Bis[1,3-bis(diphenylmethylsilylamido)propane]zirconium: A Spirocyclic Complex Containing a Sterically Demanding Chelating Amido Ligand

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Dedicated to Prof. R. Schmutzler on the occasion of his 65th birthday

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Silylamides, Zirconium Amide, Chelate Ligands, Crystal Structure

Lithiation of the diamine $CH_2(CH_2NHSiMePh_2)_2$ using *n*-butyl lithium and subsequent reaction with zirconium tetrachloride yielded the bis(chelate)-amidozirconium complex $[Zr\{CH_2(CH_2NSiMePh_2)_2\}_2]$. The spirocyclic molecule has a distorted tetrahedral coordination at the zirconium centre with overall C_2 symmetry broken only by the relative orientation of four phenyl rings. The bulky diphenylmethylsilyl substituents at the amido-N functions as well as the ligand backbone sterically protect the metal centre and render it inert towards conproportionation with zirconium chloride.

Introduction

The chemistry of group 4 metal complexes containing chelating amido ligands has recently attracted considerable attention in the quest for early transition metal complex fragments which may replace the well established metallocene derivatives. The development of several high activity olefin polymerization catalysts containing diamido chelates, in particular, has fuelled the research in this area [1 - 8]. It appears that the size of the chelate ring as well as the nature of the peripheral N-bound groups are crucial parameters determining the reactivity of the systems. Other application-oriented research focussing on spirocyclic volatile chelate-amido complexes for use in MOCVD technology has been reported by Herrmann and coworkers [9].

Apart from these applications in polymer synthesis and materials chemistry, the stabilization of reactive complex fragments which may be employed in stoichiometric organometallic reactions or as molecular building blocks has been an important aspect of research in this field. The coordination chemistry of the dianionic *N*-trimethylsilyl substituted chelating amido ligand $[CH_2(CH_2NSiMe_3)_2]^{2-}$, which was first reported by Bürger and coworkers [10] has recently been studied by us, both in connection with the synthesis of early-late heterobimetallic complexes [11 - 13] and the preparation of novel amido complexes of the heavy group 13 elements [14, 15]. The effective steric shielding of the metal atoms in the systems studied to date is due to the folded propylene chain of the chelate ring as well as the peripheral silyl groups. In order to enhance the stability of the complexes we have increased the steric demand of the N-bonded silyl functions. In this paper we wish to report first results obtained with the new *N*-methyldiphenylsilyl substituted chelating amido ligand $[CH_2(CH_2NSiMePh_2)_2]^{2-}$.

Results and Discussion

The amino precursor $CH_2(CH_2NHSiMePh_2)_2$ (**1**) of the difunctional ligand was synthesized by condensation of 1,3-diaminopropane with $Ph_2MeSiCl$ using Et_3N as auxiliary base. Lithiation with butyllithium in thf yielded the solvated lithiumamide $[CH_2\{CH_2N(Li\text{-}thf)SiMePh_2\}_2]$ (**2**) which may be

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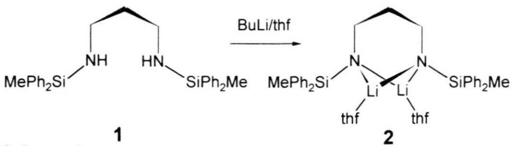
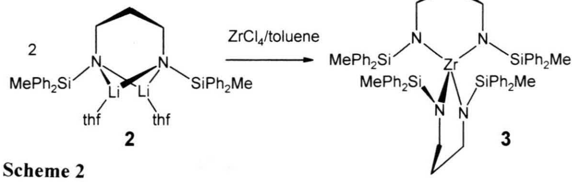
isolated as a colourless oil or, alternatively, generated in situ for further conversions (Scheme 1).



Scheme 1

Reaction of **2** with zirconium tetrachloride in a 2:1 ratio in toluene gave the spirocyclic, homoleptic zirconium complex $[Zr\{CH_2(CH_2NSiMePh_2)_2\}_2]$ (**3**) which was obtained as a crystalline colourless solid (70% yield) (Scheme 2).



Scheme 2

In order to establish the molecular structure of complex **3** and, in particular, to assess the influence of the increased steric bulk of the diphenylmethylsilyl groups, a single crystal X-ray structure analysis was carried out. Two different views of the molecular structure of **3** in the crystal are displayed in Fig. 1 and 2, while the principal bond lengths and interbond angles are listed in Table I.

Table I. Selected bond lengths and angles for $[Zr\{CH_2(CH_2NSiMePh_2)_2\}_2]$ (**3**).

a) Lengths (Å)			
Zr(1)-N(1)	2.065(3)	Zr(1)-N(2)	2.059(3)
Si(1)-N(1)	1.728(4)	Si(2)-N(2)	1.732(4)
Si(1)-C(4)	1.865(5)	Si(2)-C(5)	1.860(5)
Si(1)-C(10)	1.903(3)	Si(2)-C(30)	1.884(4)
Si(1)-C(20)	1.875(6)	Si(2)-C(40)	1.896(4)
N(1)-C1)	1.493(6)	N(2)-C(2)	1.489(6)
C(1)-C(3)	1.478(7)	C(2)-C(3)	1.484(7)
b) Angles (°)			
N(1)-Zr(1)-N(2)	101.5(2)	N(1)-Zr(1)-N(2a)	113.9(2)
N(1)-Zr(1)-N(1a)	112.4(2)	N(2)-Zr(1)-N(2a)	114.1(2)
Zr(1)-N(1)-Si(1)	128.0(2)	Zr(1)-N(2)-Si(2)	129.4(2)
Zr(1)-N(1)-C(1)	117.3(3)	Zr(1)-N(2)-C(2)	115.5(3)
Si(1)-N(1)-C(1)	114.7(3)	Si(2)-N(2)-C(2)	115.0(3)
N(1)-C(1)-C(3)	116.9(4)	N(2)-C(2)-C(3)	116.7(4)
C(1)-C(3)-C(2)	119.1(5)		

In the crystal there is a crystallographic C_2 axis through the metal atom and the midpoint between Si(1) and Si(1a) as shown in Fig. 1. However, exact C_2 symmetry for the individual molecules is ruled out by unfavourably short contacts between symmetry related phenyl rings [C(41)···C(41a) 3.221, H(41)···H(41a) 1.976 Å, *cf.* respective sums of Van der Waals radii 3.50 and 2.40 Å] as a consequence of the steric congestion in the co-ordination sphere. As a result two orientations of disordered phenyl rings C(40)/C(40A) reduce the molecular symmetry to C_1. The structural centre piece is the distorted tetrahedral tetraamidozirconium unit which links the two chelate rings to form an overall spirocyclic arrangement (Fig. 2).

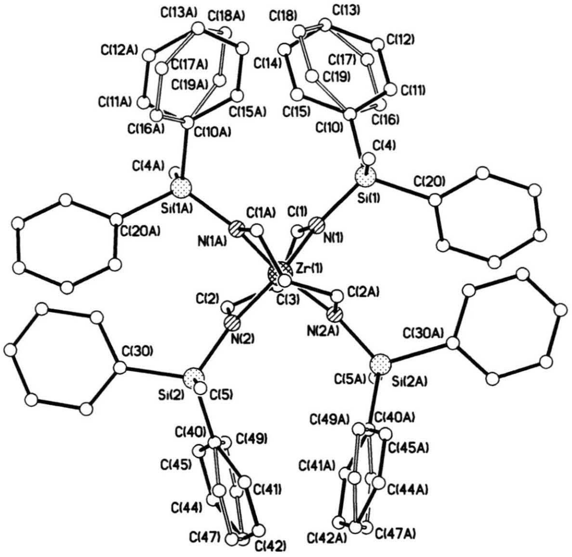


Fig. 1. A view of the disordered molecular structure of $[Zr\{CH_2(CH_2NSiMePh_2)_2\}_2]$ (**3**) which has virtual C_2 symmetry in the crystal. Unfavourably short contact distances between symmetry related components of the disordered phenyl rings [C(41)···C(41a) 3.221, H(41)···H(41a) 1.98 A] reduce the molecular symmetry to C_1 for individual molecules.

The "intra-ring" N-Zr-N angles [N(1)-Zr(1)-N(2) 101.59(13)°] are markedly smaller than the "inter-ring" N-Zr-N angles [N(1)-Zr(1)-N(1') 112.4(2), N(1)-Zr(1)-N(2') 113.80(13)°] which is a consequence of the steric constraints imposed by the ligand framework. In the only other structurally characterized example of a spirocyclic tetraamidozirconium complex reported by Bürger and coworkers, $[\{Me_2Si(N\mathit{t}Bu)_2\}_2Zr]$ [16], the distortion from a tetrahedral arrangement of the donor functions is even more pronounced due to the small bite angle defined by the chelating diamidosilane ligands.

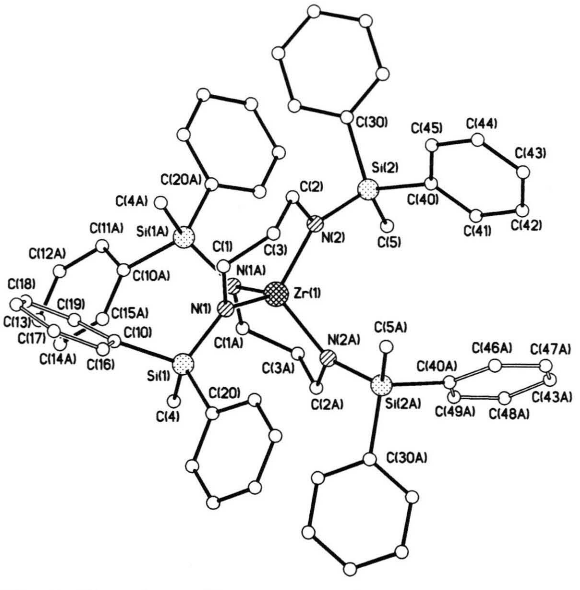


Fig. 2. The spirocyclic structure of $[Zr\{CH_2(CH_2NSiMePh_2)_2\}_2]$ (**3**) showing the distorted tetrahedral co-ordination at the zirconium centre.

The geometry at the nitrogen-N atoms in **3** is trigonal planar (sum of the interbond angles, N(1): 360.0, N(2): 359.9°) as has been observed in nearly all the established crystal structures of transition metal amides [17]. A structural consequence of the planarity of the nitrogen donor functions is the "half-twist" conformation [18] of the two six-membered chelate rings. The four diphenylmethylsilyl substituents of the amido functions in the complex adopt a very similar orientation with respect to the central structural unit. Wheras the Si-bonded methyl groups point in the direction of the amido functions the phenyl groups are oriented towards the propylene ligand backbone (Fig. 2). The pairs of phenyl groups on each silyl substituent are approximately orthogonal to each other (dihedral angles range from 73.8 to 85.0°) with the exception of one component of the disorder; the ring [C(40)-C(45)] is at an angle of 55.4° to [C(30)-C(35)]. Mutually perpendicular relative orientations for the phenyl rings are observed in many diphenylphosphido and diphenylphosphinomethane compounds [19]. The zirconium-nitrogen distances are equal within experimental error and although the mean Zr-N bond length of 2.062(3) Å is slightly longer than the mean value of 2.053(2) Å in the bischelate complex $[\{Me_2Si(N\textit{t}Bu)_2\}_2Zr]$ the difference is of low significance. The mean Zr-N bond distance in these two chelate compounds is longer that of 2.025(3) Å in the complex $[ZrCl(\mu\text{-}Cl)\{N(SiHMe_2)_2\}_2]_2$ which has monodentate amido ligands and an effectively six-coordinate geometry at zirconium [20]; in the latter compound the presence of two electronegative chloro ligands apparently enhances the π-donation from the nitrogen donors. In $[ZrCl\{N(SiMe_3)_2\}_3]$ [2.070(3) Å] [21], where there are only one chloro ligand and three monodentate amido ligands, the Zr-N bond is longer than in the dichloride, and is not significantly different from that in the present study.

The molecular structure of **3** shows, that the metal centre is very efficiently shielded by the ligand backbone as well as the peripheral substituents. This renders the compound inert towards conproportionation reactions with $ZrCl_4$ carried out in toluene at 90°C in order to obtain the amidochloro mixed-ligand complex. This contrasts the facile convertability of the trimethylsilyl-substituted analogue which we reported previously [11].

Experimental Part

All manipulations were performed under dry argon in standard (Schlenk) glassware which was flame dried with a Bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with Ar. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and dried over 4-Å molecular sieves.

The ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker AC 200 spectrometer equipped with a B-VT-2000 variable temperature unit (at 200.13, 50.32, and 39.76 MHz, respectively) with tetramethylsilane as reference. Infrared spectra were recorded on Perkin Elmer 1420 and Bruker IRS 25 FT-spectrometers. Elemental analyses were carried out in the microanalytical laboratory of the chemistry dept. at Würzburg.

1,3-Bis(diphenylmethylsilylamino)propane (**1**)

Diphenylmethylchlorosilane (7.63 g, 32.8 mmol) dissolved in 50 ml of diethyl ether was added dropwise to a stirred solution of 1,3-diaminopropane (1.22 g, 16.4 mmol) and triethylamine (3.32 g, 32.8 mmol) in diethyl ether (200 ml) which was cooled to 0°C. The reaction mixture was stirred at r.t. for 15 h, the solid triethylammonium chloride formed in the reaction subsequently removed by filtration. The solvent of the filtrate was removed in vacuo at r.t. and the oil remaining in the reaction vessel kept under vacuum (10^{-3} mbar) for 3h after which time no residual solvent could be detected by NMR spectroscopy. Yield 6.12 g (80 %).).- ^{1}H NMR (C_6D_6): δ = 0.88 (s, 6H, $SiCH_3$), 1.62 (m, 2H, CH_2CH_2N), 2.91 (vt, 4H, CH_2N), 7.43 (m, 20H, $SiPh_2$).- ^{13}C{^{1}H} NMR (C_6D_6): δ = -2.6 ($SiCH_3$), 38.8 (CH_2CH_2N), 39.7 (CH_2N), 127.7 ($C^{3,5}$, Ph), 129.5 (C^4, Ph), 134.4 ($C^{2,6}$, Ph), 137.8 (C^1, Ph).- ^{7}Li{^{1}H} NMR (C_6D_6): δ = 0.24.- ^{29}Si{^{1}H} NMR (C_6D_6): δ = -19.3.

$C_{29}H_{34}N_2Si_2$ (466.77)
Calcd C 74.62 H 7.34 N 6.00 %,
Found C 74.50 H 7.19 N 5.91 %.

Dilithium [1,3-bis(diphenylmethylsilylamido)propane] tris(tetrahydrofuran) (**2**)

Butyllithium (5.00 mmol, 2.5 ml of a 2M solution in hexane) was added to a stirred solution of $CH_2(CH_2NHSiMePh_2)_2$ (1.17 g, 2.50 mmol) in tetrahydrofuran which was cooled to -78°C. The reaction mixture was warmed to r.t. and stirred for another 30 min. After removal of the solvent the solvated lithium amide was isolated as an analytically pure viscous oil in quantitative yield (1.55g).- ^{1}H NMR (C_6D_6): δ = 0.68 (s, 6H, $SiCH_3$), 1.18 (m, 8H, CH_2CH_2O), 1.86 (m, 2H, CH_2CH_2N), 3.27 (m, 8H, CH_2CH_2O), 3.86 (vt, 4H, CH_2N), 7.16 (m, 20H, $SiPh_2$).- ^{13}C{^{1}H} NMR (C_6D_6): δ = -0.6 ($SiCH_3$), 25.2 (CH_2CH_2O), 41.5 (CH_2CH_2N), 50.5 (CH_2N), 68.5 (CH_2CH_2O), 128.0 ($C^{3,5}$, Ph), 128.2 (C^4, Ph), 134.9 ($C^{2,6}$, Ph), 145.2 (C^1, Ph).- ^{7}Li{^{1}H} NMR (C_6D_6): δ = 0.24.- ^{29}Si{^{1}H} NMR (C_6D_6): δ = -19.3.

$C_{37}H_{48}N_2Si_2Li_2O_2$ (622.85)
Calcd C 71.35 H 7.77 N 4.50 %,
Found C 71.24 H 7.45 N 4.45 %.

Bis[1,3-bis(diphenylmethylsilylamido)propane]zirconium (**3**)

Butyllithium (39.84 mmol, 99.6 ml of a 2.5 M solution in hexane) was slowly added to a stirred solution of $CH_2(CH_2NHSiMePh_2)_2$ (9.3 g, 19.92 mmol) in toluene (30 ml), which was cooled to -40°C. The reaction mixture was warmed to r.t. and, after the evolution of butane had subsided, heated briefly under reflux. After stirring at r.t. for another 30 min, the solution was cooled to -50°C. Solid $ZrCl_4$ (4.39 g, 19 mmol) was added, the reaction mixture warmed to roomtemperature and the solution stirred for another 4 d. After evaporation of the solvent in vacuo the residue was extracted with pentane (50ml) and the volume of the filtered extract reduced to *ca.* 10 ml. Storage at -35°C yielded the zirconium complex $[Zr\{CH_2(CH_2NSiMePh_2)_2\}_2]$ as a colourless crystalline solid. Yield 70%. M.p. 106°C (dec.).- ^{1}H NMR (C_6D_6): δ = 0.90 (s, 6H, $SiCH_3$), 1.77 (m, 2H, CH_2CH_2N), 3.37 (m, 4H, CH_2N), 7.00 - 7.60 (m, 20H, $SiPh_2$).- ^{13}C{^{1}H} NMR (C_6D_6): δ = 0.2 ($SiCH_3$), 39.0 (CH_2CH_2N), 52.6 (CH_2N), 127.9 ($C^{3,5}$, Ph), 129.3 (C^4, Ph), 135.5 ($C^{2,6}$, Ph), 138.2 (C^1, Ph).- ^{29}Si{^{1}H} NMR (C_6D_6): δ = -14.5.

Table II. Crystal data and structure refinement for complex **3**.

Empirical formula	$C_{58}H_{64}N_4Si_4Zr$
fw	1020.71
Crystal system	monoclinic
Space group	*I*2/*a* (No. 15)
Unit cell dimensions	
a [A]	17.564(2)
b [A]	18.4050(14)
c [A]	18.510(3)
α [°]	-
β [°]	114.942(8)
γ [°]	-
V [A^3, *Z*]	5425.7(10)
Z	4
D_{calc} / Mg m^{-3}	1.250
Radiation (λ/A)	Mo-K_α (0.71073)
μ [mm^{-1}]	0.331
F(000)	2144
Crystal size [mm]	0.52 × 0.32 × 0.30
θ-Range [°]	2.21 to 23.00
Limiting *hkl* indices	–19 to 19, –20 to 20, –20 to 20
Reflections collected	7820
Independent reflections (R_{int})	3790 (0.0422)
Max / min transmission	0.9464 / 0.4817
Data / restraints / parameters	3790 / 27 / 273
S on F^2	1.055
Final *R* indices[1]	
[I > 2σ(I)] (all data)	$R_1 = 0.0550$, $wR_2 = 0.1245$ $R_1 = 0.0843$, $wR_2 = 0.1336$
Weights a, b[1]	0.0602, 9.4998
Max and min $\Delta\rho$ [eA^{-3}]	0.509 and –0.426

[1] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ where n = number of reflections and p = total number of Parameters, $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$, $wR_2 = \Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2]^{1/2}$, $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [max(F_o^2,0) + 2(F_c^2)]/3$.

$C_{58}H_{64}N_4Si_4Zr$ (1020.74)
Calcd C 68.25 H 6.32 N 5.49 %,
Found C 68.09 H 6.11 N 5.06 %.

Crystal structure determination of **3**

Data collection for **3**. A crystal was mounted in a Lindemann capillary under argon and in an inert oil. X-ray intensity data were collected, with graphite-monochromated radiation, on a Siemens P4 four-circle diffractometer. Details of data collection, refinement and crystal data are listed in Table II. Lorentz-polarisation and absorption corrections were applied to the data.

Structure solution and refinement for **3**. The positions of the metal atom and most of the non-hydrogen atoms were located by direct methods [22]. The positions of the remaining non-hydrogen atoms were found from subsequent difference-Fourier sytheses. Two phenyl rings in the asymmetric unit were disordered corresponding to a rotation about the corresponding Si-C bond, and for both rings the *ortho*- and *meta*-carbon atoms were each resolved into two components of 50:50 occupancy. Refinement was based on F^2 [22], and the disordered phenyl rings were constrained to idealised geometry (C-C 1.39 A). All hydrogen atoms were placed in calculated positions with displacement parameters set equal to 1.2 U_{eq} of the parent carbon atoms for the methylene and phenyl groups, and 1.5U_{eq} for the methyl groups. Semi-empirical absorption corrections [22] using ψ-scans were applied to the data. All full-occupancy non-hydrogen atoms were assigned anisotropic displacement parameters in the final cycles of full-matrix least-squares refinement.

Crystallographic data for the structure of **3** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-33563. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax.: int code +(1223) 336033; e-mail: deposit@chemcrys.cam.ac.uk).

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