5358 *Organometallics* **2002,** *21,* 5358−5365

Syntheses, Structural Characterizations, and Metathesis Studies of New Dimeric Group 14 Metal Complexes Derived from Silacycloalkyl Diamide

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Received July 22, 2002

The syntheses and solid-state structures of a series of group 14 metal complexes stabilized by cyclic silyldiamide ligands (cyclo)Si(^{t}BuNH)$_2$ (**1**) derived from a silacycloalkyl unit [(cyclo)-Si = −(CH$_2$)$_n$Si−; n = 3 (**a**), 4 (**b**), and 5 (**c**)] are reported. Thus, a variety of dimeric *spiro*-siladiazametallacyclobutane complexes, [(cyclo)Si(^{t}BuN)$_2$M]$_2$ (M = Sn (**2**); Pb (**3**)), have been prepared by the reaction of the dilithium salt of **1** with MCl$_2$. The structures of **2a**, **2d**, and **3a** were determined by X-ray crystallography, which showed that all are composed of cycloadducts of two monomeric units. The reactions of **2** with AlCl$_3$ in toluene at room temperature afforded the unusual dinuclear aluminum complexes [(cyclo)Si(^{t}BuN)$_2$(AlCl$_2$)$_2$] (**4**). The complexes **4** were converted to the dimethyl complexes of the type [(cyclo)Si(^{t}BuN)$_2$-(AlMe$_2$)$_2$] (**5**) with MeMgBr. Complexes **4b** and **5c** were characterized by X-ray crystallography. As a result of the formation of the siladiazaalumacyclobutane ring, the aluminum atoms in **4** and **5** adopt distorted tetrahedral configurations with the two chloride or methyl ligands. In addition, the reactions of **2** with ZrCl$_4$·(THF)$_2$ produce unsymmetrical dinuclear bis(diamido)zirconium(IV) complexes [{(cyclo)Si(^{t}BuN)}$_2$Zr$_2$(Cl)(μ-Cl)$_3$(THF)] (**6**).

Introduction

There have been many syntheses and structural investigations of diamide ligands with a silyl substituent,[1] but most of the reported examples contain silicon atoms substituted with acyclic alkyl substituents.[2,3] The bidentate diamide ligands bearing silacycloalkyl heterocycles are unknown in most cases. However, such cyclic silacycloalkyl diamido complexes are promising precursors for olefin polymerization.[4] Indeed, the variation of the silacycloalkyl ligand backbone has been shown to have a strong effect on the kinetics of the polymerization.[5] The goal of this study was to elucidate the structures of prototypes bearing a cyclic alkyl ring as the silicon substituent and thus to understand the steric effects of the side groups. Therefore, we aim to investigate the structural chemistry of cyclic silyldiamide compounds more fully to establish a basis for the chemical behavior of this class of compounds.

As a continuation of our work, we now present the syntheses and crystal structures of a series of (silyldiamido) group 14 metal derivatives, [(cyclo)Si(^{t}BuN)$_2$M]$_2$ (M = Sn (**2**); Pb (**3**)). Herein, we report the syntheses and solid-state structures of two dimeric stannylenes, bis[*N*,*N*′-*tert*-butyl-*N*-silacyclobutyldiamido]tin(II) (**2a**) and bis[*N*,*N*′-*tert*-butyl-*N*-silacyclopentenyldiamido]tin(II) (**2d**), and one dimeric plumbylene, bis[*N*,*N*′-*tert*-butyl-*N*-silacyclobutyldiamido]lead(II) (**3a**), as shown in Chart 1.

Furthermore, we have started investigations into the use of the dimeric stannylenes **2** as potential polyolefin

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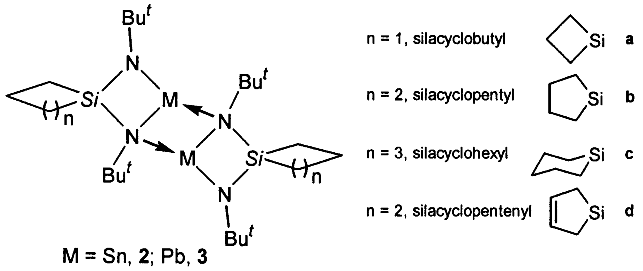
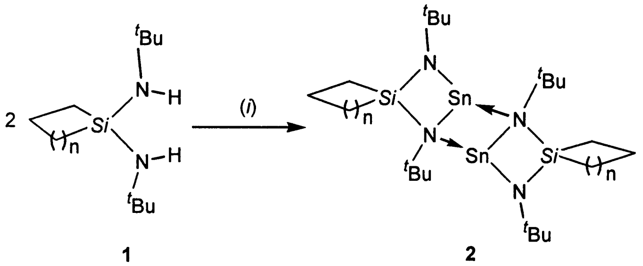
10.1021/om020587l CCC: $22.00
Publication on Web 10/23/2002

Chart 1



Scheme 1. Synthesis of Dinuclear Tin Complexes Incorporating the Ligand 1[a]



1 **2**

[a] Conditions: (*i*) (a) LiBu^n, Et$_2$O, −78 °C; (b) SnCl$_2$, Et$_2$O, −78 °C.

catalysts. In particular, the dimeric stannylenes **2** undergo metathesis with aluminum reagents to produce unusual dinuclear aluminum complexes [(cyclo)Si(^{t}BuN)$_2$(AlCl$_2$)$_2$] (**4**). Similarly, stannylenes **2** undergo facile metathesis with ZrCl$_4$·(THF)$_2$ to form a series of unsymmetrical dinuclear zirconium complexes [{(cyclo)Si(^{t}BuN)}$_2$Zr$_2$(Cl)(μ-Cl)$_3$(THF)] (**6**).

Results and Discussion

Synthesis of New Dimeric Group 14 Metal Complexes Derived from Silacycloalkyl Diamide. Chelating diamides with silyl substituents are accessible by the reaction of lithium amide with the dichlorosilacycloalkane or -alkene.[5] The reaction of SnCl$_2$ (2.2 mmol) with the dilithium salt of **1** (1 equiv) in diethyl ether leads to [(cyclo)Si(^{t}BuN)$_2$Sn]$_2$ (**2**) in moderate yield (43−86%, Scheme 1). The compounds **2** were obtained as yellow crystals by low-temperature recrystallization from toluene. Satisfactory elemental analyses were obtained for **2**, and the ^{1}H and ^{13}C NMR spectral data are consistent with the presence of the bidentate cyclic silyldiamide ligand (see Experimental Section).

The ^{1}H NMR signals for the ^{t}Bu moieties in **2** are at a lower field than for the free ligand, which is consistent with the existence of the Sn−N coordination in solution. Similar observations were found for the siladiazatitanacyclobutane ring of (cyclo)Si(^{t}BuN)$_2$TiCl$_2$.[5] The data for **2** also revealed that the replacement of the metal atom, in this case Sn for Ti, has little effect on the ^{t}Bu chemical shifts in both the ^{1}H and ^{13}C NMR spectra of this type of complex.

The ^{119}Sn NMR spectra of **2** measured in solution had a resonance at around δ −150. In addition, overlapping signals for the ^{t}BuN groups were observed in the ^{13}C (δ 33−37) and ^{1}H (δ 1.2−1.3) spectra measured in solution. Therefore, the NMR spectra did not reveal any diagnostic pattern of resonances that might reveal the nature of the solution conformation of **2**. However, evidence that compounds **2** are in fact dimeric in solution was obtained by cryoscopic measurements. A single-crystal X-ray diffraction study also showed that compounds **2** are dimeric in the solid state. Table 1 provides the crystal structure and refinement data for compound **2a**, while Table 2 lists selected bond lengths and bond angles. The tin atoms (Sn(1)/Sn(1)*) in **2a** reside at the bottom of a pocket formed by the two ^{t}BuN groups (N(1) and N(2)/N(1)* and N(2)*), which both project in the same direction (Figure 1). The dimers **2** can be considered as cycloadducts of the two monomeric units. In **2a**, the four-membered siladiazastannacyclobutane ring is almost planar and the nitrogen atoms are trigonal planar coordinated. Additionally, it is noteworthy that dimerization may be reflected in the yellow color of the compounds, as is the case for other stannylenes.[6] Therefore, we concluded that compounds **2** are covalent dimeric species, both in nonpolar solvents and in the solid state, and that they are stable with respect to redistribution.

Compound **2d** was prepared in a manner similar to **2a** in a 61% yield starting with the silacyclopentenyl backbone **1d**. A crystallographic analysis showed that, as with **2a**, the tin atoms (Sn(1)/Sn(1)*) of **2d** reside within pockets formed by the cooperative arrangement of the ^{t}BuN groups (N(1) and N(2)/N(1)* and N(2)*), as can be seen in Figure 2. Given the expected strong steric interactions between the substituents, it is likely that this conformation is also retained in solution.

The reaction of PbCl$_2$ with the dilithium salt of **1** (1 equiv) in diethyl ether afforded the plumbylenes [(cyclo)Si(^{t}BuN)$_2$Pb]$_2$ (**3**). Crystallization from toluene afforded pure **3** as orange crystals in 49−90% yield (Scheme 2). The ^{1}H and ^{13}C NMR spectra of **3** are consistent with pseudo C_2-symmetric structures and the symmetric bidentate coordination of the diamide ligand. Thus, the NMR spectra of these products were identical to those of **2**, prepared by the method summarized in Scheme 1.

The crystal data and refinement details for complex **3a** are summarized in Table 1. Selected bond distances and angles are given in Table 2. The molecular geometries and atom-labeling schemes are shown in Figure 3. The structural analysis of **3a** revealed a molecular core with similarities to complex **2a**;[7] the metal center is in a distorted tetrahedral environment consisting of the two nitrogen atoms of the silyldiamide ligand with the internuclear Pb−N interaction completing the coordination sphere.

Overall, the structures of **2a**, **2d**, and **3a** are tetrahedral with a planar conformation for the diamido-metal ring, similar to that observed in the (cyclo)Si(^{t}BuN)$_2$TiCl$_2$ complex. Thus, in all of the compounds studied, the (cyclo)Si(^{t}BuN)$_2$M core forms a nearly planar siladiazametallacyclobutane metallacyclic ring (torsional angles of N−M−N−Si < 1°). The cyclic silyldiamide ligand nearly symmetrically chelates the metal center to form a planar siladiazametallacyclobutane ring with a mean bite angle (N−M−N) of 85.4°. Common to all three molecules is a polycyclic structural element consisting of three edge-bridged perpendicular four-membered

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Table 1. X-ray Crystallographic Data and Processing Parameters for Compounds 2a, 2d, 3a, 4b, and 5c

	2a	**2d**	**3a**	**4b**	**5c**
formula	$C_{22}H_{48}N_4Si_2Sn_2$	$C_{24}H_{48}N_4Si_2Sn_2$	$C_{22}H_{48}N_4Si_2Pb_2$	$C_{12}H_{26}N_2Al_2SiCl_4$	$C_{17}H_{40}N_2Al_2Si$
fw	662.20	686.22	839.20	422.20	354.56
cryst class	triclinic	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$C2/c$	$Pbca$
Z	1	1	2	8	8
cell constants					
a, Å	8.1234(6)	7.3464(6)	9.4019(1)	18.789(4)	18.2659(1)
b, Å	9.2823(5)	10.1267(1)	9.9008(6)	23.695(5)	15.8749(1)
c, Å	10.8697(6)	11.2322(8)	16.0679(1)	13.286(3)	15.6184(7)
α, deg	66.747(5)	97.839(8)			
β, deg	89.403(5)	106.733(7)	98.984(9)	135.00(3)	
γ, deg	76.309(5)	106.356(8)			
V, Å^3	728.47(8)	746.03(1)	1477.4(3)	4182.6(2)	4528.9(5)
μ, mm^{-1}	1.812	1.773	11.47	0.703	0.182
cryst size, mm	0.5 × 0.45×0.4	0.25 × 0.3 × 0.3	0.35 × 0.3 × 0.3	0.45 × 0.3 × 0.4	0.25 × 0.3 × 0.2
d_{calcd}, g/cm^3	1.509	1.527	1.887	1.341	1.040
radiation			Mo Kα ($\lambda = 0.71073$ Å)		
$F(000)$	336	348	800	1760	1568
θ range, deg	2.05−25.97	1.95−25.95	2.36−25.96	1.72−25.95	2.14−25.97
h, k, l collected	+10, ±11, ±13	+9, ±11, ±13	+11, +12, ±19	±23, ±29, +16	+22, +19, +19
no. of reflns collected	3199	3164	3114	8488	4442
no. of unique reflns	2866	2923	2896	4116	4442
no. of reflns used in refinement ($I > 2\sigma(I)$)	2498	2375	1975	1538	1372
no. of params	142	149	143	197	210
R_1[a]	0.0360	0.0374	0.0473	0.0880	0.0722
wR_2[a]	0.0949	0.0943	0.1129	0.2112	0.1702
GOF	0.811	0.614	0.863	1.135	0.853

[a] $R_1 = \sum||F_o| - |F_c|$ (based on reflections with $F_o^2 > 2\sigma F^2$). [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma F^2$).

Table 2. Selected Interatomic Distances (Å)

Compound **2a**					
Sn(1)−N(1)	2.110(4)	Sn(1)−N(2)	2.252(3)	Sn(1)−N(2)*	2.344(3)
Sn(1)−Si(1)	2.918(1)	Si(1)−N(1)	1.699(4)	Si(1)−N(2)	1.787(4)
N(2)−Sn(1)*	2.344(3)				
Compound **2d**					
Sn(1)−N(1)	2.106(4)	Sn(1)−N(2)	2.246(4)	Sn(1)−N(2)*	2.409(4)
Sn(1)−Si(1)	2.920(1)	Si(1)−N(1)	1.702(5)	Si(1)−N(2)	1.788(4)
N(2)−Sn(1)*	2.409(4)				
Compound **3a**					
Pb(1)−N(1)	2.23(1)	Pb(1)−N(2)	2.343(1)	Pb(1)−N(2)*	2.47(1)
Pb(1)−Si(1)	3.011(4)	Si(1)−N(1)	1.685(1)	Si(1)−N(2)	1.75(1)
N(2)−Pb(1)*	2.468(1)				
Compound **4b**					
Si(1)−N(2)	1.816(5)	Si(1)−N(1)	1.816(5)	Al(1)−Si(1)	2.576(3)
Si(1)−Al(2)	2.576(3)	Al(2)−N(2)	1.946(6)	Al(1)−N(1)	1.944(6)
Al(1)−N(2)	1.951(6)	Al(2)−N(1)	1.943(6)	Al(2)−Al(1)	2.721(7)
Compound **5c**					
Si(1)−N(2)	1.772(5)	Si(1)−N(1)	1.780(5)	Si(1)−Al(1)	2.650(3)
Si(1)−Al(2)	2.656(3)	Al(1)−N(2)	1.969(5)	Al(1)−N(1)	2.014(6)
Al(1)−Al(2)	2.769(4)	Al(2)−N(1)	2.012(6)	Al(2)−N(2)	2.030(5)

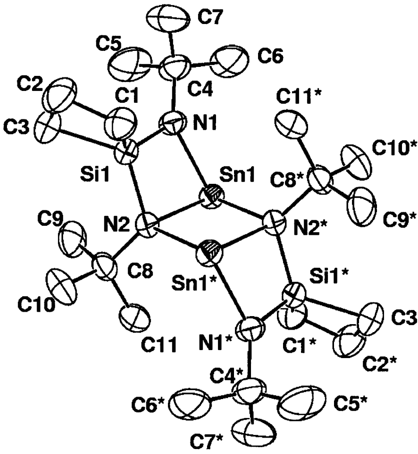

Figure 1. Molecular structure of $[(C_3H_6)Si(^tBuN)_2Sn]_2$ (**2a**) with thermal ellipsoids drawn at the 30% level.

rings ("step structure"). All the dimeric compounds that contain lower valent metals are usually less colored. The different coordination numbers at the metal centers are obviously reflected in the color of the compounds, as is also the case for tin(II) amides.[8] The electron transfer from the λ^3-N atom to the metal atom is reflected in the drastically lengthened bonds to this atom. The donor−acceptor bonds shown by the arrows for the tin and lead complexes in Schemes 1 and 2 should appreciably differ in length from the N−M single bond; this is indeed the case for the dimeric **2a**, **2d**, and **3a**.

Synthesis of Aluminum Complexes. When **2** was treated with 2 equiv of $AlCl_3$ in toluene at reflux, a white precipitate formed in 12 h (Scheme 3). Surprisingly, the X-ray crystallographic (vide infra) and elemental analyses showed that the product was an unprecedented dinuclear species, $[(cyclo)Si(^tBuN)_2(AlCl_2)_2]$ (**4**), in which each aluminum center is connected to a diamide ligand. The NMR spectra confirmed that the solid-state structure is also maintained in solution.

The structure of **4b** was determined by X-ray crystallography. The molecular structure is shown in Figure 4, and selected bond lengths and angles are summarized in Table 2 and Table 3. Complex **4b** is a dinuclear aluminum species in which the two molecular units of Cl_2AlN_2 are associated with each other. The molecule has an imposed C_2 axis through Si(1) and consists of two tetrahedral Cl_2AlN_2 moieties joined by two amido units. The four-membered AlN_2Si rings are puckered, with a dihedral angle of 120.9(9)°. Each aluminum

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[8] Corvan, P. J.; Zuckerman, J. J. *Inorg. Chim. Acta* **1979**, *34*, L255.

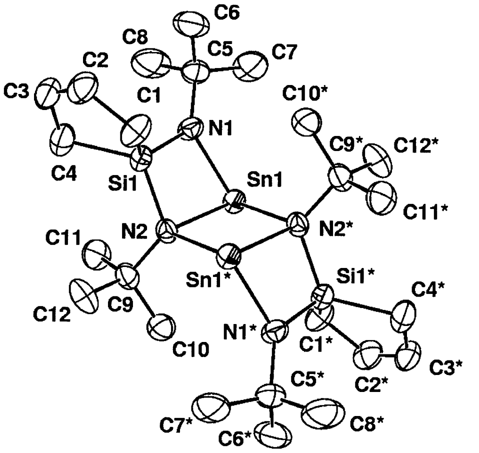
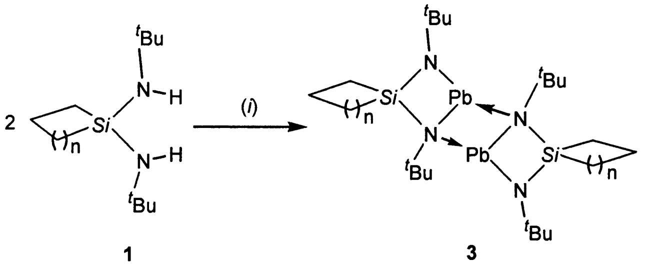


Figure 2. Molecular structure of $[(C_4H_8)Si(^tBuN)_2Sn]_2$ (**2d**) with thermal ellipsoids drawn at the 30% level.

Scheme 2. Synthesis of Dinuclear Lead Complexes Incorporating the Ligand 1[a]



[a] Conditions: (i) (a) $LiBu^n$, Et_2O, −78 °C; (b) $PbCl_2$, Et_2O, −78 °C.

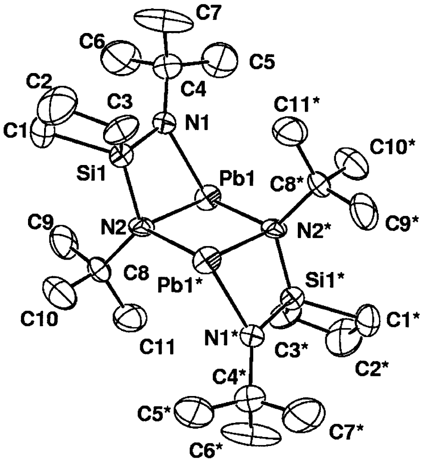


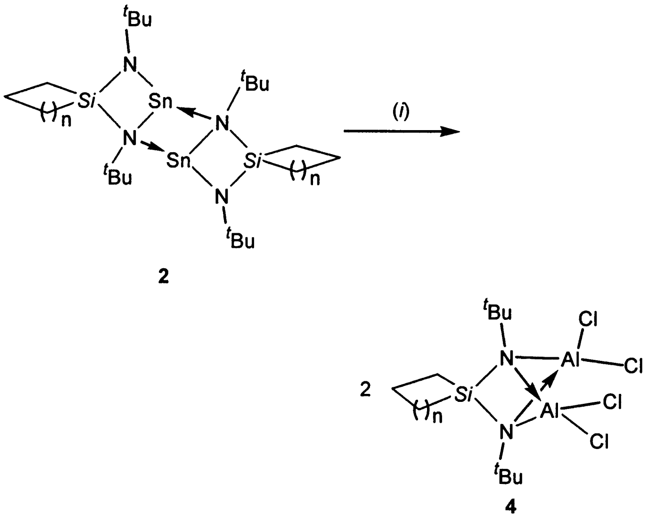
Figure 3. Molecular structure of $[(C_3H_6)Si(^tBuN)_2Pb]_2$ (**3a**) with thermal ellipsoids drawn at the 30% level.

center adopts a distorted tetrahedral geometry with a mean N−Al−N angle of 72.50(9)°.

Because dialkyl species are important precursors for active polyolefin catalysts, we synthesized the dimethyl derivatives of these diamide complexes **5**, as shown in Scheme 4. Methylation of a diethyl ether solution of **4** (1.0 mmol) with MeMgBr (4.8 mmol) afforded high yields of **5** (82−91%) as colorless crystals.

The composition of **5** was confirmed by elemental analysis. As expected, the ^1H NMR spectra of **5** were consistent with a species of pseudo C_{2v} symmetry. The characteristic ^1H and ^{13}C NMR resonances of the Al-Me groups were observed at around δ −0.5 and −1.0, respectively. The observation of two sets of ^1H and ^{13}C resonances for the Al-Me groups is in agreement with the four-membered cyclic structure. The cycloalkylsilyl groups exhibit unresolved multiplets between δ 0.7 and 1.9, and the signal of the chemically equivalent ^tBu protons is observed as a singlet at around δ 1.3.

Scheme 3. Synthesis of Dinuclear Aluminum Complexes Incorporating the Ligand 1[a]



[a] Conditions: (i) $2AlCl_3$, toluene, 110 °C.

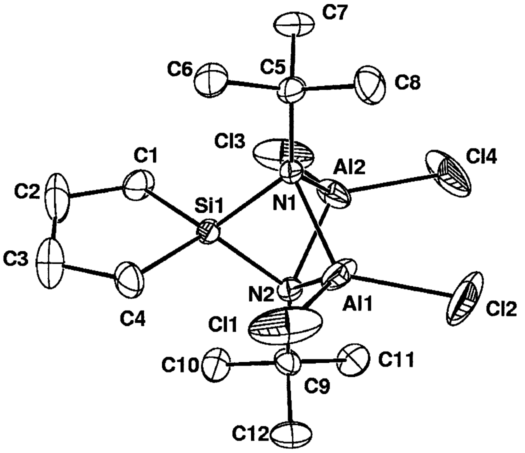


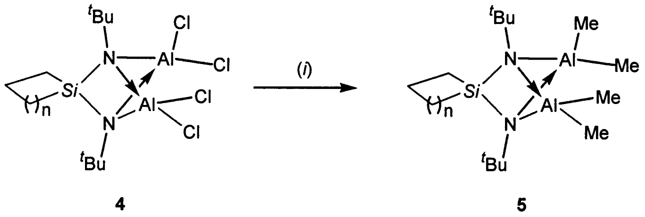
Figure 4. Molecular structure of $[(C_4H_8)Si(^tBuN)_2(AlCl_2)_2]$ (**4b**) with thermal ellipsoids drawn at the 30% level.

The molecular structure of **5c** is shown in Figure 5. Complex **5c** contains two aluminum centers, and the four methyl groups occupy two different chemical environments. The dinuclear complex **5c** has a pseudo C_{2v} symmetry; that is, there is one mirror plane passing through the Si(1), N(1), and N(2) atoms and another perpendicular plane passing through two aluminum atoms. The coordination geometry of each aluminum atom and nitrogen atom is a distorted tetrahedron. The two nitrogen and two aluminum centers comprise a butterfly-shaped metallacycle. Each aluminum center is 1.937(1) Å away from a mirror plane bisecting the aluminum centers, and the angle between the two AlN_2 planes is 113.9(2)°. The formation of the puckered Al_2N_2 ring is mainly a consequence of the rigid silacycloalkyl link. Complex **5c** is structurally similar to recently reported dinuclear aluminum complexes, $\{1,8\text{-}C_{10}H_6(NSiMe_3)_2\}Al_2Me_4$[9] and $\{^tBuNCH_2CH_2{}^tBuN\}AlH_2)_2\}$,[10] in which two aluminum alkyl moieties are symmetrically chelated by an *N,N′*-diamido ligand. As a result of

Table 3. Selected Interatomic Angles (deg)

		Compound **2a**			
N(1)−Sn(1)−N(2)	72.8(1)	N(1)−Sn(1)−N(2)*	103.1(1)	N(2)−Sn(1)−N(2)*	80.6(1)
N(1)−Si(1)−N(2)	96.0(2)	Si(1)−N(1)−Sn(1)	99.4(2)	Si(1)−N(2)−Sn(1)*	105.7(2)
Si(1)−N(2)−Sn(1)	91.8(2)	Sn(1)−N(2)−Sn(1)*	99.4(1		
		Compound **2d**			
N(1)−Sn(1)−N(2)	72.8(2)	N(1)−Sn(1)−N(2)*	104.3(2)	N(2)−Sn(1)−N(2)*	82.5(2)
N(1)−Si(1)−N(2)	95.5(2)	Si(1)−N(1)−Sn(1)	99.6(2)	Si(1)−N(2)−Sn(1)*	107.2(2)
Si(1)−N(2)−Sn(1)	92.1(2)	Sn(1)−N(2)−Sn(1)*	97.5(2)		
		Compound **3a**			
N(1)−Pb(1)−N(2)	69.0(4)	N(1)−Pb(1)−N(2)*	103.3(4)	N(2)−Pb(1)−N(2)*	80.6(4)
N(1)−Si(1)−N(2)	97.9(5)	Si(1)−N(1)−Pb(1)	99.5(5)	Si(1)−N(2)−Pb(1)*	105.3(4)
Si(1)−N(2)−Pb(1)	93.5(4)	Pb(1)−N(2)−Pb(1)*	99.4(4)		
		Compound **4b**			
N(2)−Si(1)−N(1)	78.5(3)	Al(1)−Si(1)−Al(2)	63.7(2)	N(2)−Al(1)−N(1)	72.5(3)
N(1)−Al(2)−N(2)	72.4(5)	Si(1)−N(1)−Al(2)	86.2(2)	Si(1)−N(1)−Al(1)	86.4(2)
Al(2)−N(1)−Al(1)	88.8(3)	Si(1)−N(2)−Al(1)	86.4(2)	Si(1)−N(2)−Al(2)	86.4(2)
Al(1)−N(2)−Al(2)	88.8(3)				
		Compound **5c**			
N(2)−Si(1)−N(1)	79.8(2)	Al(1)−Si(1)−Al(2)	62.9(9)	N(2)−Al(1)−N(1)	69.8(2)
N(1)−Al(2)−N(2)	68.6(2)	Si(1)−N(1)−Al(2)	88.7(2)	Si(1)−N(1)−Al(1	88.4(2)
Al(2)−N(1)−Al(1)	86.9(2)	Si(1)−N(2)−Al(1)	90.1(2)	Si(1)−N(2)−Al(2)	88.4(2)
Al(1)−N(2)−Al(2)	87.6(2)				

Scheme 4. Synthesis of Aluminum Alkyl Complexes 5[a]



[a] Conditions: (i) MeMgBr, Et_2O, −78 °C.

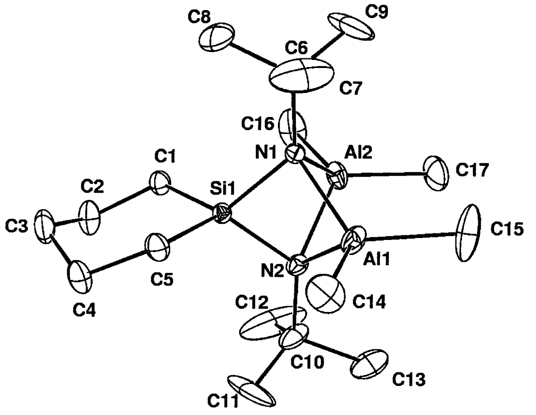
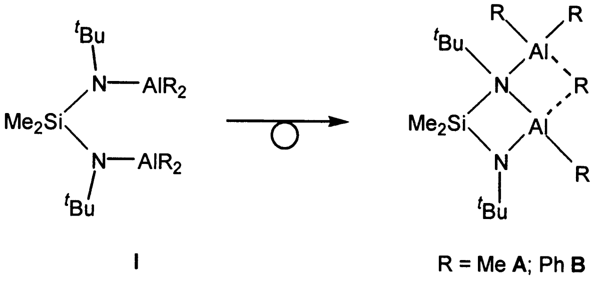


Figure 5. Molecular structure of $[(C_5H_{10})Si(^tBuN)_2(AlMe_2)_2]$ (**5c**) with thermal ellipsoids drawn at the 30% level.

the puckered Al_2N_2 ring, the mean N(1)−Al−N(2) angle (69.19(2)°) of **5c** is more acute than the mean Al(1)−N−Al(2) bond angle (87.27(1)°) (Table 2). However, the mean Al−N bond distances (2.00 Å) are comparable to those of other dimeric aluminum amido complexes containing a four-membered planar Al_2N_2 ring.[11]

Chart 2. Formation of Stable Three-Center Two-Electron Aluminum Alkyl Bond



To the best of our knowledge, the dinuclear aluminum species **4** and **5** are unusual in that most of the dinuclear aluminum complexes $[Me_2Si(^tBuN)_2AlR_2]_2$ (R = Me **A**, Ph **B**)[12] consist of equivalent monomeric units, as shown in Chart 2. Complexes **A** and **B** must originate from the reaction of the intermediates (**I**). The driving force for the formation of complexes **A** and **B** must be the large energy gain from the three-center, two-electron bond between the carbon atom of an alkyl group and the two aluminum atoms, which serves to complete the coordination sphere of the metal atoms. In contrast, the reaction of the dimeric bis(amino)stannylene **2** with aluminum chloride proceeds by the dissociation of the dimeric **2** and the addition of the aluminum metal to one of the tin−nitrogen bonds to give a tricyclic product in which both nitrogen atoms function as bases.

Only comparatively minor structural changes are displayed by the silacycloalkyl ligand backbone upon coordination to the metals. There are interactions in the ^{t}BuN portion of the molecule that are also observed in $(cyclo)Si(^tBuN)_2TiCl_2$, resulting in a Al_2 dinuclear arrangement with relatively short Al−Al distances (2.72−2.77 Å). The tricyclic framework has a central diamide bridge which is orthogonal to the terminal silacyclo alkane or alkene ring.

Synthesis of Zirconium Complexes. The reaction of the divalent stannylenes **2** with 2 equiv of $ZrCl_4\cdot$

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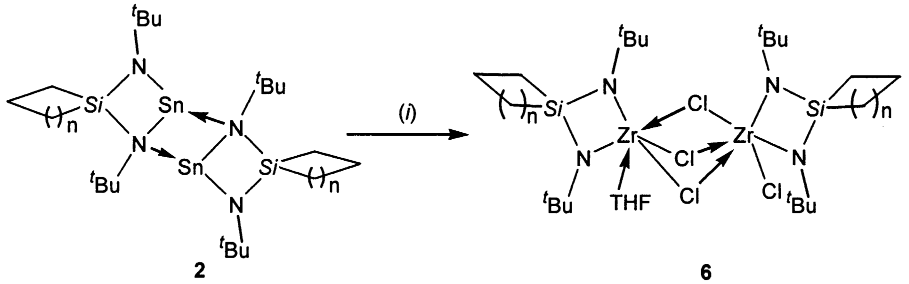
Scheme 5. Synthesis of Bimetallic Zirconium Complexes 6[a]



2

6

[a] Conditions: (i) $ZrCl_4{\cdot}(THF)_2$, Et_2O, −78 °C.

$(THF)_2$ in toluene (Scheme 5), followed by recrystallization of the crude residue from a toluene/hexane mixture, produced colorless microcrystalline complexes $[\{(cyclo)Si(^tBuN)\}_2Zr_2(Cl)(\mu\text{-}Cl)_3(THF)]$ (**6**) in 37−53% yields. Complex **6** was obtained as a spectroscopically pure solid by cooling a pentane solution of **6** to −45 °C. However, all attempts to remove the THF in vacuo from the crude product mixture at elevated temperatures led to decomposition.

The new complexes **6** were characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. Complex **6** appears to be a dizirconium species with bridging chloride ligands.[13] For unequivocal characterization, we performed an X-ray crystallographic analysis (see Supporting Information). However, the crystals were poorly diffracting, which prevented a completely satisfactory analysis. Nevertheless, the data were sufficient to firmly establish that the pair of silacyclohexyl diamide moieties in **1**$^{2-}$ bind to the Zr centers through the amide nitrogen atoms to form two four-membered chelate rings. The metal atoms are bridged by three of the four chloride ligands. In addition, the THF molecule coordinates through the oxygen atom at the *trans* sites of the bridging chlorine atom.

Summary

Silacycloalkyl diamide **1** is able to impose a well-defined coordination environment on its complexes. In **2** and **3**, for example, it produces a steric pocket that is quite reminiscent of that found in dimethylsilyl diamides and related compounds. The dimeric complexes can be considered as cycloadducts of two monomeric units. The dimers of the tin and the lead compound display a similar structural type. Common to all three molecules is a polycyclic structural element consisting of three edge-bridged perpendicular four-membered rings ("step structure"). Thus, the dimerization of **2** and **3** is reminiscent of the behavior of diamides involving silacycloalkyl substituents. The spirocyclic geometry of the tricyclic rings in **4** and **5** is novel. The bulky ^{t}BuN substituents of the ligand form a rather wide gap in the equatorial plane of the complexes that may allow selective access of substrate molecules to the Lewis acidic metal centers. Therefore, we have prepared and structurally characterized a series of chlorine-bridged dimeric zirconium diamides **6**, thereby demonstrating the utility of the silacycloalkyl diamides as precursors for the development of novel transition metal complexes.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free nitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmosphere HE-493 drybox. Diethyl ether, toluene, hexane, and pentane were distilled under nitrogen from sodium/benzophenone. Dichloromethane was dried with CaH_2. Benzene-d_6 was distilled under nitrogen from sodium and stored in a Schlenk storage flask until needed. $CDCl_3$ was predried under CaH_2 and vacuum-transferred. *n*-BuLi (1.6 M in hexanes) and $ZrCl_4$ were used as received from Aldrich. Silacyclobutyl di(*tert*-butyl)diamide, silacyclopentyl di(*tert*-butyl)diamide, silacyclohexyl di(*tert*-butyl)diamide, and silacyclopentenyl di(*tert*-butyl)diamide were obtained by literature methods.[5] $ZrCl_4(THF)_2$ was prepared according to literature procedure.[14] The NMR (^{1}H, ^{13}C, ^{119}Sn, ^{27}Al) spectra were recorded on Varian Mercury-300BB and Varian Gemini 2000 instruments, using chloroform-*d* as the lock solvent. ^{1}H and ^{13}C NMR spectra are referenced relative to TMS, and the ^{119}Sn and ^{27}Al spectra, to Me_4Sn and $[Al(H_2O)_6]Cl_3$, respectively. Elemental analyses were performed at either Galbraith Laboratories, Inc., or the chemical analysis laboratory of the Korea Institute of Science and Technology.

Preparation of the Stannylenes, $[(cyclo)Si(^tBuN)_2Sn]_2$ (2). Representative procedure: To a solution of **1** (2.0 mmol) in 20 mL of diethyl ether, precooled to −78 °C, was added 1.3 mL of *n*-BuLi (1.6 M in hexanes). The reaction mixture was warmed to room temperature and stirred for 2 h, whereupon it was transferred, via cannula, to a suspension of 2.2 equiv of tin dichloride in 20 mL of Et_2O that was cooled to −78 °C. The resultant yellow mixture was allowed to warm to room temperature and stirred for 2 h. Removal of the volatiles provided the final crude product, which was further crystallized from toluene at −10 °C to provide pure $[(cyclo)Si(^tBuN)_2Sn]_2$ (**2**) as a yellow solid.

2a: colorless crystals (0.57 g, 86%). Anal. Calcd for $C_{22}H_{48}N_4Si_2Sn_2$: C, 39.90; H, 7.31; N, 8.46. Found: C, 40.06; H, 7.50; N, 8.39. ^{1}H NMR: δ 1.21 (m, 4H, SiC*H*$_2$), 1.29 (s, 18H, ^{t}BuN), 1.72 (m, 2H, CH_2CH_2). $^{13}C\{^1H\}$ NMR: δ 11.02 (Si*C*H$_2$), 31.55 (CH_2CH_2), 33.71 (NC*Me*$_3$), 54.63 (N*C*Me$_3$). $^{119}Sn\{^1H\}$ NMR: δ −158.13.

2b: colorless crystals (0.30 g, 43%). Anal. Calcd for $C_{24}H_{52}N_4Si_2Sn_2$: C, 41.76; H, 7.59; N, 8.12. Found: C, 41.88; H, 7.70; N, 8.22. ^{1}H NMR: δ 0.89 (m, 4H, SiC*H*$_2$), 1.28 (s, 18H, ^{t}BuN), 1.66 (m, 4H, CH_2CH_2). $^{13}C\{^1H\}$ NMR: δ 15.44 (Si*C*H$_2$), 26.70 (CH_2CH_2), 33.780 (NC*Me*$_3$), 52.83 (N*C*Me$_3$). $^{119}Sn\{^1H\}$ NMR: δ −151.84.

2c: colorless powder (0.44 g, 61%). Anal. Calcd for $C_{26}H_{56}N_4Si_2Sn_2$: C, 43.47; H, 7.86; N, 7.80. Found: C, 43.56; H, 7.98; N, 7.66. ^{1}H NMR: δ 0.60 (m, 4H, SiC*H*$_2$), 1.18 (s, 18H, ^{t}BuN),

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1.40 (m, 4H, CH$_2$C*H*$_2$), 1.67 (m, 2H, CH$_2$CH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR: δ 17.94 (Si*C*H$_2$), 25.49 (CH$_2$*C*H$_2$), 30.63 (CH$_2$CH$_2$*C*H$_2$), 36.34 (NC*Me*$_3$), 50.89 (N*C*Me$_3$). ^{119}Sn{^{1}H} NMR: δ −155.42.

2d: colorless powder (0.42 g, 61%). Anal. Calcd for $C_{24}H_{48}N_4Si_2Sn_2$: C, 42.00; H, 7.05; N, 8.16. Found: C, 42.14; H, 7.12; N, 8.04. ^{1}H NMR: δ 1.25 (s, 18H, ^{t}BuN), 1.69 (m, 4H, SiC*H*$_2$), 5.95 (m, 2H, ═C*H*). ^{13}C{^{1}H} NMR: δ 19.89 (Si*C*H$_2$), 35.55 (NC*Me*$_3$), 52.45 (N*C*Me$_3$), 130.90 (═*C*H). ^{119}Sn{^{1}H} NMR: δ −154.18.

Preparation of the Plumbylenes, [(cyclo)Si(^{t}BuN)$_2$Pb]$_2$ (3). Representative procedure: To a solution of **1** (2.0 mmol) in 20 mL of diethyl ether, precooled to −78 °C, was added 1.3 mL of *n*-BuLi (1.6 M in hexanes). The reaction mixture was warmed to room temperature and stirred for 2 h, whereupon it was transferred, via cannula, to a suspension of 2.2 equiv of lead dichloride in 20 mL of Et$_2$O that was cooled to −78 °C. The resultant yellow mixture was allowed to warm to room temperature and stirred for 2 h. Removal of the volatiles provided the final crude product, which was further crystallized from toluene at −10 °C to provide pure [(cyclo)Si(^{t}BuN)$_2$Pb]$_2$ (**3**) as a yellow solid.

3a: yellow crystals (0.46 g, 55%). Anal. Calcd for $C_{22}H_{48}N_4Si_2Pb_2$: C, 31.49; H, 5.77; N, 6.68. Found: C,31.61; H, 5.89; N, 6.52. ^{1}H NMR: δ 1.19 (m, 4H, SiC*H*$_2$), 1.21 (s, 18H, ^{t}BuN), 1.46 (m, 2H, CH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR: δ 13.66 (Si*C*H$_2$), 30.89 (CH$_2$*C*H$_2$), 33.88 (NC*Me*$_3$), 49.45 (N*C*Me$_3$).

3b: yellow powder (0.78 g, 90%). Anal. Calcd for $C_{24}H_{52}N_4Si_2Pb_2$: C, 33.24; H, 6.04; N, 6.46. Found: C, 33.36; H, 6.12; N, 6.38. ^{1}H NMR: δ 0.47 (m, 4H, SiC*H*$_2$), 1.18 (s, 18H, ^{t}BuN), 1.56 (m, 4H, CH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR: δ 15.43 (Si*C*H$_2$), 26.16 (CH$_2$*C*H$_2$), 33.78 (NC*Me*$_3$), 49.52 (N*C*Me$_3$).

3c: yellow powder (0.44 g, 49%). Anal. Calcd for $C_{26}H_{56}N_4Si_2Pb_2$: C, 34.88; H, 6.30; N, 6.26. Found: C, 34.96; H, 6.40; N, 6.39. ^{1}H NMR: δ 0.62 (m, 4H, SiC*H*$_2$), 1.18 (s, 18H, ^{t}BuN), 1.38 (m, 4H, CH$_2$C*H*$_2$), 1.66 (m, 2H, CH$_2$CH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR: δ 17.96 (Si*C*H$_2$), 25.51 (CH$_2$*C*H$_2$), 30.64 (CH$_2$CH$_2$*C*H$_2$), 34.00 (NC*Me*$_3$), 49.60 (N*C*Me$_3$).

3d: yellow powder (0.56 g, 65%). Anal. Calcd for $C_{24}H_{48}N_4Si_2Pb_2$: C, 33.39; H, 5.60; N, 6.49. Found: C, 33.45; H, 5.69; N, 6.55. ^{1}H NMR: δ 1.19 (s, 18H, ^{t}BuN), 1.45 (m, 4H, SiC*H*$_2$), 5.88 (m, 2H, ═C*H*). ^{13}C{^{1}H} NMR: δ 19.92 (Si*C*H$_2$), 33.66 (NC*Me*$_3$), 49.33 (N*C*Me$_3$), 130.96 (═*C*H).

Preparation of the Tricyclic Dinuclear Aluminum Diamides, [(cycl)Si(^{t}BuN)$_2$(AlCl$_2$)$_2$] (4). Representative procedure: Complex **2** (1.0 mmol) in toluene (10 mL) was added to AlCl$_3$ (0.27 g, 2.0 mmol) in toluene (10 mL) at room temperature. The reaction mixture was heated to refluxing temperature and stirred for 12 h. The resulting orange solution was dried under vacuum to afford a yellow solid. The solid was extracted with pentane, and the filterate was concentrated and cooled to −45 °C. Yellow solid **4** was isolated by filtration, washing with cold pentane, and drying in vacuo.

4a: white powder (0.54 g, 66%) was obtained by recrystallization (−45 °C, toluene). Anal. Calcd for $C_{11}H_{24}N_2SiAl_2Cl_4$: C, 32.37; H, 5.93; N, 6.86. Found: C, 32.46, H, 5.99, N, 6.96. ^{1}H NMR: δ 1.24 (m, 4H, SiC*H*$_2$), 1.27 (s, 18H, ^{t}BuN), 1.57 (m, 2H, CH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR: δ 14.03 (Si*C*H$_2$), 30.31 (CH$_2$*C*H$_2$), 33.27 (NC*Me*$_3$), 54.34 (N*C*Me$_3$).

4b: colorless crystals (0.60 g, 71%) were obtained by recrystallization (−45 °C, toluene). Anal. Calcd for $C_{12}H_{26}N_2SiAl_2Cl_4$: C, 34.14; H, 6.21; N, 6.63. Found: C, 34.26; H, 6.29; N, 6.72. ^{1}H NMR: δ 1.15 (m, 4H, SiC*H*$_2$), 1.48 (s, 18H, ^{t}BuN), 1.77 (m, 4H, CH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR: δ 16.79 (Si*C*H$_2$), 25.49 (CH$_2$*C*H$_2$), 33.11 (NC*Me*$_3$), 53.72 (N*C*Me$_3$).

4c: colorless crystals (0.60 g, 69%) were obtained by recrystallization (−45 °C, toluene). Anal. Calcd for $C_{13}H_{28}N_2SiAl_2Cl_4$: C, 35.79; H, 6.47; N, 6.42. Found: C, 35.86; H, 6.59; N, 6.52. ^{1}H NMR: δ 1.15 (m, 4H, SiC*H*$_2$), 1.49 (s, 18H, ^{t}BuN), 1.68 (m, 4H, CH$_2$C*H*$_2$), 1.78 (m, 2H, CH$_2$C*H*$_2$CH$_2$). ^{13}C{^{1}H} NMR: δ 18.30 (Si*C*H$_2$), 24.15 (CH$_2$*C*H$_2$), 29.54 (CH$_2$CH$_2$*C*H$_2$), 33.40 (NC*Me*$_3$), 53.97 (N*C*Me$_3$).

4d: colorless crystals (0.54 g, 64%) were obtained by recrystallization (−45 °C, toluene). Anal. Calcd for $C_{12}H_{24}N_2SiAl_2Cl_4$: C, 34.30; H, 5.76; N, 6.67. Found: C, 34.42; H, 5.88; N, 6.82. ^{1}H NMR: δ 1.49 (s, 18H, ^{t}BuN), 1.86 (m, 4H, SiC*H*$_2$), 5.99 (m, 2H, ═C*H*). ^{13}C{^{1}H} NMR: δ 22.05 (Si*C*H$_2$), 27.92 (NC*Me*$_3$), 53.88 (N*C*Me$_3$), 129.27 (═*C*H).

Preparation of the Tricyclic Dinuclear Aluminumdimethyl Diamides, [(cyclo)Si(^{t}BuN)$_2$(AlMe$_2$)$_2$] (5). Representative procedure: To a solution of **4** (1.0 mmol) in 20 mL of diethyl ether, precooled to −78 °C, was added MeMgBr (3.0 M in ether, 0.80 mL, 2.4 mmol). The reaction mixture was warmed to room temperature and stirred for 2 h. The resulting yellow solution was dried under vacuum to afford a pale yellow solid. The solid was extracted with pentane, and the filterate was concentrated and cooled to −45 °C. Yellow solid **5** was isolated by filtration, washing with cold pentane, and drying in vacuo.

5a: colorless crystals (0.28 g, 85%). Anal. Calcd for $C_{15}H_{36}N_2SiAl_2$: C, 55.18; H, 11.11; N, 8.58. Found: C, 55.29; H, 11.24; N, 8.72. ^{1}H NMR: δ −0.67 (s, 6H, AlC*H*$_3$), −0.49 (s, 6H, AlC*H*$_3$), 1.23 (m, 4H, SiC*H*$_2$), 1.33 (s, 18H, ^{t}BuN), 1.98 (m, 2H, CH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR: δ −0.99 (Al*Me*), 14.63 (Si*C*H$_2$), 30.51 (CH$_2$*C*H$_2$), 34.66 (NC*Me*$_3$), 52.36 (N*C*Me$_3$). ^{27}Al{^{1}H} NMR: δ 169.64.

5b: colorless crystals (0.28 g, 82%). Anal. Calcd for $C_{16}H_{38}N_2SiAl_2$: C, 56.43; H, 11.25; N, 8.23. Found: C, 56.60; H, 11.38; N, 8.35. ^{1}H NMR: δ −0.56 (s, 6H, AlC*H*$_3$), −0.47 (s, 6H, AlC*H*$_3$), 1.095 (m, 4H, SiC*H*$_2$), 1.281 (s, 18H, N^t*Bu*), 1.701 (m, 4H, CH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR: δ −1.53 (Al*Me*), 18.08 (Si*C*H$_2$), 25.63 (CH$_2$*C*H$_2$), 34.70 (NC*Me*$_3$), 52.14 (N*C*Me$_3$). ^{27}Al{^{1}H} NMR: δ 155.65.

5c: colorless crystals (0.30 g, 85%). Anal. Calcd for $C_{17}H_{40}N_2SiAl_2$: C, 57.59; H, 11.37; N, 7.90. Found: C, 57.72; H, 11.52; N, 8.04. ^{1}H NMR: δ −0.50 (s, 12H, AlC*H*$_3$), 0.64 (m, 4H, SiC*H*$_2$), 1.32 (s, 18H, ^{t}BuN), 1.51 (m, 4H, CH$_2$C*H*$_2$), 1.87 (m, 2H, CH$_2$CH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR: δ −0.39 (Al*Me*), 20.18 (Si*C*H$_2$), 25.27 (CH$_2$*C*H$_2$), 28.39 (CH$_2$CH$_2$*C*H$_2$), 34.79 (NC*Me*$_3$), 51.78 (N*C*Me$_3$). ^{27}Al{^{1}H} NMR: δ 154.14.

5d: colorless crystals (0.31 g, 91%). Anal. Calcd for $C_{16}H_{36}N_2SiAl_2$: C, 56.77; H, 10.72; N, 8.28. Found: C, 56.90; H, 10.90; N, 8.19. ^{1}H NMR: δ −0.56 (s, 6H, AlC*H*$_3$), −0.47 (s, 6H, AlC*H*$_3$), 1.26 (s, 18H, ^{t}BuN), 1.76 (m, 4H, SiC*H*$_2$), 6.00 (m, 2H, ═C*H*). ^{13}C{^{1}H} NMR: δ −1.96 (Al*Me*), 21.83 (Si*C*H$_2$), 34.30 (NC*Me*$_3$), 51.98 (N*C*Me$_3$), 130.24 (═*C*H). ^{27}Al{^{1}H} NMR: δ 158.98.

Preparation of the Chlorine-Bridged Dinuclear Zirconium Diamides, [{(cycl)Si(^{t}BuN)}$_2$Zr$_2$(Cl)(μ-Cl)$_3$(THF)] (6). Representative procedure: Complex **2** (1.0 mmol) in toluene (10 mL) was added to ZrCl$_4$(THF)$_2$ (0.76 g, 2.0 mmol) in toluene (10 mL) at room temperature. The reaction mixture was heated to refluxing temperature and stirred for 12 h. The resulting yellow solution was dried under vacuum to afford a yellow solid. The solid was extracted with pentane, and the filterate was concentrated and cooled to −45 °C. Yellow solid **6** was isolated by filtration, washing with cold pentane, and drying in vacuo.

6a: colorless crystals (0.34 g, 42%). Anal. Calcd for $C_{26}H_{56}N_4OSi_2Cl_4Zr_2$: C, 38.03; H, 6.87; N, 6.82. Found: C, 38.20; H, 6.98; N, 6.95. ^{1}H NMR: δ 1.13 (m, 4H, SiC*H*$_2$), 1.48 (s, 18H, ^{t}BuN), 1.67 (m, 2H, CH$_2$C*H*$_2$), 2.08 (m, 4H, OCH$_2$C*H*$_2$), 4.37 (m, 4H, OC*H*$_2$). ^{13}C{^{1}H} NMR: δ 13.65 (Si*C*H$_2$), 25.80 (CH$_2$*C*H$_2$), 33.87 (NC*Me*$_3$), 60.07 (N*C*Me$_3$).

6b: colorless oil (0.31 g, 37%). Anal. Calcd for $C_{28}H_{60}N_4OSi_2Cl_4Zr_2$: C, 39.60; H, 7.12; N, 6.60. Found: C, 39.72; H, 7.26; N, 6.47. ^{1}H NMR: δ 0.86 (m, 4H, SiC*H*$_2$), 1.40 (s, 18H, ^{t}BuN), 1.80 (m, 4H, CH$_2$C*H*$_2$), 2.08 (m, 4H, OCH$_2$C*H*$_2$), 4.41 (m, 4H, OC*H*$_2$). ^{13}C{^{1}H} NMR: δ 13.25 (Si*C*H$_2$), 25.75 (CH$_2$*C*H$_2$), 34.77 (NC*Me*$_3$), 59.28 (N*C*Me$_3$).

6c: colorless crystals (0.46 g, 53%). Anal. Calcd for $C_{30}H_{64}N_4OSi_2Cl_4Zr_2$: C, 41.07; H, 7.35; N, 6.39. Found: C, 41.21; H, 7.26; N, 6.47. ^{1}H NMR: δ 0.60 (m, 4H, SiC*H*$_2$), 1.36 (m, 4H,

CH_2CH_2), 1.43 (s, 18H, ^tBuN), 1.66 (m, 2H, $CH_2CH_2CH_2$), 2.06 (m, 4H, OCH_2CH_2), 4.40 (m, 4H, OCH_2). $^{13}C\{^1H\}$ NMR: δ 17.92 ($SiCH_2$), 25.49 (CH_2CH_2), 30.62 ($CH_2CH_2CH_2$), 33.99 ($NCMe_3$), 58.08 ($NCMe_3$).

6d: colorless oil (0.38 g, 45%). Anal. Calcd for $C_{28}H_{56}N_4OSi_2Cl_4Zr_2$: C, 39.79; H, 6.68; N, 6.63. Found: C, 39.92; H, 6.90; N, 6.49. ^1H NMR: δ 1.37 (s, 18H, ^tBuN), 1.55 (m, 4H, $SiCH_2$), 2.11 (m, 4H, OCH_2CH_2), 4.44 (m, 4H, OCH_2), 6.03 (m, 2H, $=CH$). $^{13}C\{^1H\}$ NMR: δ 19.92 ($SiCH_2$), 33.69 ($NCMe_3$), 60.57 ($NCMe_3$), 130.97 ($=CH$).

Crystal Structure Determination. Crystals of **2a**, **2d**, **3a**, **4b**, and **5c** were obtained from toluene, sealed in glass capillaries under argon, and mounted on the diffractometer. Data were collected and corrected for Lorentz and polarization effects. Each structure was solved by the application of direct methods using the SHELXS-96 program[15a] and least-squares refinement using SHELXL-97.[15b] After anisotropic refinement of all non-H atoms several H atom positions could be located in difference Fourier maps. These were refined isotropically while the remaining H atoms were calculated in idealized positions and included into the refinement with fixed atomic contributions. Further detailed information is listed in Table 1.

Acknowledgment. This work was supported by Grant No. 2000-2-12200-003-1 from the Basic Research Program of the Korea Science and Engineering Foundation.

Supporting Information Available: Crystallographic data (excluding structure factors) for the structures **2a**, **2d**, **3a**, **4b**, and **5c** reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020587L

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