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Synthesis and molecular structures of zirconium complexes that contain bidentate amido ligands

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ABSTRACT

Zirconium complexes that contain bidentate amido ligands, Zr_{2} {EtN(CH₂)₃NEt}₄ (1), Zr_{2} {PhN(CH₂)₂NPh}₄ (2), Zr{Me₃SiN(CH₂)₃NSiMe₃]₂ (3) and Zr{*trans-N*,*N*'-diphenyl-1,2-diaminocyclohexane}Cl₂(THF)₂ (4), have been prepared by the reaction of lithium diamido reagents with ZrCl₄, and characterized by single crystal X-ray diffraction. The molecular structures of complexes 1–4 are discussed.

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1. Introduction

Zirconium (IV) amido complexes are useful precursors to ansazirconocenes and other Zr compounds [1]. Amine elimination reactions of Zr(NR₂)₄ and HCp'YCp'H [2] compounds provide access to ansa-(Cp'YCp')Zr(NR_2)₂ complexes [3,4], which are important in stereoselective catalysis and olefin polymerization [5]. The steric properties of the amido ligands strongly influence the rates and rac/meso selectivity of these reactions. Homoleptic Zr(NR₂)₄ compounds are also useful precursors to Zr(NR₂)₂X₂ and Zr(NR₂)₂X₂L₂ complexes [6]. Salt elimination reactions of chelated $Zr{RN(CH_2)_nNR}Cl_2(THF)_2$ (*n* = 2, 3) complexes and $Li_2[Cp'YCp']$ reagents provide access to ansa- $(Cp'YCp')Zr\{RN(CH_2)_nNR\}$ complexes, which are easily converted to ansa-(Cp'YCp')ZrCl₂ catalysts [7]. The conformations of the $Zr{RN(CH_2)_nNR}$ chelate rings control the rac/ meso selectivity in these reactions. In particular, twist conformations that place the N-R groups on opposite sides of the N-Zr-N plane favor the formation of rac-(Cp'YCp')Zr{RN(CH₂)_nNR} products [7].

Two general structure types have been observed for simple $Zr(NR_2)_4$ compounds in the solid state (Fig. 1). Complexes with sterically small amido ligands adopt dinuclear, edge-shared, trigonal bipyramidal structures with two bridging amidos, as exemplified by $Zr_2(NMe_2)_8$ (5) [8]. Sterically crowded amidos for which bridg-

ing is disfavored adopt mononuclear tetrahedral structures, as exemplified by $Zr(NPh_2)_4$ (6) [9].

The structures of chelated $Zr\{RNYNR\}_2$ complexes are similar to those of their non-chelated counterparts, as shown in Fig. 1. The homoleptic chelated-bisamido Zr complex $\{Zr[(N^iPr)_2SiMe_2]_2\}_2$ (7) has as a dinuclear trigonal bipyramidal structure similar to that of **5** [10]. In contrast, the bulky N-*R* groups and larger bisamido ligand bite angles of Zr{*trans*-1,2-(NSiMe_3)_2-cyclohexane}_2 (**8**) [11] and Zr{Ph_2MeSiN(CH_2)_3NSiMePh_2}_2 (**9**) [12] disfavor formation of dinuclear species and these complexes adopt distorted tetrahedral structures similar to that of **6**. In both **8** and **9**, the N–R groups lie in their respective N–Zr–N planes.

Several Zr{RN(CH₂)_nNR}X₂ and Zr{RN(CH₂)_nNR}X₂L₂ complexes have been prepared and representative structures are shown in Fig. 2. Five-membered chelate rings in these systems often adopt flat conformations, as observed in Zr{Ar₂BN(CH₂)₂NBAr₂}Me₂, Ar = 2,4,6-ⁱPr₃-Ph (**10**) and Zr{Cy₂BN(CH₂)₂NBCy₂}Et₂ (**11**) [13]. This conformation positions the N–*BR*₂ groups of **10** and **11** in the N–Zr–N plane. The six-membered rings in Zr{Ph₂^tBu-SiNCH₂CMe₂CH₂NSi^tBuPh₂}Cl₂ (**12**) [14] and Zr{ⁱPr₃SiN(CH₂)₃N-SiⁱPr₃Cl₂ (**13**) [15] adopt boat conformations, in which the N-*SiR*₃ groups again lie in the N–Zr–N plane. In contrast, the chelate ring in Zr{Me₃SiN(CH₂)₃NSiMe₃Cl₂(THF)₂ (**14**) [16] adopts a pronounced twist conformation, which places the N-*SiMe*₃ groups on opposite sides of the N–Zr–N plane.

Understanding the structures and conformational properties of Zr compounds with chelated-bisamido ligands may contribute to the development of improved methods for the stereoselective





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Fig. 1. Structures of $Zr_2(NMe_2)_8$ (**5**), $Zr(NPh_2)_4$ (**6**), $\{Zr[(N^iPr)_2SiMe_2]_2\}_2$ (**7**), $Zr\{trans-1,2-(NSiMe_3)_2-cyclohexane\}_2$ (**8**) and $Zr\{Ph_2MeSiN(CH_2)_3NSiMePh_2\}_2$ (**9**).



Fig. 2. Structures of $Zr{Ar_2BN(CH_2)_2NBAr_2}Me_2$ (10), $Zr{Cy_2BN(CH_2)_2NBCy_2}Et_2$ (11), $Zr{Ph_2}^tBuSiNCH_2CMe_2CH_2NSi^tBuPh_2}Cl_2$ (12), $Zr{}^tPr_3SiN(CH_2)_3NSi^tPr_3}Cl_2$ (13), and $Zr{Me_3SiN(CH_2)_3NSiMe_3}Cl_2THF_2$ (14).

synthesis of *ansa*-zirconocenes [7]. Here we describe the synthesis and structures of four Zr bisamido complexes, Zr₂{EtN(CH₂)₃NEt}₄ (**1**), Zr₂{PhN(CH₂)₂NPh}₄ (**2**), Zr{Me₃SiN(CH₂)₃NSiMe₃}₂ (**3**) [15] and Zr{*trans-N*,*N*'-diphenyl-1,2-diaminocyclohexane}Cl₂(THF)₂ (**4**).

2. Experimental

All reactions were performed under nitrogen or vacuum using standard Schlenk techniques or in a nitrogen-filled drybox. Nitrogen was purified by passage through activated molecular sieves and Q-5 oxygen scavenger. Pentane, hexanes, toluene and benzene were distilled from sodium/benzophenone or purified by passage through activated alumina and BASF R3-11 oxygen removal catalyst. Benzene- d_6 and THF- d_8 were distilled from sodium/benzophenone and stored under vacuum. ZrCl₄ was purchased from Cerac and sublimed before use. The compounds *trans*-1,2-diaminocyclohexane, EtNH(CH₂)₃NHEt and PhNH(CH₂)₂NHPh were purchased from Aldrich and used as received. Me₃SiNH(CH₂)₃NHSiMe₃ was prepared by the literature procedure [17].

NMR spectra were recorded on Bruker AMX-360, AMX-400 or AMX-500 spectrometers in flame-sealed or Teflon-valved tubes at ambient probe temperatures. ¹H and ¹³C chemical shifts are reported relative to SiMe₄ and were determined by reference to the residual ¹H and ¹³C solvent resonances. Coupling constants are given in Hz.

2.1. Synthesis

2.1.1. Li₂[EtN(CH₂)₃NEt]

A solution of ^{*n*}BuLi in hexanes (5.08 mL, 2.5 M, 13 mmol) was added to a solution of EtNH(CH₂)₃NHEt (0.819 g, 6.21 mmol) in hexanes (50 mL) over 5 min by syringe at -78 °C. The resulting slurry was stirred for 24 h during which time the mixture was allowed to warm to 25 °C. The mixture was filtered to yield a white solid. The solid was washed with hexanes (100 mL) and dried under vacuum (0.80 g, 91%). The same procedure was carried out on a 8.19 g (62.88 mmol) scale with an 81% isolated yield. ¹H NMR (THF-*d*₈): δ 3.00 (t, *J* = 6, 4H, CH₂), 2.88 (q, *J* = 8, 4H, CH₂), 1.73 (br, m, 2H, CH₂), 1.01 (t, *J* = 8, 6H, CH₃).

2.1.2. $Zr_2\{EtN(CH_2)_3NEt\}_4$ (1)

A flask was charged with ZrCl₄ (3.13 g, 14.2 mmol) and cooled to -78 °C. Et₂O (50 mL) was added and the resulting slurry was stirred for 5 min at -78 °C. A solution of Li₂[EtN(CH₂)₃NEt] (4.04 g, 28.4 mmol) in THF (50 mL) was cooled to -78 °C and added to the ZrCl₄/Et₂O slurry by cannula transfer over a 30 min period. The mixture was stirred overnight while the flask was allowed to warm to 25 °C. The volatiles were removed under vacuum. Toluene (60 mL) was added by cannula transfer and the mixture was stirred overnight at 25 °C. The mixture was filtered and the filtrate was dried under vacuum to yield an orange solid. The solid was taken up in benzene (10 mL) and hexanes (100 mL) was added by cannula transfer. The solution was cooled -35 °C overnight and filtered through a medium glass frit to yield white, X-ray quality crystals (0.965 g, 19%). The NMR spectra of **1** are complex suggesting that **1** may exist in several forms in solution.

2.1.3. $Zr_2\{PhN(CH_2)_2NPh\}_4$ (2)

The preparation and characterization of **2** were previously reported [7b]. X-ray quality crystals were obtained by recrystallization at -35 °C from a solution of CH₂Cl₂ layered with hexanes to yield pale yellow crystals.

2.1.4. Zr{Me₃SiN(CH₂)₃NSiMe₃}₂ (3)

Complex **3** was prepared by a literature method [15]. X-ray quality crystals were obtained by recrystallization from pentane at -78 °C.

2.1.5. Trans-N,N'-diphenyl-1,2-diaminocyclohexane

Trans-N,N-diphenyl-1,2-diaminocyclohexane was synthesized by a modified literature method [18]. A flask was charged with *trans*-1,2-diaminocyclohexane (1.02 g, 8.97 mmol), bromobenzene (2.95 g, 18.83 mmol) and toluene (15 mL) by cannula transfer. A separate flask was charged with Pd(OAc)₂ (0.100 g, 0.448 mmol), BINAP (0.558 g, 0.897 mmol), Na[O^tBu] (2.58 g, 26.9 mmol) and toluene (30 mL). The two mixtures were stirred for 60 min at room temperature and the solution containing 1,2-diaminocyclohexane and bromobenzene was added to the second flask by cannula transfer. The mixture was heated at 100 °C for 2 h, cooled to 25 °C, and diluted with hexanes (150 mL). The mixture was stirred for 8 h and filtered through a plug of silica gel. The silica was washed with CH_2Cl_2 (25 mL), and the wash and filtrates were combined and dried under vacuum to yield an amber oil. The oil was purified by column chromatography (silica gel, CH_2Cl_2 eluent) to yield an amber gel which was pure enough for use subsequent reactions (0.708 g, 71%). ¹H NMR (CDCl₃): δ 7.16 (t, *J* = 8.0, 4H, *m*-Ph), 6.70 (t, *J* = 8.0, 2H, *p*-Ph), 6.61 (d, *J* = 8.0, 4H, *o*-Ph), 3.80 (br s, 2H, NH), 3.19 (m, 2H, CH₂), 2.35 (m, 2H, CH₂), 1.76 (m, 2H, CH₂), 1.40 (m, 2H, CH₂), 1.22(m, 2H).

2.1.6. Li₂[trans-N,N'-diphenyl-1,2-diaminocyclohexane]

A solution of ^{*n*}BuLi in hexanes (5.1 mL, 2.5 M, 12.8 mmol) was added to a solution of *trans-N*,*N'*-diphenyl-1,2-diaminocyclohexane (1.7 g, 6.4 mmol) in benzene (150 mL) over 5 min by syringe at 23 °C. The resulting slurry was stirred for 2 h at 23 °C and filtered to yield a pale yellow solid. The solid was washed with hexanes (70 mL) and dried under vacuum to yield a pale yellow solid (1.65 g, 92%). ¹H NMR (THF-*d*₈): δ 6.96 (t, *J* = 8.0, 4H, *m*-Ph), 6.17 (d, *J* = 8.0, 4H, *o*-Ph), 5.78 (t, *J* = 8.0, 2H, *p*-Ph), 2.94 (d, *J* = 8.0, 2H, CH₂), 2.46 (d, *J* = 8.0, 2H, CH₂), 1.73 (obscured by solvent, 2H, CH₂), 1.41 (t, *J* = 8.0, 2H, CH₂), 0.08 (br m, 2H, CH₂).

2.1.7. Zr{trans-N,N'-diphenyl-1,2-diaminocyclohexane}Cl₂(THF)₂ (4)

A flask was charged with ZrCl₄ (0.420 g, 1.80 mmol) and Li₂[trans-N,N'-diphenyl-1,2-diaminocyclohexane] (0.500 g, 1.80 mmol). A mixture of THF and Et₂O (1/1 by volume, 175 mL) was added by vacuum transfer at -196 °C. The mixture was placed in an ice bath at 0 °C and stirred for 12 h, during which time it was allowed to warm to room temperature. The volatiles were removed under vacuum at 30 °C to yield a yellow solid. Benzene (75 mL) was added by vacuum transfer at -196 °C and the mixture was stirred for 2 h at room temperature. The mixture was filtered through a medium porosity glass frit (10-20 um pore size) and the volatiles were removed from the filtrate under vacuum at 35 °C, yielding an orange solid (0.708 g, 68%). X-ray quality crystals were grown from a 7/1 (by volume) toluene/hexanes solution at -35 °C. ¹H NMR (C_6D_6): δ 7.39 (br d, I = 8.0, 4H, o-Ph), 7.19 (t, I = 8.0, 4H, m-Ph), 6.88 (t, J = 8.0, 2H, p-Ph), 4.70 (br s, 2H) 3.64 (br s, 8H, THF), 1.85 (br d, J = 8.0, 2H, CH₂), 1.48 (br d, J = 8.0, 2H, CH₂), 1.16 (br s, 4H, CH₂), 1.07 (br s, 8H, THF). ¹³C{¹H} NMR (C_6D_6) δ 149.4, 128.8, 124.7, 122.4, 73.3, 70.8, 30.7, 25.7, 25.1.

2.2. X-ray structure determinations

Crystallographic data are summarized in Tables 1 and 2. ORTEP plots are drawn at the 50% probability level. Non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The asymmetric unit of $2 \cdot (CH_2Cl_2)$ contains a disordered solvent molecule, in which atom Cl(1) is disordered over two positions in an 85/15 ratio.

3. Results and discussion

3.1. Synthesis and structure of $Zr_2\{EtN(CH_2)_3NEt\}_4$ (1)

The reaction of $Li_2[EtN(CH_2)_3NEt]$ with $ZrCl_4$ yields **1**. As shown in Fig. 3, **1** adopts a dinuclear structure comprising two edge-shared, trigonal bipyramidal units, which is similar to those of **5**

Table 1

Summary of X-ray diffraction data for $Zr_2\{EtN(CH_2)_3NEt\}_4$ (1) and $Zr_2\{PhN(CH_2)_2NPh\}_4$ (2).

	1	$\bm{2}\cdot CH_2Cl_2$
Formula	$C_{28}H_{64}N_8Zr_2$	C57H58N8Cl2Zr2
Formula weight	695.31	1108.49
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	Р
a (Å)	12.052(2)	9.9109(6)
b (Å)	13.159(3)	11.640(1)
c (Å)	21.385(4)	12.677(1)
α (°)	90.0	92.882(1)
β (°)	100.44(3)	109.265(3)
γ (°)	90.0	112.284(1)
V (Å ³)	3335.2(1)	1349.0(2)
Ζ	4	2
T (K)	100(2)	173(2)
Crystal color, habit	Transparent, fragment	Yellow, fragment
GOF on F ²	1.167	1.026
<i>R</i> indices $(I > 2\sigma(I))^a$	$R_1 = 0.0436, wR_2 = 0.0890$	$R_1 = 0.0248, wR_2 = 0.0710$
R indices (all data) ^a	$R_1 = 0.0507$, $wR_2 = 0.092$	$R_1 = 0.0276, wR_2 = 0.0726$
(all data)	$R_1 = 0.0307, WR_2 = 0.032$	$R_1 = 0.0270, WR_2 = 0.072$

^a $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; \quad wR_2 = \left[\sum \left[w \left(F_o^2 - F_c^2 \right)^2 \right] / \sum \left[w \left(F_o^2 \right)^2 \right] \right]^{1/2}, \text{ where } w = q \left[\sigma^2 \left(F_o^2 \right) + (aP)^2 + bP \right]^{-1}.$

Table 2

Summary of X-ray diffraction data for $Zr\{Me_3SiN(CH_2)_3NSiMe_3\}_2$ (**3**) and $Zr\{trans-N,N'-diphenyl-1,2-diaminocyclohexane\}Cl_2(THF)_2$ (**4**).

	3	4
Formula	C ₁₈ H ₄₈ N ₄ Si ₄ Zr	C ₂₆ H ₃₆ N ₂ Cl ₂ O ₂ Zr
Formula weight	524.18	662.82
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	$P2_1/n$
a (Å)	17.159(3)	14.280(2)
b (Å)	10.427(2)	11.044(3)
c (Å)	17.175(3)	21.120(4)
β (°)	111.32(3)	107.310(4)
V (Å ³)	2862.6(10)	3179.8(1)
Ζ	4	4
T (K)	100(2)	100(2)
Crystal color, habit	Clear, fragment	Yellow, fragment
GOF on F ²	1.108	1.007
R indices $(I > 2\sigma(I))^a$	$R_1 = 0.0515, wR_2 = 0.1509$	$R_1 = 0.0263$, wR2 = 0.0617
R indices (all data) ^a	$R_1 = 0.0515, wR_2 = 0.1509$	$R_1 = 0.0330, wR_2 = 0.0625$

^a $R_1 = \Sigma ||F_0| - |F_c||/\Sigma |F_0|;$ $wR_2 = \left[\sum \left[w \left(F_0^2 - F_c^2 \right)^2 \right] / \sum \left[w \left(F_0^2 \right)^2 \right] \right]^{1/2},$ where $w = q \left[\sigma^2 \left(F_0^2 \right) + (aP)^2 + bP \right]^{-1}.$

and **7**. At Zr(1), N(3) and N(7) occupy the axial positions, and N(4), N(6) and N(8) occupy the equatorial sites. At Zr(2), N(1) and N(8) occupy the axial positions and N(2), N(5) and N(7) occupy the equatorial sites. The N(1)–N(2) bisamido ligand chelates to Zr(2), and the N(3)–N(4) bisamido chelates to Zr(1). In both cases, the bisamido ligand occupies an axial and an equatorial site, and as shown in Fig. 3, the chelate rings have twist conformations. The N(5)–N(6) bisamido ligand bridges the two Zr centers by monodentate *terminal* coordination at an equatorial site at each Zr, and as shown in Fig. 3, has a twist conformation. Finally, the N(7)–N(8) bisamido ligand forms a double bridge in which each N forms a μ^2 -bridge between the two Zr centers. This bisamido ligand has a slightly puckered conformation.

3.2. Synthesis and structure of $Zr_2\{PhN(CH_2)_2NPh\}_4(2)$

The reaction of $Li_2[PhN(CH_2)_2NPh]$ with $ZrCl_4$ yields **2**. As shown in Fig. 4, **2** has a dinuclear structure comprising two edge-shared,



highly distorted, trigonal bipyramidal Zr units, which are related by a crystallographically imposed inversion center. This structure is again grossly similar to those of **5** and **7**. N(1) and N(4) occupy axial positions, and N(2), N(3) and N(4A) occupy equatorial sites. The principal distortion is a displacement of the "axial" N(4) atom toward the equatorial plane by ca. 36°. The connectivity of the Zr bisamido units and the conformations of the chelate rings in **2** are different from those in **1**. The N(1)–N(2) bisamido ligand of **2** chelates to Zr(1), occupies one axial and one equatorial site, and has a flat envelope conformation. The N(3)–N(4) bisamido ligand binds in a terminal fashion to Zr(1) via N(3) and in a μ^2 -bridging mode to both Zr centers via N(4). These differences in the structures of **2** and **1** may be due to the smaller natural bite angle of



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Fig. 4. Molecular structure and views of the chelate rings of $Zr_2\{PhN(CH_2)_2NPh\}_4$ (**2**). H atoms are omitted. Bond distances (Å): Zr(1)-C(23) 2.807(2), Zr(1)-N(1) 2.081(2), Zr(1)-N(2) 2.049(2), Zr(1)-N(3) 2.150(2), Zr(1)-N(4) 2.302(2). Bond angles (°): N(1)-Zr(1)-N(2) 84.18(6), N(3)-Zr(1)-N(4) 74.36(5), N(1)-Zr(1)-N(3) 97.59(5), N(1)-Zr(1)-N(4) 144.25(5), N(2)-Zr(1)-N(3) 113.71(5), N(2)-Zr(1)-N(4) 131.25(5). Sums of angles at N (°): N(1) 357.1(3), N(2) 359.7(4), N(3) 359.9(5), N(4) 335.1(5). Angles between planes (°): C(9)-N(2)-C(2)/N(1)-Zr(1)-N(2) 7.2, C(1)-N(1)-C(3)/N(1)-Zr(1)-N(2) 25.9. Deviations of atoms from the N(1)-Zr(1)-N(2) plane (Å): C(9) 0.176, C(2) -0.099, C(1) -0.611, C(3) 0.082. Deviations of atoms from the N(3)-Zr(1)-N(4) plane (Å): C(23) 1.405, C(16) -0.602, C(15) 0.262, C(17) 0.194.

the $[PhN(CH_2)_2NPh]^{2-}$ ligand versus the $[EtN(CH_2)_3NEt]^{2-}$ ligand. Interestingly, in **2** there is a close contact between Zr and the ipso carbon of the phenyl ring in the bridging amido unit (Zr(1)–C(23), 2.807(2) Å), and the corresponding Zr–N–C_{ipso} angle is small (Zr(1)–N(4)–C(23), 95.10(9) deg). These data indicate that a weak Ph–Zr donor interaction is present, analogous to the M– η^2 -CH₂Ph interactions commonly observed in unsaturated metal benzyl complexes [19]. Related donor interactions are observed in Zr{1,2-(NSi^PPr₃)₂-C₆H₄}₂ [20] and Zr{1,2-(NSiMe₃)₂-C₁₀H₆}₂ [21]. Additionally, in **2**, the N–Ph rings of N(1), N(4A) and N(2A) are arranged for staggered π -stacking with an average distance between the planes of 3.32 Å (Fig. 4) [22].

3.3. Synthesis and structure of $Zr\{Me_3SiN(CH_2)_3NSiMe_3\}_2$ (3)

The reaction of Li₂[Me₃SiN(CH₂)₃NSiMe₃] with ZrCl₄ yields **3**. As shown in Fig. 5, **3** adopts a monomeric, distorted tetrahedral structure. The major distortion is a 14° reduction of the N–Zr–N angle of the chelate ring from the ideal tetrahedral angle. The angles between the N–Zr–N planes (N(1)–Zr–N(2)/N(1A)–Zr–N(2A), 88.4°; (N(1)–Zr–N(1A)/N(2)–Zr–N(2A), 71.1°) also deviate from the ideal tetrahedral value of 90°. The chelate ring of **3** adopts an envelope conformation, which places the N-SiMe₃ groups in the N(1)–Zr(1)–N(2) plane.

3.4. Synthesis and structure of Zr{trans-N,N'-diphenyl-1,2diaminocyclohexane}Cl₂(THF)₂ (**4**)

The reaction of Li₂[*trans-N*,*N*'-diphenyl-1,2-diaminocyclohexane] with $ZrCl_4$ yields **4**. As shown in Fig. 6, **4** adopts a monomeric octahedral structure. The major distortion from ideal octahedral geometry is the reduced Cl–Zr–Cl angle of 164°. The chelate ring of **4** adopts a puckered conformation, which places the N–Ph groups in the N(1)–Zr(1)–N(2) plane. The cyclohexane ring adopts a normal chair conformation.

4. Conclusion

The structures of **1–4** provide useful insights to the nuclearity, metal coordination geometries and bisamido chelate ring conformations of zirconium amido complexes. The steric bulk of the N–*R* groups of the amido ligands influences the preference for mononuclear or dinuclear species. Small N–*R* groups favor dinuclear complexes, while large N–*R* substituents favor mononuclear species. The six-membered $Zr{EtN(CH_2)_3NEt}$ chelate rings in **1** adopt twist conformations that position the N–*Et* groups on opposite sides of their respective N–Zr–N planes. In contrast, the $Zr{Me_3}_{SiN(CH_2)_3NSiMe_3}$ chelate rings in **3**, which contain larger N–*SiMe_3* groups, adopt an envelope conformation that places the N–*SiMe_3* groups in the N–Zr–N plane. The five-membered chelate rings in complexes **2** and **4** adopt slightly puckered conformations that place the N–*R* groups close to the N–Zr–N plane.



Fig. 5. Molecular structure and views of the chelate ring of $Zr\{Me_3SiN(CH_2)_2NSiMe_3\}_2$ (**3**). H atoms are omitted. Bond distances (Å): Zr(1)-N(1) 2.060(4), Zr(1)-N(2) 2.048(4). Bond angles (°): N(1)-Zr(1)-N(2) 98.5(1), N(1)-Zr(1)-N(2A) 116.0(1), N(1)-Zr(1)-N(1A) 112.0(2). Sums of angles at N (°): N(1) 359.7(4), N(2) 359.9(4). Angles between planes (°): Si(1)-N(1)-C(4)/N(1)-Zr(1)-N(2) 5.5, Si(2)-N(2)-C(6)/N(1)-Zr(1)-N(2) 9.0. Deviations of atoms from the N(1)-Zr(1)-N(2) plane (Å): Si(1) 0.091, C(4) - 0.230, C(5) - 0.416, C(1) - 0.132, Si(2) 0.092.



Fig. 6. Molecular structure and view of the chelate ring of $Zr\{trans-1,2-(NPh)_2-cyclohexane\}Cl_2(THF)_2$ (**4**). H atoms are omitted with the exception of H(1A) and H(2A) in the view at the top right. Bond distances (Å): Zr(1)-N(1) 2.063(2), Zr(1)-N(2) 2.061(2), Zr(1)-Cl(1) 2.490(7), Zr(1)-Cl(2) 2.489(7), Zr(1)-O(1) 2.300(2), Zr(1)-O(2) 2.284(2). Bond angles (°): N(1)-Zr(1)-N(2) 80.98(6), O(1)-Zr(1)-O(2) 80.59(5), Cl(1)-Zr(1)-Cl(2) 164.98(2). Sums of angles at N (°): N(1) 356.6(4), N(2) 356.5(4). Angles between planes (deg): C(1)-N(1)-Cr(7)/N(1)-Zr(1)-N(2) 15.3, C(13)-N(2)-C(2)/N(1)-Zr(1)-N(2) 22.4. Deviations of atoms from the N(1)-Zr(1)-N(2) plane (Å): C(1) - 0.085, C(2) 0.085, C(13) 0.020, C(7) - 0.281.

5. Supplementary material

CCDC 704612, 704477, 704493 and 704494 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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