Synthesis and Characterization of Unusual Dichloro(amido)-Bridged Zirconium Complexes. X-ray Crystal Structures of $(Me_2N)_3Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_2(THF)$ and $Cl(Me_2N)_2Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_2(THF)$

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Reactions of 3 and 2 equiv of lithium dimethylamide with $ZrCl_4$ in THF afford dinuclear complexes $(Me_2N)_3Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_2(THF)$ (**1**) and $Cl(Me_2N)_2Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_2(THF)$ (**2**), respectively. These complexes were found to have unusual structures containing dichloro(amido) bridges between Zr atoms. Both complexes **1** and **2** crystallize in the monoclinic space group $P2_1/c$ ($a = 8.735(3)$ Å, $b = 21.498(7)$ Å, $c = 13.997(5)$ Å, $\beta = 92.56(3)°$, $Z = 4$ for **1**; $a = 8.550(3)$ Å, $b = 20.673(7)$ Å, $c = 14.229(6)$ Å, $\beta = 95.11(3)°$, $Z = 4$ for **2**). Each Zr atom in **1** and **2** has a trigonal antiprismatic coordination geometry. Reaction of 1 equiv of lithium dimethylamide with $ZrCl_4$ in THF gave the monosubstituted complex as the LiCl adduct $(Me_2N)(THF)ZrCl_2(\mu\text{-}Cl)_2Li(THF)_2$ (**4**), which crystallizes in the triclinic space group $P\bar{1}$ ($a = 10.078(6)$ Å, $b = 11.003(7)$ Å, $c = 11.039(6)$ Å, $\alpha = 84.75(5)°$, $\beta = 78.38(5)°$, $\gamma = 66.65(5)°$, $Z = 2$). In **4**, the Zr atom has a distorted octahedral coordination geometry. These new amido complexes add to the missing members of the $Zr(NMe_2)_xCl_{4-x}$ series. The dynamic NMR of **1** has also been studied.

Introduction

Early-transition-metal dialkylamido chloride complexes are versatile starting materials for inorganic and organometallic amide derivatives. The syntheses and structural studies of group IV metal dialkylamides and chloro(dialkylamides) have attracted wide interest.[1−4] Titanium amide (and ammonia) complexes have also been used in the chemical vapor deposition (CVD) of titanium nitride thin films.[5] The crystal structures of $Ti(NR_2)_3Cl$ (R = Me, Et),[2] $[Zr(NMe_2)_4]_2$,[3] $Zr(NMe_2)_6Li_2(THF)_2$,[3] and $(R_2N)_2ZrCl_2(THF)_2$ (R = Me, Et)[4] have been reported by Stephan, Chisholm, Kempe, and their co-workers. Winter and co-workers have recently prepared titanium complexes bearing η^2-pyrazolato ligands.[6] Our interest lies in exploring the chemistry of d^0 early-transition-metal silyl complexes free of cyclopentadienyl (Cp^-) or other anionic π ligands, and we have reported a series of Cp-free alkyl silyl complexes of d^0 early transition metals (M = Ti, Zr, Ta, W).[7] Our interest in these zirconium amido chloro complexes was stimulated by their use as precursors to amido silyl complexes, as well as by our recent discovery that $(Me_3CCH_2)_3ZrCl$ has a unique structure containing linear symmetric polymeric −Zr−Cl−Zr−Cl− chains.[8] The structure of this alkyl chloro complex led us to study its amido analogue $(Me_2N)_3ZrCl$.[9] Consequently we were able to prepare new amido chloro complexes $(Me_2N)_3Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_2(THF)$ (**1**) and $Cl(Me_2N)_2Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_2(THF)$ (**2**), and we found that they contain unusual dichloro(amido) bridges between Zr atoms. We report here the syntheses, characterization, and structures of these dinuclear zirconium complexes, as well as the synthesis and structure of $(Me_2N)(THF)ZrCl_2(\mu\text{-}Cl)_2Li(THF)_2$ (**4**). These new amido complexes add to the missing members of the $Zr(NMe_2)_xCl_{4-x}$ family.

Experimental Section

All manipulations were performed either in a glovebox or using Schlenk techniques under nitrogen. All solvents were purified by distillation from potassium benzophenone ketyl. NMR solvents were dried and stored over 5 Å molecular sieves. $ZrCl_4$ (Strem) was sublimed before use. $LiNMe_2$ (Aldrich) was used as received. NMR spectra were recorded on Bruker AC-250 and AMX-400 Fourier transform spectrometers. Chemical shifts were referenced to solvents (residual protons in the ^1H spectra). Elemental analyses were carried out by E+R Microanalytical Laboratory, Inc., Corona, NY.

Synthesis of Pentakis(dimethylamido)(tetrahydrofuran)bis(μ-chloro)(μ-dimethylamido)dizirconium, $(Me_2N)_3Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_2(THF)$ (1). $ZrCl_4$ (5.0 g, 21.5 mmol) and 30 mL of THF were stirred at 0 °C to form a white slurry. At −40 °C, 3.28 g (64.3 mmol) of $LiNMe_2$ in 20 mL of THF was added dropwise with stirring.

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The reaction solution was then slowly warmed to room temperature. After 3 h, the THF was removed to yield a pale yellow solid, which was extracted with hot hexanes (50 °C) to give a pale yellow solution. This hot hexane solution was filtered and slowly cooled to room temperature, producing 2.15 g of **1** as yellow crystals. The mother solution was then filtered, concentrated, and cooled to −16 °C to give another 2.0 g of product (overall yield 65%). ^{1}H NMR (250.1 MHz, benzene-d_6, 24 °C): δ 3.66 (m, 4H, THF), 2.94 (s, 36H, N*Me*$_2$), 1.31 (m, 4H, THF). ^{1}H NMR (400.1 MHz, toluene-d_8, −80 °C): δ 3.74 (m, 4H, THF), 3.51 (s, 18H, N*Me*$_2$), 3.12 (s, 6H, μ-N*Me*$_2$), 2.98 (s, 12H, N*Me*$_2$), 0.90 (m, 4H, THF). ^{13}C{^{1}H} NMR (62.9 MHz, benzene-d_6, 24 °C): δ 69.7 (THF), 43.9 (N*Me*$_2$), 5.6 (THF). ^{13}C{^{1}H} NMR (100.6 MHz, toluene-d_8, −80 °C): δ 73.6 (THF), 45.8 (N*Me*$_2$), 45.4 (μ-N*Me*$_2$), 44.4 (N*Me*$_2$), 25.3 (THF). Anal. Calcd for $C_{16}H_{44}N_6OCl_2Zr_2$: C, 32.58; H, 7.52. Found: C, 32.41; H, 7.38.

Synthesis of Chlorotetrakis(dimethylamido)(tetrahydrofuran)bis(μ-chloro)(μ-dimethylamido)dizirconium, $Cl(Me_2N)_2Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_2(THF)$ (2), and Dichlorobis(dimethylamido)bis(tetrahydrofuran)zirconium, $(Me_2N)_2ZrCl_2(THF)_2$ (3). To a slurry of $ZrCl_4$ (5.0 g, 21.5 mmol) in 40 mL of THF at −40 °C was added dropwise 2 equiv of $LiNMe_2$ (2.19 g, 42.9 mmol) in 30 mL of THF. The reaction solution was stirred at room temperature for 2 days. After removal of THF in vacuo, the pale yellow residue was extracted with hot hexanes (40 °C). A large amount of pale yellow crystals formed, along with some rodlike yellow crystals, when the resulting solution was slowly cooled to room temperature. The two crystalline domains were separated, yielding 0.62 g of **2** as yellow crystals (10% yield based on $ZrCl_4$) and 3.23 g of **3** as pale yellow crystals (38% yield based on $ZrCl_4$). The NMR spectra of **3** were found to be identical to those reported in the literature.[4] ^{1}H NMR for **2** (250.1 MHz, benzene-d_6, 24 °C): δ 3.72 (m, 4H, THF), 3.12 (s, 30H, N*Me*$_2$), 1.16 (m, 4H, THF). ^{13}C{H} NMR (62.9 MHz, benzene-d_6, 24 °C): δ 72.3 (THF), 44.8 (NMe_2), 25.4 (THF). Anal. Calcd for $C_{14}H_{38}Cl_3N_5OZr_2$ (**2**): C, 28.93; H, 6.59. Found: C, 28.73; H, 6.66.

Formation of 2 by Reaction of 1 and 3. ^{1}H and ^{13}C NMR spectra of a mixture of **1** (25 mg) and 2 equiv of **3** (33.4 mg) in benzene-d_6 showed **2** to be the only species in solution.

Formation of 1 by Reaction of 3 and $(Me_2N)_4Zr$. ^{1}H and ^{13}C NMR spectra of a mixture of **3** (30 mg) and 1 equiv of $(Me_2N)_4Zr$ (20 mg) in benzene-d_6 showed the product to be **1**.

Synthesis of Dichloro(dimethylamido)tris(tetrahydrofuran)bis(μ-chloro)lithiumzirconium, $(Me_2N)(THF)ZrCl_2(\mu\text{-}Cl)_2Li(THF)_2$ (4). $ZrCl_4$ (5.0 g, 21.5 mmol) was mixed with THF (30 mL) to afford a white slurry. $LiNMe_2$ (1.09 g, 21.3 mmol) in 30 mL of THF was then added dropwise with stirring at −5 °C. The reaction solution gradually turned pale yellow and was allowed to warm to room temperature overnight. The solution was then concentrated to 20 mL and layered with Et_2O (20 mL), initiating crystallization. After 12 h, the resultant pale yellow crystals were filtered and dried, yielding 8.55 g of **4** (80.0% yield). ^{1}H NMR (250.1 MHz, benzene-d_6, 24 °C): δ 3.80 (m 12H, THF), 3.36 (s, 6H, N*Me*$_2$), 1.30 (m, 12H, THF). ^{13}C{H} NMR (62.9 MHz, benzene-d_6, 24 °C): δ 71.8 (THF), 45.7 (NMe_2), 25.4 (THF). Anal. Calcd: C, 33.61; H, 6.04. Found: C, 33.43; H, 5.91.

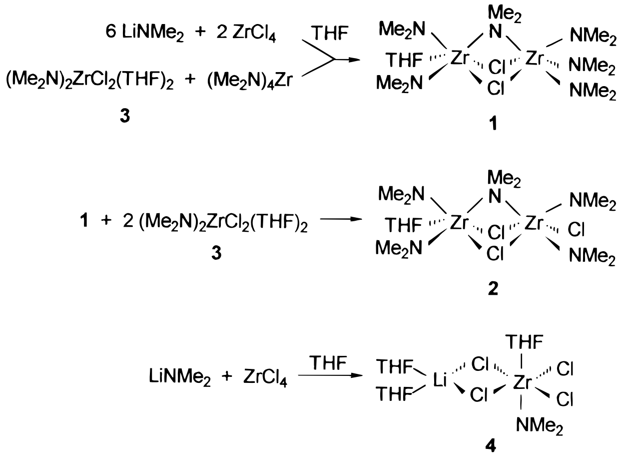
X-ray Structural Determinations. X-ray-quality crystals of **1**, **2**, and **4** were obtained from the procedures described above. Data were collected at −100 °C on a Siemens R3m/V diffractometer fitted with a Nicolet LT-2 low-temperature device. Suitable crystals were coated with Paratone oil (Exxon) and mounted under a stream of nitrogen. The unit cell dimensions were calculated from the angular settings of 30−40 randomly located reflections in reciprocal space and were confirmed by the use of axial photographs. The complexes **1** and **2** were found to crystallize in the monoclinic system, and **4** was found to crystallize in the triclinic system. Crystal data are summarized in Table 1. The data were corrected for Lorentz and polarization effects during data reduction. Absorption corrections based on ψ-scans were applied to the data for **1** and **2**.

Table 1. Crystallographic Data for Complexes **1**, **2**, and **4**

	1	**2**	**4**
formula	$C_{16}H_{44}Cl_2N_6OZr_2$	$C_{14}H_{38}Cl_3N_5OZr_2$	$C_{14}H_{30}Cl_4NO_3LiZr$
fw	589.91	581.28	500.35
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	8.735(3)	8.550(3)	10.078(6)
b, Å	21.498(7)	20.673(7)	11.003(7)
c, Å	13.997(5)	14.229(6)	11.039(6)
α, deg	90	90	84.75(5)
β, deg	92.56(3)	95.11(3)	78.38(5)
γ, deg	90	90	66.65(5)
V, Å^3	2626(2)	2505(2)	1100.7(11)
Z	4	4	2
ρ_{calc}, g/cm^3	1.492	1.541	1.510
μ, cm^{-1}	10.14	11.64	9.96
T, °C	−100	−100	−100
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73
R1 (wR2)[a]	0.0434 (0.0950)	0.0283 (0.0685)	0.0491 (0.1159)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$.

Scheme 1



The structures were solved by direct methods using the Siemens SHELXTL-93 (Version 5.0) proprietary software package and were completed by successive Fourier syntheses. All non-hydrogen atoms in the structures of **1**, **2**, and **4** were anisotropically refined by full-matrix least squares. In **4**, the NMe_2 ligand, as well as one of the THF molecules bonded to Li, was found to be disordered. The NMe_2 group was refined as two rotamers separated by ca. 90°, and the site occupation factors of the two sets of Me carbons were refined to values of 0.61 and 0.39, respectively. The disordered THF molecule was fitted to a five-membered ring whose 1,2 and 1,3 distances were restrained to be approximately equal by the use of similarity restraints in the refinement. The hydrogen atoms were placed at calculated positions and introduced into the refinement as fixed contributors with isotropic *U* values of 0.08 Å^2.

We also determined the X-ray structure of **3**, which was found to be the same as reported in the literature.[4]

Results and Discussion

Syntheses. Mononuclear titanium amido and amido chloro complexes $(Me_2N)_4Ti$,[10] $(Me_2N)_3TiCl$,[2] and $(Me_2N)_2TiCl_2$[11] were prepared either by the replacement of chloride in $TiCl_4$ by $LiNMe_2$ or through comproportionation reactions between $(Me_2N)_4Ti$ and $TiCl_4$ in nonpolar solvents such as benzene, toluene, or hexane. However, comproportionation reactions between $(Et_2N)_4Zr$ and $ZrCl_4$ in ether or toluene were reported to give mixtures of products, but utilization of Et_2O/THF as solvent afforded mononuclear complexes $(R_2N)_2ZrCl_2(THF)_2$ (R = Me, **3**; Et).[4]

The syntheses of the new complexes **1**, **2**, and **4** in the current study are shown in Scheme 1. The dinuclear complexes were synthesized by the direct reactions of $ZrCl_4$ and $LiNMe_2$ in THF.

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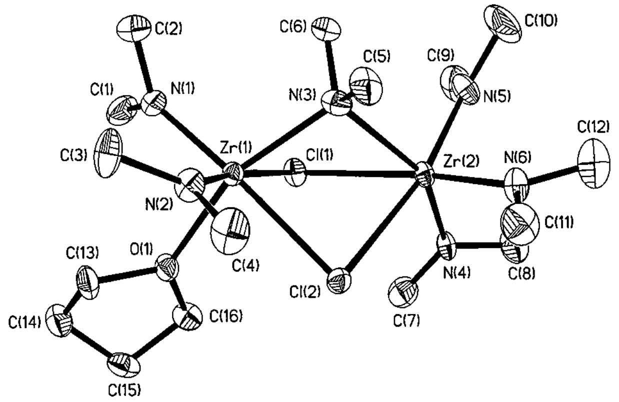

Figure 1. ORTEP view of the molecular structure of $(Me_2N)_3Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_2(THF)$ (**1**), showing 50% thermal ellipsoids.

Complex $(Me_2N)_3Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_2(THF)$ (**1**) was prepared by reaction of 3 equiv of $LiNMe_2$ with $ZrCl_4$ in THF and purified by crystallization from hexanes. **1** can also be prepared by the ligand redistribution reaction between **3** and $(Me_2N)_4Zr$ in benzene. Recently, the solvent-free $(Me_2N)_3ZrCl$ complex has been prepared by reaction of $ZrCl_4$ with $LiNMe_2$ in ether.[9]

Pure $Cl(Me_2N)_2Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)(THF)$ (**2**) can be prepared by ligand redistribution between **1** and 2 equiv of **3** in benzene (Scheme 1). However, all attempts to prepare pure **2** directly from $ZrCl_4$ and $LiNMe_2$ were unsuccessful, as mixtures of **2** and **3** were produced.

$(Me_2N)_2ZrCl_2(THF)_2$ (**3**) was recently prepared through comproportionation of $(Me_2N)_4Zr$ and $ZrCl_4$ in ether containing 2 equiv of THF.[4] In the current study, **3** was made from $ZrCl_4$ and 2 equiv of $LiNMe_2$ in THF. In addition, we also prepared the monosubstituted complex $(Me_2N)(THF)ZrCl_2(\mu\text{-}Cl)_2Li(THF)_2$ (**4**) (Scheme 1), which crystallizes from THF/Et_2O as the LiCl adduct.

Solid-State Structures. $(Me_2N)_3Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_2(THF)$ (1). An ORTEP view of the molecule is shown in Figure 1, and selected bond distances and angles are listed in Table 2. Both zirconium atoms are hexacoordinate: one by two bridging chloride ligands and one bridging and three terminal amido ligands; the other by one bridging and two terminal Me_2N ligands, two bridging chloride ligands, and a THF molecule. The geometry around each zirconium atom can be described as a distorted trigonal antiprism, and the terminal ligands around each Zr are nearly staggered with respect to the bridging ligands.

Zr(IV) complexes usually tend to form doubly bridging planar structures, as observed in $[(Me_2N)_3Zr(\mu\text{-}NMe_2)]_2$[3] and $-[-ZrCl_2(\mu\text{-}Cl)_2ZrCl(\mu\text{-}Cl)_2-]-$.[12] In $(Me_3CCH_2)_3ZrCl$, a linear symmetric polymeric $Zr-Cl-Zr-Cl-$ structure is adopted.[8] The most interesting feature of the structure of **1** is the unusual mixed triply bridging unit $Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr$. Triply bridged Zr complexes are rare, as only three other structures containing trichloro-bridged Zr atoms have, to our knowledge, been reported by Cotton,[13] Floriani,[14] and their co-workers. The structures of **1** and **2** (see discussion below) represent the first Zr(IV) complexes containing triply bridged Zr centers with different bridging ligands. In contrast, the solvent-free $(Me_2N)_3ZrCl$ complex, prepared recently by Kempe et al., adopts a Me_2N-bridging dimeric structure $[Cl(Me_2N)_2Zr(\mu\text{-}NMe_2)]_2$.[9] The Ti analogue of **1**, $(Me_2N)_3TiCl$, was found to have a monomeric structure.[2] This difference is probably due to the larger size of Zr(IV) relative to Ti(IV); ZrL_4-type complexes usually are sterically and coordinatively unsaturated and tend to form bridging or solvated complexes as shown in the trigonal pyramidal structures of $[Zr(NMe_2)_4]_2$,[3] $[Cl(Me_2N)_2Zr(\mu\text{-}NMe_2)]_2$,[9] and $(Me_3CCH_2)_3ZrCl$[8] and octahedral structures of $ZrCl_4$[12] and $(Me_2N)_2ZrCl_2(THF)_2$.[4] An exception to this observation is the unsolvated monomeric structures observed in $[(Me_3Si)_2N]_3ZrCl$[15d] and $(Me_3CCH_2)_3ZrSi(SiMe_3)_3$,[7e] which contain bulky silylamido and silyl ligands, respectively.

Table 2. Selected Bond Distances (Å) and Angles (deg) in **1**

Distances

Zr(1)−Zr(2)	3.5792(14)	Zr(2)−N(3)	2.408(5)
Zr(1)−N(1)	2.035(5)	Zr(2)−N(4)	2.078(5)
Zr(1)−N(2)	2.047(5)	Zr(2)−N(5)	2.056(6)
Zr(1)−N(3)	2.221(5)	Zr(2)−N(6)	2.083(6)
Zr(1)−Cl(1)	2.649(2)	Zr(2)−Cl(1)	2.742(2)
Zr(1)−Cl(2)	2.645(2)	Zr(2)−Cl(2)	2.733(2)
Zr(1)−O(1)	2.244(4)	$C-N_{av}$	1.457(9)

Angles

Cl(1)−Zr(1)−Cl(2)	78.16(6)	Cl(1)−Zr(2)−Cl(2)	75.12(5)
N(1)−Zr(1)−Cl(1)	89.3(2)	N(3)−Zr(2)−Cl(1)	71.54(14)
N(2)−Zr(1)−Cl(1)	171.8(2)	N(4)−Zr(2)−Cl(1)	82.7(2)
N(1)−Zr(1)−Cl(2)	165.4(2)	N(5)−Zr(2)−Cl(1)	96.3(2)
N(2)−Zr(1)−Cl(2)	93.8(2)	N(6)−Zr(2)−Cl(1)	165.5(2)
N(3)−Zr(1)−Cl(1)	76.17(14)	N(3)−Zr(2)−Cl(2)	74.76(13)
N(3)−Zr(1)−Cl(2)	79.6(2)	N(4)−Zr(2)−Cl(2)	90.6(2)
N(1)−Zr(1)−N(2)	98.9(2)	N(5)−Zr(2)−Cl(2)	168.7(2)
N(1)−Zr(1)−N(3)	104.7(2)	N(6)−Zr(2)−Cl(2)	91.9(2)
N(2)−Zr(1)−N(3)	100.8(2)	N(3)−Zr(2)−N(4)	152.8(2)
N(1)−Zr(1)−O(1)	88.9(2)	N(3)−Zr(2)−N(5)	95.7(2)
N(2)−Zr(1)−O(1)	96.5(2)	N(3)−Zr(2)−N(6)	99.2(2)
N(3)−Zr(1)−O(1)	155.9(2)	N(4)−Zr(2)−N(5)	95.6(2)
O(1)−Zr(1)−Cl(1)	84.38(12)	N(4)−Zr(2)−N(6)	104.1(2)
O(1)−Zr(1)−Cl(2)	82.59(12)	N(5)−Zr(2)−N(6)	95.7(2)
Zr(1)−N(3)−Zr(2)	101.2(2)	Zr(1)−Cl(1)−Zr(2)	83.17(5)
Zr(1)−Cl(2)−Zr(2)	83.43(5)		

The trans angles around the Zr atoms in **1** are close to those found in the octahedral structure of $(Me_2N)_2ZrCl_2(THF)_2$.[4] The bridging Zr−N−Zr angle is about 3° smaller than that in $[Zr(NMe_2)_4]_2$.[3] The Cl−Zr−Cl angles (78.16(6)° and 75.12(5)°) are similar to that (79.5°) found in $ZrCl_4$.[12] However, the Zr−Cl−Zr angles (83.17(5)° and 83.43(5)°) are close to those in $[Ph_4P][Zr_2Cl_9]$ (78.20(8)°, 87.45(9)°, and 87.7(11)°)[13] and $[\eta^2\text{-}(C_6Me_6)Zr_2(\mu\text{-}Cl)_3Cl_5]$ (88.4(1)° and 90.3(1)°)[14] and much smaller than that in $ZrCl_4$ (100.5°).[12]

The distance between the two Zr atoms is 3.5792(14) Å, which is close to that found in $[Ph_4P][Zr_2Cl_9]$ (3.562(3) Å)[13] and significantly shorter than the distances in the dimeric structures of $[Zr(NMe_2)_4]_2$ (3.704(1) Å)[3] and $ZrCl_4$ (3.962 Å).[12] This short distance may account for the smaller Zr−Cl−Zr angle in **1**. The terminal Zr(1)−N bond lengths (2.035(5) and 2.047(5) Å) are slightly shorter than those (2.078(5), 2.056(6), and 2.083(6) Å) of Zr(2), though all of the terminal Zr−N bond distances in **1** are consistent with those observed in other Zr(IV) amido complexes.[3,4,15] This bond deviation suggests larger

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(15) Some representative Zr−N bond lengths for Zr(IV) amide complexes: (a) 2.06 Å, $(Me_2N)_2Zr(\mu\text{-}NBu^t)_2Zr(NMe_2)_2$ (Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030); (b) 2.06 Å, *rac*-$[C_2H_4(C_9H_6)_2]Zr(NMe_2)_2$ (Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 8024); (c) 2.07 Å, *rac*-$[SiMe_2(C_9H_6)]_2Zr(NMe_2)_2$; 2.04 Å, $[\mu\text{-}SiMe_2(C_9H_6)_2]Zr_2(NMe_2)_6$ (Christopher, J. N.; Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4038); (d) 2.07 Å, $[(Me_3Si)_2N]_3ZrCl$; 2.08 Å, $[(Me_3Si)_2N]_3ZrMe$ (Bradley, D. C.; Chudzynska, H.; Becker-Dirks, J. D.; Hursthouse, M. B.; Ibrahim, A. A.; Montevalli, M.; Sullivan, A. C. *Polyhedron* **1990**, *9*, 1423).

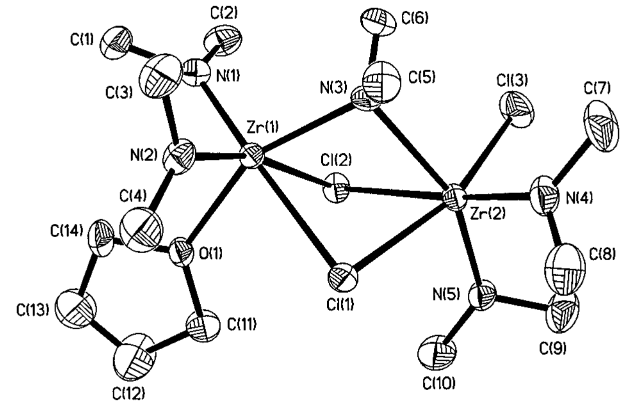

Figure 2. ORTEP view of the molecular structure of $Cl(Me_2N)_2Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_2(THF)$ (**2**), showing 50% thermal ellipsoids.

Table 3. Selected Bond Distances (Å) and Angles (deg) in **2**

Distances			
Zr(1)−Zr(2)	3.5413(11)	Zr(2)−N(3)	2.417(3)
Zr(1)−N(1)	2.035(3)	Zr(2)−N(4)	2.034(3)
Zr(1)−N(2)	2.029(3)	Zr(2)−N(5)	2.039(3)
Zr(1)−N(3)	2.226(3)	Zr(2)−Cl(1)	2.6130(12)
Zr(1)−Cl(1)	2.7066(12)	Zr(2)−Cl(2)	2.7214(12)
Zr(1)−Cl(2)	2.6179(12)	Zr(2)−Cl(3)	2.4409(12)
Zr(1)−O(1)	2.249(3)	$C-N_{av}$	1.462(5)
Angles			
N(1)−Zr(1)−Cl(1)	172.21(9)	N(3)−Zr(2)−Cl(1)	74.07(8)
N(1)−Zr(1)−Cl(2)	93.95(9)	N(3)−Zr(2)−Cl(2)	74.20(8)
N(2)−Zr(1)−Cl(1)	89.24(9)	N(3)−Zr(2)−Cl(3)	93.78(8)
N(2)−Zr(1)−Cl(2)	165.98(9)	N(4)−Zr(2)−Cl(1)	97.94(10)
N(3)−Zr(1)−Cl(1)	75.19(8)	N(4)−Zr(2)−Cl(2)	171.20(9)
N(3)−Zr(1)−Cl(2)	79.40(8)	N(4)−Zr(2)−Cl(3)	94.90(11)
O(1)−Zr(1)−Cl(1)	82.44(7)	N(5)−Zr(2)−Cl(1)	87.63(10)
O(1)−Zr(1)−Cl(2)	82.96(7)	N(5)−Zr(2)−Cl(2)	88.56(10)
O(1)−Zr(1)−N(1)	96.37(11)	N(5)−Zr(2)−Cl(3)	100.87(10)
O(1)−Zr(1)−N(2)	89.16(12)	Cl(1)−Zr(2)−Cl(2)	78.09(4)
O(1)−Zr(1)−N(3)	153.85(10)	Cl(1)−Zr(2)−Cl(3)	163.29(4)
Cl(1)−Zr(1)−Cl(2)	78.27(4)	Cl(2)−Zr(2)−Cl(3)	87.68(4)
N(1)−Zr(1)−N(2)	98.45(13)	N(3)−Zr(2)−N(4)	97.20(12)
N(1)−Zr(1)−N(3)	103.94(12)	N(3)−Zr(2)−N(5)	156.92(11)
N(2)−Zr(1)−N(3)	103.74(13)	N(4)−Zr(2)−N(5)	99.18(13)
Zr(1)−N(3)−Zr(2)	99.33(11)	Zr(1)−Cl(1)−Zr(2)	83.46(3)
Zr(1)−Cl(2)−Zr(2)	83.07(4)		

steric crowding around Zr(2). The bridging Zr(1)−N(3) and Zr(2)−N(3) bond lengths are 2.221(5) and 2.408(5) Å, respectively, which are close to the values (2.22 and 2.45 Å) reported for the two bridging amide bonds in $[Zr(NMe_2)_4]_2$.[3] The bridging Zr−Cl bond lengths range from 2.645(2) to 2.742(2) Å, which are close to those reported for $[\eta^2\text{-}(C_6Me_6)Zr_2(\mu\text{-}Cl)_3Cl_5]$ (2.518(3)−2.760(2) Å)[14] and are slightly longer than those found in $[Ph_4P][Zr_2Cl_9]$ (2.576(3) Å),[13] $ZrCl_4$ (2.576(2) Å),[12] and $(Me_3CCH_2)_3ZrCl$ (2.547(1) Å).[8]

$Cl(Me_2N)_2Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_2(THF)$ (2). An ORTEP view of the molecule is shown in Figure 2, and selected bond distances and angles are given in Table 3. The complex has a structure similar to **1**, except one terminal amide ligand on Zr(2) is replaced by a chloride atom. This molecule can be viewed as the association of $(Me_2N)_3ZrCl$ and $(Me_2N)_2ZrCl_2(THF)$ moieties. In the bridging $Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr$ unit, the bond lengths and angles are similar to those in **1**. The terminal Zr−N bond distances of two Zr atoms are similar (2.029(3)−2.039(3) Å). This is in contrast to the structure of **1**, in which the terminal Zr(2)−N bonds are slightly longer than the Zr(1)−N bonds. In **2**, one of the terminal Me_2N ligands is replaced by a less bulky chloride ligand. We believe that the steric repulsion around Zr(2) in **2** is less than that in **1**, leading to the shorter terminal Zr(2)−N bond lengths in **2**. The terminal Zr(2)−Cl(3) bond length is 2.4409(12) Å, which is slightly shorter than the Zr−Cl bonds in $(Me_2N)ZrCl_2(THF)_2$ (2.499(1) and 2.486(1) Å)[4] and is longer than the terminal Zr−Cl bond in $ZrCl_4$ (2.307(2) Å).[12]

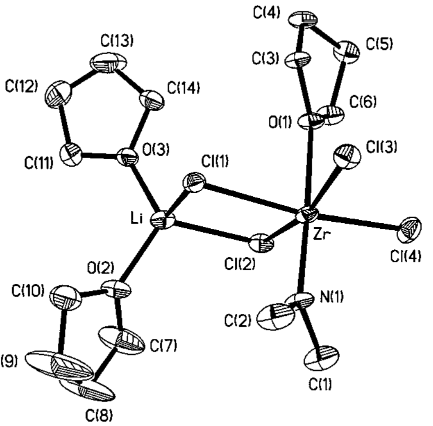

Figure 3. ORTEP view of the molecular structure of $(Me_2N)(THF)ZrCl_2(\mu\text{-}Cl)_2Li(THF)_2$ (**4**), showing 30% thermal ellipsoids.

There are amido and chloride ligands in both dinuclear complexes **1** and **2**. It is interesting to note that both complexes adopt the structure with dichloro(amido) bridges between the metal atoms, leaving one chloride ligand in **2** in the terminal position.

$(Me_2N)(THF)ZrCl_2(\mu\text{-}Cl)_2Li(THF)_2$ (4). An ORTEP view of the structure of **4** is shown in Figure 3. The zirconium is surrounded by two terminal and two bridging chlorides, one amido ligand, and one THF molecule in a distorted octahedral geometry. The four chloride atoms occupy the equatorial plane, and the THF and Me_2N ligands occupy axial positions with an O−Zr−N angle (176.3(2)°) near 180°. An interesting feature of the structure is that the equatorial chlorine atoms are all bent toward the THF molecule; the O−Zr−Cl angles range from 81.72(12)° to 85.88(12)°, and the N−Zr−Cl angles range from 93.9(2)° to 97.5(2)°. Such distortion indicates that the Me_2N ligand is more sterically demanding than the THF molecule, causing all the equatorial chloride atoms to bend toward the THF molecule.

The terminal Zr−Cl bond lengths (2.438(2)−2.441(3) Å) are similar to those found in **2** and **3**.[16] However, the bridging Zr−Cl bond distances in **4** (2.538(3)−2.535(2) Å) are shorter than the corresponding distances in **1** and **2** (Table 4). The Zr−N bond length of 1.990(5) Å is consistent with those observed in other Zr(IV) amido complexes.[3,4,15]

NMR studies. There are three types of NMe_2 ligands in the solid structure of **1** (Figure 1): one bridging and two terminal on Zr(1), and three terminal on Zr(2). At room temperature, the ^1H NMR spectrum (400 MHz) of **1** displays a single peak at 2.94 ppm assignable to the coordinated Me_2N ligands, indicating that the complex is fluxional in solution at this temperature. The variable-temperature NMR of **1** has been studied; at −70 °C, the ^1H NMR spectrum consists of three amido signals at 2.98, 3.12, and 3.51 ppm in a 2:1:3 ratio, which is consistent with the solid-state structure. As the temperature is raised, the signals of the two amido ligands on Zr(1) (2.98

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(16) The Zr−Cl bond lengths are close to those found in **2**, **3**, $[Ph_4P][ZrCl_6]\cdot 4MeCN$ (2.469(1) Å),[13] $[NEt_4][ZrCl_6]$ (2.463(8) Å),[17] and $[Ph_4P][ZrCl_6]$ (2.463(1) Å),[18] but longer than those in $ZrCl_4$[12] and $[\eta^2\text{-}(C_6Me_6)Zr_2(\mu\text{-}Cl)_3Cl_5]$ (2.345(2), 2.359(4), and 2.373(2) Å).[14]

(17) Ruhlandt-Senge, V. K.; Bacher, A.-D.; Muller, U. *Acta Crystallogr.* **1990**, *C46*, 1925.

(18) Hartmann, E.; Dehnicke, K.; Fenske, D.; Goesmann, H.; Baum, G. *Z. Naturforsch. B* **1989**, *44*, 1155.

Table 4. Selected Bond Distances (Å) and Angles(deg) in **4**

Distances

Zr(1)−N(1)	1.990(5)	Li(1)−Cl(2)	2.378(12)
Zr(1)−O(1)	2.322(4)	Li(1)−O(2)	1.880(12)
Zr(1)−Cl(1)	2.538(3)	Li(1)−O(3)	1.901(12)
Zr(1)−Cl(2)	2.535(2)	N(1)−C(1)	1.462(13)
Zr(1)−Cl(3)	2.438(2)	N(1)−C(2)	1.459(12)
Zr(1)−Cl(4)	2.441(3)	N(1)−C(1A)	1.57(2)
Li(1)−Cl(1)	2.390(12)	N(1)−C(2A)	1.37(2)

Angles

N(1)−Zr(1)−O(1)	176.3(2)	Cl(1)−Zr(1)−Cl(3)	88.30(8)
Cl(1)−Zr(1)−Cl(4)	169.11(6)	Cl(2)−Zr(1)−Cl(4)	90.24(8)
Cl(2)−Zr(1)−Cl(3)	166.14(6)	Cl(3)−Zr(1)−Cl(4)	94.87(9)
O(1)−Zr(1)−Cl(1)	84.78(13)	Cl(1)−Zr(1)−N(1)	93.9(2)
O(1)−Zr(1)−Cl(2)	81.72(12)	Cl(2)−Zr(1)−N(1)	94.2(2)
O(1)−Zr(1)−Cl(3)	85.88(12)	Cl(3)−Zr(1)−N(1)	97.5(2)
O(1)−Zr(1)−Cl(4)	85.06(13)	Cl(4)−Zr(1)−N(1)	96.0(2)
Cl(1)−Zr(1)−Cl(2)	84.43(8)		

ppm) and the bridging amide ligand (3.12 ppm) coalesce first at −44 °C, and all signals coalesce to one peak at −37 °C. The free energies of activation $\Delta G^{\ddagger}$ were estimated to be 11.4 ± 0.5 kcal/mol (for ligand exchange from terminal to bridging) for the first coalescence at −44 °C and 11.1 ± 0.5 kcal/mol for the second coalescence at −37 °C, respectively.[19]

Although complex **2** also has three different types of amide ligands, the room temperature NMR spectra only show one amido peak at 3.12 ppm, indicating a rapid exchange between the ligands. However, attempts to study the variable-temperature NMR of **2** were hampered by the complexity of the low-temperature NMR spectra. At low temperature, the NMR spectra show three sets of THF resonances and many amido peaks corresponding to at least three different complexes, perhaps resulting from the isomerization of **2**. To date, all attempts to isolate these complexes have been unsuccessful. At −20 °C, the NMR spectra are consistent with the presence of two isomers in toluene-d_8 solution; only one isomer was obtained from crystallization from hexanes at this temperature.

Complex **4** is only slightly soluble in benzene or toluene. Its ^{1}H NMR spectrum in benzene-d_6 at room temperature shows one amido peak at 3.36 ppm and one set of THF signals at 1.30 and 3.80 ppm, indicating that the coordinated THF molecules on lithium and zirconium exchange rapidly at room temperature.

In conclusion, several chloro amido zirconium complexes have been prepared. Dinuclear complexes **1** and **2** are found to contain unusual structures with three ligand bridges between zirconium atoms in their solid-state structures. The terminal and bridging amido ligands in **1** and **2** undergo rapid exchange at room temperature. In the $Zr(NMe_2)_xCl_{4-x}$ family, complexes with amido:Zr ratios of 6 in $Zr(NMe_2)_6Li_2(THF)_2$,[3] 4 in $[Zr(NMe_2)_4]_2$,[3] 3 in $[(Me_2N)_3ZrCl]_2$,[9] and 2 in $(Me_2N)_2ZrCl_2(THF)_2$[4] have been reported. The amido:Zr ratios in the new complexes **2** and **4** (2.5 and 1, respectively) reported here add to the missing members of the $Zr(NMe_2)_xCl_{4-x}$ series.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles for **1**, **2**, and **4** and dynamic NMR spectra for **1** (16 pages). Ordering information is given on any current masthead page.

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[19] For the evaluation of exchange rate constants from unequally populated doublets in NMR spectra, see: Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; p 81.