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Application of Amine Elimination for the Efficient Preparation of Electrophilic *ansa*-Monocyclopentadienyl Group 4 Complexes Containing an Appended Amido Functionality. Structural Characterization of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_2(NMe_2H)$

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The homologous series of *ansa*-monocyclopentadienyl amido complexes $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]M(NMe_2)_2$ (M = Ti (**2**), Zr (**3**), Hf (**4**)) and $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(NMe_2)_2$ (**8**) are prepared in 70−85% isolated yields by heating the neat 1:1 reaction mixture of (C_5R_4H)-$SiMe_2(N(H)\text{-}t\text{-}Bu)$, where R = H, Me, and $M(NMe_2)_4$, at 110−120 °C for 24−48 h under a N_2 purge. Whereas the reactions of **2** with 2 equiv of $[NEt_3H]Cl$ or HCl produce a mixture of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$ (**5**) and $[(C_5H_4)SiMe_2Cl]TiCl_2(NMe_2)(NMe_2H)$ (**6**), the reaction of **2** with $SiMe_3Cl$ in toluene provides a suitable route for the quantitative conversion of **2** to **5**. Alternatively, the reactions of **3** and **8** with 2 equiv of $[NEt_3H]Cl$ or HCl afford solely the dimethylamine adduct $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_2(NMe_2H)$ (**7**) and the dichloride derivative $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_2$ (**1**), respectively. Compounds **1**−**8** have been characterized in solution by NMR measurements, and the molecular structures of **2**, **7**, and **8** have been determined by X-ray crystallography. The M−N(appended amido) bond distances and Cp(centroid)−M−N bond angles in **2**, **7**, and **8** are 1.972(4), 2.055(5), 2.108(4) Å and 105.5, 101.1, 100.2°, respectively.

Introduction

Since the discovery in 1957 that bis(cyclopentadienyl)titanium dichloride in the presence of alkylaluminum chloride acts as a homogeneous Ziegler−Natta catalyst[1] for the polymerization of ethylene, research efforts have been devoted to the development of modified metallocene-based catalysts that not only exhibit high activity but also provide stereochemical control over polymer composition and structure. A significant milestone occurred in 1980, when Kaminsky and co-workers[2] reported that group 4 metallocene compounds in the presence of an excess of methylalumoxane offer highly active catalysts for olefin polymerization. With the introduction of a short interannular bridge, Brintzinger[3] and others[4] were able to reduce the steric congestion and modify the Lewis acidity at the electrophilic metal center associated with these *ansa*-metallocene complexes. This structural modification was instrumental in the development of chiral, C_2-symmetric *ansa*-metallocene reagents that in the presence of methylalumoxane behave as enantioselective catalysts for α-olefin polymerization[5] and the cyclopolymerization of 1,5-hexadienes.[6] The catalytically active species associated with these metallocene-based systems is generally assumed to be a 14-electron metallocene alkyl cation.[7]

More recently, Bercaw and co-workers[8] prepared a series of neutral 14-electron scandocene alkyl complexes and found that the activity displayed by these one-component catalysts could be enhanced by replacement

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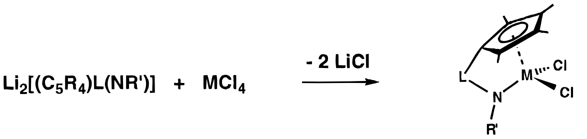
of the two linked or unlinked cyclopentadienyl rings with the dianionic bifunctional chelating ligand $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]^{2-}$. The weaker π-donating character and the lower steric requirements of the amido group enhance the metal's Lewis acidity by the simultaneous reduction of the formal electron count and the steric crowding at the electrophilic d^0 Sc center. Although the rates of ethylene polymerization for these one-component Sc-based catalysts are relatively slow, the rates of chain transfer observed for the Sc complexes containing a chelating *ansa*-monocyclopentadienyl amido ligand are substantially slower than those observed for the parent scandocene complexes.

Following Bercaw's findings, researchers at Dow Chemical Co.[9] and Exxon[10] independently demonstrated that $[(\eta^5\text{-}C_5R_4)SiR'_2(\eta^1\text{-}NR'')]MCl_2$ compounds (M = Ti, Zr, Hf; R = alkyl; R′, R″ = alkyl or aryl) in the presence of methylalumoxane are highly active Ziegler–Natta polymerization catalysts for the copolymerization of ethylene and 1-alkenes. For these 14-electron *ansa*-monocyclopentadienyl amido complexes, the Cp(c)–M–N bite angle (c = centroid) is 25–30° smaller than the typical Cp(c)–M–Cp(c) angle in the corresponding 16-electron metallocene systems.[11] The less crowded metal coordination sphere, coupled with the more electron-deficient d^0 metal center associated with these $[(\eta^5\text{-}C_5R_4)SiR'_2(\eta^1\text{-}NR'')]MCl_2$ precursors, presumably enhances the ability of the active catalyst to promote facile migratory olefin insertion into the metal–carbon bond of the growing polymer chain. The apparent reduction in the tendency of the bulk polymer chain to undergo chain transfer for these "constrained geometry" catalysts further aids in the production of high-molecular-weight copolymers.

In view of the industrial importance of these compounds, considerable interest exists in the development of efficient synthetic procedures for complexation of a bifunctional *ansa*-monocyclopentadienyl amido ligand to an electrophilic group 4 metal center. The synthetic approach initially employed by Bercaw and co-workers[8] and described in detail in subsequent Dow[9] and Exxon[10] patents utilizes the metathetical reaction of the dilithio salt of $[(C_5R_4)L(NR')]^{2-}$ with the appropriate metal halide (eq 1). Okuda and co-workers[12] have employed this strategy to prepare various *ansa*-monocyclopentadienyl and *ansa*-monofluorenyl amido Ti and Zr compounds.

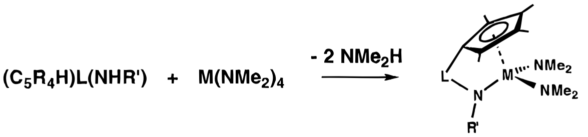
Unfortunately, in some instances this route leads to low isolated yields or isomeric mixtures. Specifically, we found that the reactions of $TiCl_4(THF)_2$ or $TiCl_3(THF)_3$ with $Li_2[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]$ consistently give



(1)

less than 5% isolated yields of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$. Furthermore, the reaction of $ZrCl_4(THF)_2$ with $Li_2[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]$ affords a nearly equimolar mixture of $\{[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl(\mu\text{-}Cl)\}_2$[13] and a THF adduct, which on the basis of NMR evidence is formulated as the lithium zirconate compound $Li(THF)_n\{[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_3\}$.[14,15] In contrast, the reactions of $Li_2[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]$ with $ZrCl_4$ or $ZrCl_4(THF)_2$ give solely $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_2$ in good isolated yields of >80%.

An alternative strategy relies upon Lappert's earlier observation that group 4 metallocene compounds can be prepared by an amine elimination reaction.[16] Teuben and co-workers[17] have adapted this strategy (eq 2) for



(2)

the synthesis of *ansa*-monocyclopentadienyl amido complexes, with L being a three-carbon linkage. The range of *ansa*-monocyclopentadienyl amido group 4 metal complexes that are accessible by this amine elimination route was recently expanded by Herrmann and co-workers,[18] who prepared a series of half-sandwich compounds featuring a dimethylsilyl linkage between a cyclopentadienyl ring or indenyl group from homoleptic $M(NMe_2)_4$ and $M(NEt_2)_4$. Jordan and co-workers[19] have also shown that the amine elimination reaction of 1,2-bis(3-indenyl)ethane and $Zr(NMe_2)_4$ provides an efficient method for the preparation of *rac*-$[C_2H_4(indenyl)_2]ZrL_2$ (L = Cl, NMe_2).

In view of the difficulties we encountered with the preparation of group 4 metal complexes of $[(C_5H_4)SiMe_2$-

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[11] For the structures of the *ansa*-monocyclopentadienyl amido Ti and Zr complexes with a dimethylsilyl bridge reported by Stevens *et al.*,[10] the Cp(centroid)–M–N bond angles range from 99.1° in $\{[(\eta^5\text{-}C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl(\mu\text{-}Cl)\}_2$ to 106.1° in $[(\eta^5\text{-}C_5Me_4)SiMe_2(NC_6H_5)]TiCl_2$.

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[13] The dimeric structure of $\{[(\eta^5\text{-}C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl(\mu\text{-}Cl)\}_2$, as confirmed by an X-ray structural analysis,[10] is maintained in solution. ^1H NMR spectrum ($CDCl_3$): δ 6.55, 6.40, 5.89, 5.56 (C_5H_4, m), 1.25 ($NCMe_3$, s), 0.57, 0.42 ($SiMe_2$, s). Gated nondecoupled ^{13}C NMR spectrum ($CDCl_3$): δ 116.8, 115.8, 114.7, 112.7 (proximal and distal carbons of C_5H_4, d, 175), 55.8 ($N\mathbf{C}Me_3$, s), 32.5 ($NC\mathbf{Me}_3$, q, 124), 5.02, 2.04 ($SiMe_2$, q, 118).

[14] ^1H NMR spectrum ($CDCl_3$): δ 6.92, 6.42 (C_5H_4, t, 2.3), 4.60 (α-CH_2(THF), br s), 2.12 (β-CH_2(THF), br s), 1.38 ($NCMe_3$, s), 0.54 ($SiMe_2$, s). Gated nondecoupled ^{13}C NMR spectrum ($CDCl_3$): δ 122.0, 121.3 (proximal and distal carbons of C_5H_4, d, 177), 78.3 (α-CH_2(THF), t, 149), 57.5 ($N\mathbf{C}Me_3$, s), 32.7 ($NC\mathbf{Me}_3$, q, 125), 25.7 (β-CH_2(THF), t, 134), 0.9 ($SiMe_2$, q, 119).

[15] Other examples of lithium organometallate compounds include the following. (a) $[Li(OEt_2)_2][(tritox)_2ZrCl_3]$: Lubben, T. V.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* **1984**, *3*, 977. (b) $[Li(THF)_3][(C_5Me_5)(C_2B_9H_{11})Sc(CH(SiMe_3)_2)]$: Bazan, G. C.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1993**, *12*, 2126. (c) $[Li(OEt_2)_2][(C_5Me_5)(C_4H_4BN(i\text{-}Pr)_2)ZrCl_2]$: Quan, R. W.; Bazan, G. C.; Kiely, A. F.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4489. (d) $[Li(TMEDA)][(C_5Me_5)(TMM)ZrCl_2]$: Bazan, G. C.; Rodriquez, G.; Cleary, B. P. *J. Am. Chem. Soc.* **1994**, *116*, 2177.

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[18] Herrmann, W. A.; Morawietz, M. J. A. *J. Organomet. Chem.* **1994**, *482*, 169.

[19] Diamond, G. M.; Rodewald, S.; Jordan, R. F. *Organometallics* **1995**, *14*, 5.

(N-*t*-Bu)]$^{2-}$ by the metathesis route, an effort was undertaken to investigate the utility of the amine elimination reaction for the syntheses of [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]M(NMe$_2$)$_2$ (M = Ti, Zr, Hf) and examine the ease of their conversion with HCl or [NEt$_3$H]Cl to the corresponding chloride adducts. In this paper we report high yield-syntheses of [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]M(NMe$_2$)$_2$ (M = Ti, Zr, Hf) and [(C$_5$Me$_4$)SiMe$_2$(N-*t*-Bu)]Zr(NMe$_2$)$_2$ from the corresponding amine elimination reaction. Treatment of [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]Ti(NMe$_2$)$_2$ with either 2 equiv of HCl or [NEt$_3$H]Cl affords a mixture of products, whereas the corresponding reactions for [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]Zr(NMe$_2$)$_2$ and [(C$_5$Me$_4$)SiMe$_2$(N-*t*-Bu)]Zr(NMe$_2$)$_2$ give the dimethylamine adduct [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]ZrCl$_2$(NMe$_2$H) and [(C$_5$Me$_4$)SiMe$_2$(N-*t*-Bu)]ZrCl$_2$, respectively. The molecular structures of [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]Ti(NMe$_2$)$_2$, [(C$_5$Me$_4$)SiMe$_2$(N-*t*-Bu)]Zr(NMe$_2$)$_2$, and [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]ZrCl$_2$(NMe$_2$H) were determined by X-ray crystallography, and the results are described herein.

Experimental Section

Reagents. Reagent grade hydrocarbon and ethereal solvents were purified using standard methods.[20] Pentane, toluene, and THF were refluxed under nitrogen over Na/K and then transferred to storage flasks containing [(C$_5$H$_5$)$_2$Ti(μ-Cl)$_2$]$_2$Zn.[21] Hexamethyldisiloxane was dried over CaH$_2$. The deuterated solvents C$_6$D$_6$ (Aldrich, 99.5%) and CDCl$_3$ (Aldrich, 99.8%) were dried over activated 4A molecular sieves prior to use, as was *t*-BuNH$_2$ (Aldrich). TiCl$_4$(THF)$_2$,[22] ZrCl$_4$(THF)$_2$,[22] HfCl$_4$(THF)$_2$,[22] C$_5$Me$_4$H$_2$,[23] and Li(C$_5$Me$_4$H)[23] were prepared by literature procedures. Ti(NMe$_2$)$_4$, Zr(NMe$_2$)$_4$, and Hf(NMe$_2$)$_4$ were prepared by treatment of TiCl$_4$(THF)$_2$, ZrCl$_4$, and HfCl$_4$ with 4 equiv of LiNMe$_2$, respectively.[19,24] Whereas Ti(NMe$_2$)$_4$ is extracted from the product residue with pentane as a yellow oil, Zr(NMe$_2$)$_4$ and Hf(NMe$_2$)$_4$ were obtained as semicrystalline solids by sublimation at 10^{-4} Torr and 40 and 60 °C, respectively. [NEt$_3$H]Cl was prepared by the stoichiometric addition of HCl to a pentane solution of NEt$_3$. TiCl$_4$ (Aldrich), *n*-BuLi (Aldrich, 1.6 M in hexanes), HCl (Matheson), LiNMe$_2$ (Aldrich), NEt$_3$ (Aldrich), dicyclopentadiene (Kodak), SiMe$_3$Cl (Aldrich), and SiMe$_2$Cl$_2$ (Aldrich or Hüls Petrarch) were used without further purification, whereas ZrCl$_4$ (Alfa) and HfCl$_4$ (Boulder Chemical) were further purified by sublimation.

General Considerations. All syntheses and manipulations were carried out on a double-manifold, high-vacuum line or in a Vacuum Atmospheres glovebox equipped with an HE-493 Dri-Train. Reactions were typically carried out in pressure-equalizing filter-frits equipped with high-vacuum Teflon stopcocks and Solv-Seal joints. Nitrogen was purified by passage over reduced BTS catalysts and activated 4A molecular sieves. All glassware was thoroughly oven-dried and/or flame-dried under vacuum prior to use. NMR sample tubes were sealed under approximately 500 Torr of nitrogen. The instrumentation employed for the ^{1}H and ^{13}C NMR measurements has been described previously.[4c] Elemental analyses were performed by Robertson Microlit Laboratories of Madison, NJ.

Syntheses of Compounds. Preparation of (*tert*-Butylamino)cyclopentadienyldimethylsilane, (C$_5$H$_5$)SiMe$_2$(N(H)-*t*-Bu). The preparation of (C$_5$H$_5$)SiMe$_2$(N(H)-*t*-Bu) was accomplished in two separate steps (eqs 3a and 3b).

$$\mathrm{NaC_5H_5} + \text{excess } \mathrm{SiMe_2Cl_2} \rightarrow \mathrm{(C_5H_5)SiMe_2Cl} + \mathrm{NaCl} \quad (3a)$$

$$\mathrm{(C_5H_5)SiMe_2Cl} + 2t\text{-}\mathrm{BuNH_2} \rightarrow \mathrm{(C_5H_5)SiMe_2(N(H)}\text{-}t\text{-}\mathrm{Bu)} + t\text{-}\mathrm{BuNH_2{\cdot}HCl} \quad (3b)$$

A 6.00 g (68.1 mmol) sample of NaC$_5$H$_5$ was added to an addition sidearm, which was then attached to a 250 mL three-neck flask. Diethyl ether (*ca.* 150 mL) and 33.0 mL (272.5 mmol) of Me$_2$SiCl$_2$ were introduced by vacuum distillation. The reaction mixture was cooled with a liquid N$_2$/propanol bath while the NaC$_5$H$_5$ was added in small portions over a 2 h period. The reaction mixture was then stirred at room temperature overnight. Following filtration, the solvent and excess Me$_2$SiCl$_2$ were collected in a liquid-N$_2$-cooled trap while the reaction flask was kept at 0 °C, leaving 8.43 g (53.1 mmol, 78% yield) of (C$_5$H$_5$)SiMe$_2$Cl as a light yellow oil.

THF (*ca.* 100 mL) and 11.2 mL of *t*-BuNH$_2$ (106.2 mmol) were added by vacuum distillation to (C$_5$H$_5$)SiMe$_2$Cl. As the reaction proceeded, a white precipitate formed. The solution was filtered and the solvent was removed under reduced pressure, leaving 8.51 g (82% yield) of (C$_5$H$_5$)SiMe$_2$(N(H)-*t*-Bu) as a yellow oil. The ^{1}H NMR spectrum of the product contains three separate sets of methyl resonances for the *tert*-butyl substituent and the dimethylsilyl linkage, consistent with the presence of three cyclopentadiene isomers.[18]

Preparation of (*tert*-Butylamino)(tetramethylcyclopentadienyl)dimethylsilane, (C$_5$Me$_4$H)SiMe$_2$(N(H)-*t*-Bu), and its Dilithio Salt. (a) Preparation of (C$_5$Me$_4$H)SiMe$_2$(N(H)-*t*-Bu). The preparation of (C$_5$Me$_4$H)SiMe$_2$(N(H)-*t*-Bu) was accomplished in two separate steps (eqs 4a and 4b). This compound was used in its protonated form for the amine elimination reactions or metalated with 2 equiv of *n*-butyllithium to produce the corresponding dilithio salt.

$$\mathrm{Li(C_5Me_4H)} + \text{excess } \mathrm{SiMe_2Cl_2} \rightarrow \mathrm{(C_5Me_4H)SiMe_2Cl} + \mathrm{LiCl} \quad (4a)$$

$$\mathrm{(C_5Me_4H)SiMe_2Cl} + 2t\text{-}\mathrm{BuNH_2} \rightarrow \mathrm{(C_5Me_4H)SiMe_2(N(H)}\text{-}t\text{-}\mathrm{Bu)} + t\text{-}\mathrm{BuNH_2{\cdot}HCl} \quad (4b)$$

THF (*ca.* 50 mL) and 9.5 mL (78.0 mmol) of SiMe$_2$Cl$_2$ were added sequentially to 3.01 g (23.0 mmol) of Li(C$_5$Me$_4$H). The reaction mixture was stirred overnight at ambient temperature. The excess SiMe$_2$Cl$_2$ and solvent were removed under vacuum and replaced by an equal volume of pentane. After filtration, the pentane was removed, leaving 4.33 g (88% yield) of (C$_5$Me$_4$H)SiMe$_2$Cl as a light yellow oil. ^{1}H NMR spectrum of the 5-isomer of (C$_5$Me$_4$H)SiMe$_2$Cl (C$_6$D$_6$): δ 2.88 (SiCH, s), 1.91, 1.70 (C$_5$Me$_4$, s), 0.13 (SiMe$_2$, s).

The entire product (20.0 mmol) was transferred to another swivel frit assembly. THF (*ca.* 50 mL) and 5.25 mL (48.0 mmol) of *tert*-butylamine were introduced, and the reaction mixture was stirred at ambient temperature. Following the removal of all of the volatiles, the product was extracted with *ca.* 30 mL of pentane, which was then removed, leaving 4.12 g (82% yield) of (C$_5$Me$_4$H)SiMe$_2$(N(H)-*t*-Bu) as a light yellow oil. ^{1}H NMR spectrum of the 5-isomer of (C$_5$Me$_4$H)SiMe$_2$(N(H)-*t*-Bu) (C$_6$D$_6$): δ 2.76 (SiCH, s), 2.01, 1.84 (C$_5$Me$_4$, s), 1.09 (NCMe$_3$, s), 0.11 (SiMe$_2$, s).

(b) Preparation of Li$_2$[(C$_5$Me$_4$)SiMe$_2$(N(H)-*t*-Bu)]. A solution of 4.12 g (16.0 mmol) of (C$_5$Me$_4$H)SiMe$_2$(N(H)-*t*-Bu) in 50 mL of diethyl ether was cooled to −78 °C. Under a N$_2$ flush 20.0 mL (32.0 mmol) of 1.6 M *n*-butyllithium was added with the aid of a syringe through the pressure-equalizing sidearm of the swivel frit. The reaction mixture was stirred overnight, and the white precipitate was collected by filtration. The product residue was washed once with 20 mL of ether

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and then dried under vacuum to afford 3.91 g (93% yield) of Li$_2$[(C$_5$Me$_4$)SiMe$_2$(N-*t*-Bu)] as a white powder.

Preparation of [(C$_5$Me$_4$)SiMe$_2$(N-*t*-Bu)]ZrCl$_2$ (1). A 2.50 g sample (9.49 mmol) of Li$_2$[(C$_5$Me$_4$)SiMe$_2$(N-*t*-Bu)] was combined with 3.58 g (9.49 mmol) of ZrCl$_4$(THF)$_2$ as a toluene solution (*ca.* 50 mL), and the mixture was stirred at ambient temperature for 3 days. After solvent removal, the product was dissolved in diethyl ether and filtered. After the product residue was washed with hexamethyldisiloxane, off-white single crystals of **1** (1.56 g, 85% yield) were obtained by recrystallization from an ether/pentane (5:1) solution. ^{1}H NMR spectrum (CDCl$_3$): δ 2.01, 1.95 (C$_5$Me$_4$, s), 1.32 (NCMe$_3$, s), 0.41 (SiMe$_2$, s). Gated nondecoupled ^{13}C NMR spectrum (CDCl$_3$): δ 134.2, 131.5 (**C**$_5$Me$_4$, s), 56.6 (N**C**Me$_3$, s), 33.1 (NC**Me**$_3$, q, 125), 14.7, 11.8 (C$_5$**Me**$_4$, q, 128), 6.0 (SiMe$_2$, q, 120). Anal. Calcd for C$_{15}$H$_{27}$Cl$_2$NSiZr: C, 43.77; H, 6.61; N, 3.40. Found: C, 42.84; H, 6.92; N, 3.13.

Preparation of [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]Ti(NMe$_2$)$_2$ (2). A 3.17 g sample (14.1 mmol) of Ti(NMe$_2$)$_4$ was combined with 2.76 g (14.1 mmol) of (C$_5$H$_5$)SiMe$_2$(N(H)-*t*-Bu) in a 100 mL Solv-Seal flask equipped with a high-vacuum adapter. The neat reaction mixture was heated at 120 °C under a modest N$_2$ purge. During the course of the reaction, an orange crystalline solid, **2**, formed and migrated up the walls of the reaction flask. Following the evacuation of volatiles, the product was collected via sublimation at 40 °C and 10^{-4} Torr. Recrystallization of **2** by slow removal of solvent from a concentrated pentane solution yielded orange crystals suitable for X-ray crystallographic analysis. Overall yield: 4.05 g (87.1% yield). ^{1}H NMR spectrum (C$_6$D$_6$): δ 6.25, 5.99 (C$_5$H$_4$, t, 2.3), 2.95 (NMe$_2$, s), 1.31 (NCMe$_3$, s), 0.51 (SiMe$_2$, s). Gated nondecoupled ^{13}C NMR spectrum (C$_6$D$_6$): δ 117.9, 116.3 (proximal and distal carbons of C$_5$H$_4$, d, 169), 107.0 (bridgehead C, s), 59.6 (N**C**Me$_3$, s), 49.6 (NMe$_2$, q, 133), 34.0 (NC**Me**$_3$, q, 124), 1.7 (SiMe$_2$, q, 119). Anal. Calcd for C$_{15}$H$_{31}$N$_3$SiTi: C, 54.69; H, 9.49; N, 12.76. Found: C, 54.40; H, 9.41; N, 12.85.

Preparation of [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]Zr(NMe$_2$)$_2$ (3). The neat reaction mixture containing 3.18 g (11.9 mmol) of Zr(NMe$_2$)$_4$ and 2.35 g (12.0 mmol) of (C$_5$H$_5$)SiMe$_2$(N(H)-*t*-Bu) was heated at 120 °C for 36 h. The NMe$_2$H was removed by a slow purge of N$_2$ and periodic evacuation. As the reaction proceeded, an off-white solid formed on the walls of the flask. The product residue was sublimed at 45 °C and 10^{-4} Torr, giving 3.33 g (75.1% yield) of **3** as a waxy solid. ^{1}H NMR spectrum (C$_6$D$_6$): δ 6.31, 6.18 (C$_5$H$_4$, t, 2.4), 2.80 (NMe$_2$, s), 1.28 (NCMe$_3$, s), 0.55 (SiMe$_2$, s). Gated nondecoupled ^{13}C NMR spectrum (C$_6$D$_6$): δ 118.4, 114.8 (proximal and distal carbons of C$_5$H$_4$, d, 169), 108.3 (bridgehead C, s), 55.9 (N**C**Me$_3$, s), 44.0 (NMe$_2$, q, 132), 34.5 (NC**Me**$_3$, q, 124), 2.34 (SiMe$_2$, q, 117). Anal. Calcd for C$_{15}$H$_{31}$N$_3$SiZr: C, 48.34; H, 8.38; N, 11.27. Found: C, 46.67; H, 8.62; N, 11.14. The low carbon analysis may reflect zirconium carbide formation.

Preparation of [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]Hf(NMe$_2$)$_2$ (4). A 0.700 g sample (1.97 mmol) of Hf(NMe$_2$)$_4$ was combined with 0.39 g (2.00 mmol) of (C$_5$H$_5$)SiMe$_2$(N(H)-*t*-Bu), and the reaction mixture was heated at 120 °C for 2 days. The volatile NMe$_2$H was removed by a N$_2$ purge and periodic evacuation of the reaction flask. As the reaction proceeded, an off-white solid collected on the walls of the flask. Sublimation of the product residue at 60 °C and 10^{-4} Torr yielded 0.715 g (70% yield) of a white waxy solid. ^{1}H NMR spectrum (C$_6$D$_6$): δ 6.30, 6.14 (C$_5$H$_4$, t, 2.5), 2.84 (NMe$_2$, s), 1.25 (NCMe$_3$, s), 0.53 (SiMe$_2$, s). Gated nondecoupled ^{13}C NMR spectrum (C$_6$D$_6$): δ 118.2, 114.7 (proximal and distal carbons of C$_5$H$_4$, d, 169), 108.0 (bridgehead C, s), 55.9 (N**C**Me$_3$, s), 44.1 (NMe$_2$, q, 132), 35.0 (NC**Me**$_3$, q, 124), 2.5 (SiMe$_2$, q, 119). Anal. Calcd for C$_{15}$H$_{31}$N$_3$SiHf: C, 39.17; H, 6.79; N, 9.13. Found: C, 37.39; H, 6.86; N, 8.70. The low carbon analysis may reflect hafnium carbide formation.

Reactions of 2 with HCl or [NEt$_3$H]Cl. A 0.200 g sample (0.607 mmol) of [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]Ti(NMe$_2$)$_2$ was placed in a two-neck flask equipped with an addition sidearm containing 0.167 g (1.21 mmol) of [NEt$_3$H]Cl. After the addition of *ca.* 50 mL of pentane, the reaction mixture was cooled with an ice bath, [NEt$_3$H]Cl was added incrementally over a period of several hours, and then the mixture was stirred overnight. The volatiles were removed, and the product residue was sublimed, yielding 0.109 g. ^{1}H NMR measurements revealed that the sublimate contained a *ca.* 3:1 mixture of [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]TiCl$_2$ (**5**) and a compound tentatively formulated as [(C$_5$H$_4$)SiMe$_2$Cl]TiCl$_2$(NMe$_2$)(NMe$_2$H) (**6**). Although crystals of **5** were obtained by slow removal of pentane from a concentrated solution of this product mixture, repeated attempts to separate **5** and **6** were unsuccessful due to their similar solubility properties. The reaction was also performed by substituting [NEt$_3$H]Cl with 2−4 equiv of HCl and adding the HCl from a calibrated gas bulb. The ^{1}H NMR spectrum of the sublimed residue consistently contained a mixture of **5** and **6**, with the relative amount of the latter compound increasing as the amount of excess HCl increased. **5**: ^{1}H NMR spectrum (C$_6$D$_6$) δ 6.60, 6.07 (C$_5$H$_4$, t, 2.3), 1.38 (NCMe$_3$, s), 0.18 (SiMe$_2$, s); ^{13}C{^{1}H} NMR spectrum (C$_6$D$_6$) δ 126.3, 125.6 (proximal and distal carbons of C$_5$H$_4$), 110.0 (bridgehead C), 63.7 (N**C**Me$_3$), 32.2 (NC**Me**$_3$), −0.2 (SiMe$_2$).[10] **6**: ^{1}H NMR spectrum (C$_6$D$_6$): δ 6.49, 6.15 (C$_5$H$_4$, t, 2.4), 3.27 (NMe$_2$, s), 2.43 (NMe$_2$H, s), 0.47 (SiMe$_2$, s); gated nondecoupled ^{13}C NMR spectrum (C$_6$D$_6$) δ 134.1 (CSi, s), 125.7, 119.4 (proximal and distal carbons of C$_5$H$_4$, d, 169), 51.2 (NMe$_2$, q, 137), 38.2 (NMe$_2$H, q, 133), 0.95 (SiMe$_2$, q, 119).

Conversion of 2 with SiMe$_3$Cl to 5. A 0.503 g sample (1.53 mmol) of **2** was dissolved in 5 mL of toluene. SiMe$_3$Cl (0.55 mL, 4.33 mmol) was added by vacuum transfer, and the reaction mixture was stirred for 24 h at 65 °C. As the reaction proceeded, the original reddish orange color of the solution became dark red and then turned orange once the reaction was complete. After removal of the volatiles, a sublimator was attached and 0.433 g (1.39 mmol) of **5** (91%) was collected by sublimation at 50−60 °C and 10^{-4} Torr. Heating the reaction mixture was necessary to ensure complete conversion; otherwise, the sublimed material contains an appreciable amount of [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]TiCl(NMe$_2$). ^{1}H NMR spectrum of **5** (CDCl$_3$): δ 7.07, 6.45 (C$_5$H$_4$, t, 2.4), 1.45 (NCMe$_3$, s), 0.60 (SiMe$_2$, s). ^{1}H NMR spectrum of [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]TiCl(NMe$_2$) (CDCl$_3$): δ 6.88, 6.35, 6.08 (C$_5$H$_4$, multiplets of 1:2:1 relative intensity, 4H), 3.01 (NMe$_2$, s), 1.33 (NCMe$_3$, s), 0.54, 0.52 (SiMe$_2$, s).

Synthesis of [(C$_5$H$_4$)SiMe$_2$(N-*t*-Bu)]ZrCl$_2$(NMe$_2$H) (7). Pentane (*ca.* 50 mL) was added to a reaction mixture of 0.709 g (1.90 mmol) of **3** and 0.524 g (3.80 mmol) of [NEt$_3$H]Cl. The reaction mixture was stirred for 6 h at ambient temperature. After removal of the volatiles, the product residue was dissolved in toluene and the resulting solution was filtered. Slow removal of toluene afforded large colorless crystals of **7** suitable for an X-ray crystallographic analysis. Recrystallization from pentane yielded 0.591 g (77.6% isolated yield) of **7**. The corresponding reaction of **3** with 2−3 equiv of HCl also leads to comparable isolated yields of **7**. ^{1}H NMR spectrum (C$_6$D$_6$): δ 6.61, 6.53 (C$_5$H$_4$, t, 2.5), 2.64 (NH, br s), 2.49 (NMe$_2$, s), 1.34 (NCMe$_3$, s), 0.49 (SiMe$_2$, s). Gated nondecoupled ^{13}C NMR spectrum (C$_6$D$_6$): δ 122.5, 119.0 (proximal and distal carbons of C$_5$H$_4$, d, 171), 110.4 (bridgehead C, s), 57.9 (N**C**Me$_3$, s), 39.6 (N**Me**$_2$H, q, 135), 31.2 (NC**Me**$_3$, q, 125), 0.95 (SiMe$_2$, q, 119). Anal. Calcd for C$_{13}$H$_{26}$N$_2$Cl$_2$SiZr: C, 38.98; H, 6.54; N, 6.99. Found: C, 38.85; H, 6.67; N, 6.83.

Preparation of [(C$_5$Me$_4$)SiMe$_2$(N-*t*-Bu)]Zr(NMe$_2$)$_2$ (8). This compound can be prepared either by the metathetical reaction of **1** with 2 equiv of LiNMe$_2$ or by the amine elimination reaction of (C$_5$Me$_4$H)SiMe$_2$(N(H)-*t*-Bu) with Zr(NMe$_2$)$_4$.

(a) Metathetical Reaction. Pentane (*ca.* 50 mL) was added to a reaction mixture of 1.00 g (2.43 mmol) of **1** and 0.248 g (4.86 mmol) of LiNMe$_2$. The reaction mixture was stirred overnight at room temperature and filtered. Slow removal of pentane yielded off-white crystals of **8** suitable for

Table 1. Crystallographic Data for the X-ray Structural Analyses of the *ansa*-Monocyclopentadienyl Amido Complexes 2, 7, and 8

	2	**7**	**8**
A. Crystal Data			
emp formula	$C_{15}H_{31}N_3SiTi$	$C_{13}H_{26}Cl_2N_2SiZr$	$C_{19}H_{39}N_3SiZr$
dimens, mm	0.10 × 0.20 × 0.50	0.20 × 0.24 × 0.50	0.28 × 0.30 × 0.38
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/n$	$P2_1/n$
a, Å	8.277(1)	7.782(1)	9.179(1)
b, Å	17.207(3)	27.915(3)	14.146(2)
c, Å	26.800(3)	8.950(1)	18.234(3)
α, deg	90	90	90
β, deg	90	101.39(1)	101.43(1)
γ, deg	90	90	90
V, $Å^3$	3816.9(9)	1906.0(4)	2320.7(6)
Z	8	4	4
fw	329.42	400.57	428.84
density, g/cm^3	1.146	1.396	1.227
μ, cm^{-1}	5.07	9.11	5.31
F(000)	1424	824	912
B. Data Collection and Structural Analyses			
scan type	ω, variable	ω, variable	ω, variable
scan rate, deg/min	2.5−10.0	2.50−10.0	2.0−10.0
2θ range, deg	3.0−45.0	3.0−45.0	3.0−50.0
rflns sampled	h ($-1 \le h \le 9$) k ($-1 \le k \le 20$) l ($-21 \le l \le 28$)	h ($-1 \le h \le 8$) k ($-1 \le k \le 30$) l ($-9 \le l \le 9$)	h ($0 \le h \le 10$) k ($0 \le k \le 16$) l ($-21 \le l \le 21$)
no. of rflns	3257	3236	4310
no. of unique data	2086	2147	3533
agreement factor	$R_{int} = 0.0429$	$R_{int} = 0.0401$	$R_{int} = 0.0299$
no. of data ($I > 2\sigma(I)$)	1283	1532	2458
abs cor	none	none	empirical, ψ scans
R indices ($I > 2\sigma(I)$)	R1 = 0.0544 wR2 = 0.0938	R1 = 0.0463 wR2 = 0.0705	R1 = 0.0515 wR2 = 0.0907
R indices (all data)	R1 = 0.1392 wR2 = 0.1221	R1 = 0.1035 wR2 = 0.0870	R1 = 0.1107 wR2 = 0.1104
σ_1, GOF	0.989	0.986	1.007
values of *a* and *b*	0.0398, 0.0	0.0235, 0.0	0.0411, 0.0
no. of variables	191	183	230
data to param ratio	10.9:1	11.7:1	15.4:1
largest diff peak and hole, e/$Å^3$	0.204, −0.201	0.297, −0.311	0.297, −0.326

X-ray crystallographic analysis. Sublimation of the product at 60 °C and 10^{-4} Torr gave 0.75 g (72% yield) of **8**.

(b) Amine Elimination Reaction. The neat reaction mixture containing 0.53 g (1.98 mmol) of $Zr(NMe_2)_4$ and 0.50 g (1.99 mmol) of $(C_5Me_4H)SiMe_2(N(H)$-*t*-Bu) was stirred at 110 °C, with the NMe_2H being flushed out with a moderate flow of N_2. As the reaction proceeded, **8** crystallized on the walls of the reaction flask. The product residue was washed with cold pentane and then purified by sublimation to give 0.58 g (67% isolated yield) of **8**. ^1H NMR spectrum (C_6D_6): δ 2.84 (NMe_2, s), 2.14, 1.90 (C_5Me_4, s), 1.33 ($NCMe_3$, s), 0.65 ($SiMe_2$, s). Gated nondecoupled ^{13}C NMR spectrum (C_6D_6): δ 127.4, 124.6 (proximal and distal carbons of C_5Me_4, s), 100.9 (bridgehead C, s), 56.0 (N**C**Me_3, s), 44.5 (NMe_2, q, 136), 34.6 (NC**Me**$_3$, q, 125), 14.0, 11.1 (C_5Me_4, q, 128), 7.44 ($SiMe_2$, q, 120). Anal. Calcd for $C_{19}H_{39}N_3SiZr$: C, 53.22; H, 9.17; N, 9.80. Found: C, 52.97; H, 9.24; N, 9.47.

X-ray Structural Analyses. The X-ray structural analyses of $[(C_5H_4)SiMe_2(N$-*t*-$Bu)]Ti(NMe_2)_2$ (**2**), $[(C_5H_4)SiMe_2(N$-*t*-$Bu)]ZrCl_2(NMe_2H)$ (**7**), and $[(C_5Me_4)SiMe_2(N$-*t*-$Bu)]Zr(NMe_2)_2$ (**8**) were performed by following the same general procedures. A single crystal of each compound was sealed in a capillary tube under a nitrogen atmosphere and then optically aligned on the goniostat of a Siemens P4 automated X-ray diffractometer. The unit cell dimensions were initially determined by indexing a set of reflections whose angular coordinates were obtained either with a rotation photograph or with the automatic peak search routine provided with XSCANS.[25] The corresponding lattice parameters and orientation matrix for the unit cell were determined from a nonlinear least-squares fit of the orientation angles of at least 20 higher order reflections at 22 °C. Pertinent crystallographic information is summarized in Table 1.

Intensity data were measured with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) and variable ω scans. Background counts were measured at the beginning and at the end of each scan with the crystal and counter kept stationary. The intensities of three standard reflections were measured after every 100 reflections. The intensity data were corrected for Lorentz−polarization and crystal decay (when appropriate). An empirical absorption correction based upon ψ-scan data was performed on **8**.

Preliminary atomic coordinates were provided by the first E-map, calculated on the basis of the phase assignments made by the direct methods structure solution software available with SHELXL-93.[26] The coordinates of all remaining non-hydrogen atoms that were not revealed on the initial E-map were located in subsequent Fourier maps. All hydrogen atoms were idealized with isotropic temperature factors set at 1.2 times that of the adjacent carbon. The initial position for the amine hydrogen atom, H(1A), bonded to N(2) of $[(C_5H_4)SiMe_2(N$-*t*-$Bu)]ZrCl_2(NMe_2H)$ was resolved in a difference Fourier map and then refined with an isotropic temperature factor. The positions of all the methyl hydrogens were optimized by a rigid rotating group refinement with idealized tetrahedral angles. Full-matrix least-squares refinements, based upon the minimization of $\sum w_i|F_o^2 - F_c^2|^2$, with $w_i^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$, were performed with

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[25] XSCANS (version 2.0) is a diffractometer control system developed by Siemens Analytical X-ray Instruments, Madison, WI.

[26] SHELXL-93 is a FORTRAN-77 program (Professor G. Sheldrick, Institut für Anorganische Chemie, University of Göttingen, D-37077 Göttingen, Germany) for single-crystal X-ray structural analyses.

Table 2. Interatomic Distances (Å) and Bond Angles (deg) for the *ansa*-Monocyclopentadienyl Dimethylsilyl-Bridged *tert*-Butylamido Group 4 Complexes 2, 7, and 8

	2	**7**	**8**
	A. Interatomic Distances		
M−N(1)	1.972(4)	2.055(5)	2.108(4)
M−Cp(c)[a]	2.083	2.195	2.233
M−L	1.924(5) (N(2)) 1.906(4) (N(3))	2.424(5) (N(2)) 2.529(2) (Cl(1)) 2.448(2) (Cl(2))	2.060(5) (N(2)) 2.064(4) (N(3))
Si−C_b[b]	1.856(6)	1.858(7)	1.871(5)
Si−N(1)	1.722(4)	1.736(5)	1.730(4)
	B. Bond Angles (deg)		
Cp(c)−M−N(1)	105.5	101.1	100.2
Cp(c)−M−L	118.7 (N(2)) 115.9 (N(3))	108.9 (Cl(1)) 108.7 (N(2)) 111.5 (Cl(2))	117.4 (N(2)) 118.2 (N(3))
Cp(c)−C_b−Si	150.3	153.4	154.2
N(1)−M−L	110.2(2) (N(2)) 102.2(2) (N(3))	91.5(2) (Cl(1)) 150.0(2) (N(2)) 93.9(1) (Cl(2))	105.6(2) (N(2)) 111.2(2) (N(3))
L−M−L	103.2(2)	75.7(2) 78.8(2) 137.3(1)	103.6(2)
C_b−Si−N(1)	93.9(2)	93.6(2)	94.5(2)
Si−N(1)−M	103.7(2)	106.0(3)	105.5(2)
C_t[c]−N(1)−Si	127.6(4)	125.6(4)	126.1(3)
C_t−N(1)−M	128.1(4)	128.4(4)	128.0(3)

[a] Cp(c) denotes the centroid of the cyclopentadienyl ring. [b] C_b corresponds to the bridgehead carbon. [c] C_t corresponds to the quaternary carbon of the *tert*-butyl group.

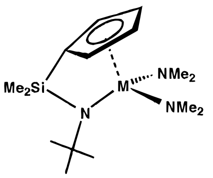
SHELXL-93[26] operating on a Silicon Graphics Iris Indigo workstation. The final values of the discrepancy indices are provided in Table 1. Their values were calculated from the expressions $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum(w_i(F_o^2 - F_c^2)^2)/\sum(w_i(F_o^2)^2)]^{1/2}$, and the standard deviation of an observation of unit weight σ_1 is equal to $[\sum(w_i(F_o^2 - F_c^2)^2)/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters varied during the last refinement cycle. Selected interatomic distances and bond angles for **2**, **7**, and **8** are compared in Table 2.

Results and Discussion

Synthesis and Characterization of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]M(NMe_2)_2$ (M = Ti, Zr, Hf) Prepared via the Amine Elimination Reaction. The homologous series of *ansa*-monocyclopentadienyl amido complexes $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]M(NMe_2)_2$ (M = Ti (**2**), Zr (**3**), Hf (**4**)) is prepared by heating the respective neat 1:1 reaction mixtures of $(C_5H_5)SiMe_2(N(H)\text{-}t\text{-}Bu)$ and $M(NMe_2)_4$ (eq 5) at 110−120 °C. The evolved NMe_2H is removed by purging the reaction mixture with nitrogen gas and/or by periodic evacuation. These compounds are isolated by sublimation of the product residue at 10^{-4} Torr and 45−60 °C. Compound **2** sublimes to produce a reddish orange semicrystalline solid, whereas compounds **3** and **4** give nearly colorless waxy solids.

$$(C_5H_5)SiMe_2(N(H)\text{-}t\text{-}Bu) + M(NMe_2)_4 \xrightarrow{-2\ NMe_2H}$$

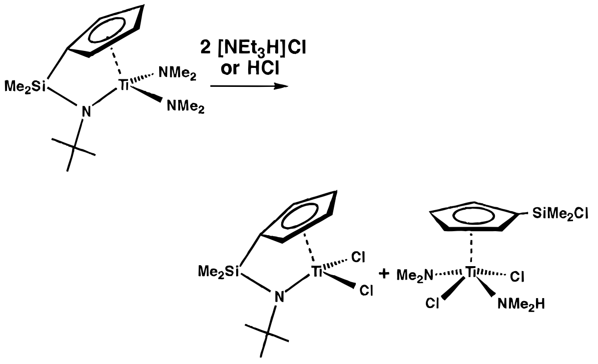
M = Ti, Zr, Hf



(5)

The overall yields obtained from these reactions typically range from 70 to 85%. These compounds were characterized in solution by ^1H and ^{13}C NMR measurements, and the molecular structure of **2** was confirmed by an X-ray structure determination (*vide infra*).

Conversion of the $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]M(NMe_2)_2$ Species to Their Chloride Derivatives. The reactions of **2** and **3** with HCl or $[NEt_3H]Cl$ were performed in an effort to produce the corresponding dichloride derivatives. The reaction of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti(NMe_2)_2$ with 2 equiv of anhydrous HCl gas or $[NEt_3H]Cl$ in toluene proceeds with the formation of two distinctly different products (eq 6). The desired dichloride derivative, $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$ (**5**), was identified by comparison of the chemical shifts of its ^1H and ^{13}C NMR resonances with those measured for an authentic sample of **5**. Several reddish orange crystals of **5** were also isolated after slow removal of solvent from a pentane solution of the product mixture. Its molecular structure was confirmed by an X-ray structural analysis.[27]



(6)

5 **6**

The remaining prominent resonances in the solution ^1H and ^{13}C NMR spectra of the product mixture are readily assigned to the other product, **6**. Surprisingly, a singlet at *ca.* δ 1.3−1.4 for the nine methyl protons of an appended *tert*-butylamido group is not observed. The pair of downfield pseudotriplets is consistent with a monosubstituted cyclopentadienyl ring bound to Ti. The quaternary ring carbon resonance is located downfield relative to the carbon resonances for the distal and proximal ring carbons, rather than upfield as in **5**. This reversal of their relative positions[28] is further evidence that the cyclopentadienyl ring in **6** is no longer chelated to the Ti through a *tert*-butylamido functionality. The ^1H resonance at δ 2.43 and the ^{13}C resonance at δ 38.2 ($^1J_{C-H}$ = 133 Hz) indicate that a molecule of NMe_2H is coordinated to Ti. The ^1H resonance at δ 3.27 and ^{13}C resonance at δ 51.2 ($^1J_{C-H}$ = 137 Hz) are consistent with the presence of a coordinated NMe_2^- group. On the basis of the NMR data, **6** is tentatively formulated as $[(C_5H_4)SiMe_2Cl]TiCl_2(NMe_2)(NMe_2H)$, which is presumably formed by the formal addition of HCl across the Si−N bond of a dimethylsilyl-*tert*-butylamino group. The

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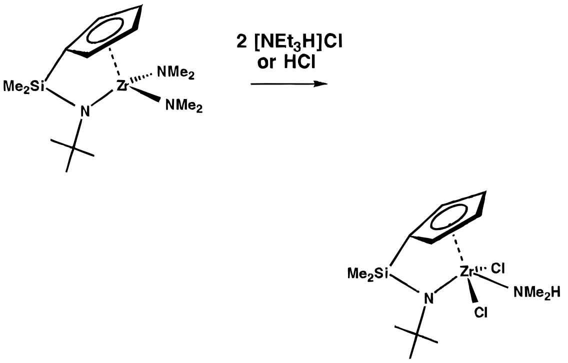
[27] Crystallographic data for **5**: triclinic, $P\bar{1}$, a = 8.348(1) Å, b = 8.482(1) Å, c = 12.863(1) Å, α = 73.75(1)°, β = 89.09(1)°, γ = 62.45(1)°, V = 768.3(2) Å^3, Z = 2, d_c = 1.349 g/cm^3, T = 295 K. Full-matrix refinement (on F_o^2) on 16 non-hydrogen atoms and 19 idealized hydrogen atoms converged with R1 = 0.0415 for 2052 data with $I > 2\sigma(I)$ and GOF = 1.078.

[28] Davis, J. H.; Sun, H.; Redfield, D.; Stucky, G. D. *J. Magn. Reson.* **1980**, *37*, 441.

driving force behind this reaction is the formation of the stronger Si−Cl bond, with a bond energy of *ca.* 13 kcal/mol higher than that of the Si−N bond.[29]

In contrast, treatment of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(NMe_2)_2$ with 2 equiv of either anhydrous HCl or $[NEt_3H]Cl$ affords only a single product, **7** (eq 7). The



(7)

7

^1H and ^{13}C NMR data are consistent with **7** being the dimethylamine adduct $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_2(NMe_2H)$, with the NMe_2H ligand situated between the two chloride ligands and lying trans to the appended amido group. The identity of **7** was confirmed by an X-ray structural analysis (*vide infra*).

The results obtained for the reactions of **2** and **3** with 2 equiv of $[NEt_3H]Cl$ or HCl indicate that the appended *tert*-butylamido ligand of **2** is susceptible to protonolysis and cleavage of the Si−N bond. The observed difference in behavior is probably a consequence of the smaller radial size of Ti, thereby resulting in a more strained metal coordination sphere and a decrease in the relative degree of $N(p_\pi)-M(d_\pi)$ overlap for the appended amido N in **2**. This combination of steric and electronic effects weakens the Ti−N(appended amido) bond, as reflected by a substantial increase in this Ti−N bond distance as determined by the X-ray structural analysis of **2** (*vide infra*).

In an effort to find an alternative strategy for its conversion to **5**, **2** was reacted with the nonprotic Cl-containing reagents $SiMe_3Cl$ and PCl_5. Although both reactions proceed with the formation of **5**, the former occurs with nearly quantitative conversion and therefore is preferred.

Descriptions of the Molecular Structures of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti(NMe_2)_2$ and $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(NMe_2)_2$. The molecular structures of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti(NMe_2)_2$ (**2**) and the related zirconium dimethylamido complex $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(NMe_2)_2$ (**8**) were determined by X-ray crystallography. Whereas **2** was produced via an amine elimination reaction (eq 5), **8** was obtained initially from the reaction of 2 equiv of $LiNMe_2$ with $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_2$ (**1**) (eq 8). The results of these structural analyses provide the opportunity to evaluate the structural changes due to the replacement of Ti with Zr and the stereoelectronic influence of the four electron-donating methyl substituents of the cyclopentadienyl ring in the chelating *ansa*-monocyclopentadienyl amido ligand.

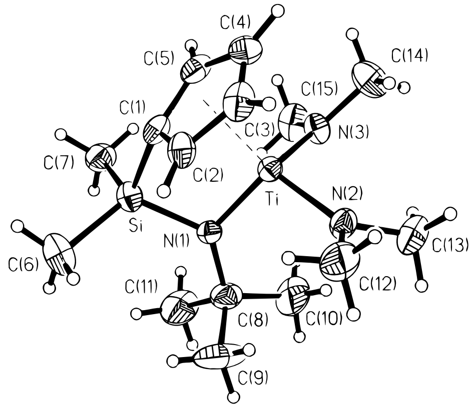


Figure 1. Perspective view of the molecular structure of **2** with the non-hydrogen atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

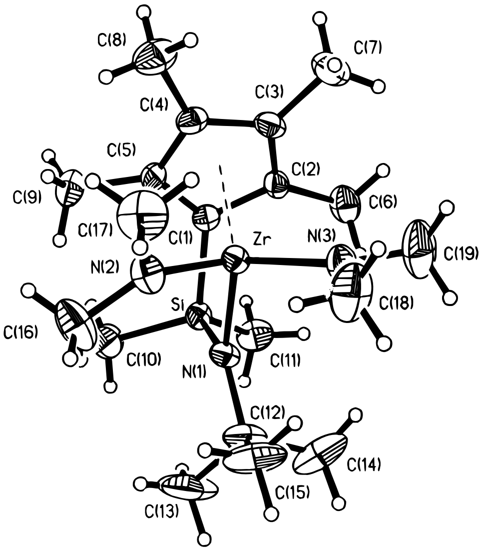


Figure 2. Perspective view of the molecular structure of **8** with the non-hydrogen atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

(8)

1 **8**

Perspective views of the molecular structures of compounds **2** and **8** are depicted in Figures 1 and 2, respectively, along with the non-hydrogen labeling scheme. These compounds exhibit the expected pseudotetrahedral geometry consisting of a bifunctional *ansa*-monocyclopentadienyl amido ligand and two terminal dimethylamido groups. The sum of the bond angles around the *tert*-butylamido N atom is essentially 360°, consistent with sp^2 hybridization. The similarity of the $C_t-N(1)-M$ and $C_t-N(1)-Si$ bond angles reflects the symmetric disposition of the *tert*-butyl substituent at the planar appended amido N.

The presence of the $SiMe_2$ bridge in **2** and **8** produces a substantial reduction of the Cp(c)−M−N(1) angle as compared to the values reported for the structurally similar unlinked monocyclopentadienyl group amido complexes listed in Table 3. For the series of uncon-

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(29) The Si−Cl bond energy in Me_3Si-Cl is 113 kcal/mol, compared to the Si−N bond energy of 100 kcal/mol in $Me_3Si-NHMe$. See: Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

Table 3. Selected Interatomic Distances (Å) and Bond Angles (deg) for Related Monocyclopentadienyl Ti and Zr Amido Complexes[a,b]

compd	M−N	M−Cp(c)	M−Cl	Cp(c)−M−N	Cl−M−Cl	ref
$(C_5H_5)Ti[N(i\text{-}Pr)_2]Cl_2$	1.865(2)	2.035	2.290(1) 2.305(1)	116.2	103.38(4)	30
$(C_5Me_5)Ti[N(i\text{-}Pr)_2]Cl_2$	1.865(5)	2.077	2.274(2) 2.291(2)	129.5	99.17(10)	30
$(C_5H_5)Ti[NH(t\text{-}Bu)]Cl_2$	1.879(3)	2.032	2.271(1)	110.7	100.28(5)	31
$(C_5H_4Me)Ti[NH(t\text{-}Bu)]Cl_2$	1.871(5)	2.036	2.261(3) 2.277(2)	110.0	100.40(9)	31
$(C_5H_5)Ti[N(SiMe_3)_2]Cl_2$	1.879(2)	2.050	2.278(1) 2.264(2)	121.2	102.97(7)	32
$[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$ (**5**)	1.901(3)	2.019	2.264(1) 2.264(2)	107.0	103.27(6)	27
$[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$	1.907(4)	2.030	2.2635(11)	107.6	102.97(7)	33
$(C_5Me_5)Ti(NMe_2)_3$	1.919(9) 1.923(14)	2.132		119.4 116.5		34
$(C_5H_5)Zr[N(i\text{-}Pr)_2]Cl_2$	1.988(4)	2.191	2.403(2) 2.416(2)	114.5	100.92(6)	30
$(C_5Me_5)Zr[N(i\text{-}Pr)_2]Cl_2$	2.003(4)	2.215	2.399(2) 2.401(2)	128.0	100.41(7)	30
$(C_5H_5)Zr[N(SiMe_3)_2]Cl_2$	2.025(3)	2.212	2.380(1) 2.398(1)	118.3	97.53(5)	35
$[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_2$ (**1**)	2.052(2)	2.163	2.4065(10) 2.4082(10)	102.0	104.92(4)	33
$[(C_5Me_4)SiMe_2(NCH_2CH_2NMe_2)]ZrCl_2$	2.077(2)		2.450(1)av		109.60(3)	36

[a] Cp(c) denotes the centroid of the cyclopentadienyl ring. [b] The esd's for the interatomic distances and bond angles were calculated from the standard errors of the fractional coordinates of the corresponding atomic positions.

strained $(C_5R_5)M[N(i\text{-}Pr)_2]Cl_2$ complexes,[30] the Cp(c)−M−N angle ranges from 114.5° in $(C_5H_5)Zr[N(i\text{-}Pr)_2]Cl_2$ to 129.5° in $(C_5Me_5)Ti[N(i\text{-}Pr)_2]Cl_2$. For the constrained $[(C_5R_4)SiMe_2(N\text{-}t\text{-}Bu)]ML_2$-type compounds (Tables 2 and 3), the "effective" bite angle of the chelating $[(C_5R_4)SiMe_2(N\text{-}t\text{-}Bu)]^{2-}$ ligand decreases with an increase in the atomic size of the metal. The Cp(c)−Ti−N angles of 105.5, 107.0, and 107.6° in **2**, $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$,[27] and $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$,[33] respectively, are consistently several degrees larger than the Cp(c)−Zr−N angles of 100.2 and 102.0° in **8** and $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_2$,[33] respectively. The constrained geometry imposed by the chelating $[(C_5R_4)SiMe_2(N\text{-}t\text{-}Bu)]^{2-}$ ligand is characterized by a substantial displacement (0.85−0.95 Å) of the Si atom from the cyclopentadienyl ring plane, as indicated by the $Cp(c)-C_b-Si$ angles, which range from 150 to 154°, and results in the internal C_b-Si-N and Si−N−M bond angles lying between 90 and 95° and between 104 and 106°, respectively.

A comparison of the pertinent bond distances of $(C_5R_5)Ti[N(i\text{-}Pr)_2]Cl_2$ with those of $[(C_5R_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$ (Table 3) indicates that the presence of the interannular bridge leads to a reduction in the Ti−Cp(c) distance and an increase in the Ti−N distance. The Ti−Cp(c) distances in $(C_5R_5)Ti[N(i\text{-}Pr)_2]Cl_2$ are 2.035 Å (R = H) and 2.077 Å (R = Me), compared to 2.019 Å (R = H) and 2.030 Å (R = Me) in $[(C_5R_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$; the Ti−N distances in $(C_5R_5)Ti[N(i\text{-}Pr)_2]Cl_2$ are 1.865(2) Å (R = H) and 1.865(5) Å (R = Me) compared to 1.901(3) Å (R = H) and 1.907(4) Å (R = Me) in $[(C_5R_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$. The longer Ti−N bonds in the latter systems are probably a consequence of the constrained geometry introduced by the chelated $[(C_5R_4)SiMe_2(N\text{-}t\text{-}Bu)]^{2-}$ ligand, preventing optimal overlap of the amido nitrogen p_π orbital with the appropriate vacant Ti d_π orbital. The observed increase in the Ti−N bond distance is compensated somewhat by a *ca.* 0.03 Å decrease in the average Ti−Cl bond distance. This variation in Ti−Cl distances is an indication that the $[(C_5R_4)SiMe_2(N\text{-}t\text{-}Bu)]^{2-}$ ligand of $[(C_5R_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$ is a poorer π-donor than the collective donation of the unlinked anionic C_5R_5 and $N(i\text{-}Pr)_2$ ligands of $(C_5R_5)Ti[N(i\text{-}Pr)_2]Cl_2$.

The structural analysis of **2** shows that the replacement of the two chloride ligands of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$ with a pair of NMe_2^- groups leads to a *ca.* 0.07 Å increase in both the Cp(c)−Ti and Ti−N(appended amido) distances. The Ti−N(appended amido) distance of 1.972(4) Å is substantially longer than the two terminal Ti−N(2) and Ti−N(3) distances of 1.924(5) and 1.906(4) Å, which are comparable in magnitude to the two crystallographically independent Ti−N distances of 1.919(9) and 1.923(14) Å in the related tris(dimethylamido) Ti(IV) complex $(C_5Me_5)Ti(NMe_2)_3$[34] and to the average Ti−N distance of 1.940(10) Å in $Ti[N(SiMe_3)_2]_3Cl$.[37] The presence of three anionic N π-donor ligands obviates their individual ability to

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(30) Pupi, R. M.; Coalter, J. N.; Petersen, J. L. *J. Organomet. Chem.* **1995**, *497*, 17.

(31) Giolando, D. M.; Kirschbaum, K.; Graves, L. J.; Bolle, U. *Inorg. Chem.* **1992**, *31*, 3887.

(32) Bai, Y.; Roesky, H. W.; Noltemeyer, M. Z. *Z. Anorg. Allg. Chem.* **1991**, *595*, 21.

(33) Crystallographic data for $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$: orthorhombic, *Pnma*, $a = 11.594(1)$ Å, $b = 13.495(1)$ Å, $c = 12.184(1)$ Å, $V = 1906.3(3)$ Å^3, $Z = 4$, $d_c = 1.283$ g/cm^3, $T = 295$ K. Full-matrix refinement (on F_o^2) on 14 independent non-hydrogen atoms and 18 idealized hydrogen atoms converged with R1 = 0.0438 for 1152 data with $I > 2\sigma(I)$ and GOF = 1.045. Crystallographic data for $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_2$ (**1**): orthorhombic, $P2_12_12_1$, $a = 8.412(1)$ Å, $b = 13.734(1)$ Å, $c = 16.812(2)$ Å, $V = 1942.3(4)$ Å^3, $Z = 4$, $d_c = 1.408$ g/cm^3, $T = 295$ K. Full-matrix refinement (on F_o^2) on 20 non-hydrogen atoms and 27 idealized hydrogen atoms converged with R1 = 0.0307 for 3886 data with $I > 2\sigma(I)$ and GOF = 1.026.

(34) Martin, A.; Mena, M.; Yelamos, C.; Serrano, R.; Raithby, P. R. *J. Organomet. Chem.* **1994**, *467*, 79.

(35) Crystallographic data for $(C_5H_5)Zr[N(SiMe_3)_2]Cl_2$: orthorhombic, $P2_12_12_1$, $a = 7.0976(4)$ Å, $b = 13.5722(11)$ Å, $c = 18.9760(16)$ Å, $V = 1828.0(2)$ Å^3, $Z = 4$, $d_c = 1.408$ g/cm^3, $T = 295$ K. Full-matrix refinement (on F_o^2) on 17 independent non-hydrogen atoms and 23 idealized hydrogen atoms converged with R1 = 0.0299 for 2849 data with $I > 2\sigma(I)$ and GOF = 1.029.

(36) du Plooy, K. E.; Moll, U.; Wocaldo, S.; Massa, W.; Okuda, J. *Organometallics* **1995**, *14*, 3129.

donate fully their respective p_π electron pair to the electrophilic d^0 Ti center. Consequently, it is not surprising to find that all of the Ti−N distances in these three tris(amido) Ti complexes are substantially longer than the Ti−N bonds observed in $(C_5R_5)Ti(NR_2)Cl_2$.

The orientations of the two planar NMe_2^- ligands with respect to the Ti, N(2), N(3) plane in **2** are quite different. The plane passing through N(2), C(12), C(13) exhibits a dihedral angle of 11.6°, whereas the other plane passing through N(3), C(14), C(15) is rotated in the opposite direction by 55.4°. As this dihedral angle increases from 0° to 90°, the orientation of the filled N p_π orbital of NMe_2^- becomes better aligned to donate into a vacant Ti d_π orbital lying in the Ti, N(2), N(3) plane and therefore should be accompanied by a reduction in the corresponding Ti−N distance. In this case, the larger dihedral angle for the N(3), C(14), C(15) plane is accompanied by only a modest (*ca.* 0.02 Å) decrease in the Ti−N(3) distance.

The molecular structure of **8** exhibits essentially the same general structural features as noted for **2**. The Cp(c)−Zr and Zr−N(1) distances of 2.233 and 2.108(4) Å in **8** are noticeably longer than the corresponding distances of 2.163 and 2.052(2) Å in the dichloride precursor, $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_2$ (Table 3). The planar NMe_2^- ligand containing N(3), C(18), C(19) lies nearly parallel (11.4°) to the Zr, N(2), N(3) plane, whereas the other amido ligand containing N(2), C(16), and C(17) is rotated by 52.2° in the opposite direction. However, the larger dihedral angle for the latter does not produce a noticeable reduction in the Zr−N(2) distance. The nearly equal Zr−N(2) and Zr−N(3) distances of 2.060(5) and 2.064(4) Å, respectively, are comparable to the average Zr−N distances of 2.07 Å in $Zr(NMe_2)_4$,[38] of 2.06 Å in $(Me_2N)_2Zr(\mu\text{-}N\text{-}t\text{-}Bu)_2Zr(NMe_2)_2$,[39] of 2.06 Å in *rac*-$[C_2H_4(indenyl)_2]Zr(NMe_2)_2$,[40] and of 2.070 and 2.080 Å in $Zr[(N(SiMe_3)_2]_3X$ (X = Cl,[41] Me[41]) and are thereby typical for an amido ligand bound to a d^0 Zr center with appreciable π-bonding. However, they are substantially longer than the Zr−N bond distances of 1.988(4) and 2.003(4) Å in $(C_5H_5)Zr[N(i\text{-}Pr)_2]Cl_2$ and $(C_5Me_5)Zr[N(i\text{-}Pr)_2]Cl_2$, respectively, in which the lone amido ligand competes more effectively with the weaker Cl ligands as a π-donor.

Description of the Molecular Structure of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_2(NMe_2H)$. The molecular structure determination of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_2(NMe_2H)$ (**7**) provides the opportunity to evaluate the structural consequences resulting from the incorporation of another ligand, in this case NMe_2H, into the pseudotetrahedral metal coordination sphere of a $[(C_5R_4)SiMe_2(N\text{-}t\text{-}Bu)]ML_2$-type complex. The perspective view of **7** depicted in Figure 3 shows that its molecular geometry resembles that of a four-legged piano stool. The amine ligand is situated symmetrically between the two terminal chlorides and lies trans to the appended amido N atom with the N(1)−Zr−N(2) bond angle being 150.0(2)°. The N(1)−Zr−Cl(1) and N(1)−Zr−Cl(2) bond angles in **7** are 91.5(2) and 93.9(1)°, respectively, and the corresponding Cl(1)−Zr−Cl(2) bond angle is 137.3(1)°. The Zr−N(2) distance of 2.424(5) Å is consistent with a Zr−N(sp^3) single bond. Recently, Okuda and coworkers[36] reported the synthesis and structural characterization of $[(C_5Me_4)SiMe_2(NCH_2CH_2NMe_2)]ZrCl_2$, in which the amido group contains an appended dimethylamino functionality that also coordinates to Zr. The short ethylene linkage between the amido and amino nitrogens constrains the amino group to occupy an apical position trans to the cyclopentadienyl ring of the trigonal-bipyramidal geometry at Zr. This ligand arrangement results in an acute N(amido)−Zr−N(amine) bond angle of 70.69(9)°, a Cl(1)−Zr−Cl(2) bond angle of 109.60(3)°, and a rather long Zr−N(amine) bond distance of 2.491(2) Å. Jordan and co-workers[42] observed a similarly long $Zr-N(NMe_2H)$ distance of 2.497(4) Å in the seven-coordinate complex $(Me_4taen)ZrCl_2(NMe_2H)$, where Me_4taen is a dianionic 14-membered N_4 macrocyclic ligand.

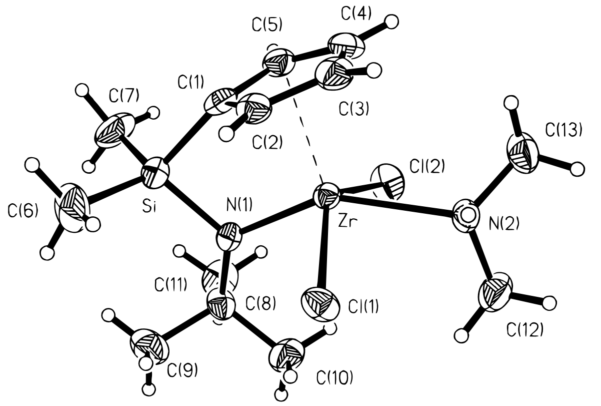

Figure 3. Perspective view of the molecular structure of **7** with the non-hydrogen atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

A comparison of the relevant bond distances of **7** with those of $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_2$ (Table 3) reveals that the NMe_2H ligand in the former has little or no influence on the Cp(c)−Zr or the Zr−N(1) distance. The more congested Zr coordination sphere in **7** leads to an elongation of both Zr−Cl bonds and is accompanied by expected decreases in the Cp(c)−Zr−L bond angles. Whereas the Zr−Cl(2) bond distance of 2.448(2) Å is compatible with that observed in 16-electron Cp_2ZrCl_2-type complexes,[4c,43] the Zr−Cl(1) bond of 2.529(2) Å is unusually long. This large disparity in the two Zr−Cl bonds of **7** is apparently due to intermolecular hydrogen bonding between the amine hydrogen, H(1A), and Cl(1) of a each pair of molecules of **7** related by a crystallographic center of inversion in the crystal lattice. This interaction is depicted in Figure 4. After the refined coordinates of H(1A) are corrected to account

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(37) Airoldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Abdul Malik, K. M.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2010.

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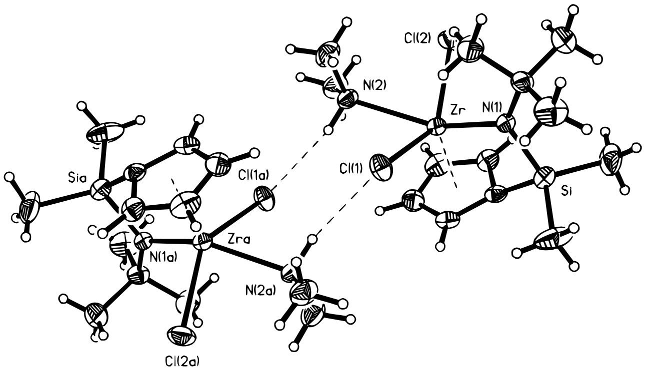

Figure 4. Perspective view of the intermolecular hydrogen bonding between molecular pairs of **7** that are related by a crystallographic center of inversion.

for the inherent shortening of its X-ray-determined position, the H(1A)···Cl(1a) separation is *ca.* 2.4 Å.

Concluding Remarks. The thermally induced amine elimination reactions of $(C_5H_5)SiMe_2(N(H)\text{-}t\text{-}Bu)$ with $M(NMe_2)_4$ offer convenient synthetic routes for the preparation of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]M(NMe_2)_2$ (M = Ti (**2**), Zr (**3**), Hf (**4**)) in consistently good isolated yields. Although we were successful in extending this strategy to the preparation of $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(NMe_2)_2$ (**8**), our parallel effort to prepare the Ti analog by the 1:1 neat reaction of $(C_5Me_4H)SiMe_2(N(H)\text{-}t\text{-}Bu)$ with $Ti(NMe_2)_4$ led to a myriad of products. Protonolyses of **3** and **8** with 2 equiv of either $[NEt_3H]Cl$ or HCl afford $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_2(NMe_2H)$ (**7**) and $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_2$ (**1**), respectively. The ligation of NMe_2H in **7** prevents dimer formation and thereby provides a more attractive reagent for the preparation of other derivatives for future reactivity studies. In contrast, the corresponding reaction of **2** with 2 equiv of $[NEt_3H]Cl$ yields a product mixture containing mainly $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$ (**5**) contaminated with a substantial amount of **6**, tentatively formulated as $[(C_5H_4)SiMe_2Cl]TiCl_2(NMe_2)(NMe_2H)$. Its presence indicates that the appended *tert*-butylamido functionality of **2** is susceptible to protonolysis and cleavage of its Si−N bond. Alternatively, the reaction of **2** with $SiMe_3Cl$ provides a convenient method for its efficient conversion to **5**.

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Supporting Information Available: Tables of the positional and thermal parameters for all of the non-hydrogen and hydrogen atoms and of the interatomic distances and bond angles for **2**, **7**, and **8** (16 pages). Ordering information is given on any current masthead page. Structure factor tables for these compounds are available from the authors upon written request.

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