely determined space group $P2_1/c$ (No. 14) by using the direct methods of the SHELX-90[14] program and refined by the least-squares method on F^2 with SHELXL-93, incorporated in SHELXTL-PC V 5.03.[19] Hydrogen atoms were calculated by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection.

$\{(\mathrm{MeSiN^tBu})_2(\mathrm{N^tBu})_2\}\mathrm{ZrMe}_2$, 3. A colorless plate of approximate dimensions 0.5 × 0.2 × 0.1 mm was glued inside an argon-filled capillary tube and was optically aligned on an Enraf-Nonius CAD 4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A monoclinic unit cell of dimensions a = 18.867(2) Å, b = 9.361(1) Å, c = 18.059(3) Å, β = 119.49(1)° was obtained from a least-squares fit of 24 centered reflections. The measured intensities of two independent octants ($-20 \le h \le 17$, $0 \le k \le 10$, $1 \le l \le 19$) of the reciprocal lattice were collected via ω−2Θ scans over 2.0° ≤ 2Θ ≤ 45.0°. Of the 1817 data collected, 1279 with $I \ge 1.5\sigma(I)$ were used in the structure refinement. The probable space group $C2/c$ (No. 15) was later corroborated by the successful structure refinement.

The data were corrected for Lorentz and polarization effects and for decay (3.9% based on the measured intensities of two check reflections). An empirical absorption correction based on ψ-scans was applied.

Patterson methods were used to locate the zirconium atom. Successive Fourier syntheses coupled with least-squares refinement yielded the positions of all remaining non-hydrogen atoms. Idealized coordinates for the hydrogen atoms of the methyl groups were calculated with site occupations tied to the associated carbon atoms. Isotropic refinement of all nonhydrogen atoms was followed by anisotropic refinement of all non-hydrogen atoms, with the exception of C(8), which had a nonpositive definite value upon initial anisotropic refinement. Refinement converged with R = 0.084, R_w = 0.086. A final difference map revealed no unusual features. The following software was used for data reduction, solution, and refinement: NRCVAX Datrdr, NRCVAX Solver, and NRCVAX LstSq.[20]

$\{(\mathrm{MeSiN^tBu})_2(\mathrm{N^tBu})_2\}\mathrm{HfMe}_2$, 4. Hardware, software, acquisition, and data reduction parameters were identical to those for **2**. A thin, colorless plate of approximate dimensions 0.2 × 0.15 × 0.15 mm was glued to a glass capillary with silicone grease. A total of 1271 frames with 7662 reflections in the index ranges $-25 \le h \le 22$, $-8 \le k \le 12$, $-21 \le l \le 23$ were collected with a final resolution of 0.75 Å. Of these reflections, 3280 were unique and observed ($I \ge 2\,\sigma(I)$), R_{int} = 0.0373. The first 50 frames were re-collected at the end of data acquisition to monitor for decay; none was observed. The structure was solved in space group $C2/c$ (No. 15) by direct methods. The centrosymmetric space group was indicated by the diffraction intensity distribution and confirmed by the successful refinement of the structure in this space group. The structure was solved with direct methods. Carbon-bound hydrogen atoms were placed in idealized positions (C−H = 0.96 Å) with fixed thermal parameters proportional to the thermal parameter of the carbon atoms to which they are attached (riding model). The hydrogen atom parameters were not refined.

Results and Discussion

The interactions of $\{(\mathrm{MeSiN^tBu})_2(\mathrm{N^tBuLi})_2\}$ species with MCl_4 (M = Zr (**1**), Hf (**2**)) in hot toluene according to eq 1

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(14) Sheldrick, G. M. *Program for the Solution of Crystal Structures , SHELXS-86*; University of Göttingen: Göttingen, Germany, 1990.

(15) Sheldrick, G. M. *Program for Crystal Structure Refinement SHELXL-93*; University of Göttingen: Göttingen, Germany, 1993.

(16) *SMART V 4.043 Software for the CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, 1995.

(17) *SAINT V 4.043 Software for the CCD Detector System*; Siemens Analytical X-ray Systems: Madison, WI, 1995.

(18) SADABS program for absorption corrections using the Siemens CCD Detector System. Based on: Blessing, R. *Acta Crystallogr.*, **1995**, *A 51*, 33.

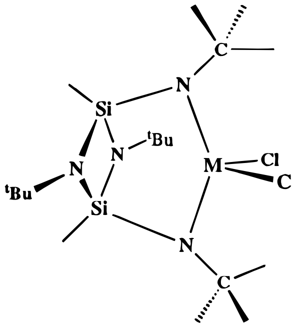
(19) *SHELXTL-PC V 5.03 (PC-Version), Program Library for Structure Solution and Molecular Graphics*; Siemens Analytical X-ray Systems: Madison, WI, 1995.

(20) Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.*, **1989**, *22*, 384.

Table 1. Crystallographic Data for **1**−**4**

	1	**2**	**3**	**4**
empirical formula	$C_{18}H_{42}Cl_2N_4Si_2Zr$	$C_{18}H_{42}Cl_2N_4Si_2Hf$	$C_{20}H_{48}N_4Si_2Zr$	$C_{20}H_{48}N_4Si_2Hf$
formula weight	532.86	620.13	492.03	579.30
space group	$P2_1/n$ (No.14)	$P2_1/n$ (No.14)	$C2/c$ (No.15)	$C2/c$ (No.15)
lattice constants:				
a, Å	9.174(6)	9.1871(1)	18.867(2)	18.8066(4)
b, Å	18.027(13)	17.8553(2)	9.361(1)	9.3208(2)
c, Å	16.515(14)	16.4770(3)	18.059(3)	17.8725(3)
β, deg	98.81(6)	99.339(1)	119.49(1)	119.508(1)
V, $Å^3$	2699(4)	2688.4(4)	2776.4(4)	2726.53(9)
Z	4	4	4	4
ρ(calc), g cm^{-3}	1.31	1.544	1.177	1.411
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73
temp, K	293(2)	213(2)	293(2)	213(2)
μ, cm^{-1}	7.05	42.13	4.8	39.26
R^a	0.0311	0.0315	0.084	0.0424
$R_w{}^b$	0.0992	0.0754	0.086 (F)	0.0911

[a] For **1**−**4**: $R = \sum|F_o - F_c|/\sum|F_o|$. [b] For **1**, **2**, and **4**: $R_w = \{[\sum w(F_o{}^2 - F_c{}^2)^2]/[\sum w(F_o{}^2)^2]\}1/^2$, $w = 1/[\sigma^2(F_o)^2 + (xP)^2 + yP]$, $P = (F_o{}^2 + 2F_c{}^2)/3$. For **3**: $R_w = \{\sum w|F_o - F_c|^2/\sum w|F_o|^2\}^{1/2}$, $w = 1/\sigma^2|(F_o)|$.



M = Zr (1), Hf (2)

produced $\{(MeSiN^tBu)_2(N^tBu)_2\}MCl_2$ in ca. 70% yields. The light-yellow (**1**) and colorless (**2**), hydrocarbon-soluble solids can be handled in air for brief periods of time but hydrolyze on prolonged exposure to the atmosphere. Flame tests on a variety of samples were consistently negative for the presence of lithium. Both compounds have simple ^1H NMR spectra consisting of one sharp line each for the *tert*-butylamido, *tert*-butylimido, and methyl groups. For the zirconium complex these signals appear at δ 1.46, 1.20, and 0.46, respectively, while the analogous hafnium complex displays these signals at δ 1.45, 1.22, and 0.47. These data and the virtually identical five-line ^{13}C NMR spectra suggested that these compounds are isostructural and have C_{2v} molecular symmetry in solution. The robustness of these amido−dichlorides is convincingly demonstrated by their relatively high air and thermal stabilities and the presence of molecular ion peaks in the mass spectra. Single

$$\{(MeSiN^tBu)_2(N^tBuLi)_2\} + MCl_4 \xrightarrow[-2LiCl]{\text{toluene, 80 °C}} \{(MeSiN^tBu)_2(N^tBu)_2\}MCl_2 \quad (1)$$

$$M = Zr\ (\mathbf{1}),\ Hf\ (\mathbf{2})$$

crystals of excellent quality were obtained from cold, concentrated toluene solutions, and these afforded the opportunity for X-ray structural investigations on both compounds. Relevant crystal data for **1** and **2** are collected in Table 1. Selected interatomic distances and angles for these compounds are summarized in Table 2. The isotypic bis(*tert*-butylamido)cyclodisilazane complexes crystallize as close-packed molecular solids with four molecules in the monoclinic unit cells having

Table 2. Selected Bond Distances and Angles for **1** and **2**

	1		
	Bond Distances (Å)		
Zr−N(4)	2.075(3)	Zr−N(3)	2.089(3)
Zr−Cl(1)	2.401(2)	Zr−Cl(2)	2.413(2)
Zr−N(1)	2.523(3)	Si(1)−N(4)	1.723(3)
Si(1)−N(2)	1.750(3)	Si(1)−N(1)	1.767(3)
Si(1)−C(1)	1.843(4)	Si(2)−N(3)	1.714(3)
Si(2)−N(2)	1.746(3)	Si(2)−N(1)	1.770(3)
Si(2)−C(2)	1.855(4)	N(1)−C(3)	1.490(4)
N(2)−C(7)	1.474(4)	N(3)−C(11)	1.483(4)
N(4)−C(15)	1.486(4)		
	Bond Angles (deg)		
N(4)−Zr−N(3)	124.41(11)	N(4)−Zr−Cl(1)	111.88(8)
N(3)−Zr−Cl(1)	112.72(9)	N(4)−Zr−Cl(2)	99.46(8)
N(3)−Zr−Cl(2)	98.96(8)	Cl(1)−Zr−Cl(2)	105.47(7)
N(4)−Zr−N(1)	68.35(10)	N(3)−Zr−N(1)	68.13(10)
Cl(1)−Zr−N(1)	107.12(8)	Cl(2)−Zr−N(1)	147.41(6)
N(4)−Si(1)−N(2)	111.77(13)	N(4)−Si(1)−N(1)	96.75(12)
N(2)−Si(1)−N(1)	84.92(13)	N(4)−Si(1)−C(1)	120.1(2)
N(2)−Si(1)−C(1)	115.7(2)	N(1)−Si(1)−C(1)	121.4(2)
N(3)−Si(2)−N(2)	112.32(13)	N(3)−Si(2)−N(1)	96.94(14)
N(2)−Si(2)−N(1)	84.96(13)	N(3)−Si(2)−C(2)	120.1(2)
N(2)−Si(2)−C(2)	114.6(2)	N(1)−Si(2)−C(2)	121.9(2)
C(3)−N(1)−Si(1)	130.0(2)	C(3)−N(1)−Si(2)	129.3(2)
Si(1)−N(1)−Si(2)	94.30(13)	Si(2)−N(2)−Si(1)	95.76(14)
	2		
	Bond Distances (Å)		
Hf−N(4)	2.075(4)	Hf−N(3)	2.084(4)
Hf−Cl(1)	2.378(1)	Hf−Cl(2)	2.398(1)
Hf−N(1)	2.466(4)	Si(1)−N(4)	1.731(5)
Si(1)−N(2)	1.747(4)	Si(1)−N(1)	1.786(4)
Si(1)−C(1)	1.857(6)	Si(2)−N(3)	1.723(5)
Si(2)−N(2)	1.748(4)	Si(2)−N(1)	1.782(4)
Si(2)−C(2)	1.850(6)	N(1)−C(3)	1.500(7)
N(2)−C(7)	1.486(7)	N(3)−C(11)	1.481(7)
N(4)−C(15)	1.484(6)		
	Bond Angles (deg)		
N(4)−Hf−N(3)	124.2(2)	N(4)−Hf−Cl(1)	113.82(13)
N(3)−Hf−Cl(1)	112.75(13)	N(4)−Hf−Cl(2)	97.81(13)
N(3)−Hf−Cl(2)	99.03(13)	Cl(1)−Hf−Cl(2)	104.17(5)
N(4)−Hf−N(1)	69.1(2)	N(3)−Hf−N(1)	69.1(2)
Cl(1)−Hf−N(1)	107.31(11)	Cl(2)−Hf−N(1)	148.52(11)
N(4)−Si(1)−N(2)	113.8(2)	N(4)−Si(1)−N(1)	95.1(2)
N(2)−Si(1)−N(1)	85.1(2)	N(4)−Si(1)−C(1)	121.0(3)
N(2)−Si(1)−C(1)	113.2(3)	N(1)−Si(1)−C(1)	122.4(3)
N(3)−Si(2)−N(2)	113.8(2)	N(3)−Si(2)−N(1)	95.7(2)
N(2)−Si(2)−N(1)	85.2(2)	N(3)−Si(2)−C(2)	120.0(3)
N(2)−Si(2)−C(2)	114.7(3)	N(1)−Si(2)−C(2)	121.3(2)
C(3)−N(1)−Si(1)	128.8(4)	C(3)−N(1)−Si(2)	129.2(4)
Si(1)−N(1)−Si(2)	93.5(2)	Si(2)−N(2)−Si(1)	96.0(2)

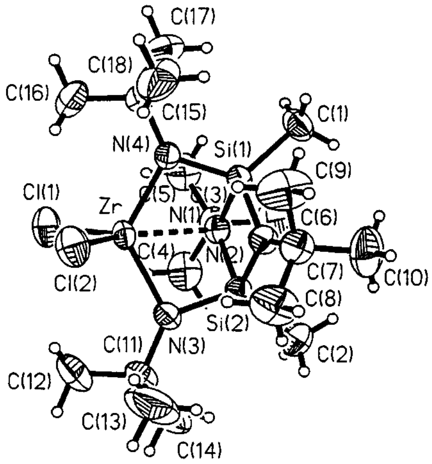


Figure 2. Molecular structure and labeling scheme for $\{(MeSiN^tBu)_2(N^tBu)_2\}ZrCl_2$.

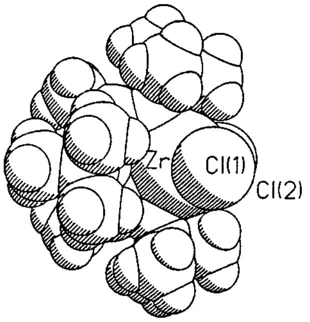


Figure 3. Space-filling drawing of $\{(MeSiN^tBu)_2(N^tBu)_2\}ZrCl_2$, **1**, that shows the coordination gap in the equatorial plane of the complex.

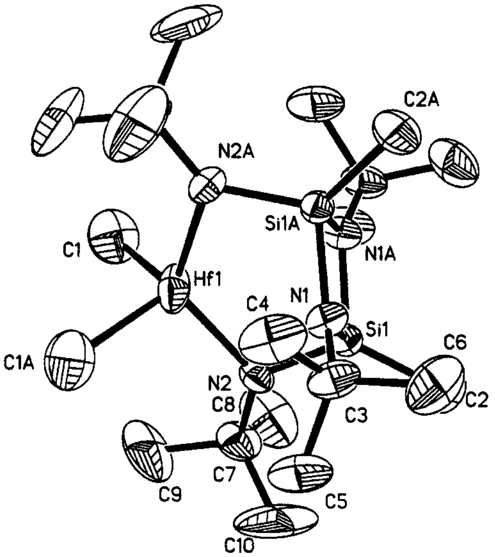


Figure 4. Perspective view of $\{(MeSiN^tBu)_2(N^tBu)_2\}HfMe_2$, **4**, that demonstrates the truly four-coordinate metal center of the dimethyl complexes.

space group $P2_1/n$. Representative drawings of **1** are depicted in Figures 2, 3, and 5.

The structures of the pseudotetrahedral molecules are dominated by the four *tert*-butyl groups, which almost completely surround one hemisphere of the metal. The U-shaped N$-$(Si$-$N)$_2-$N moiety wraps tightly around the zirconium atom and brings all its constituent atoms into close contact with the metal, cf. Zr- - -Si = 2.81 Å. Of special interest is the N$-$M$-$N angle, which at 124.4° is almost identical to the centroid$-$Zr$-$centroid angles in *ansa*-metallocene dichlorides and metallocene dichlorides. The coordination geometry about the amido nitrogen atoms is indicative of sp^2 hybridization, and this, together with the relatively short bond distances, suggests that these nitrogen atoms function as 3-electron donors in these molecules. The Cl$-$Zr$-$Cl angle of 105.5(1)° is significantly larger, by about 10°, than the corresponding angle in Cp_2ZrCl_2[21] and much closer to the ideal tetrahedral value. This opening of the Cl$-$M$-$Cl angle in these cyclodisilazane complexes is likely an indication of lesser steric crowding in the equatorial plane of these compounds. The N(amide)$-$M$-$Cl angles are decidedly nonequivalent as a result of an additional donor interaction between a ring nitrogen and the zirconium atom (*vide infra*) and range from 99° to 110°.

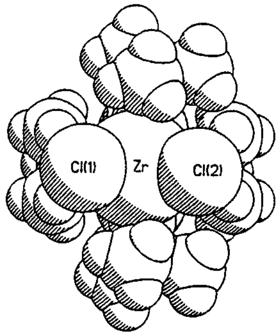


Figure 5. Frontal view of a space-filling representation of $\{(MeSiN^tBu)_2(N^tBu)_2\}ZrCl_2$, **1.**

The Zr$-$N(amido) distances of 2.075(3) and 2.089(3) Å are normal for these three-coordinate, planar nitrogen atoms, and they compare well with those of truly four-coordinate monochlorotris{bis(trimethylsilyl)amido}zirconium compounds for which an average Zr$-$N bond distance of 2.070(3) Å was determined.[6b] The Zr$-$Cl distances, 2.403(2) and 2.413(2) Å, are relatively short and asymmetric. They are shorter than both the sum of their covalent radii and the zirconium$-$chloride bonds in Cp_2ZrCl_2. The shortness is likely due to the lesser crowding and perhaps also the greater Lewis acidity of the metal centers in **1** and **2** and is suggestive of some Cl to metal π-donation. The apparent asymmetry, on the other hand, is likely the result of the N(imido)$-$Zr interaction *(vide infra)* which has lengthened the Zr$-$Cl bond *trans* to itself.

One of the most intriguing aspects of these structures is the proximity of the cyclodisilazane plane to the metal and the extent to which this ring interacts with the metal. The four endocyclic Si$-$N bonds are of equal length (1.76 Å) and considerably shorter than the sum of the covalent radii of silicon and nitrogen (1.87 Å);[22] both features indicate electron delocalization in the ring.

This conclusion is also supported by the planarity of the ring, with atomic displacements—silicon toward and nitrogen away from the metal—being less than 0.015 Å, and the endocyclic angle sum being 360.0(2)°. The Zr$-$(SiN)$_2$ separation of 2.472 Å places the metal almost within bonding distance of the ring's constituent atoms. Because the σ-bond framework of the amide groups holds the zirconium atom at an essentially fixed distance to the cyclodisilazane ring, however, it is difficult to determine the relative importance of the ring$-$zirconium interaction. Given the electron-deficient nature of the zirconium atom in this complex, this secondary interaction between metal and ligand is not surprising, and it may also explain the short nonbonding distances.[23] In the related cyclophosphazene$-$metal

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(21) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr.*, **1974**, *B 30*, 2290.

(22) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960.

(23) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 108.

adducts where the ring–metal donor interaction is the only form of bonding between cyclophosphazene and metal, this interaction is clearly quite strong.[24] Here the X-ray structural evidence, Zr–N = 2.523(3) Å, suggests that in **1** the nitrogen–zirconium donor bond is relatively weak. Despite its weakness this interaction has caused a reduction of the molecular symmetry from C_{2v} to C_s and a noticeable pyramidalization of the donor nitrogen atom (angle sum = 353.6°). We were unable to freeze out this ground state in solution at temperatures as low as −80 °C, but are able to estimate an upper limit of ca. 7.9 kcal/mol for the activation energy of the equilibration process.

The isotypic relationship between **1** and **2** obviates a detailed structural discussion of the hafnium analogue. Metal–ligand bond distances are in line with the trends typically observed in isostructural zirconium and hafnium compounds.[25] Thus the metal–ligand distances in the hafnium complex are slightly, but consistently, shorter than those in $\{(MeSiN^tBu)_2(N^tBu)_2\}ZrCl_2$. The Hf–N and Hf–Cl distances average 2.080(4) and 2.388(1) Å, respectively, and these values are quite comparable to those in $\{(Me_3Si)_2N\}_3HfCl$, for which Hf–N = 2.040(10) Å and Hf–Cl = 2.436(5) Å were found.[6b] It is important to note, however, that the hafnium–chloride distances are shorter in **2** whereas the hafnium–nitrogen distances are shorter in the bis(trimethylsilyl)amido complex.

Because dialkyl species are important precursors for active polyolefin catalysts, we synthesized dimethyl derivatives of these diamido–dichloro compounds. This transformation is easily accomplished by treating **1** and **2** with 2 equiv of MeMgCl in ether (eq 2). The resulting organometallic complexes $\{(MeSiN^tBu)_2(N^tBu)_2\}ZrMe_2$, **3**, and $\{(MeSiN^tBu)_2(N^tBu)_2\}HfMe_2$, **4**, were isolated as colorless crystalline solids in fair yields. In contrast to the often incomplete methylations of metallocene dichlorides, alkylation appears to be fast for these complexes, as indicated by the rapid appearance of $MgCl_2$ in the reaction mixture.

$$\{(MeSiN^tBu)_2(N^tBu)_2\}MCl_2 + 2MeMgCl \xrightarrow[-2MgCl_2]{Et_2O,\ 0\ °C} \{(MeSiN^tBu)_2(N^tBu)_2\}MMe_2 \quad (2)$$

$$M = Zr\ (\mathbf{3}),\ Hf\ (\mathbf{4})$$

The organometallic products of this reaction are more air-stable and almost as thermally stable as the dichlorides, having decomposition points of ca. 234 °C. Qualitative tests on solid samples of **3** and **4** were consistently negative for the presence of chloride. The dimethyl complexes have the very simple ^1H and ^{13}C NMR spectra expected for molecules of C_{2v} symmetry with one signal each for the *tert*-butylamido, *tert*-butylimido, and Si-methyl groups at δ 1.53 (1.45), 1.19 (1.20), and 0.53 (0.52) respectively for **3** (**4**). Both **3** and **4** display one sharp signal at δ 0.69 (0.54) for the methyl ligands in their ^1H NMR spectra.

Single-crystal X-ray studies on these compounds were carried out in order to have a complete set of structural parameters for **1**–**4** and to determine to what extent these molecules are similar to the corresponding dimethylmetallocenes and the related amido–methyl compounds of these metals. Table 1 contains the crystal data for these complexes. Single crystals of **3** were of relatively poor quality, making all metric data of this compound's X-ray diffraction study subject to relatively high statistical uncertainty. Because of the complications which had accompanied the early structural investigations of metallocene dimethyl complexes of zirconium and hafnium,[26] each batch of X-ray crystals was tested to confirm the absence of chloride. The results of the X-ray structural investigations on **4** are shown in Figure 4. Selected bond distances and angles for these compounds are summarized in Table 3.

Table 3. Selected Bond Distances and Angles for **3** and **4**

3

Bond Distances (Å)

Zr(1)–N(2)	2.128(8)	Si(1)–N(1A)	1.753(8)
Zr(1)–N(1)	2.836(8)	Si(1)–C(2)	1.85(1)
Zr(1)–C(1)	2.22(1)	N(1)–C(3)	1.49(1)
Si(1)–N(2)	1.73(1)	N(2)–C(7)	1.45(2)
Si(1)–N(1)	1.752(8)		

Bond Angles (deg)

N(2)–Zr(1)–N(2A)	127.7(4)	N(2)–Si(1)–N(1A)	105.7(4)
N(2)–Zr(1)–C(1A)	107.1(4)	N(1)–Si(1)–N(1A)	83.0(4)
N(2A)–Zr(1)–C(1A)	104.1(4)	C(7)–N(2)–Zr(1)	130.8(8)
C(1A)–Zr(1)–C(1)	104.7(4)	Si(1)–N(2)–Zr(1)	95.9(4)
N(2)–Si(1)–N(1)	106.2(4)	Si(1)–N(1)–Si(1A)	97.0(4)

4

Bond Distances (Å)

Hf(1)–N(2)	2.097(4)	Si(1)–N(1A)	1.753(4)
Hf(1)–N(1)	2.835(4)	Si(1)–C(2)	1.860(5)
Hf(1)–C(1)	2.218(8)	N(1)–C(3)	1.483(6)
Si(1)–N(2)	1.706(4)	N(2)–C(7)	1.486(6)
Si(1)–N(1)	1.752(4)		

Bond Angles (deg)

N(2)–Hf(1)–N(2A)	126.6(2)	N(2)–Si(1)–N(1A)	105.8(2)
N(2)–Hf(1)–C(1A)	106.7(2)	N(1)–Si(1)–N(1A)	84.1(2)
N(2)–Hf(1)–C(1)	105.1(2)	C(7)–N(2)–Hf(1)	130.1(4)
C(1A)–Hf(1)–C(1)	104.8(4)	Si(1)–N(2)–Hf(1)	97.1(2)
N(2)–Si(1)–N(1)	105.1(2)	Si(1)–N(1)–Si(1A)	95.9(2)

The bis(alkylamido)cyclodisilazane–dimethyl complexes crystallize as close-packed molecular solids in the monoclinic space group *C*2/*c*. Like the dichloro analogues, these compounds are isotypic, i.e., they have virtually identical cell parameters and atomic positions. The following discussion on the structures of these compounds pertains to the hafnium dimethyl complex, because its derived metric parameters have greater accuracy. The isolated molecules of **4** are situated on crystallographic 2-fold axes that pass through the hafnium atom and render the symmetry strictly C_2, although the molecules are almost C_{2v} symmetric.

Figure 4 shows a perspective drawing of **4** that emphasizes the coordination geometry about the hafnium atom. While a structural similarity between the two sets of compounds (**1**, **2** and **3**, **4**) is readily apparent, the truly four-coordinate nature of the metal center in the latter two compounds provides a noteworthy difference. Due to the missing ring–metal donor interaction in **4**, the hafnium atom is ca. 0.13 Å farther from the cyclodisilazane ring than in the dichloro derivative. All metal–ligand bonds in the dimethyl compound are slightly but consistently longer than those in **2**. Thus, for example, the Hf–N distances average 2.097(4) Å versus 2.077(7) Å in **2**. The hafnium–methyl distance of 2.218(8) Å appears normal for a four-coordinate metal center and is quite comparable to that in dimethylhafnocene (2.236(12) Å)[26] and the monomethyl derivative $(^tBu_3SiNH)_3ZrCH_3$ 2.231(7) Å.[6e] Bond distances and angles within the cyclodisilazane moiety are essentially identical to those in **1**–**3**.

The metal–amide bond angles in **3** and **4** are again much closer to those in metallocenes and *ansa*-metallocenes than those

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(24) See, for example: (a) Coxon, G. E.; Sowerby, D. B. *J. Chem. Soc. A* **1969**, 3012. (b) Calhoun, H. P.; Paddock, N. L.; Trotter, J. *J. Chem.Soc., Dalton Trans.* **1973**, 2708. (c) Harrison, W.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1973**, 61.

(25) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and Organo-Hafnium Compounds*; John Wiley: New York, 1986.

(26) Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.

Table 4. Selected Bond Distances (Å) and Angles (deg) for **1**−**4**

	1	**2**	**3**	**4**
M−N(av)	2.082(3)	2.077(7)	2.128(8)	2.097(4)
M−Cl(av)	2.407(2)	2.382(3)		
M−C(av)			2.22(1)	2.218(8)
Si−N(amido)	1.719(3)	1.704(6)	1.73(1)	1.707(4)
Si−N(imido)	1.758(3)	1.760(8)	1.753(8)	1.753(4)
Si−C	1.849(4)	1.855(11)	1.85(1)	1.860(5)
N−M−N	124.4(1)	124.0(3)	127.7(4)	126.6(2)
Cl−M−Cl	105.47(7)	104.2(1)		
C−M−C			104.7(4)	104.8(4)
M−N(ring)	2.523(3)	2.466(4)	2.836(8)	2.835(4)
M−ct(ring)	2.472(2)	2.417(2)	2.564(5)	2.565(2)

in four-coordinate complexes of monodentate-amido complexes. For example, the N−Hf−N angle of 126.6(2)° approaches the value found for the centroid−Hf−centroid angle of 133.0° in dimethylhafnocene. This is ca. 2° larger than that of the dichloro species **1** and **2** and likely arises from electronic influences, since it is difficult to explain in steric terms. The angle enclosed by the methyl groups is 104.8(4)° and therefore ca. 10° larger than in the related dimethylhafnocene; this increase presumably reflects the lesser steric crowding in the equatorial plane of **4**.

A comparative listing of the salient bond parameters of **1**−**4** in Table 4 shows that these novel bis(*tert*-butylamido)cyclodisilazane complexes of zirconium and hafnium constitute a homogeneous group. The bond angles and distances for the $\{(MeSiN^tBu)_2(N^tBu)_2\}M$ moieties of the four new compounds are almost identical, the hafnium compounds having consistently shorter metal−ligand bonds. The central structural feature of these compounds is the pseudotetrahedral metal center, which is almost completely enveloped on one side by the cyclodisilazane ligand and which remains fairly exposed on the opposite side due to the presence of the comparatively small chloro and methyl substituents, as shown in Figures 3 and 5. This deviation from ideal tetrahedral geometry is due to the rigid structure of the ligand, which constrains the geometry of its metal complexes much like the $Cp-SiMe_2-N^tBu$ group does.

While the title compounds share many structural characteristics with conventional bis(amido) complexes, the chelating cyclodisilazane **A** does form a very compact and stable Si_2N_4M moiety whose differences may prove advantageous in some situations. The encapsulating ability of $\{(MeSiN^tBu)_2(N^tBu)_2\}^{2-}$, for example, obviates the presence of extremely bulky substituents on the amide−nitrogen atoms, thereby enhancing substrate access to the metal center and thus reactivity.

According to the neutral-ligand formalism the nitrogen atoms of the bis(alkylamido)cyclodisilazane ligand are 3-electron donors, making the title complexes 12-electron species. This high Lewis acidity, paired with a four-coordinate metal center and a well-defined steric pocket, should render these molecules catalytically active. Reactivity studies on the title compounds and related molecules with a variety of cocatalysts are currently underway.

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Supporting Information Available: Tables of crystal data and atomic positional and displacement parameters, complete tables of interatomic distances and angles, and additional packing and ORTEP diagrams (27 pages). Ordering information is given on any current masthead page.

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