

Preparation of Group 4 metal complexes of a bulky amido-fluorenyl ligand

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Abstract

The synthesis, spectroscopic and structural characterization of new amido-fluorenyl ligand $[(\text{Me}_3\text{CN}(\text{H})-\text{Si}(\text{Me})_2\text{CH}_2-\text{C}_{13}\text{H}_8)\text{Li}(\text{THF})]$ (**1**) is reported. The treatment of **1** with BuLi followed by the reaction with Group 4 metal chlorides led to crystalline, solvent free, metal complexes $[(\eta^1\text{-NCMe}_3)\text{Si}(\text{Me})_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)\text{MCl}_2]$ (where M = Ti (**3**), Zr (**4**) or Hf (**5**)) in good yield. The X-ray crystal structures of **4** and **5** are also reported. Both these compounds possess monomeric structures with relatively short M–N and M–Cl bonds. The M–N distances of **4** and **5** are 2.060(3) Å and 2.065(3) Å respectively. The metal ion is coordinated to the fluorene group in η^5 -fashion. The X-ray data also indicate the presence of a relatively unstrained ligand backbone in these metal complexes.

Keywords: Alkali metals; Group 4; Crystal structure; Amide; Metallocene

1. Introduction

The *ansa*-metallocene complexes of Group 4 metals are of importance in many areas including in catalytic alkene polymerizations and in the asymmetric induction [1–16]. Recently there has been increasing interest in the synthesis of ligands where one of the cyclopentadiene groups of *ansa*-metallocene has been replaced with groups such as amido or alkoxy donors [17–25]. The Group 3 and 4 metal complexes of these monocyclopentadiene-amido or -alkoxy ligands have also been found to act as catalysts for olefin polymerization reactions [17–19,21,26–30]. Furthermore, metal complexes of such amido-cyclopentadienyl ligands show higher Lewis acidity compared to the corresponding bis(cyclopentadienyl)metal complexes [19]. This increased electrophilicity of the metal center has been attributed largely to the reduction in the number of electrons donated to the metal center by the ligands [17,31]. In the absence of adequate steric protection, the metal complexes derived from these hybrid *ansa*-ligands often tend to form adducts with solvents, Lewis bases, alkali metal halides, or to form aggregates [17,21,25]. In certain instances,

this increased reactivity even leads to the formation of bis-ligand complex. For example, irrespective of the molar ratio, the reaction between $[\text{Me}_3\text{CNSi}(\text{Me})_2\text{-C}_5\text{H}_4]\text{Li}_2$ and ZrCl_4 leads exclusively to $[\text{Me}_3\text{CNSi}(\text{Me})_2\text{C}_5\text{H}_4]_2\text{Zr}$ [24].

We have focused our attention on the synthesis of sterically demanding *ansa*-ligand systems containing fluorene [32]. In this paper, we describe the synthesis of an amido-fluorenyl ligand with a $-\text{Si}(\text{Me})_2\text{CH}_2-$ backbone and its use in the synthesis of the dichloro metal complexes of Ti, Zr and Hf. Such systems could be expected to have relatively less strained ligand backbone compared to systems with $-\text{CR}_2-$ or $-\text{SiR}_2-$ (where R = alkyl or aryl group) bridges and should offer better protection to the central metal ion.

2. Experimental details

All operations were carried out under an atmosphere of purified nitrogen using either standard Schlenk techniques or in a Vacuum Atmospheres single station dry box equipped with a -25°C refrigerator. Solvents were distilled from conventional drying agents and degassed twice prior to use [33]. Glassware was oven-dried at 150°C overnight. The ^1H and ^{13}C NMR spectra were recorded in C_6D_6 at 25°C on a Bruker MSL-300 spec-

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trometer (^1H , 300.15 MHz; ^{13}C , 75.47 MHz) or Nicolet NT-200 spectrometer (^1H , 200.06 MHz; ^{13}C , 50.31 MHz), unless otherwise noted. Chemical shifts for ^1H NMR spectra are relative to internal Me_4Si or to residual protium in the deuterated solvents (C_6D_6 , 7.15 ppm). The ^{13}C NMR spectra were run with ^1H decoupling and the chemical shifts are reported in ppm vs. Me_4Si (C_6D_6 at 128.0 ppm). Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Elemental analyses were performed by Texas Analytical Laboratories, Inc., Houston, TX.

Fluorene ($\text{C}_{13}\text{H}_{10}$), $^n\text{BuLi}$ (1.6 M solution in hexanes), TiCl_4 , ZrCl_4 and HfCl_4 were obtained from Aldrich and used as received. $\text{TiCl}_4(\text{THF})_2$ was prepared according to literature method [34]. The $\text{ClCH}_2\text{Si}(\text{Me})_2\text{N}(\text{H})\text{CMe}_3$ was synthesized from Me_3CNH_2 and $\text{ClCH}_2\text{Si}(\text{Me})_2\text{Cl}$ as described for the related species, purified by vacuum distillation and used immediately in the synthesis of **1** [35,36].

2.1. $\{[\text{Me}_3\text{CN}(\text{H})\text{Si}(\text{Me})_2\text{CH}_2-\text{C}_{13}\text{H}_8]\text{Li}(\text{THF})\}$ (**1**)

Fluorene (2.0 g, 12.0 mmol) in thf (20 ml) was cooled to 0°C and treated with $^n\text{BuLi}$ in hexane (7.5 ml of 1.6 M solution, 12.0 mmol) over a period of 15 min. The color of the solution became red immediately. The solution was then allowed to warm up to room temperature and stirred for further 30 min. This mixture was added dropwise into $\text{ClCH}_2\text{Si}(\text{Me})_2\text{N}(\text{H})\text{CMe}_3$ (1.08 g, 6.0 mmol, 20 ml) in THF (20 ml) at 0°C , allowed to warm up to room temperature and stirred overnight. All of the volatiles were removed under vacuum and the residue was extracted into toluene. The mixture was filtered and the toluene was removed from the filtrate to obtain a red solid. This red solid was rinsed several times with hexane and dried under vacuum to obtain **1** in 67% yield. The product was recrystallized from toluene–hexane at -25°C . m.p. $105\text{--}108^\circ\text{C}$. ^1H $\delta = 0.22$ (s, 6H, SiMe), 0.67 (s, 9H, ^tBu), 1.01 (m, 4H, THF), 2.48 (m, 4H, THF), 2.62 (s, 2H, CH_2), 7.08–8.37 (m, 8H, C_{13}H_8); $^{13}\text{C}\{^1\text{H}\}$ $\delta = 2.72$ (SiMe), 14.87 (SiCH₂), 25.08 (THF), 32.93 (^tBu), 50.24 (^tBu), 67.53 (THF), 85.06, 111.78, 115.57, 119.41, 120.83, 121.77, 130.73 (C_{13}H_8). Anal. Calc. for $\text{C}_{24}\text{H}_{34}\text{NOSiLi}$: C, 74.38; H, 8.84; N, 3.61. Found: C, 74.32; H, 8.81; N, 3.58.

2.2. $\{[(\eta^1\text{-NCMe}_3)\text{Si}(\text{Me})_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{TiCl}_2\}$ (**3**)

A solution of **1** (0.50 g, 1.29 mmol) in toluene (20 ml) was treated with $^n\text{BuLi}$ in hexane (0.8 ml of 1.6 M solution, 1.29 mmol) at 0°C and allowed to stir for 10 min. After 30 min stirring at room temperature, this mixture was added dropwise to $\text{TiCl}_4(\text{THF})_2$ (0.45 g, 1.34 mmol) in toluene (15 ml) over a period of 15 min at -78°C . The color of the mixture changed from red

to dark green. The solution was allowed to warm up to room temperature and stirred overnight. The resulting mixture was filtered and the filtrate was concentrated to ca. 5 ml. Hexane was added and the solution was cooled to -25°C to obtain a dark green microcrystalline precipitate. A second crop of crystals were obtained from the concentrated filtrate. Yield 0.34 g (63%), m.p. $205\text{--}210^\circ\text{C}$. ^1H $\delta = 0.40$ (s, 6H, SiMe), 1.28 (s, 9H, ^tBu), 2.61 (s, 2H, CH_2), 7.16–7.60 (m, 8H, C_{13}H_8); $^{13}\text{C}\{^1\text{H}\}$ $\delta = 7.07$ (SiMe), 17.46 (SiCH₂), 33.00 (^tBu), 63.40 (^tBu), 116.70, 119.55, 124.26, 125.33, 129.15 (C_{13}H_8). Anal. Calc. for $\text{C}_{20}\text{H}_{25}\text{Cl}_2\text{NSiTi}$: C, 56.35; H, 5.91; N, 3.29. Found: C, 56.13; H, 5.97; N, 3.29.

2.3. $\{[(\eta^1\text{-NCMe}_3)\text{Si}(\text{Me})_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{ZrCl}_2\}$ (**4**)

A solution of **1** (0.50 g, 1.29 mmol) in diethyl ether (20 ml) was treated with $^n\text{BuLi}$ in hexane (0.8 ml of 1.6 M solution, 1.29 mmol) at 0°C . After 5 min, the solution was allowed to warm up to room temperature and stirred for further 30 min. The reaction mixture was then added dropwise to ZrCl_4 (0.30 g, 1.29 mmol) in Et_2O (15 ml) at -78°C . The color of the solution changed from red to brown. The reaction system was allowed to warm up to room temperature and stirred overnight. The volatiles were removed under reduced pressure. The resulting solid was taken up in toluene, the solution was filtered and the filtrate was concentrated. Addition of hexane followed by cooling to -25°C afforded dark yellow crystals of **4** in 75% yield. m.p. $245\text{--}248^\circ\text{C}$. ^1H $\delta = 0.40$ (s, 6H, SiMe), 1.26 (s, 9H, ^tBu), 2.43 (s, 2H, CH_2), 7.14–7.75 (m, 8H, C_{13}H_8); $^{13}\text{C}\{^1\text{H}\}$ $\delta = 7.51$ (SiMe), 15.01 (SiCH₂), 32.91 (^tBu), 56.69 (^tBu), 103.32, 120.09, 121.41, 125.10, 125.64, 129.09 (C_{13}H_8). Anal. Calc. for $\text{C}_{20}\text{H}_{25}\text{Cl}_2\text{NSiZr}$: C, 51.15; H, 5.37; N, 2.98. Found: C, 51.09; H, 5.31; N, 2.82.

2.4. $\{[(\eta^1\text{-NCMe}_3)\text{Si}(\text{Me})_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{HfCl}_2\}$ (**5**)

A solution of **1** (0.50 g, 1.29 mmol) in diethyl ether (20 ml) was treated with $^n\text{BuLi}$ in hexane (0.8 ml of 1.6 M solution, 1.29 mmol) at 0°C . After 5 min, the solution was allowed to warm up to room temperature and stirred for further 30 min. The reaction mixture was then added dropwise to an Et_2O (15 ml) solution of HfCl_4 (0.41 g, 1.29 mmol) at -78°C . The color of the solution changed from red to brown. The resulting mixture was then stirred overnight at room temperature. The volatiles were removed under reduced pressure. The resulting solid was taken up in toluene, the solution was filtered and the filtrate was concentrated. Addition of hexane followed by cooling to -25°C afforded dark yellow crystals of **5** in 81% yield. m.p. $225\text{--}228^\circ\text{C}$. ^1H $\delta = 0.42$ (s, 6H, SiMe), 1.25 (s, 9H, ^tBu), 2.47 (s, 2H, CH_2), 7.12–7.75 (m, 8H, C_{13}H_8); $^{13}\text{C}\{^1\text{H}\}$ $\delta = 7.96$

(SiMe), 14.61 (SiCH₂), 33.63 (¹Bu), 55.95 (¹Bu), 97.82, 118.78, 121.13, 124.58, 125.47, 128.96 (C₁₃H₈). Anal. Calc. for C₂₀H₂₅Cl₂NSiHf: C, 43.13; H, 4.52; N, 2.52. Found: C, 43.04; H, 4.67; N, 2.40.

2.5. X-ray structure determination of 1

X-ray quality crystals of **1** were obtained by slow crystallization from toluene–hexane at –25°C. A suitable crystal was selected and mounted under nitrogen in a Lindemann capillary on a goniometer head and transferred to the goniostat of an Enraf-Nonius CAD 4 diffractometer. The unit cell parameters were determined by least-squares refinement of 25 reflections. Data were collected at room temperature. Three standard reflections were measured at every 3600 s of exposure time to check for crystal deterioration and/or misalignment. No significant deterioration in intensity was observed. Data were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods (SHELX 86) [37]. Anisotropic refinement was carried out by full-matrix least-squares on *F*. All non-hydrogen atoms with the exception of the carbons in the 5-membered ring and Li were refined with anisotropic thermal parameters. The H on the nitrogen was located on the difference map, and the remaining hydrogen atoms were included in the model at calculated position (*U*(H) = 1.3 [*U*(C)]). Refinement converged at *R* = 0.0546, *R*_w = 0.0526 (*w* = [0.04*F*² + (σ*F*)²]⁻¹) [38]. Further details of the crystal structure are provided in the supplementary material.

2.6. X-ray structure determination of 4

Crystals of **4** were obtained by slow crystallization from toluene–hexane at –25°C. A suitable crystal was selected and mounted under nitrogen in a Lindemann capillary on a goniometer head and transferred to the goniostat of an Enraf-Nonius CAD 4 diffractometer. The unit cell parameters were determined by least-squares refinement of 25 reflections. Data were collected at room temperature. Three standard reflections were measured at every 3600 s of exposure time to check for crystal deterioration and/or misalignment. No significant deterioration in intensity was observed. Data were corrected for Lorentz and polarization effects, and a Fourier absorption correction was applied. The structure was solved by Patterson methods. Anisotropic refinement was carried out by full-matrix least-squares for all the non-hydrogen atoms, and hydrogen atoms were included in the model at calculated position (*U*(H) = 1.3 [*U*(C)]). Refinement on *F* converged at *R* = 0.0268, *R*_w = 0.0317 (*w* = [0.04*F*² + (σ*F*)²]⁻¹) [38]. Further details of the crystal structure are available in the supplementary material.

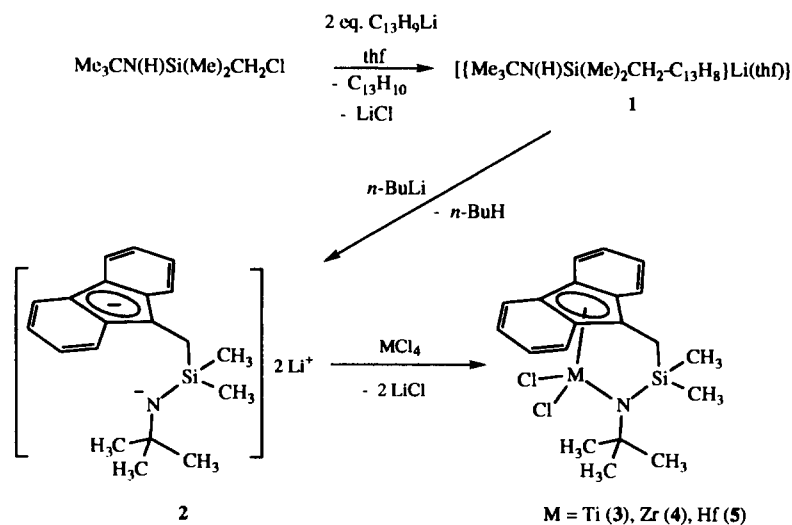
2.7. X-ray structure determination of 5

Crystals of **5** were obtained by slow crystallization from toluene–hexane at –25°C. The crystals were removed from the Schlenk tube under nitrogen and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected and attached to a glass fiber and immediately placed in the low temperature nitrogen stream of the Siemens P4 diffractometer with a LT-2A device [39]. The unit cell parameters were determined by least-squares refinement of 50 reflections. Data were collected at –80°C. Three standard reflections were measured at every 97 data points to check for crystal deterioration and/or misalignment. No significant deterioration in intensity was observed. Data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied [40]. The structure was solved by direct methods. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement at calculated position (*U*(H) = 1.2 [*U*(C)]). Refinement on *F* converged at *R* = 0.0212, *R*_w = 0.0212; [*w* = 1/σ²(*F*)]. All the software programs and the sources of scattering factors are contained in the SHELXTL PC (Version 4.2) software package provided by Siemens Analytical X-ray Instruments, Inc. [41]. Further details of the crystal structure are available in the supplementary material.

3. Results and discussion

The monolithium complex of the amido-fluorenyl ligand, [(Me₃CN(H)Si(Me)₂CH₂–C₁₃H₈)Li(THF)] (**1**) was prepared in 67% yield by the treatment of Me₃CN(H)SiMe₂CH₂Cl with two equivalents of fluorenyllithium in THF (Scheme 1). This compound has been isolated as a red solid and characterized by ¹H, ¹³C NMR spectroscopy and elemental analysis. These data also show the presence of one molecule of THF for each Li atom in **1**. The ¹H NMR signals due to the THF appear as two multiplets around 1.01 and 2.48 ppm. This somewhat upfield shift may be due to the shielding effects of fluorenyl ring current [25]. Compound **1** could be stored under dry nitrogen (preferably at –25°C) without any apparent decomposition.

[(Me₃CNSi(Me)₂CH₂–C₁₃H₈)Li]₂ **2** was prepared by the addition of one equivalent of ⁿBuLi to **1** in toluene and used directly in the preparation of Group 4 metal complexes (Scheme 1). The treatment of **2** with an equivalent of TiCl₄(THF)₂ at low temperature led to dark green, air and moisture sensitive crystals of [(η¹-NCMe₃)Si(Me)₂CH₂(η⁵-C₁₃H₈)]TiCl₂ (**3**). Compounds [(η¹-NCMe₃)Si(Me)₂CH₂(η⁵-C₁₃H₈)]ZrCl₂ (**4**) and [(η¹-NCMe₃)Si(Me)₂CH₂(η⁵-C₁₃H₈)]HfCl₂ (**5**) were prepared in Et₂O by treating **2** with the



Scheme 1.

corresponding metal(IV) chloride, and isolated as dark yellow crystals in 75 and 81% yield respectively.

Compounds 3–5 were characterized by elemental analysis and ¹H and ¹³C NMR spectroscopy. All three complexes show similar spectra with only minor differences in the chemical shift values, suggesting closely related structures in solution. However, the ¹H NMR chemical shift values of ^tBu and fluorenyl hydrogens of 3, 4 and 5 show significant differences when compared to the corresponding signals of 1. For example, the ^tBu hydrogens of 4 appear about 0.6 ppm downfield from that of 1. The ¹H NMR signals due to the fluorenyl hydrogens of 4 are spread over a relatively narrow region of about 0.6 ppm, whereas in 1, the spread is much wider (1.3 ppm).

The NMR and elemental analysis data of 3–5 show no evidence for the presence of solvent molecules or LiCl coordinated to the metal center. It is notable that the related alkoxy-fluorenyl Zr(IV) complexes, $\{(\eta^5\text{-C}_{13}\text{H}_8)\text{CHR-CHR-O}\}\text{ZrCl}_2(\text{THF})_2$ (6) (where CHR-CHR = cyclohexyl, cyclopentyl) have been isolated as bis-tetrahydrofuran adducts [21]. The attempted synthesis of THF free 6 using CH₂Cl₂ has resulted in products which contain one equivalent of LiCl or NaCl. The dimethylsilylene bridged amido-fluorenyl complex $\{[(\eta^1\text{-NCMe}_3)\text{SiMe}_2(\eta^5\text{-C}_{13}\text{H}_8)]\}\text{ZrCl}_2$ (7) has been synthesized and characterized as its Et₂O or THF coordinated species [25]. The loss of coordinated solvent from this compound results in the formation of oligomeric or polymeric solids which are insoluble even in hot THF. In contrast, compounds 3–5 show excellent solubility in Et₂O, THF, toluene or benzene. The relatively low coordination number in complexes 3, 4 or 5 is probably an indication of increased crowding around the central metal ion. The increased bulk of the amido-fluorenyl ligand, $\{[(\text{NCMe}_3)\text{Si}(\text{Me})_2\text{CH}_2(\text{C}_{13}\text{H}_8)]\}^{2-}$,

may be due to a combination of effects of having a sterically demanding *t*-butylamido group and a relaxed ligand backbone.

3.1. Structural descriptions

Compound 1 crystallizes easily from toluene at –20°C. The structure of 1 has been confirmed by X-ray crystallography. A summary of crystal data, selected bond lengths and angles and atomic positional parameters are listed in Tables 1, 2 and 3 respectively.

Compound 1 adopts a monomeric structure (Fig. 1) in which the lithium atom is coordinated to the THF oxygen (Li–O distance of 1.85 (1) Å), nitrogen (Li–N distance of 2.16(1) Å) and to the fluorenyl group in a η^2 -fashion (Li–C distances of 2.28(1) and 2.31(1) Å). The remaining Li–C(fluorenyl) distances are 2.62, 2.68 and 2.87 Å, and thus are not indicative of any interaction. The Li–O distance is relatively short, indicating a strong interaction between the two centers [42–44]. The amino nitrogen center is pyramidal as expected.

The X-ray crystal structures of 4 and 5 have been determined to examine the structural effects of the dimethylsilylmethylene ligand backbone. The ORTEP diagrams of 4 and 5 are shown in Figs. 2 and 3 respectively [45]. The Zr and the Hf compounds are essentially isostructural. The summary of crystal data for 4 and 5 are listed in Table 1, and selected bond lengths and angles and atomic parameters are listed in Tables 4 and 5.

In 4, the Zr atom adopts a formal octahedral structure, being coordinated in an η^5 -fashion to the fluorenyl ring (Zr to C distances range from 2.430(5) to 2.587(4) Å), the nitrogen and two chlorines [46,47]. The nitrogen atom adopts a planar geometry. The Zr–N bond distance is 2.060 (3) Å. This distance is slightly shorter

Table 1
Crystal data and summary of data collection and refinement

Formula	C ₂₄ H ₃₄ LiNOSi (1)	C ₂₀ H ₂₅ Cl ₂ NSiZr (4)	C ₂₀ H ₂₅ Cl ₂ NSiHf (5)
fw	387.57	469.64	556.91
Crystal color and habit	scarlet blocks	orange blocks	orange blocks
Cryst. dimensions (mm)	0.25 × 0.32 × 0.35	0.50 × 0.62 × 0.68	0.26 × 0.30 × 0.40
Crystal system	monoclinic	triclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	14.755(3)	8.634(1)	8.667(2)
<i>b</i> (Å)	11.494(2)	9.6930(9)	9.713(3)
<i>c</i> (Å)	14.836(3)	14.346(2)	14.463(4)
α (deg)	90	82.964(9)	82.62(2)
β (deg)	110.52(1)	75.30(1)	75.09(1)
γ (deg)	90	65.299(9)	65.02(2)
<i>V</i> (Å ³)	2356.4(7)	1054.9(2)	1066.1(5)
<i>Z</i>	4	2	2
<i>D</i> _{calc} (g cm ⁻³)	1.092	1.478	1.735
abs. coeff. (cm ⁻¹)	1.08	8.27	52.02
<i>F</i> (000)	848	480	544
Scan method	θ -2 θ	θ -2 θ	θ -2 θ
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Siemens P4
Radiation	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)
Monochromator	graphite	graphite	graphite
<i>T</i> (K)	ambient	ambient	193
2 θ range	2° to 44°	2° to 44°	3.5° to 50.0°
Scan rate (deg min ⁻¹)	variable	variable	variable
Bckgd/scan time	0.5	0.5	0.5
No. of reflections measd	3198	2584	4559
No. of indep rflns	3073	2584	3750
No. of obsd rflns	1563 [<i>F</i> > 6 σ (<i>F</i>)]	2330 [<i>F</i> > 6 σ (<i>F</i>)]	3578 [<i>F</i> > 4 σ (<i>F</i>)]
Weighting scheme	$w = [0.04F^2 + (\sigma F)^2]^{-1}$	$w = [0.04F^2 + (\sigma F)^2]^{-1}$	$w = [\sigma^2(F)]^{-1}$
<i>R</i> , <i>R</i> _w	0.0546, 0.0526	0.0268, 0.0317	0.0212, 0.0212 ^{a,b}
Data : parameter ratio	7.0 : 1	10.3 : 1	14.3 : 1

^a $R = \sum(|F_o| - |F_c|) / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$.

than the Zr–N bond lengths observed for zirconocene complexes [(η^5 -C₅H₅)₂Zr(η^1 -NC₄H₂Me₂)₂] (2.22(2) Å), [(Me₂Si(η^5 -C₅H₄)(NPh))₂Zr] (2.137(2), 2.127(2) Å), and [(η^5 -C₅H₅)₂Zr(Cl)(Me₃CNSiMe₂H)] (2.139(3) Å) [23,48,49]. In fact, the Zr–N distance of **4** is very similar to the corresponding bond lengths found in closely related compounds, [(η^1 -NCMe₃)SiMe₂(η^5 -C₁₃H₈)Zr(CH₂SiMe₂)₂] (**8**) (2.061(2) Å) and [(η^1 -NCMe₃)SiMe₂(η^5 -C₁₃H₈)ZrCl₂] (2.056(6) Å) [25,50,51]. The Zr–Cl distances of 2.408(1) and 2.402(1)

Å in **4** are shorter than the average distance of 2.44 Å observed for 16-electron complex [(η^5 -C₅H₅)₂ZrCl₂], and are much closer to the Zr–Cl(terminal) values in the formally 14-electron complex, [(η^5 -C₅Me₅)ZrCl₃]₂ (av. 2.38 Å) [52,53]. For comparison, the Zr–Cl dis-

Table 2
Selected bond distances (Å) and bond angles (deg) for [(Me₃CN(H)-Si(Me)₂CH₂-C₁₃H₈)Li(THF)] (**1**)

Si–N	1.748(4)	Si–C(14)	1.864(7)
Si–C(15)	1.845(8)	Si–C(16)	1.853(8)
O–Li	1.85(1)	N–C(17)	1.495(6)
N–Li	2.16(1)	C(1)–C(14)	1.510(8)
C(1)–Li	2.28(1)	C(13)–Li	2.31(1)
N–Si–C(14)	101.3(2)	N–Si–C(15)	110.1(3)
N–Si–C(16)	115.7(3)	C(14)–Si–C(15)	109.5(3)
C(14)–Si–C(16)	111.0(3)	C(15)–Si–C(16)	108.9(4)
Si–N–C(17)	127.9(4)	Si–N–Li	100.2(3)
C(17)–N–Li	117.6(4)	C(2)–C(1)–Li	86.9(4)
C(13)–C(1)–Li	73.4(4)	C(14)–C(1)–Li	106.2(4)

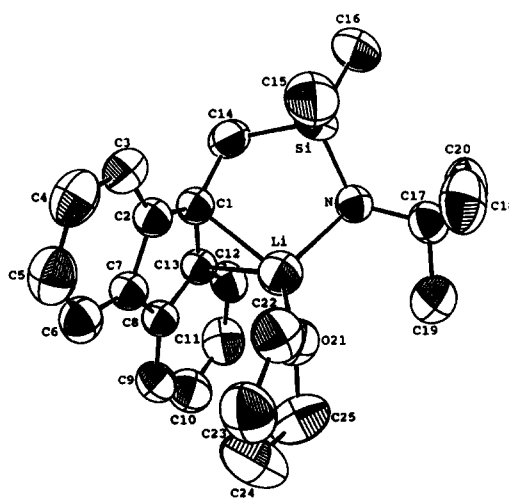


Fig. 1. Computer generated drawing of **1**. Hydrogen atoms omitted for clarity.

Table 3
Atomic coordinates ($\times 10^4$) for $[\{\text{Me}_3\text{CN}(\text{H})\text{-Si}(\text{Me})_2\text{CH}_2\text{-C}_{13}\text{H}_8\}\text{Li}(\text{THF})] (\mathbf{1})$

Atom	x	y	z
Si	6643(1)	1453(2)	2289(1)
O	7751(3)	-2028(3)	3697(2)
N	7693(3)	1053(4)	3235(3)
C(1)	7325(3)	-306(4)	1330(3)
C(2)	6781(3)	-1343(5)	1136(3)
C(3)	5790(4)	-1573(6)	764(4)
C(4)	5453(4)	-2701(6)	608(4)
C(5)	6102(4)	-3638(6)	812(4)
C(6)	7072(4)	-3458(5)	1169(4)
C(7)	7439(3)	-2320(5)	1322(3)
C(8)	8390(3)	-1854(5)	1653(3)
C(9)	9301(4)	-2383(5)	1934(4)
C(10)	10116(4)	-1707(6)	2218(4)
C(11)	10042(4)	-510(6)	2202(4)
C(12)	9163(4)	40(5)	1923(4)
C(13)	8303(3)	-619(4)	1644(3)
C(14)	6918(4)	912(5)	1228(4)
C(15)	5591(4)	660(7)	2379(5)
C(16)	6365(6)	3030(6)	2179(6)
C(17)	7994(4)	1404(5)	4268(4)
C(18)	7195(5)	1164(7)	4645(4)
C(19)	8877(5)	688(7)	4826(5)
C(20)	8275(6)	2667(7)	4410(5)
C(22)	6924(4)	-2722(6)	3622(4)
C(23)	7246(5)	-3929(6)	3823(5)
C(24)	8281(5)	-3922(7)	4047(6)
C(25)	8597(5)	-2705(7)	4186(5)
Li	7758(7)	-773(9)	2922(7)

tance in 18-electron complex is much longer; e.g., the Zr–Cl in $[\{\text{Me}_2\text{C}(\eta^5\text{-C}_5\text{H}_4)(\eta^3\text{-C}_{13}\text{H}_8)\}\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$ is 2.560 (1) Å [54]. The Si–N distance of 1.765(4) Å in **4** is relatively long (e.g., 1.738(2) Å for **8**). The short Zr–Cl and Zr–N bonds and the trigonal planar nitrogen center in **4** possibly indicate the effects of increased metal Lewis acidity due to the replacement

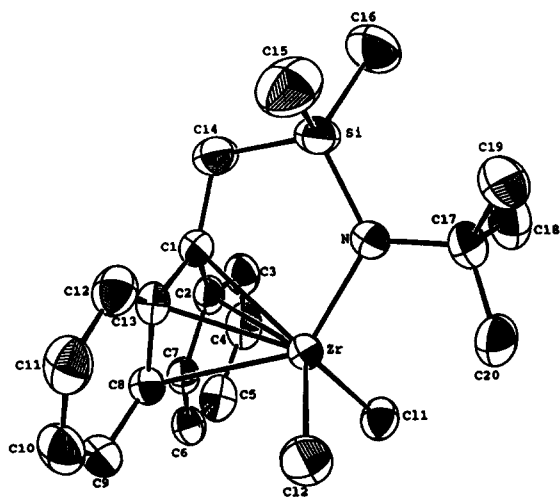


Fig. 2. Computer generated drawing of **4**. Hydrogen atoms omitted for clarity.

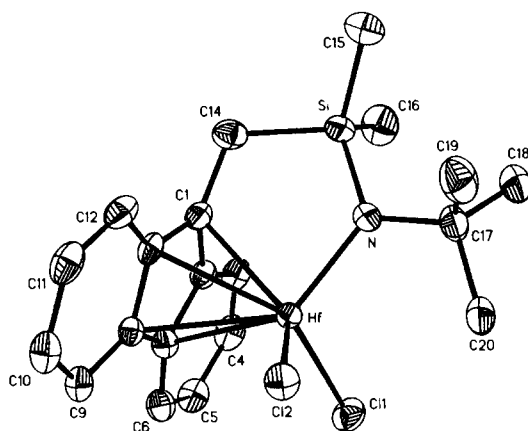


Fig. 3. Computer generated drawing of **5**. Hydrogen atoms omitted for clarity.

of 6-electron $\eta^5\text{-C}_5\text{H}_5^-$ donor with the 4 (or 2) electron donor amido group [19,31].

The effects of having an extra $-\text{CH}_2-$ moiety in the backbone is clearly evident from the X-ray data. For

Table 4
Selected bond distances (Å) and bond angles (deg) for $[\{\eta^1\text{-NCMe}_3\}\text{Si}(\text{Me})_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)\}\text{MCl}_2]$ (where M = Zr (**4**), Hf (**5**))

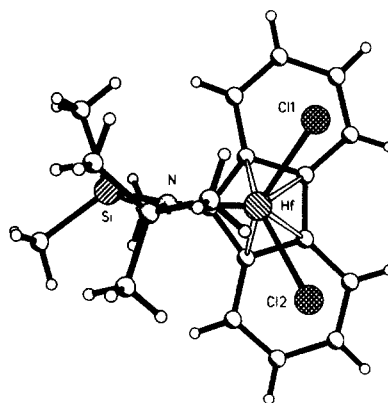
Compound 4			
Zr–Cl(1)	2.408(1)	Zr–Cl(2)	2.402(1)
Zr–N	2.060(3)	Zr–C(1)	2.430(5)
Zr–C(2)	2.515(4)	Zr–C(7)	2.587(4)
Zr–C(8)	2.587(4)	Zr–C(13)	2.508(5)
Si–N	1.765(4)	Si–C(14)	1.853(5)
Si–C(15)	1.867(6)	Si–C(16)	1.859(4)
N–C(17)	1.503(6)	C(1)–C(14)	1.493(5)
Cl(1)–Zr–Cl(2)	103.20(4)	Cl(1)–Zr–N	109.0(1)
Cl(1)–Zr–C(1)	123.61(9)	Cl(1)–Zr–C(2)	91.6(1)
Cl(1)–Zr–C(7)	85.2(1)	Cl(1)–Zr–C(8)	110.84(9)
Cl(1)–Zr–C(13)	139.25(9)	Cl(2)–Zr–N	110.47(9)
Cl(2)–Zr–C(1)	126.01(9)	Cl(2)–Zr–C(2)	138.97(8)
Cl(2)–Zr–C(7)	110.02(7)	Cl(2)–Zr–C(8)	85.31(8)
Cl(2)–Zr–C(13)	93.05(9)	Zr–N–Si	122.8(2)
Zr–C(1)–C(14)	117.4(3)	N–Si–C(14)	104.3(2)
C(1)–C(14)–Si	112.2(3)	Zr–N–C(17)	118.2(2)
Compound 5			
Hf–Cl(1)	2.396(1)	Hf–Cl(2)	2.399(1)
Hf–N	2.065(3)	Hf–C(1)	2.430(5)
Hf–C(2)	2.507(5)	Hf–C(7)	2.607(5)
Hf–C(8)	2.602(4)	Hf–C(13)	2.521(5)
Si–N	1.778(4)	Si–C(14)	1.891(5)
Si–C(15)	1.878(5)	Si–C(16)	1.889(6)
N–C(17)	1.534(7)	C(1)–C(14)	1.509(5)
Cl(1)–Hf–Cl(2)	102.7(1)	Cl(1)–Hf–N	109.0(1)
Cl(1)–Hf–C(1)	126.8(1)	Cl(1)–Hf–C(2)	93.8(1)
Cl(1)–Hf–C(7)	85.6(1)	Cl(1)–Hf–C(8)	110.5(1)
Cl(1)–Hf–C(13)	139.8(1)	Cl(2)–Hf–N	107.6(1)
Cl(2)–Hf–C(1)	123.8(1)	Cl(2)–Hf–C(2)	140.1(1)
Cl(2)–Hf–C(7)	111.9(1)	Cl(2)–Hf–C(8)	85.8(1)
Cl(2)–Hf–C(13)	91.7(1)	Hf–N–Si	121.7(2)
Hf–C(1)–C(14)	116.6(3)	N–Si–C(14)	104.4(2)
C(1)–C(14)–Si	112.1(4)	Hf–N–C(17)	120.1(3)

example, a comparison of the X-ray structural data between **4** and **8** shows that the Zr–N–CMe₃ (118.2(2)°) and Zr–N–Si (122.8(2)°) angles in **4** are significantly different from the corresponding values of 130.1(2)° and 103.1(1)° for **8**. These data are indicative of a

Table 5

Atomic coordinates ($\times 10^4$) for $[(\eta^1\text{-NCMe}_3)_2\text{Si}(\text{Me})_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{MCl}_2$ (where M = Zr (**4**), Hf (**5**))

Atom	x	y	z
Compound 4			
Zr	1425.9(4)	1108.1(4)	2133.7(3)
Cl(1)	2723(1)	2868(1)	1421(5)
Cl(2)	3673(1)	–828(1)	2831(8)
Si	–2778(1)	2074(1)	3294(7)
N	–756(4)	2194(3)	3192(2)
C(1)	–768(4)	749(4)	1533(3)
C(2)	20(5)	1453(4)	738(3)
C(3)	–639(5)	2928(4)	303(3)
C(4)	419(6)	294(4)	–467(3)
C(5)	2148(5)	2287(5)	–836(3)
C(6)	2852(5)	883(4)	–431(3)
C(7)	1799(4)	445(4)	375(3)
C(8)	2115(4)	–944(4)	917(3)
C(9)	3574(5)	–2372(4)	836(3)
C(10)	3445(6)	–3526(5)	1445(3)
C(11)	1914(6)	–3334(4)	2150(3)
C(12)	470(5)	–2007(4)	2253(3)
C(13)	517(5)	–770(4)	1620(3)
C(14)	–2613(5)	1411(5)	2101(3)
C(15)	–3155(6)	655(6)	4225(4)
C(16)	–4747(6)	3892(6)	3525(4)
C(17)	–597(5)	3096(5)	3915(3)
C(18)	–1352(7)	4786(5)	3642(4)
C(19)	–1518(6)	2822(6)	4936(3)
C(20)	1310(6)	2608(5)	3941(3)
Compound 5			
Hf	3588(1)	3911(1)	2886(1)
Cl(1)	1353(2)	5825(1)	2179(1)
Cl(2)	2308(1)	2148(1)	3576(1)
N	5732(4)	2812(4)	1815(2)
Si	7770(2)	2920(1)	1701(1)
C(1)	5775(5)	4254(4)	3485(3)
C(2)	4499(5)	5778(4)	3389(3)
C(3)	4550(6)	7026(5)	2743(3)
C(4)	3094(7)	8373(5)	2832(3)
C(5)	1549(6)	8582(5)	3541(3)
C(6)	1417(6)	7418(5)	4161(3)
C(7)	2881(5)	5995(4)	4088(3)
C(8)	3193(5)	4577(4)	4642(3)
C(9)	2112(6)	4138(5)	5447(3)
C(10)	2811(6)	2723(5)	5859(3)
C(11)	4575(6)	1688(5)	5488(3)
C(12)	5650(6)	2045(5)	4715(3)
C(13)	4976(5)	3548(4)	4282(3)
C(14)	7635(6)	3558(5)	2912(3)
C(15)	9759(7)	1085(6)	1449(4)
C(16)	8135(8)	4374(7)	772(4)
C(17)	5581(6)	1906(5)	1074(3)
C(18)	6524(7)	2199(7)	52(3)
C(19)	6346(7)	206(6)	1344(4)
C(20)	3652(6)	2387(7)	1052(3)

Fig. 4. View of **5** perpendicular to the fluorene ring plane.

relatively unstrained ligand backbone in **4**. The structure of **4** also shows that the ^tBu group is directed more towards the open face of the metal complex, providing increased protection to the Zr center.

The cell dimensions and the structural features of $[(\eta^1\text{-NCMe}_3)_2\text{Si}(\text{Me})_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{HfCl}_2$ (**5**) are very similar to those of the zirconium analog, **4**. Such close similarities between the zirconium and hafnium species have been observed previously [55,56]. As in **4**, compound **5** exists as discrete molecules in the solid state. Fig. 4 shows the orientation of the t-butyl group on nitrogen with respect to the two chlorine atoms.

The bond distances between the Hf to carbons of the five membered ring in the fluorene group (2.430(5) to 2.607(5) Å) suggest η^5 -coordination [55,57]. The Hf–N distance 2.065(3) is somewhat longer than that found in $[(\eta^5\text{-C}_5\text{Me}_5)\text{Hf}(\text{H})\text{NHMe}]$ (2.027(8) Å) but much closer to the distances found in $[(\eta^5\text{-C}_5\text{Me}_5)\text{Hf}\{\text{NH}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\}_3]$ (2.041(4), 2.048(4), and 2.065(3) Å) or $[\text{HfCl}\{\text{N}(\text{SiMe}_3)_2\}_3]$ (2.040(10) Å) [58–60]. The Hf–Cl distances (2.396(1), 2.399(1) Å) may be compared with the values of 2.510(1) Å in $[\text{Me}_2\text{C}(\eta^5\text{-C}_5\text{H}_4)_2\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$, 2.42 Å in $[(\text{CH}_2)_3(\eta^5\text{-C}_5\text{H}_4)_2\text{HfCl}_2]$ and 2.436(5) Å in $[\text{HfCl}\{\text{N}(\text{SiMe}_3)_2\}_3]$ [56,60,61].

In conclusion, we have reported the synthesis of an amido-fluorenyl ligand system and its utility in the synthesis and isolation of solvent free, monomeric Group 4 metal dichloro complexes. The longer $-\text{CH}_2\text{Si}(\text{Me})_2-$ bridge increases the effectiveness of the protection offered by the ligand to the metal ion. The X-ray structures of **4** and **5** also represent rare examples of mono(flourenyl) complexes of Group 4 metal ions [25]. The Group 4 metal complexes based on this amido-fluorenyl ligand could be useful as catalyst precursors in the olefin polymerization reactions [26–30]. We are currently studying the chemistry of **3–5**, and the reactions of **2** with various other metal ions. We are also currently investigating the chemistry of $[(\text{N-}^i\text{Pr})\text{Si}(\text{Me})_2\text{-CH}_2(\text{C}_{13}\text{H}_8)]^{2-}$ ligand [62].

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