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Triamidoamine Chemistry of Zirconium

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The reactions of $H_3(NN'_3)$ ($NN'_3 = N(CH_2CH_2NSiBu^tMe_2)_3$) with $[Zr(CH_2Ph)_4]$ and $[Zr(NMe_2)_4]$ give the azazirconatranes $[Zr(NN'_3)(CH_2Ph)]$ and $[Zr(NN'_3)(NMe_2)]$, respectively. The reaction of $[Li_3(NN'_3)(THF)_3]$ with $[ZrCl_4(THF)_2]$ fails to yield $[Zr(NN'_3)Cl]$ cleanly, but this compound is accessible by reaction of $[Zr(NN'_3)(CH_2Ph)]$ with BCl_3 or of $[Zr(NN'_3)(NMe_2)]$ with $SiMe_3Cl$. The molecular structures of $[Zr(NN'_3)X]$ (X = CH_2Ph, NMe_2, Cl) show that the triamidoamine ligands adopt the usual 3-fold symmetric arrangement to give approximately trigonal-bipyramidal complexes. Attempted sublimation of $[Zr(NN'_3)(CH_2Ph)]$ or its treatment with H_2 leads to clean conversion to the metallacyclic complex $[Zr\{N(CH_2CH_2NSiBu^tMe_2)_2CH_2CH_2NSiBu^tMeCH_2\}]$ via deprotonation of a silylmethyl group and elimination of toluene. The molecular structure of this complex contrasts with those above in that the *tert*-butyldimethylsilyl groups adopt an upright conformation as a consequence of the presence of the metallacyclic unit. The dihedral angles $N_{ax}-Zr-N_{eq}-Si$ are in the range 173.8−177.2°. Exposure of the metallacycle to D_2 gas leads to deuteration of all three Me_2Si groups via sequential deuteriolysis/σ-bond metathesis. The less acidic ^tBuSi and backbone CH_2 groups are unaffected.

Introduction

While triamidoamine $[N(CH_2CH_2NR)_3]^{3-}$ ligand chemistry is well-developed for most of the early transition metals,[1] complexes of the later group 4 elements Zr and Hf are limited to those of the type $[M(NR'_2)\{N(CH_2CH_2NR)_3\}]$.[2] Titanium triamidoamines have been reported by Verkade,[3] Schrock,[4] and Gade;[5] the last author has also reported closely related triamide complexes (vide infra).[6] We have recently found that 3-fold symmetric complexes of metals with large van der Waals radii such as the lanthanides[7] and actinides[8] can be isolated by using the triamidoamine ligand with the substituent R = $SiBu^tMe_2$ (henceforth NN'_3).[9] Use of the ligand R = $SiMe_3$, on the other hand, is either unsuccessful or leads to complexes with unsymmetrical structures.[10] In this paper we show that the $SiBu^tMe_2$-substituted ligand can be successfully applied to the synthesis of triamidoamine complexes of zirconium.

Experimental Section

All manipulations were carried out under an inert atmosphere of argon either using standard Schlenk techniques or in an MBraun drybox. Sublimation was performed by oven heating (±1 °C) of the material under study contained in one end of a horizontal glass tube, dynamic vacuum in the system being maintained by a turbomolecular pumping system protected by a wide-bore liquid-nitrogen-cooled trap. NMR samples were made up in the drybox, and the sample tubes were sealed in vacuo or using Young type concentric stopcocks. Pentane was predried over sodium wire and then distilled over sodium−potassium alloy under an atmosphere of dinitrogen. Deuterated solvents were dried by refluxing over molten potassium in vacuo and were then distilled trap-to-trap, also in vacuo. NMR spectra were recorded at ca. 295 K on Bruker AC-250, AC-400, or DMX-300 spectrometers and the spectra referenced internally using residual protio solvent resonances relative to tetramethylsilane (δ 0 ppm). EI mass spectra were obtained on a VG Autospec mass spectrometer. Elemental analyses were performed by Warwick Analytical Services. BCl_3 and $SiMe_3Cl$ were purchased from Aldrich Chemical Co. Ltd., while H_2 (grade 6.0, 99.999%) was purchased from Air Products. $[Zr(CH_2Ph)_4]$[11] and $[Zr(NMe_2)_4]$[12] were synthesized by literature methods.

$[Zr(NN'_3)(CH_2Ph)]$ (1). Pentane (30 cm^3) was added to a mixture of $[H_3(NN'_3)]$[13,14] (0.27 g, 0.55 mmol) and $[Zr(CH_2Ph)_4]$

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(0.25 g, 0.55 mmol) at room temperature. The Schlenk vessel was wrapped in aluminum foil, and the solution was stirred at ambient temperature for 3 days. After filtration, the pale orange solution was concentrated by evaporation in vacuo and cooled to −30 °C to afford colorless crystals (0.33 g, 90%).

Anal. Calcd for $C_{31}H_{64}N_4Si_3Zr$: C, 55.83; H, 9.68; N, 8.41. Found: C, 54.18; H, 9.47; N, 8.14. ^1H NMR (293 K, d_6-benzene): δ 7.36 (m, 2H, Ph), 7.28 (m, 2H, Ph), 6.92 (m, 1H, Ph), 3.32 (t, 6H, CH_2), 2.63 (s, 2H, CH_2Ph), 2.21 (t, 6H, CH_2), 1.04 (s, 27H, Bu^t), 0.33 (s, 18H, Me_2Si). $^{13}C\{^1H\}$ NMR (293 K, d_6-benzene): δ 150.99 (s, Ph), 125.94 (s, Ph), 120.11 (s, Ph), 63.95 (s, CH_2Ph), 63.35 (s, CH_2), 48.15 (s, CH_2), 27.12 (s, *Me*$_3$C), 20.72 (s, Me_3*C*), −3.59 (s, Me_2Si). MS (EI): *m*/*z* 575 (28%, $M^+ - CH_2Ph$), 536 (57%, $M^+ - SiMe_2Bu^t - Me$), 517 (55%, $M^+ - CH_2Ph - Bu^t$).

[Zr(NN′₃)(NMe₂)] (2). Pentane (30 cm^3) was added to a mixture of $[H_3(NN'_3)]$ (0.91 g, 1.87 mmol) and $[Zr(NMe_2)_4]$ (0.5 g, 1.87 mmol) at room temperature. The solution was stirred at ambient temperature for 3 days with periodic evacuation of the vessel. After filtration, the pale orange solution was concentrated and cooled to −30 °C, which on standing overnight afforded colorless crystals (1.01 g, 87%). NMR spectroscopic data were in accord with those of the original report.[2]

[Zr(NN′₃)Cl] (3). Method A. Boron trichloride (0.45 cm^3, 1 M solution in hexanes, 1 equiv) was added to a solution of **1** (0.30 g, 0.45 mmol) in pentane (10 cm^3) at −78 °C. The mixture was stirred and warmed to room temperature to give a cloudy white solution. After evaporation of volatiles, the residue was extracted with warm pentane (2 × 20 cm^3), filtered, and evaporated under reduced pressure to give a white solid (0.14 g, 51%).

Method B. Chlorotrimethylsilane (1.07 g, 9.90 mmol) was added to a solution of **2** (1.15 g, 1.80 mmol) in toluene (10 cm^3). After the mixture was refluxed for 3 days, all volatiles were removed under reduced pressure. The residue was sublimated at 180 °C and 10^{-6} mbar to give a colorless crystalline solid (0.93 g, 85%).

Anal. Calcd for $C_{24}H_{57}ClN_4Si_3Zr$: C, 47.05; H, 9.38; N, 9.14. Found: C, 46.01; H, 9.32; N, 9.15. ^1H NMR (293 K, d_6-benzene): δ 3.32 (t, 6H, CH_2), 2.26 (t, 6H, CH_2), 1.13 (s, 27H, Bu^t), 0.37 (s, 18H, Me_2Si). $^{13}C\{^1H\}$ NMR (293 K, d_6-benzene): δ 63.67 (s, CH_2) 47.88 (s, CH_2), 27.00 (s, *Me*$_3$C), 20.93 (s, Me_3*C*). MS (EI): *m*/*z* 611 (12%, M^+), 596 (63%, $M^+ - Me$), 576 (28%, $M^+ - Cl$), 554 (95%, $M^+ - Bu^t$).

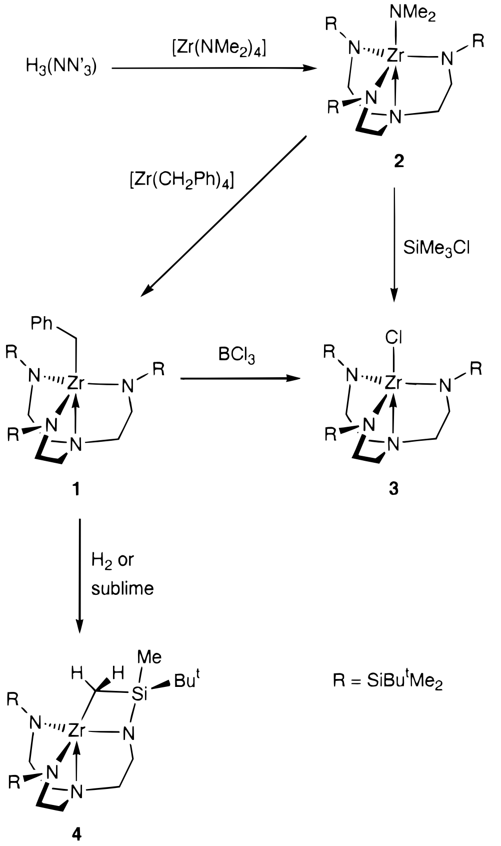
[Zr(bitNN′₃)] (4). Method A. Sublimation of **1** (0.50 g, 0.87 mmol) at 200 °C and 10^{-6} mbar gave a colorless crystalline solid (0.45 g, 96%) which was recrystallized from pentane at −30 °C.

Method B. Hydrogen was added to an NMR tube containing a solution of **1** in d_6-benzene. The tube was shaken at room temperature for 24 h. ^1H NMR spectroscopy indicated essentially quantitative conversion.

Anal. Calcd for $C_{24}H_{56}N_4Si_3Zr$: C, 50.03; H, 9.80; N, 9.72. Found: C, 49.98; H, 9.79; N, 9.78. ^1H NMR (293 K, d_6-benzene): δ 3.68 (m, 2H, CH_2), 3.23 (m, 4H, CH_2), 2.31 (m, 6H, CH_2), 1.23 (s, 9H, Bu^t), 1.04 (s, 18H, Bu^t), 0.49 (s, 3H, MeSi), 0.43 (s, 3H, MeSi), 0.42 (s, 3H, MeSi), 0.30 (s, 3H, MeSi), 0.29 (d, 1H, CH_2Si), 0.16 (d, 1H, CH_2Si), 0.15 (s, 3H, MeSi). $^{13}C\{^1H\}$ NMR (293 K, d_6-benzene): δ 57.49 (s, CH_2), 57.14 (s, CH_2), 56.39 (s, CH_2), 50.59 (s, CH_2), 47.29 (s, CH_2), 47.21 (s, CH_2), 28.67 (s, CH_2Si), 27.22 (s, *Me*$_3$C), 27.15 (s, Me_3*C*), 27.01 (s, *Me*$_3$C), 20.18 (s, Me_3*C*), 20.04 (s, Me_3*C*), 19.77 (s, Me_3*C*), −3.13 (s, Me_2Si), −3.83 (s, Me_2Si), −4.59 (s, Me_2Si), −4.81 (s, Me_2Si), −4.97 (s, Me_2Si). MS (EI): *m*/*z* 575 (96%, M^+), 518 (93%, $M^+ - Bu^t$).

Crystallography. Crystals were coated with inert oil and transferred to the cold N_2 gas stream on the diffractometer (Siemens SMART three-circle with CCD area detector). Graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) was used. Absorption correction was performed by multiscan (SADAB). The structures were solved by direct methods using SHELXS[15] with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups. The structures were refined using SHELXL 96.[16] In the structure of **3** the *tert*-butyl group at Si(3) shows resolved disorder with two positions of half-occupancy. Correspondingly, Si(3) itself, the methyl groups at C(19) and C(20), and the backbone methylene groups at C(5) and C(6) have relatively large thermal ellipsoids but these were not modeled with alternative positions. For **4** the C atoms of a pentane molecule in the lattice was modeled at half-occupancy and the absolute structure of the individual crystal chosen was checked by refinement of the $\Delta F''$ multiplier.

Scheme 1. Synthesis of the Complexes 1−4



Results and Discussion

Syntheses and Spectroscopic Characterization. The pure triamine $H_3(NN'_3)$ reacts smoothly with $[Zr(CH_2Ph)_4]$ in pentane to give the benzyl complex $[Zr(NN'_3)(CH_2Ph)]$ (**1**) in 90% isolated yield. (Scheme 1). The $ZrCH_2$ group in **1** gives rise to a singlet at δ 2.63 ppm in the ^1H NMR spectrum and at 63.95 ppm in the ^{13}C spectrum, as assigned by $^{13}C-^1H$ correlation spectroscopy.

Verkade has reported a range of group 4 amido complexes, including $[Zr(NN'_3)(NMe_2)]$ (**2**), which was synthesized by refluxing $H_3(NN'_3)$ with $[Zr(NMe_2)_4]$ in THF in the presence of catalytic $(NH_4)_2SO_4$.[2] We found that the reaction in pentane is complete within 3 days

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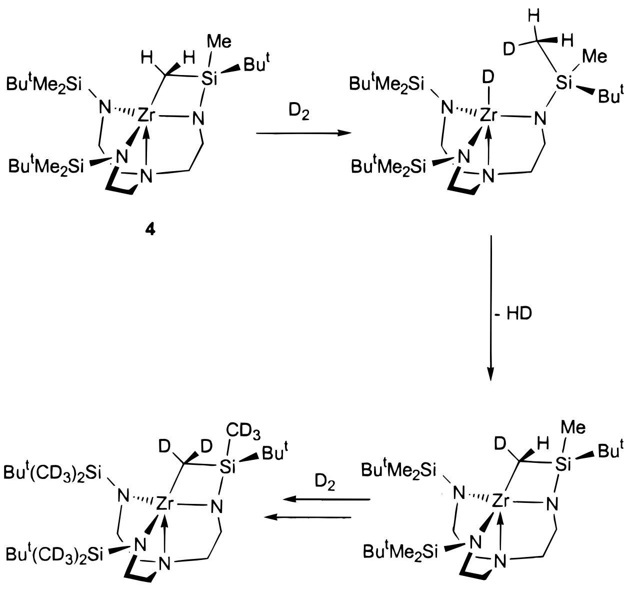
Scheme 2. Selective H/D Exchange Process for 4



at room temperature with no added catalyst. Concentration of the solvent gives large crystals of **2** directly.

Reaction of the trilithium compound $[Li_3(THF)_3(NN'_3)]$[9] with $[ZrCl_4(THF)_2]$ gives a low yield of $[Zr(NN'_3)Cl]$ (**3**) that is inseparable from oily coproducts. The complex is more efficiently synthesized by the reaction of **1** with BCl_3 or the reaction of **2** with $SiMe_3Cl$ in pentane. Colorless, crystalline **3** is best purified by sublimation.

The reaction of **1** at ambient temperature with pure hydrogen (1 atm) leads to clean metalation of one of the relatively acidic SiMe groups, presumably via elimination of hydrogen from the unobserved hydrido species $[Zr(NN'_3)H]$ (Scheme 2), to give the colorless zirconacycle $[Zr(bitNN'_3)]$ (**4**). By comparison, the equilibrium conversion of **II** (X = H) to its metallacycle by a similar process occurs only slowly, at elevated temperatures.[13] Also, while sublimation of **1** also leads to pure **4** with elimination of toluene, no metallacycle is formed when **II** (X = Me) decomposes. The ^{13}C NMR spectrum of **4** recorded in d_6-benzene contains a total of 18 resonances, indicating that the product is chiral; the metallacyclic Si atom is stereogenic.[17] Of these, 17 resonances are assigned to methyl and *tert*-butyl groups or methylene groups in the ligand backbone. A resonance at 28.67 ppm, assigned to the $Si-CH_2-Zr$ group, correlates in the ^1H NMR spectrum with a pair of AB doublets at apparent chemical shifts 0.29 and 0.16 ppm.

All CH groups in Andersen's uranacycle $[U\{N(SiMe_3)_2\}_2\{N(SiMe_3)(CH_2SiMe_2)\}]$ are deuterated on exposure of the complex to D_2.[18] Under similar conditions (d_8-toluene at ambient temperature) addition of dry D_2 to **4** leads to deuteration of all $SiMe_2$ groups and the metallacyclic CH_2 group. Figure 1 shows the ^1H NMR spectrum due to (a) the five inequivalent silyl methyl groups and the metallacyclic CH_2 group of **4** and (b) the same region after exposure to D_2 for 2 h, i.e., nearing complete deuteration. The remaining low-intensity overlapping multiplets in (b) are due to mixtures of isotopomers containing, for example, $SiCHD_2$ groups. The deuteration process presumably occurs via sequential deuteriolysis/metalation reactions as depicted in Scheme 2. The less acidic *t*-Bu and backbone CH_2 groups are not affected, as evidenced by integration of the ^1H NMR spectrum.

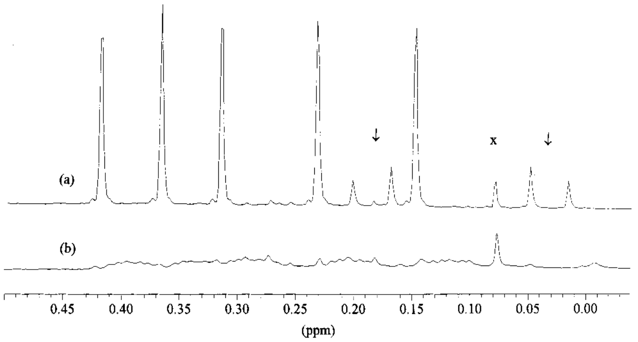
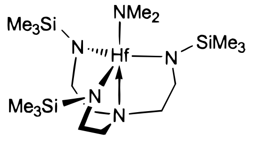


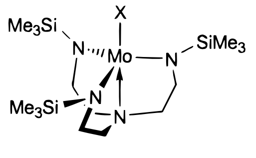
Figure 1. Part of the ^1H NMR spectrum of **4** in d_8-toluene measured (a) before and (b) after admission of D_2 (1 atm). The metallacyclic methylene group AB doublets are indicated by arrows, and the peak marked "x" is due to an impurity.

Molecular Structures. Single crystals of the compounds **1**, **2**, and **4** were readily grown by slow cooling of saturated solutions of the pure compounds in pentane. Crystals of **3** were grown by heating an evacuated and sealed tube of the presublimed material to 120 °C for a few days. The molecular structures were determined by X-ray crystallography (Table 1).

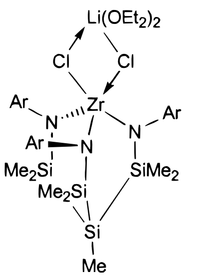
The molecular structure of **1** is shown in Figure 2 along with selected bond lengths and angles. It is instructional to compare the structure of this compound with that of Verkade's trimethylsilyl-substituted azahafnatrane **I**,[2] Schrock's range of molybdenum complexes **II**[19] and Gade's tri(amidosilyl)silane of zirconium **III**.[6b] The triamidoamine ligand in **1** is disposed with approximate 3-fold symmetry about the metal atom, as



I



II



III

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(17) If **3** had dimerized in solution via $Zr-C$ σ-bond metathesis (in order perhaps to relieve metallacycle ring strain), we would expect to see evidence in the NMR spectra for the presence of diastereomeric pairs (i.e. 36 ^{13}C resonances).

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Table 1. Experimental Data for the X-ray Diffraction Studies of 1−4

	1	**2**	**3**	**4**
mol formula	$C_{31}H_{64}N_4Si_3Zr$	$C_{26}H_{63}N_5Si_3Zr$	$C_{24}H_{57}ClN_4Si_3Zr$	$C_{26.5}H_{56}N_4Si_3Zr$
fwt	668.35	621.30	612.68	606.24
cryst syst	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	12.0082(15)	9.69980(10)	12.4097(2)	12.8111(2)
b/Å	18.663(3)	13.1685(3)	15.66210(10)	13.2448(2)
c/Å	18.131(3)	15.2304(4)	18.2802(2)	13.2748(2)
α/deg		106.48		60.3260(10)
β/deg	108.883(5)	103.5540(10)	92.74	67.9120(10)
γ/deg		95.8210(10)		86.0950(10)
cell vol/$Å^3$	3844.7(9)	1783.89(6)	3548.91(7)	1793.84(5)
Z	4	2	4	2
D_{calcd}/(Mg/m^3)	1.155	1.157	1.147	1.122
F(000)	1440	672	1312	650
μ/mm^{-1}	0.403	0.430	0.504	0.426
temp/K	160(2)	180(2)	180(2)	180(2)
cryst size/mm	0.4 × 0.4 × 0.4	0.4 × 0.1 × 0.07	0.5 × 0.2 × 0.1	0.4 × 0.3 × 0.2
θ_{max}/deg	28.54	28.34	28.47	22.50
total no. of rflns	22792	10552	20875	7279
no. of indep rflns	8927 (R(int) = 0.0268)	7706 (R(int) = 0.0275)	8332 (R(int) = 0.0493)	4650 (R(int) = 0.0201)
no. of significant rflns, $I > 2\sigma(I)$	6868	5321		3918
no. of params	367	333	353	328
T_{max}, T_{min}	0.93, 0.78	0.93, 0.77	0.928, 0.769	0.928, 0.707
GOF on F^2	1.021	0.907	1.153	1.049
$\Delta\rho_{max,min}$/(e $Å^{-3}$) (near U)	0.382, −0.611	0.537, −0.852	0.567, −7.30	0.737, −0.749
R1, wR2 ($I > 2\sigma(I)$)	0.0316, 0.0784	0.0450, 0.0929	0.0595, 0.0935	0.0527, 0.1215

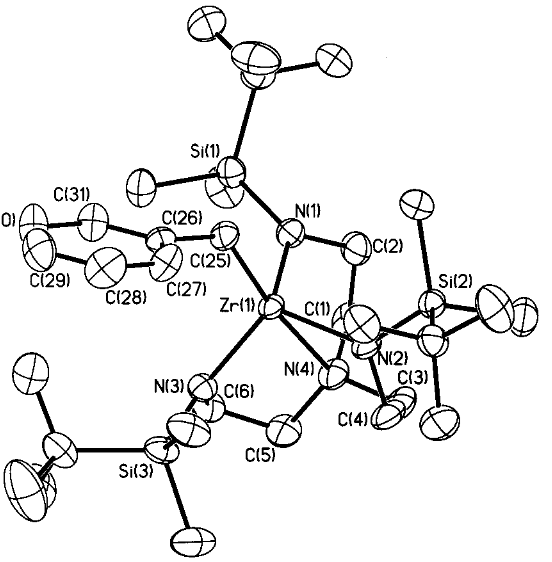

Figure 2. Thermal ellipsoid plot of the molecular structure of [Zr(NN′$_3$)(CH$_2$Ph)] (**1**) (non-hydrogen atoms). Selected distances (Å) and angles (deg): Zr(1)−N(3) = 2.0727(15), Zr(1)−N(2) = 2.0796(15), Zr(1)−N(1) = 2.0885(16), Zr(1)−C(25) = 2.3243(18), Zr(1)−N(4) = 2.5484(15); N(3)−Zr(1)−N(2) = 112.75(6), N(3)−Zr(1)−N(1) = 112.55(6), N(2)−Zr(1)−N(1) = 111.12(6), N(3)−Zr(1)−C(25) = 112.99(6), N(2)−Zr(1)−C(25) = 104.12(6), N(1)−Zr(1)−C(25) = 102.57(6), N(3)−Zr(1)−N(4) = 73.40(6), N(2)−Zr(1)−N(4) = 73.59(6), N(1)−Zr(1)−N(4) = 73.07(6), C(25)−Zr(1)−N(4) = 173.50(6).

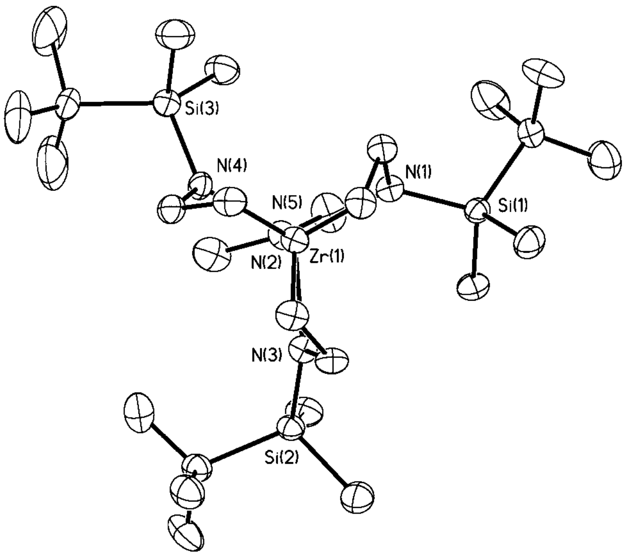

Figure 3. Thermal ellipsoid plot of the molecular structure of [Zr(NN′$_3$)(NMe$_2$)] (**2**) (non-hydrogen atoms) oriented along the apical N(2)−Zr axis. Selected distances (Å) and angles (deg): Zr(1)−N(5) = 2.063(2), Zr(1)−N(1) = 2.096(2), Zr(1)−N(4) = 2.124(3), Zr(1)−N(3) = 2.130(2), Zr(1)−N(2) = 2.509(2); N(5)−Zr(1)−N(1) = 109.75(9), N(5)−Zr(1)−N(4) = 99.96(10), N(1)−Zr(1)−N(4) = 114.44(10), N(5)−Zr(1)−N(3) = 107.11(10), N(1)−Zr(1)−N(3) = 108.30(9), N(4)−Zr(1)−N(3) = 116.62(10), N(5)−Zr(1)−N(2) = 173.21(10), N(1)−Zr(1)−N(2) = 74.75(8), N(4)−Zr(1)−N(2) = 73.36(9), N(3)−Zr(1)−N(2) = 75.53(9).

in **I** and **II**. The maximum deviation of any atom from the least-squares planes of the amidozirconium fragments, e.g. Si(1),N(1),C(2),Zr(1), is ca. 0.08 Å. The dihedral angles N_{ax}−Zr−N_{eq}−Si of 128.8−133.1° are similar to those observed in uranium complexes of NN′$_3$ (125−140°)[8] but are smaller than those in **I** (131−154°) and are at the lower end of the range observed for **II**, where the angle approaches 180° for small ligands X. The effect of this on the structure of **1** is that the SiMe$_2$Bu^t groups encircle the equatorial plane of the zirconium atom rather than surround the apical coordination site as in, for example, **II** (X = Cl). The equatorial amido N−Zr distances of 2.073(2)−2.089(2) Å are, as expected, similar to those in **I** (ca. 2.08 Å) and **III** (2.03−2.12 Å) but slightly longer than those in **II** (1.98−2.01 Å). The amino Mo−N_{ax} distances in **II** are strongly influenced by steric compression in the apical coordination site and range from 2.171(9) Å (X = OTf) to 2.422(10) (X = cyclohexyl). Hence, the Zr−N(4) distance of 2.5484(15) Å in **1** is not unduly long compared to that of 2.488(6)

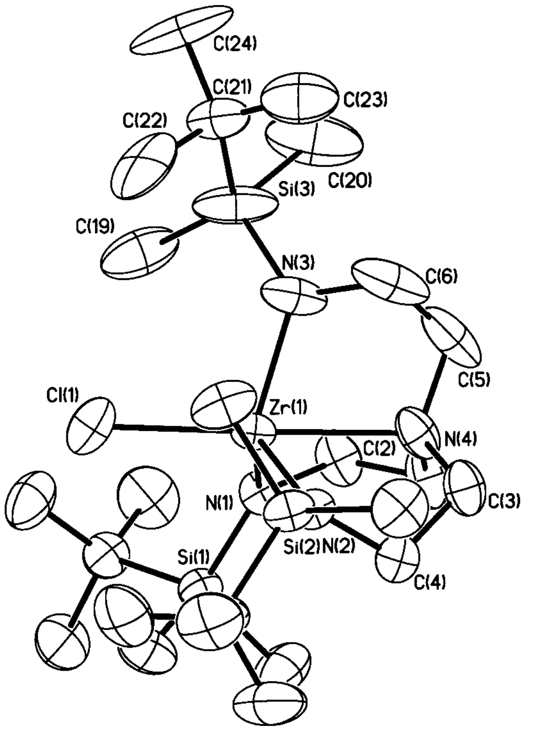

Figure 4. Thermal ellipsoid plot of the molecular structure of $[Zr(NN'_3)Cl]$ (**3**) (non-hydrogen atoms). Selected distances (Å) and angles (deg): Zr(1)−N(1) = 2.064(3), Zr(1)−N(2) = 2.066(3), Zr(1)−N(3) = 2.066(3), Zr(1)−Cl(1) = 2.4231(11), Zr(1)−N(4) = 2.444(3); N(1)−Zr(1)−N(2) = 112.84(11), N(1)−Zr(1)−N(3) = 112.59(12), N(2)−Zr(1)−N(3) = 114.94(12), N(1)−Zr(1)−Cl(1) = 106.50(9), N(2)−Zr(1)−Cl(1) = 104.42(9), N(3)−Zr(1)−Cl(1) = 104.42(12), N(1)−Zr(1)−N(4) = 75.17(11), N(2)−Zr(1)−N(4) = 75.30(11), N(3)−Zr(1)−N(4) = 74.22(14), Cl(1)−Zr(1)−N(4) = 178.22(8).

Å in **I**. The Zr atom sits ca. 0.60 Å out of the plane formed by the three amido nitrogen atoms compared with that of 0.55 Å in **I** and 0.94 Å in **III**, which has no axial donor atom. The η^1-benzyl ligand in **1** has no unusual features.

The molecular structures of **2** and **3** are shown in Figures 3 and 4. The triamidoamine unit in **2** is oriented with 3-fold symmetry as usual, but while the silyl groups at Si(1) and Si(3) are oriented “anticlockwise” in the figure, the group at Si(2) is “clockwise”. All other structures recorded which incorporate this ligand have these groups circulating in one direction only. We can offer no explanation for this unusual behavior but note that the dihedral angle N(2)−Zr(1)−N(3)−Si(2) is unusually large at 165.3° compared to 131.0 and 123.8° for the other two silyl groups. The equatorial amido N−Zr distances of 2.096(2)−2.124(3) Å in **2** are slightly larger than those in **1**, perhaps as a consequence of the greater steric demand of the ligand in the fifth coordination site. Those in the chloride complex **3** are correspondingly shorter at 2.064(3)−2.066(3) Å.

The molecular structure of **4** is shown in Figure 5. The metallacyclic Zr−C(14) distance is 2.613(11) Å, and although there is a relatively large error associated with this measurement, the bond length is nevertheless considerably greater than those of 2.324(3) and 2.309(3) Å in the related metallacycle $[Zr\{CH_2SiMe_2N(SiMe_3)\}_2(dmpe)]$.[20] This is presumably a consequence of the conformational constraints imposed by the triamidoamine framework in **4**. In the analogous trimethylsilyl-substituted complex of molybdenum the metallacyclic Mo−C distance is at most 0.1 Å longer than that found in the acyclic alkyls.[19] In **4** the orientations of the maximum amplitudes of the thermal ellipsoid plots of C(14) and C(20) *along* the C−Zr vectors are consistent with the presence of some sort of disorder. Given that the overall geometry of the molecule is little distorted from 3-fold symmetry, it seems likely that there is a significant occupancy in the crystal where the metallacyclic carbon is C(20). This may be related also to the twist disorder in the backbone carbon atoms indicated by their large thermal ellipsoids. To bring the metallacyclic carbon atom within the above-mentioned bonding distance of the zirconium center, the silyl groups in **4** must assume a more “upright” position than in the structures of **1**−**3** with dihedral angles N_{ax}−Zr−N_{eq}−Si in the range 173.8−177.2°.

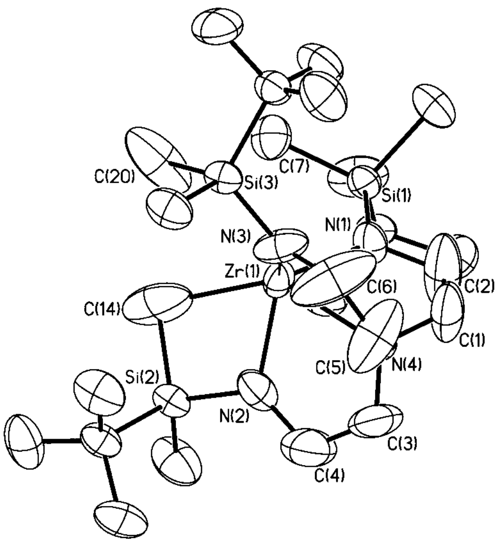

Figure 5. Thermal ellipsoid plot of the molecular structure of the metallacycle $[Zr(bitNN'_3)]$ (**4**) (non-hydrogen atoms). Selected distances (Å) and angles (deg): Zr(1)−N(3) = 2.054(5), Zr(1)−N(2) = 2.062(5), Zr(1)−N(1) = 2.077(4), Zr(1)−N(4) = 2.399(4), Zr(1)−C(14) = 2.613(11); N(3)−Zr(1)−N(2) = 113.37(19), N(3)−Zr(1)−N(1) = 112.7(2), N(2)−Zr(1)−N(1) = 113.7(2), N(3)−Zr(1)−N(4) = 75.17(17), N(2)−Zr(1)−N(4) = 72.64(17), N(1)−Zr(1)−N(4) = 76.13(15), N(3)−Zr(1)−C(14) = 123.8(2), N(2)−Zr(1)−C(14) = 67.8(2), N(1)−Zr(1)−C(14) = 117.1(2), N(4)−Zr(1)−C(14) = 140.34(18).

Conclusion

The steric demand of the substituent groups in triamidoamine ligands has a profound effect on their ability to coordinate effectively to early transition metals and f elements. In the latter case the geometries of the complexes formed are also strongly influenced. It is becoming increasingly clear that while triamidoamines with smaller substituents (up to, for example, $SiMe_3$) have great synthetic utility for the first-row metals and most of the transition metals of groups 5 onward, the larger metals (group 3, heavier group 4 and f elements) are better served by more sterically demanding substituents. The $SiMe_2Bu^t$-substituted triamidoamine NN'_3

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[20] Planalp, R. P.; Andersen, R. A. *Organometallics* **1983**, *2*, 1675.

forms volatile crystalline monomeric complexes with these elements, but the SiMe groups are unstable with respect to deprotonation by early-transition-metal alkyls and hydrides. Schrock's more recently introduced aryl-substituted triamidoamine ligands[21] may be more resistant to this type of reaction.

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Supporting Information Available: Four X-ray crystallographic files (for **1**−**4**) in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.

OM990347E

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[21] Greco, G. E.; Popa, A. I.; Schrock, R. R. *Organometallics* **1998**, *17*, 5591.