

Synthesis and characterization of organozirconium complexes bearing a new trianionic multidentate cyclopentadienyl ligand by use of amine elimination

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Received 24 August 1999; received in revised form 2 February 2000

Abstract

The new multidentate ligand *o*-(NH(C₆H₅)(N'H(Si(CH₃)₂(C₅(CH₃)₄H))C₆H₄) (1), was synthesized by the reaction of (C₅(CH₃)₄(H)Si(CH₃)₂Cl) with *o*-C₆H₄(NH₂)(N'HPh) in the presence of NEt₃. The ligand was bound to Zr using the amine elimination method through the reaction of 1 with Zr(N(CH₃)₂)₄. Because of the incomplete removal of HCl generated in the synthesis of 1, two complexes were isolated and characterized from the reaction of 1 with Zr(N(CH₃)₂)₄, *o*-C₆H₄{N(C₆H₅)N'[Si(CH₃)₂(C₅(CH₃)₄)]}Zr(N(CH₃)₂)(NH(CH₃)₂) (2) and *o*-C₆H₄{N(C₆H₅)N'[Si(CH₃)₂(C₅(CH₃)₄)]}Zr(Cl)(NH(CH₃)₂)₂ (3). The structures of both 2 and 3 were confirmed by X-ray crystallography. Crystals of 2 are triclinic, space group *P* $\bar{1}$, with *a* = 10.9864(1), *b* = 11.8841(2), *c* = 12.3633(1) Å, and *Z* = 2. Compound 2 has a square-pyramidal geometry with the -NMe₂ group occupying the apical position. Crystals of 3 are monoclinic, space group *P*2₁/*c*, with *a* = 12.1925(2), *b* = 18.9677(4), *c* = 12.2218(2) Å, and *Z* = 4. Complex 3 has a distorted octahedral geometry with the cyclopentadienyl and the amido groups of the chelating ligand occupying pseudo-meridional positions. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Zirconium; *ansa*-Metallocene; Cyclopentadienyldiamide; Amine elimination

1. Introduction

Among the large number of cyclopentadienyl ligands that have been synthesized to date, there are systems which contain a cyclopentadienyl ring linked to additional pendent groups such as amides [1], alkoxides [1a,2], amines [1a,j–1,3], phosphines [1o,p] and olefins [1a,h,l]. The pendent donors on the cyclopentadienyl rings can provide an effective means of altering the coordination environment of these cyclopentadienyl metal complexes [1]. In recent years, these chelating cyclopentadienyl ligands have generated increasing interest with respect to their use as ancillary ligands for homogeneous olefin polymerization catalysts [1b].

The CpSiNR class of ligands, in which a (dimethylsilyl)amide is linked to the cyclopentadienyl moiety, have been successfully used as alternatives to the bridged bis(cyclopentadienyl) ligands that have been

employed as ancillary ligands in α -olefin polymerization catalysts [1c,d,4]. The substitution of a cyclopentadienyl ring with an amido ligand increases the Lewis acidity and electrophilicity of the metal center in these complexes because of reduced steric crowding and electron count compared to their bis(cyclopentadienyl) analogs. For example, scandium complexes such as (η^5, η^1 -C₅Me₄SiMe₂NCMe₃)ScR, synthesized by Bercaw et al. [1c,d,4a] using the C₅Me₄SiMe₂NCMe₃ ligand, have been shown to have significantly enhanced Lewis acidity compared to *ansa*-metallocenes.

To date, most of the 'CpSiNR' type ligands that have been synthesized have been dianionic, and with or without additional neutral donors. We were interested in synthesizing similar chelating mixed cyclopentadienyl ligands that are trianionic to examine their ability to coordinate to early transition metals. This paper reports the synthesis of two zirconium compounds that have a CpSi(NR)₂ hybrid ligand system in which the diamide piece of the ligand is derived from an *o*-phenylenediamine derivative.

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2. Experimental

2.1. General considerations

All procedures were performed using standard Schlenk techniques or in a nitrogen-filled Vacuum Atmospheres glovebox. Diethyl ether (Et₂O), pentane, and hexanes were distilled from sodium benzophenone ketyl; toluene was previously deoxygenated by washing twice with cold H₂SO₄ followed by water and bicarbonate, and was then distilled from potassium metal. Dichloromethane (CH₂Cl₂) was distilled from CaH₂. After collection, all solvents were stored under argon and over molecular sieves. Glassware was oven dried before use. The compound C₅(CH₃)₄(H)Si(CH₃)₂Cl was synthesized according to published procedures [4]. *N*-phenyl-*o*-phenylenediamine was purchased from Aldrich and was used without further purification. Homoleptic amido complexes Zr(N(CH₃)₂)₄ and Ta(N(CH₃)₂)₅ were synthesized according to the procedure reported by Jordan and co-workers [6]. All NMR solvents were purchased from Cambridge Isotope Laboratories and were degassed and stored over molecular sieves in a drybox prior to use.

NMR spectra were measured either on a Varian VXR or Gemini-300 (300 MHz) spectrometer. Chemical shifts for the ¹H spectra were referenced to residual protons in the deuterated solvents and are reported relative to tetramethylsilane. Mass spectrometry was performed by the UF Department of Chemistry Analytical Services. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA.

2.2. *o*-(NH(C₆H₅)(N'H((C₅(CH₃)₄H)Si(CH₃)₂)C₆H₄) (1)

To a –78°C Et₂O solution of (C₅(CH₃)₄H)Si(CH₃)₂Cl (1.17 g, 5.44 mmol) an Et₂O solution of *N*-phenyl-*o*-phenylenediamine (1.03 g, 5.59 mmol) was slowly added. The reaction mixture was warmed to room temperature (r.t.) and stirred for ~6 h. At this time the reaction mixture was light pink in color and a small amount of a pink solid had precipitated. To this reaction mixture excess Et₃N (3 ml, 40.9 mmol) was added at r.t. resulting in a color change from pink to pale orange. The reaction was stirred for 1 h after which the Et₂O was removed under reduced pressure, and a waxy pale-orange solid was obtained. Extraction of the solid with four portions of cold pentane followed by filtration and removal of the pentane under reduced pressure gave **1** as a thick, pale orange, oil (yield: 1.6 g, 82%). ¹H-NMR (25°C, C₆D₆): δ 0.14 (s, 6H, Si(CH₃)₂), 1.72, 1.87 (s, 6H each, C₅(CH₃)₄H), 2.91 (s, 1H, C₅(CH₃)₄H), 4.10, 4.38 (broad s, 1H each, N–H), 6.49–7.09 (phenyl region, 9H). ¹³C-NMR (25°C, C₆D₆): δ 2.97 (–Si(CH₃)₂), 11.25, 14.38 (C₅(CH₃)₄H), 54.88 (CHC₄(CH₃)₄), 115.09, 115.98,

118.31, 119.30 (CHC₄(CH₃)₄), 126.98, 127.47, 129.38, 130.04, 132.45, 136.48, 144.84, 146.80 (aromatic C's). CIMS/CH₄: M + 1 = 363.109 amu.

2.3. *o*-C₆H₄{N(C₆H₅)N'[Si(CH₃)₂(C₅(CH₃)₄)]}-Zr(N(CH₃)₂)(NH(CH₃)₂) (2)

To a stirring hexane solution of Zr(N(CH₃)₂)₄ (0.126 g, 0.47 mmol) at r.t., was added dropwise a solution of **1** (0.18 g, 0.48 mmol) in hexanes. The reaction mixture immediately became light orange and when approximately half of the ligand had been added, compound **2** began precipitating as a yellow solid. After addition of **1** was completed, the reaction mixture was allowed to stir for an additional 6 h. The precipitate was allowed to settle, the supernatant was removed, and the remaining solid was extracted with pentane until the extracts were clear. Removal of the pentane from the combined extracts gave crude **2** as a yellow–orange solid. Compound **2** was recrystallized from a toluene–pentane mixture. The ¹H-NMR of the first crop of crystals isolated from the toluene–pentane mixture contained ca. 60% of **2** with the remaining 40% being complex **3** (overall yield of **2**: 0.07 g, 25%). Repeated recrystallizations separated **2** from **3**. Similar results were observed when the reaction was performed in Et₂O. X-ray quality crystals formed from a r.t. C₆D₆ solution of **2**. Anal. Calc. for C₂₇H₄₀N₄Zr: C, 60.1; H, 7.47; N, 10.4. Found: C, 59.2; H, 7.25; N, 9.93%. ¹H-NMR (25°C, C₆D₆): δ 0.79, 0.86 (s, 6H each, Si(CH₃)₂), 1.61, 1.77, 2.07, 2.14 (s, 3H each, C₅(CH₃)₄), 1.62 (6H, N(CH₃)₂H), 2.71 (s, 6H, –N(CH₃)₂), 6.88–7.21 (multiplets, 9H, aromatic H). The N(CH₃)₂H is hidden in the baseline. ¹³C-NMR (25°C, C₆D₆): δ 3.53, 3.92 (–Si(CH₃)₂), 12.05, 13.35, 13.49, 14.04 (C₅(CH₃)₄H), 38.37 (NH(CH₃)₂), 46.51 (N(CH₃)₂), 102.70, 110.94, 114.00, 116.17, 118.90, 123.63, 128.81, 129.94, 144.48, 151.97, 155.21 (C₅(CH₃)₄H and aromatic C's).

2.4. *o*-C₆H₄{N(C₆H₅)N'[Si(CH₃)₂(C₅(CH₃)₄)]}-Zr(Cl)(NH(CH₃)₂) (3)

To a hexane solution of **1** (0.14 g, 0.39 mmol, 2.1 equivalents) at r.t., a hexane solution of Zr(N(CH₃)₂)₄ (0.05 g, 0.18 mmol) was added dropwise. An immediate color change to orange and precipitation of a yellow–orange solid was observed. The reaction mixture was stirred for an additional 15 min and was left to settle. The supernatant was removed and the solid was washed twice with pentane to remove the excess ligand (yield: 0.03 g, 28%). X-ray quality crystals were obtained within 4 days from a r.t. C₇D₈ solution of **3**. Anal. Calc. for C₂₇H₄₀ClN₄Zr: C, 56.4; H, 7.01; N, 9.74. Found: C, 55.3; H, 6.58; N, 9.52. ¹H-NMR

(25°C, C₆D₆): δ 0.70 (s, 6H, –Si(CH₃)₂), 1.88, 1.93 (s, 6H each, C₅(CH₃)₄H), 2.00 (broad s, 12H, NH(CH₃)₂), 3.28 (very broad s, 2H, NH(CH₃)₂), 6.57–7.41 (multiplets, 9H, aromatic protons). ¹³C-NMR (25°C, C₆D₆): δ 3.46 (–Si(CH₃)₂), 12.21, 14.05 (C₅(CH₃)₄H), 40.40 (NH(CH₃)₂), 112.58, 115.12, 115.92, 121.10, 123.62, 126.24, 127.31, 129.51, 143.51, 155.09 (C₅(CH₃)₄H and aromatic C's).

2.5. X-ray data collection and structure refinement for compounds **2** and **3**

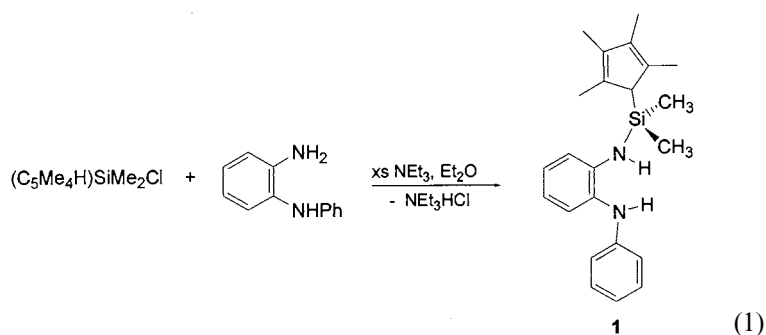
Data for both compounds were collected at 173 K on a Siemens CCD SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo–K α radiation ($\lambda = 0.71073$ Å). Cell parameters were refined using 8192 reflections from each data set. A hemisphere of data (1381 frames) was collected using the ω -scan method (0.3° frame width).

The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on *I* was < 1%). Absorption corrections were applied based on the ψ -scan using the entire data sets.

Both structures were solved by direct methods in SHELXTL [7] and were refined using full-matrix least-squares on *F*². The non-H atoms were refined with anisotropic thermal parameters. All of the H atoms were refined without any constraints. Compound **2** also has disordered benzene molecules located on centers of inversion. They were refined as two dependent parts and their site occupation factors refined to 0.56(3) and 0.44(3), respectively. The benzene H atoms were included in the final cycle of refinement in a riding mode on their parent atoms. For compound **2**, 514 parameters were refined in the final cycle of refinement using 6040 reflections with *I* > 2 σ (*I*) to yield *R*₁ and *wR*₂ of 2.38 and 5.92, respectively. For compound **3**, 472 parameters were refined in the final cycle of refinement using 5484 reflections with *I* > 2 σ (*I*) to yield *R*₁ and *wR*₂ of 2.37 and 5.79, respectively. Refinement was performed using *F*².

3. Results and discussion

In order to synthesize a bis-amido cyclopentadienyl chelating trianionic ligand we chose unsubstituted or monosubstituted phenyldiamines as the bis-amido part of the ligand. Initially, we attempted reaction of *o*-C₆H₄(NH₂)₂ or *o*-C₆H₄(NH₂)(N'(H)SiMe₃) with C₅Me₄HSiMe₂Cl, however, these reactions produced multiple products. In both cases one of the products were identified by mass spectrometry to be the bis-cyclopentadienyl compound *o*-C₆H₄[(C₅Me₄H)SiMe₂(NH)]₂. To avoid the problem of multiple substitution and/or cleavage of the already existing substituents on the nitrogens, we pursued the reaction of *o*-(PhNH)C₆H₄(NH₂) with C₅Me₄HSiMe₂Cl in which case the desired product, *o*-(NHPh)C₆H₄((C₅Me₄H)SiMe₂NH) (**1**) was obtained in good yield (though always contaminated with small amounts of an impurity that was tentatively identified as **1**·HCl as described below) (Eq. (1)).



Although a number of cyclopentadienyl isomers are possible via possible proton or silicon sigmatropic shifts [8], the ¹H-NMR spectrum of **1** indicates the presence of only one isomer with the tetramethylcyclopentadienyl methine proton and –SiMe₂ group bound at the 5 position of the Cp ring. The methine proton resonates at 2.91 ppm, whereas the two secondary amine protons are observed as two singlets at 4.10 and 4.38 ppm, respectively. Compound **1** is relatively air and moisture sensitive, and unstable in chlorinated solvents, with cleavage of the Si–N bond a likely decomposition pathway. Alternatively, **1** could be isolated in low yield by initial deprotonation of *o*-(PhNH)C₆H₄(NH₂) with *n*-BuLi and subsequent addition of (C₅Me₄H)SiMe₂Cl.

The usual synthetic approach to Group III and IV transition metal complexes that contain cyclopentadienyl–amido ligands employs the metathetical reaction of the alkali salts of these ligands with the appropriate metal halides [1c,d,g,h,j,l,n,4]. Therefore, we attempted the synthesis of alkali salts of **1** by reaction with MeLi, *n*-BuLi, LiN(CH₃)₂ and KH with no success. Additionally, when we attempted in situ deprotonation of **1** and subsequent addition to ZrCl₄ or TaCl₅, intractable mixtures of compounds were observed.

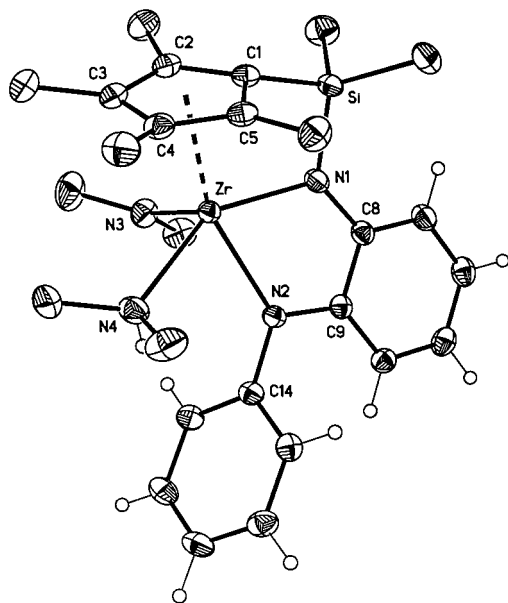


Fig. 1. Thermal ellipsoid plot of the molecular structure of *o*-C₆H₄{N(C₆H₅)N[Si(CH₃)₂(C₅(CH₃)₄)]}Zr(N(CH₃)₂)(NH(CH₃)₂) (**2**).

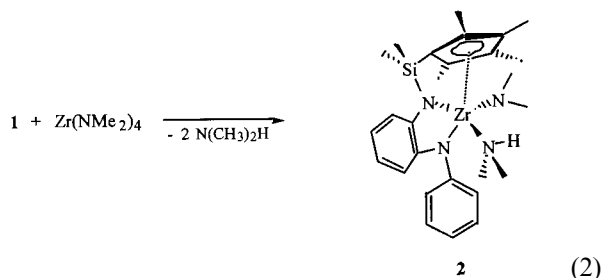
Table 1

Summary of crystallographic data, collection parameters, and refinement parameters for **2** and **3**^a

	2	3
<i>Crystal data</i> (173 K)		
Empirical formula	C ₂₇ H ₄₀ N ₄ SiZr·1/2(C ₆ H ₆)	C ₂₇ H ₄₁ ClN ₄ SiZr
FW	578.99	576.40
Crystal size (mm)	0.34 × 0.26 × 0.11	0.34 × 0.26 × 0.13
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	10.9864(1)	12.1925(2)
<i>b</i> (Å)	11.8841(2)	18.9677(4)
<i>c</i> (Å)	12.3633(1)	12.2218(2)
α (°)	77.310(1)	
β (°)	70.304(1)	91.407(1)
γ (°)	77.732(1)	
<i>V</i> (Å ³)	1465.68(3)	2825.6(9)
<i>Z</i>	2	4
<i>D</i> _{calc} (Mg m ⁻³)	1.312	1.355
<i>F</i> (000), electrons	610	1208
<i>Structure refinement</i>		
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
<i>S</i> , goodness-of-fit	1.092	1.022
<i>R</i> ₁ /reflections	0.0238/6040 > 2σ(<i>I</i>)	0.0237/5464 > 2σ(<i>I</i>)
<i>wR</i> ₂ /reflections	0.0592/6040 > 2σ(<i>I</i>)	0.0579/5464 > 2σ(<i>I</i>)
<i>R</i> _{int} (%)	2.25	2.50

^a $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$, $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$, $S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}$, $w = 1 / [\sigma^2(F_o^2) + (0.0370p)^2 + 0.31p]$, $p = [\max(F_o^2, 0) + 2F_c^2] / 3$.

The methods of amine [1e,i,5] and alkane elimination [1k,m] are alternative strategies for the attachment of cyclopentadienyl-amido type ligands to transition metals. We therefore pursued these possibilities in order to coordinate **1** to zirconium and tantalum. As a model reaction, we initially investigated the amine elimination route by addition of one equivalent of **1** to a solution of Zr(NMe₂)₄. This resulted in the isolation of *o*-C₆H₄{N(C₆H₅)N[Si(CH₃)₂(C₅(CH₃)₄)]}Zr(N(CH₃)₂)(NH(CH₃)₂) (**2**) in low yield (Eq. (2)). We found that the coordinated NMe₂H could not be removed even when the reaction mixture was heated in an open system.



The ¹H-NMR spectrum of **2** exhibits four Cp ring methyl (1.61, 1.77, 2.07, 2.14 ppm) and two silyl methyl (0.79, 0.86 ppm) resonances reflecting an asymmetric geometry. The methyls of the coordinated NMe₂H appear as a broad singlet at 1.62 ppm, whereas the amine proton is either broadened into the baseline or overlaps with the Me peaks of the amine or amide groups. The structure in Eq. (2) is consistent with the NMR spectra and was confirmed via a single-crystal X-ray diffraction study (vide infra).

The single-crystal X-ray diffraction study performed on **2** confirmed the proposed structure of this complex. A thermal ellipsoid plot of **2** is found in Fig. 1. The crystallographic data are presented in Table 1, while selected bond lengths and angles for **2** are summarized in Table 2.

The geometry around zirconium is best described as a distorted square pyramid with the dimethylamido ligand occupying the apical position. The dimethylamine, the centroid of the cyclopentadienyl ligand (Cp(c)), and the two amido groups of the phenylenediamine define the base of the pyramid. The angles between both sets of *trans* ligands are less than 180°. Therefore, the Zr atom is slightly displaced from the equatorial plane of the square pyramid. The 2.059 Å distance between Zr–N(3) is comparable to the average Zr–N distances in compounds such as Zr(NMe₂)₄ [9], *rac*-[C₂H₄(indenyl)₂]Zr(NMe₂)₂ [6], and [(C₅Me₄)-SiMe₂(N-*t*-Bu)]Zr(NMe₂)₂ [11], and is consistent with the presence of π-donation from the nitrogen of the amido ligand to the Zr center.

The sum of the angles around the chelating nitrogens, N(1) and N(2) are approximately 360°, indicating

Table 2
Selected bond distances (Å) and angles (°) for **2**^a

<i>Bond lengths</i>	
Zr–N(1)	2.1451(12)
Zr–N(2)	2.2513(12)
Zr–N(3)	2.0599(13)
Zr–N(4)	2.4005(13)
Zr–Cp(c)	2.332(2)
Si–N(1)	1.7173(13)
N(1)–C(8)	1.385(2)
N(2)–C(9)	1.401(2)
N(2)–C(14)	1.432(2)
N(3)–C(20)	1.462(2)
N(3)–C(21)	1.452(2)
Si–C(1)	1.874(2)
<i>Bond angles</i>	
N(1)–Zr–N(2)	71.34(4)
N(1)–Zr–N(3)	102.88(5)
N(1)–Zr–N(4)	145.90(5)
N(1)–Zr–Cp(c)	97.4(5)
N(2)–Zr–N(3)	96.47(5)
N(2)–Zr–N(4)	77.72(5)
N(2)–Zr–Cp(c)	153.0
N(3)–Zr–N(4)	94.38(5)
N(3)–Zr–Cp(c)	109.61
N(4)–Zr–Cp(c)	104.32
N(1)–Si–C(1)	92.86(6)
Si–N(1)–Zr	107.25(6)
C(8)–N(1)–Zr	121.87(9)
C(8)–N(1)–Si	130.64(10)
C(9)–N(2)–Zr	117.62(9)
C(9)–N(2)–C(14)	113.35(11)
C(14)–N(2)–Zr	128.71(9)
C(20)–N(3)–Zr	117.44(11)
C(20)–N(3)–C(21)	109.49(14)
C(21)–N(3)–Zr	132.83(12)
Si–C(1)–Cp(c)	159.42

^a Cp(c) denotes the centroid of the cyclopentadienyl ring.

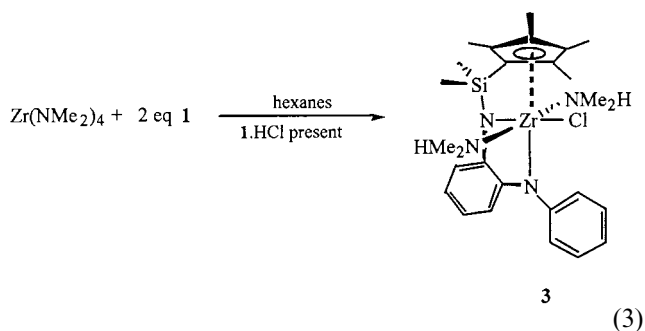
sp²-hybridization. The Zr–N(1) and Zr–N(2) distances of the chelating ligand however, are ~0.10–0.20 Å longer, respectively, compared to those in [*o*-C₆H₄(NSiⁱPr₃)₂]₂Zr [10]. This reflects either a weaker ππ–dπ interaction between N(1), N(2) and Zr, or excessive steric congestion around the metal center.

The bond lengths between zirconium and the carbon atoms of the cyclopentadienyl ring range from 2.474 to 2.769 Å revealing a significant tilt due to the constraints imposed by the rest of the chelating ligand. The Zr–Cp(c) distance (where Cp(c) is the centroid of the cyclopentadienyl ring) is comparable to values reported in the literature for similar complexes [1i]. The presence of the –SiMe₂ bridge leads to reduction of the Cp(c)–Zr–N(1) angle compared to similar complexes with unlinked cyclopentadienyl and amido ligands [1i,11]. The geometry imposed by the chelating ligand is also characterized by the substantial displacement of the Si atom from the plane of the cyclopentadienyl ring (Cp(c)–C(1)–Si = 159.4°), and results in the internal C(1)–Si–N(1) and Si–N(1)–Zr angles being 92.86 and

107.25°, respectively. The bite angle of the phenylenediamido fragment is 71.34°, which is considerably smaller than the 86.8° angle reported for complex [*o*-C₆H₄(NSiⁱPr₃)₂]₂Zr [10].

Isolation of a pure sample of **2** was troublesome. Its synthesis was accompanied by formation of a second zirconium complex that, by ¹H-NMR, appeared to be a symmetric species. We were able to isolate this second complex in low yields, by dropwise addition of Zr(NMe₂)₄ to two or more equivalents of **1**. ¹H-NMR spectroscopy together with X-ray crystallography, confirmed that this complex was *o*-C₆H₄{N(C₆H₅)N[Si(CH₃)₂(C₅(CH₃)₄)]}Zr(Cl)(NH(CH₃)₂)₂ (**3**) (Eq. (3)). Consistent with our assignment, the bridging silyl methyls of **3** appear as a sharp singlet at 0.70 ppm in the ¹H-NMR spectrum, whereas the methyls of the Cp ring appear as two singlets at 1.88 (6H) and 1.93 (6H) ppm, respectively. The methyls of the coordinated NMe₂H groups appear as a sharp singlet at 2.00 ppm. In this case, the two amine protons were observed as a very broad singlet at 3.28 ppm.

The isolation of complex **3** was due to presence of chloride impurity in **1**. The source of chloride could be attributed either to NEt₃HCl or **1**·HCl, which are both generated during the preparation of **1**. Although we cannot be absolutely certain, two points support **1**·HCl being responsible for the isolation of **3**. First, **1** was extracted several times with cold pentane, which should have separated **1** from the NEt₃HCl byproduct. Second, addition of NEt₃HCl to pure **2** produced only a minimal amount **3**. Therefore, it is more likely that the formation of **3** arises from the presence of **1**·HCl. This suggests that **1**·HCl is a stable adduct that is not completely converted to **1** even when an excess of NEt₃ is present. It also cannot be successfully separated from **1** due to its similar solubility to **1** even in non-polar solvents.



Orange crystals suitable for an X-ray diffraction study were isolated from a C₇D₈ solution of **3** after four days at r.t. A thermal ellipsoid plot of **3** is shown in Fig. 2, whereas crystallographic data are summarized in Table 1. Table 3 contains selected bond lengths and angles for **3**. The structure of *o*-C₆H₄{N(C₆H₅)N[Si(CH₃)₂(C₅(CH₃)₄)]}Zr(Cl)(NH(CH₃)₂)₂ (**3**) is best described as a distorted octahedron with the centroid of

the cyclopentadienyl ring, the NPh group of the phenylenediamido ligand, occupying mutually *trans* positions. The silicon atom is displaced from the plane of the cyclopentadienyl ring as indicated by the $\text{Cp(c)-C(1)-Si} = 156.5^\circ$ due to the constraints imposed by the chelating ligand.

The sums of the angles around the nitrogens of the phenylenediamido fragment of the chelating ligand are approximately 360° indicating sp^2 -hybridization at both N atoms. The Zr–N(1) and Zr–N(2) distances in **3** (2.124 and 2.302 Å respectively) are comparable to those of **2**. The substitution of the $-\text{NMe}_2$ ligand in **2** by chloride which is not as good a π -donor renders the metal center more electron deficient and allows coordination of an additional amine group. The zirconium–amine bonds Zr–N(3) and Zr–N(4) in **3** are similar in length to the Zr–N(4) distance in **2** and are consistent with a Zr–N(sp^3) single bond.

The isolation of complexes **2** and **3** supported the idea that amine elimination is a viable route for the synthesis of other transition metal complexes of **1**. However, our efforts to extend this chemistry to tantalum have met with little success. For example, addition of **1** to $\text{Ta}(\text{NMe}_2)_5$ produced a number of products that had $^1\text{H-NMR}$ spectra that were similar to those of **2** and **3**, but these products could not be unequivocally identified or separated. In contrast, reaction of **1** with $\text{Ta}(\text{CH}_2\text{Ph})_3\text{Cl}_2$ did not proceed even under forced conditions.

The synthesis of the trianionic mixed cyclopentadienyl–diamido ligand **1** was achieved in good yield. The amine elimination method was a viable route for attachment of **1** to zirconium and resulted in the isolation

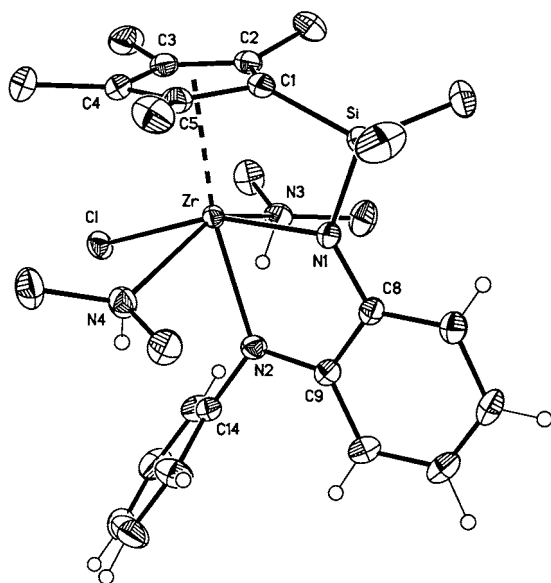


Fig. 2. Thermal ellipsoid plot of the molecular structure of $o\text{-C}_6\text{H}_4\{\text{N}(\text{C}_6\text{H}_5)\text{N}[\text{Si}(\text{CH}_3)_2\text{C}_5(\text{CH}_3)_4]\}\text{Zr}(\text{Cl})(\text{NH}(\text{CH}_3)_2)_2$ (**3**).

Table 3

Selected bond distances (Å) and angles ($^\circ$) for **3**^a

Bond lengths	
Zr–N(1)	2.1245(12)
Zr–N(2)	2.3024(13)
Zr–N(3)	2.4511(14)
Zr–N(4)	2.4190(13)
Zr–Cl	2.5376(4)
Zr–Cp(c)	2.300(2)
Si–N(1)	1.7296(14)
Si–C(1)	1.873(2)
N(1)–C(8)	1.399(2)
N(2)–C(9)	1.399(2)
N(2)–C(14)	1.432(2)
Bond angles	
N(1)–Zr–N(2)	71.84(5)
N(1)–Zr–N(3)	92.33(5)
N(1)–Zr–N(4)	97.92(5)
N(1)–Zr–Cl	158.74(4)
N(1)–Zr–Cp(c)	97.1
N(2)–Zr–N(3)	74.95(5)
N(2)–Zr–N(4)	74.19(5)
N(2)–Zr–Cl	87.13(3)
N(2)–Zr–Cp(c)	168.9
N(3)–Zr–N(4)	142.42(5)
N(3)–Zr–Cl	78.82(4)
N(3)–Zr–Cp(c)	107.1
N(4)–Zr–Cl	78.73(4)
N(4)–Zr–Cp(c)	107.4
Zr–Cl–Cp(c)	104.0
N(1)–Si–C(1)	92.64(7)
Si–N(1)–Zr	108.93(6)
C(8)–N(1)–Si	128.54(11)
C(8)–N(1)–Zr	122.50(10)
C(9)–N(2)–C(14)	114.71(12)
C(9)–N(2)–Zr	115.78(10)
C(14)–N(2)–Zr	128.40(10)
Si–C(1)–Cp(c)	156.5

^a Cp(c) denotes the centroid of the cyclopentadienyl ring.

of complexes **2** and **3**. The unexpected isolation of the chloride complex **3** is likely to be due to presence of the **1**·HCl adduct rather than NEt_3HCl , both of which are generated during the synthesis of **1**. The crystal structures of both **2** and **3** indicate that the rigid trianionic cyclopentadienyl–bisamido ligand is not very sterically demanding and leaves a large area of the Zr center exposed. This behavior is evidenced by the strong coordination of amine groups in both **2** and **3**.

References

- [1] (a) J. Okuda, *Comments Inorg. Chem.* 16 (1994) 185 and references therein. (b) M.J. Bochman, *J. Chem. Soc. Dalton Trans.* (1996) 255 and references therein. (c) P.J. Shapiro, E. Bunel, W.P. Schaefer, J.E. Bercaw, *Organometallics* 9 (1990) 867. (d) P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, *J. Am. Chem. Soc.* 116 (1994) 4623. (e) W. Herrmann, W. Baratta, J.A. Morawietz, *J. Organomet.*

- Chem. 497 (1995) C4. (f) J. Okuda, F. Schattermann, S. Wocadlo, W. Massa, *Organometallics* 14 (1995) 789. (g) A.K. Hughes, A. Meetsma, J.H. Teuben, *Organometallics* 12 (1993) 1936. (h) R. Spence, W.E. Piers, *Organometallics* 14 (1995) 4617. (i) D.W. Carpenetti, L. Kloppenburg, J.T. Kupec, J.L. Petersen, *Organometallics* 5 (1996) 1572. (j) J. Okuda, K.E. du Plooy, W. Massa, H.C. Kang, U. Rose, *Chem. Ber.* 129 (1996) 275. (k) Y. Mu, W.E. Piers, D.C. McQuarrie, M.J. Zaworotko, V.G. Young, *Organometallics* 15 (1996) 2720 and references therein. (l) K.E. du Plooy, U. Moll, S. Wocadlo, W. Massa, J. Okuda, *Organometallics* 14 (1995) 3129. (m) Y.X. Chen, T.J. Marks, *Organometallics* 16 (1997) 3649. (n) F. Amor, T.P. Spaniol, J. Okuda, *Organometallics* 16 (1997) 4765. (o) M.D. Fryzuk, P.B. Duval, S.H. Mao, S.J. Rettig, M.J. Zaworotko, L.R. Macgillivray, *J. Am. Chem. Soc.* 121 (1999) 2478. (p) M.D. Fryzuk, P.B. Duval, S.H. Mao, S.J. Rettig, M.J. Zaworotko, L.R. Macgillivray, *J. Am. Chem. Soc.* 121 (1999) 1707.
- [2] S. Ciruelos, T. Cuenca, P. Gomez-Sal, A. Manzano, P. Royo, *Organometallics* 14 (1995) 177.
- [3] (a) P. Jutzi, U. Siemeling, *J. Organomet. Chem.* 500 (1995) 175. (b) M. Enders, R. Rudolph, H. Pritzkow, *Chem. Ber.* 129 (1996) 459. (c) P. Jutzi, J. Dahlhaus, *Synthesis* (1993) 684.
- [4] (a) W.E. Piers, P.J. Shapiro, E. Bunel, J.E. Bercaw, *Synlett* 1 (1990) 74. (b) J.M. Canich, *Eur. Patent Appl.* EP-420-436-A1, 1991. (c) J.M. Canich, *US Patent Appl.* 5,026,798, 1991. (d) J.M. Canich, G.G. Hlatky, H.W. Turner, *PCT Appl.* WO92-00333, 1992. (e) J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickias, R.K. Rosen, G.W. Knight, S. Lai, *Eur. Patent Appl.* EP-416-815-A2, 1991.
- [5] W.A. Hermann, W.J. Baratta, *J. Organomet. Chem.* 506 (1996) 357.
- [6] G.M. Diamond, R.F. Jordan, J.L. Petersen, *J. Am. Chem. Soc.* 118 (1996) 8024.
- [7] G.M. Sheldrick, *SHELXTL*, Nicolet XRD, Madison, WI, 1986.
- [8] P. Jutzi, *Chem. Rev.* 86 (1986) 983.
- [9] K. Hagen, C.J. Holwill, D.A. Rice, J.D. Runnacles, *Inorg. Chem.* 27 (1988) 2032.
- [10] K. Ayogi, K. Gantzel, K. Kalai, T.D. Tilley, *Organometallics* 15 (1996) 923.
- [11] R.M. Pupi, J.N. Coalter, J.L. Petersen, *J. Organomet. Chem.* 497 (1995) 172.