

# Syntheses and characterization of zirconium and hafnium complexes of amido-fluorenyl ligands $[(\text{NBu}^t)\text{SiMe}_2\text{CH}_2(\text{C}_{13}\text{H}_8)]^{2-}$ and $[(\text{NPr}^i)\text{SiMe}_2\text{CH}_2(\text{C}_{13}\text{H}_8)]^{2-}$

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## Abstract

The reaction of  $\text{Pr}^i\text{N}(\text{H})\text{SiMe}_2\text{CH}_2\text{Cl}$  with two equivalents of fluorenyllithium in THF led to  $[\text{Pr}^i\text{N}(\text{H})\text{SiMe}_2\text{CH}_2(\text{C}_{13}\text{H}_8)]\text{Li}(\text{THF})$  (**1**) in high yield. X-ray diffraction studies of **1** revealed a monomeric structure with an  $\eta^2$ -coordinated fluorenyl ligand. Lithiation followed by the treatment with zirconium or hafnium tetrachloride afforded the corresponding dichloro complexes  $[(\eta^1\text{-NPr}^i)\text{SiMe}_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{ZrCl}_2$  (**2**) and  $[(\eta^1\text{-NPr}^i)\text{SiMe}_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{HfCl}_2$  (**3**). These metal adducts were characterized by NMR spectroscopy, and in the case of **3** also by X-ray diffraction. Compound **3** shows a weak interaction between the formally 14-electron Hf center and the C–H of the isopropyl group. The dialkyl compound  $[(\eta^1\text{-NBu}^t)\text{SiMe}_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{Zr}(\text{CH}_2\text{SiMe}_3)_2$  (**4**) was prepared from  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  and  $[(\eta^1\text{-NBu}^t)\text{SiMe}_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{ZrCl}_2$ . The NMR spectroscopic and X-ray data point to a fairly congested environment around the zirconium atom. In contrast to the  $-\text{SiMe}_2-$  bridged analogs, the  $-\text{SiMe}_2\text{CH}_2-$  linked amido-fluorenyl complex **4** features a relatively unstrained ligand backbone with a close to ideal trigonal planar geometry at the amido nitrogen atom. © 1997 Elsevier Science S.A.

**Keywords:** Zirconium; Cyclopentadienyl groups; NMR spectroscopy

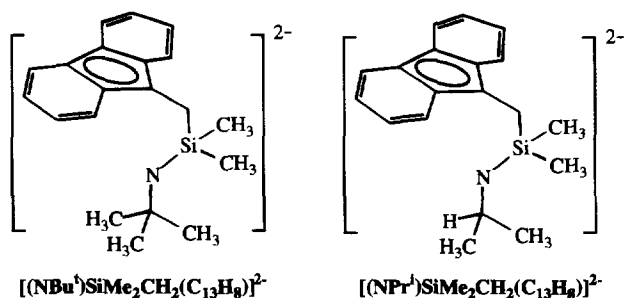
## 1. Introduction

The *ansa*-metallocene complexes of Group 4 metal ions are of particular interest due to their importance as catalyst precursors in the syndiospecific  $\alpha$ -olefin polymerization processes [1–16]. A variety of sterically and electronically different cyclopentadienyl ligands, ring annelated  $\eta^5$ -donors such as fluorenyl or indenyl ligands, and various bridging moieties (e.g.  $-(\text{CH}_2)_2-$ ,  $-(\text{CH}_2)_3-$ ,  $-\text{CMe}_2-$ ,  $-\text{SiMe}_2-$ ,  $-\text{SnMe}_2-$ ) have been used to modulate properties of these metal adducts [8,10,11,17–21]. More drastic modifications involve the use of ligands other than cyclopentadienyl (or related ring-annelated) systems. Recently, there has been increasing activity in the latter direction. For example,

there is growing interest in the synthesis and use of ligands where one of the cyclopentadienyl groups of *ansa*-metallocene has been replaced with groups such as amido or alkoxy donors [7,21–40]. The Group 3 and 4 metal complexes of these monocyclopentadienyl-amido or -alkoxy ligands have also been found to act as catalyst precursors for olefin polymerization reactions [21,24,28,37,38,41–43]. Furthermore, metal complexes of these bifunctional amido-cyclopentadienyl ligands show higher Lewis acidity compared to the corresponding bis(cyclopentadienyl)metal complexes [23]. 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 [23,44]. 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 [24,26,28,36].

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In certain instances, this increased reactivity even leads to the formation of bis-ligand complexes [31].



We have focused our attention on the study of sterically demanding *ansa*-ligand systems containing fluorene. Recently, we have reported the synthesis of an amido-fluorenyl ligand  $[(NBu^t)SiMe_2CH_2(C_{13}H_8)]^{2-}$  which contains a  $-SiMe_2CH_2-$  backbone and its use in the synthesis of titanium, zirconium and hafnium complexes [27]. Unlike the corresponding  $-SiMe_2-$  bridged analog, this  $-SiMe_2CH_2-$  bridged ligand easily allows the isolation of Group 4 metal adducts in monomeric form, free of any coordinated solvents [26,27]. Furthermore,  $[(\eta^1-NBu^t)SiMe_2CH_2(\eta^5-C_{13}H_8)]MCl_2$  (where  $M = Ti, Zr$  or  $Hf$ ) shows good solubility in hydrocarbon solvents. The X-ray data indicate the presence of a relatively unstrained ligand backbone in these metal complexes. In order to further evaluate the steric effect of ligands on the properties of metal adducts, we have decided to explore the chemistry of sterically less demanding *N*-isopropyl analog. In this paper, we report the synthesis of  $[(NPr^i)SiMe_2CH_2(C_{13}H_8)]^{2-}$  ligand, and its use in the zirconium and hafnium chemistry. The synthesis and X-ray structural characterization of the solvent-free dialkyl derivative  $[(\eta^1-NBu^t)SiMe_2CH_2(\eta^5-C_{13}H_8)]Zr(CH_2SiMe_3)_2$  is also described.

## 2. Experimental details

All manipulations 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  $-25^\circ C$  refrigerator. Solvents were distilled from conventional drying agents and degassed twice prior to use [45]. Glassware was oven-dried at  $150^\circ C$  overnight. The  $^1H$  and  $^{13}C$  NMR spectra were recorded in  $C_6D_6$  at room temperature on a Bruker MSL-300 spectrometer ( $^1H$ , 300.13 MHz;  $^{13}C$ , 75.47 MHz) or Nicolet NT-200 spectrometer ( $^1H$ , 200.07 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 parts per million 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 ( $C_{13}H_{10}$ ), *n*-BuLi (1.6 M solution in hexanes),  $ClCH_2SiMe_2Cl$ ,  $Me_3SiCH_2MgCl$ ,  $ZrCl_4$  and  $HfCl_4$  were obtained from Aldrich and used as received.  $[(\eta^1-NBu^t)SiMe_2CH_2(\eta^5-C_{13}H_8)]ZrCl_2$  was prepared according to the literature method [27].

### 2.1. $ClCH_2SiMe_2N(H)Pr^i$

A mixture of  $Pr^iNH_2$  (3.0 g, 50.8 mmol) and triethylamine (5.14 g, 50.8 mmol) in hexane (150 ml) was added dropwise to a hexane solution of  $ClCH_2SiMe_2Cl$  (7.27 g, 50.8 mmol) at room temperature. The temperature was maintained using a water bath. A white precipitate was formed immediately. The mixture was stirred overnight, and filtered to remove the white  $Et_3NHCl$  precipitate. The product was isolated from the filtrate by vacuum distillation at  $89^\circ C$  (50% yield), and used immediately in the preparation of **1**.  $^1H$   $\delta = 0.06$  (s, 6H, SiMe), 0.91 (d,  $J = 6.9$  Hz, 6H, *i*-Pr), 2.51 (s, 2H,  $CH_2$ ), 2.86 (m, 1H, *i*-Pr);  $^{13}C\{^1H\}$   $\delta = -3.2$  (SiMe), 28.0 ( $SiCH_2$ ), 31.4 (*i*-Pr), 43.4 (*i*-Pr).

### 2.2. $[Pr^iN(H)SiMe_2CH_2(C_{13}H_8)]Li(THF)$ (**1**)

Fluorene (6.10 g, 36.2 mmol) in tetrahydrofuran (80 ml) was cooled to  $0^\circ C$  and treated with *n*-BuLi in hexane (22.6 ml of 1.6 M solution, 36.2 mmol) over a period of 30 min. The color of the solution became red immediately. The solution was then allowed to warm to room temperature and stirred for an additional 30 min. This mixture was added dropwise into  $ClCH_2SiMe_2N(H)Pr^i$  (3.00 g, 18.1 mmol) in tetrahydrofuran (50 ml) at  $0^\circ C$ , and stirred overnight at room temperature. All 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 78% yield. The product was recrystallized from toluene-hexane-tetrahydrofuran at  $-25^\circ C$ . M.p.  $85-89^\circ C$ .  $^1H$   $\delta = 0.11$  (s, 6H, SiMe), 0.34 (d,  $J = 4.2$  Hz, 6H, *i*-Pr), 1.00 (m, 4H, THF), 2.45 (m, 4H, THF), 2.50 (m, 1H, *i*-Pr), 2.59 (s, 2H,  $CH_2$ ), 7.04 (t,  $J = 7.3$  Hz, 2H), 7.42 (t,  $J = 7.3$  Hz, 2H), 7.57 (d,  $J = 8.2$  Hz, 2H), 8.33 (d,  $J = 8.2$  Hz, 2H);  $^{13}C\{^1H\}$   $\delta = 0.3$  (SiMe), 13.5 ( $SiCH_2$ ), 25.0 (THF), 26.5 (*i*-Pr), 43.8 (*i*-Pr), 67.4 (THF), 84.6, 111.7, 115.6, 119.6, 120.7, 121.6, 130.5 ( $C_{13}H_8$ ). Anal. Calcd for

$C_{19}H_{24}LiNSi \cdot 1.5(C_4H_8O)$ : C, 73.31; H, 8.86; N, 3.42. Found: C, 73.35; H, 9.36; N, 3.61.

### 2.3. $[(\eta^1-NPr^i)SiMe_2CH_2(\eta^5-C_{13}H_8)]ZrCl_2$ (2)

A solution of **1** (1.00 g, 2.68 mmol) in diethyl ether (60 ml) was treated with *n*-BuLi in hexane (1.68 ml of 1.6 M solution, 2.68 mmol) at  $-78^\circ\text{C}$ . After 10 min, the solution was allowed to warm to  $0^\circ\text{C}$  and stirred for an additional 30 min. The reaction mixture was then added dropwise to  $ZrCl_4$  (0.62 g, 2.68 mmol) in diethyl ether (20 ml) over a period of 15 min at  $-78^\circ\text{C}$ . This temperature was maintained for a further 2 h. Then the reaction mixture was brought to room temperature and stirred overnight. The color of the solution changed from red to brown. The solution was filtered to remove the precipitate and the filtrate was concentrated. Addition of hexane followed by cooling to  $-25^\circ\text{C}$  afforded brown microcrystalline **2** in 65% yield. Carefully dried samples show only a trace amount of  $\text{Et}_2\text{O}$ . M.p.  $202\text{--}206^\circ\text{C}$ .  $^1\text{H}$   $\delta = 0.34$  (s, 6H, SiMe), 0.98 (d,  $J = 6.0$  Hz, 6H, *i*-Pr), 2.42 (s, 2H,  $\text{CH}_2$ ), 4.02 (hepta, 1H, *i*-Pr), 7.13 (m, 4H,  $\text{C}_{13}\text{H}_8$ ), 7.39 (m, 4H,  $\text{C}_{13}\text{H}_8$ );  $^{13}\text{C}\{^1\text{H}\}$   $\delta = 5.8$  (SiMe), 14.2 (Si $\text{CH}_2$ ), 24.5 (*i*-Pr), 44.8 (*i*-Pr), 104.0, 117.0, 120.8, 124.2, 125.2, 129.0, 129.3 ( $\text{C}_{13}\text{H}_8$ ). Anal. Calcd for  $C_{19}H_{23}Cl_2NSiZr$ : C, 50.09; H, 5.09; N, 3.07. Found: C, 49.90; H, 5.14; N, 3.12.

### 2.4. $[(\eta^1-NPr^i)SiMe_2CH_2(\eta^5-C_{13}H_8)]HfCl_2$ (3)

A solution of **1** (1.00 g, 2.68 mmol) in diethyl ether (60 ml) was treated with *n*-BuLi in hexane (1.68 ml of 1.6 M solution, 2.68 mmol) at  $-78^\circ\text{C}$ . After 10 min, the

solution was allowed to warm to  $0^\circ\text{C}$  and stirred for an additional 30 min. The reaction mixture was then added dropwise to  $\text{HfCl}_4$  (0.86 g, 2.68 mmol) in diethyl ether (20 ml) over a period of 15 min at  $-78^\circ\text{C}$ . This low temperature was maintained for a further 2 h. Then the mixture was brought to room temperature and stirred overnight. The color of the solution changed from red to bright yellow. The solution was filtered to remove the precipitate and the filtrate was concentrated. Addition of hexane followed by cooling to  $-25^\circ\text{C}$  afforded light brown crystals of **3** in 75% yield. M.p.  $185\text{--}188^\circ\text{C}$ .  $^1\text{H}$   $\delta = 0.31$  (s, 6H, SiMe), 0.99 (d,  $J = 6.0$  Hz, 6H, *i*-Pr), 2.44 (s, 2H,  $\text{CH}_2$ ), 3.93 (m, 1H, *i*-Pr), 7.08 (m, 4H,  $\text{C}_{13}\text{H}_8$ ), 7.40 (m, 4H,  $\text{C}_{13}\text{H}_8$ );  $^{13}\text{C}\{^1\text{H}\}$   $\delta = 6.3$  (SiMe), 14.0 (Si $\text{CH}_2$ ), 24.6 (*i*-Pr), 44.2 (*i*-Pr), 99.9, 115.6, 120.7, 123.7, 125.3, 128.9, 129.0 ( $\text{C}_{13}\text{H}_8$ ). Anal. Calcd for  $C_{19}H_{23}Cl_2HfNSi$ : C, 42.04; H, 4.27; N, 2.58. Found: C, 42.21; H, 4.46; N, 2.24.

### 2.5. $[(\eta^1-NBu^t)SiMe_2CH_2(\eta^5-C_{13}H_8)]Zr(CH_2SiMe_3)_2$ (4)

A solution of  $[(\eta^1-NBu^t)SiMe_2CH_2(\eta^5-C_{13}H_8)]ZrCl_2$  (0.50 g, 1.06 mmol) in diethyl ether (30 ml) was treated with two equivalents of  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  in diethyl ether (2.13 ml of 1.0 M solution, 2.13 mmol) at  $-78^\circ\text{C}$  over a 10 min period. After 30 min stirring, the reaction mixture was slowly brought to room temperature and stirred for a further 4 h. Volatile materials were then removed by reduced pressure, leaving a brown solid. This solid was taken up in hexane-toluene, filtered and the filtrate was concentrated. Cooling to  $-25^\circ\text{C}$  afforded yellow crystals of **4** in 68%

Table 1  
Crystal data and summary of data collection and refinement

	1	3	4
Formula	$C_{23}H_{32}LiNOSi$	$C_{19}H_{23}Cl_2HfNSi$	$C_{28}H_{47}NSi_3Zr$
Fw	373.53	542.86	573.16
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>Cc</i>
<i>a</i> (Å)	8.538(2)	8.417(1)	11.413(1)
<i>b</i> (Å)	15.665(3)	9.708(1)	16.410(1)
<i>c</i> (Å)	32.392(4)	14.304(1)	16.762(1)
$\alpha$ (deg)	90	84.81(1)	90
$\beta$ (deg)	90	73.52(1)	101.301(6)
$\gamma$ (deg)	90	65.86(1)	90
Vol. (Å <sup>3</sup> )	4332.4(13)	1022.3(2)	3076.8(4)
<i>Z</i>	8	2	4
<i>T</i> (K)	183(2)	188(2)	188(2)
$\lambda(\text{Mo K}\alpha)$ (Å)	0.71073	0.71073	0.71073
Density (calc) (g cm <sup>-3</sup> )	1.145	1.763	1.237
Absorption coefficient (mm <sup>-1</sup> )	0.120	5.423	0.490
<i>R</i> 1, <i>wR</i> 2 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup> (%)	5.06, 10.57	3.75, 10.07	2.62, 6.52
<i>R</i> 1, <i>wR</i> 2 [all data] <sup>a</sup> (%)	10.02, 12.75	4.20, 12.26	2.88, 6.79

<sup>a</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]\}^{1/2}$ .

Table 2  
Selected bond distances (Å) and bond angles (deg) for  
[Pr<sup>i</sup>N(H)SiMe<sub>2</sub>CH<sub>2</sub>(C<sub>13</sub>H<sub>8</sub>)]Li(THF)

Si–N	1.757(3)	Si–C(14)	1.878(3)
Si–C(15)	1.856(4)	Si–C(16)	1.854(3)
O–Li	1.889(7)	N–C(17)	1.496(5)
N–Li	2.147(7)	C(1)–C(14)	1.505(5)
C(1)–Li	2.279(7)	C(13)–Li	2.325(7)
C(2)–Li	2.513(8)	C(8)–Li	2.562(7)
C(7)–Li	2.677(7)	C(14)–C(15)	2.325(7)
N–Si–C(14)	106.3(2)	N–Si–C(15)	104.2(2)
N–Si–C(16)	114.9(2)	C(14)–Si–C(15)	112.4(2)
C(14)–Si–C(16)	109.0(2)	C(15)–Si–C(16)	110.1(2)
Si–N–C(17)	119.3(2)	Si–N–Li	102.4(2)
C(17)–N–Li	108.1(3)	C(1)–C(14)–Si	113.1(2)

yield. M.p.: dec. around 100°C. <sup>1</sup>H δ = –1.18 (d, J = 11.7 Hz, 2H, ZrCH<sub>2</sub>), –0.40 (d, J = 11.7 Hz, 2H, ZrCH<sub>2</sub>), 0.12 (s, 18H, SiMe), 0.47 (s, 6H, SiMe), 1.38 (s, 9H, t-Bu), 2.37 (s, 2H, CH<sub>2</sub>), 7.11 (m, 4H, C<sub>13</sub>H<sub>8</sub>), 7.47 (d, J = 7 Hz, 2H, C<sub>13</sub>H<sub>8</sub>), 7.82 (d, J = 7 Hz, 2H, C<sub>13</sub>H<sub>8</sub>); <sup>13</sup>C{<sup>1</sup>H} δ = 3.7 (ZrCH<sub>2</sub>SiMe), 7.9 (SiMe), 14.6 (CH<sub>2</sub>), 33.1 (t-Bu), 55.0 (t-Bu), 57.8 (ZrCH<sub>2</sub>), 97.6, 119.9, 121.9, 122.4, 124.8, 127.2, 129.1 (C<sub>13</sub>H<sub>8</sub>). Anal. Calcd for C<sub>28</sub>H<sub>47</sub>NSi<sub>3</sub>Zr: C, 58.68; H, 8.27; N, 2.44. Found: C, 58.31; H, 8.33; N, 2.40.

### 3. X-ray structure determination

#### 3.1. General procedure

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 [46]. Data were col-

lected using a Siemens P4 diffractometer equipped with an LT-2A device for low temperature work and graphite monochromated Mo Kα radiation (λ = 0.71073). Three standard reflections were measured at every 97 data points to check for crystal deterioration and/or misalignment. All the software programs and the sources of scattering factors are contained in the SHELXTL (PC Version 5 based on SHELXL-93) software package [47] provided by Siemens Analytical X-ray Instruments, Inc. A summary of crystal data, data collection and refinement parameters are given in Table 1. Selected bond distances and angles are provided in Tables 2–4. Further details of the crystal structure are available in the supporting material.

#### 3.2. [Pr<sup>i</sup>N(H)SiMe<sub>2</sub>CH<sub>2</sub>(C<sub>13</sub>H<sub>8</sub>)]Li(THF)

The unit cell parameters were determined by least squares refinement of 39 reflections. Data were corrected for Lorentz and polarization effects. Structures were solved by direct methods followed by successive cycles of full-matrix least squares refinement on F<sup>2</sup> and difference Fourier analysis. All the non-hydrogen atoms were refined anisotropically. The hydrogen on the nitrogen atom was located from the difference map, and refined freely. The remaining hydrogen atoms were included at calculated positions. They were treated as riding atoms with isotropic displacement parameters fixed 1.2 or 1.5 times the value refined for the respective host atom.

#### 3.3. [(η<sup>1</sup>-NPr<sup>i</sup>)SiMe<sub>2</sub>CH<sub>2</sub>(η<sup>5</sup>-C<sub>13</sub>H<sub>8</sub>)]HfCl<sub>2</sub>

The unit cell parameters were determined by least squares refinement of 25 reflections. Data were corrected for Lorentz, polarization, and absorption (using ψ

Table 3  
A comparison of structural parameters of dichloro hafnium adducts

	[(η <sup>1</sup> -NPr <sup>i</sup> )SiMe <sub>2</sub> CH <sub>2</sub> (η <sup>5</sup> -C <sub>13</sub> H <sub>8</sub> )]HfCl <sub>2</sub>	[(η <sup>1</sup> -NBu <sup>t</sup> )SiMe <sub>2</sub> CH <sub>2</sub> (η <sup>5</sup> -C <sub>13</sub> H <sub>8</sub> )]HfCl <sub>2</sub>
Hf–N	2.013(9)	2.065(3)
Hf–C1	2.423(11)	2.430(5)
Hf–C2	2.495(11)	2.507(5)
Hf–C13	2.472(10)	2.521(5)
Hf–C7	2.558(11)	2.607(5)
Hf–C8	2.536(10)	2.602(4)
Hf–Cl1	2.376(3)	2.396(1)
Hf–Cl2	2.386(3)	2.399(1)
Si–N	1.740(10)	1.778(4)
N–C17	1.49(2)	1.534(7)
Hf–N–Si	129.3(5)	121.7(2)
Hf–N–C17	104.8(8)	120.2(3)
Si–N–C17	125.8(8)	118.2(2)
Cl1–Hf–Cl2	103.1(1)	102.7(1)
F(c)–Hf–N	108.4	112.4

Table 4  
A comparison of structural parameters of dialkyl zirconium adducts ( $R = CH_2SiMe_3$ )

	$[(\eta^1-NBu^i)SiMe_2(\eta^5-C_{13}H_8)]ZrR_2$	$[(\eta^1-NBu^i)SiMe_2CH_2(\eta^5-C_{13}H_8)]ZrR_2$
Zr–N	2.061(2)	2.075(3)
Zr–C1	2.400(3)	2.474(4)
Zr–C2	2.538(2)	2.588(4)
Zr–C13	2.548(2)	2.558(3)
Zr–C7	2.695(3)	2.683(4)
Zr–C8	2.708(3)	2.669(4)
Zr–CSiMe <sub>3</sub>	2.232(3)	2.251(3)
	2.248(3)	2.259(4)
Si–N	1.738(2)	1.747(3)
Zr–N–Si	103.4(1)	122.8(2)
Zr–N–C	130.1(2)	117.4(2)
Si–N–C	126.3(2)	119.8(2)
Zr–C–SiMe <sub>3</sub>	136.1(2)	133.4(2)
	123.8(2)	126.4(2)
C–Zr–C	103.8(1)	107.5(1)

scans) effects. Structures were solved by the Patterson method followed by successive cycles of full-matrix least squares refinement on  $F^2$  and difference Fourier analysis. The hydrogen atom on C17 was located on the difference map but could not be refined isotropically. Therefore, it was included with fixed  $U(H)$ . The remaining hydrogen atoms were included at calculated positions. They were treated as riding atoms with isotropic displacement parameters fixed 1.2 or 1.5 times the value refined for the respective host atom. All the non-hydrogen atoms were refined anisotropically.

### 3.4. $[(\eta^1-NBu^i)SiMe_2CH_2(\eta^5-C_{13}H_8)]Zr(CH_2SiMe_3)_2$

The unit cell parameters were determined by least squares refinement of 43 reflections. Data were corrected for Lorentz, polarization, and absorption (using  $\psi$  scans) effects. Structures were solved by direct methods followed by successive cycles of full-matrix least squares refinement on  $F^2$  and difference Fourier analysis. The hydrogen atoms were included at calculated positions. They were treated as riding atoms with isotropic displacement parameters fixed 1.2 or 1.5 times the value refined for the respective host atom. All the non-hydrogen atoms were refined anisotropically.

## 4. Results and discussion

The  $Pr^iN(H)SiMe_2CH_2Cl$  was prepared from isopropylamine and  $ClSiMe_2CH_2Cl$  following a procedure described previously for a related species [48]. This compound is very sensitive to air, and used immediately in the next step. The reaction of  $Pr^iN(H)SiMe_2CH_2Cl$  with two equivalents of fluorenyllithium in THF led to  $[Pr^iN(H)SiMe_2CH_2(C_{13}H_8)]Li$  which can be isolated as its THF adduct in 78% yield.  $[Pr^iN(H)SiMe_2CH_2(C_{13}H_8)]Li(THF)$  (**1**) is an air-sensi-

tive, red crystalline solid. Compound **1** was characterized by  $^1H$ ,  $^{13}C$  NMR spectroscopy, and X-ray crystallography. The  $^1H$  NMR signals due to the THF appear as two multiplets at 1.00 and 2.45 ppm. This somewhat upfield shift may be due to the shielding effects of fluorenyl ring current [26,27]. Fluorenyl ring hydrogens appear as two sets of doublets and two sets of triplets in the range spanning 7.02–8.34 ppm. This pattern is very similar to that seen for the related  $[Bu^iN(H)SiMe_2CH_2(C_{13}H_8)]Li(THF)$  [27]. Compound **1** is less stable compared to the corresponding *N*-*t*-butyl analog. However, this lithium adduct can be stored at low temperature without any significant decomposition.

The X-ray crystal study revealed a monomeric structure for **1** (Fig. 1). The lithium atom is coordinated to the THF oxygen (Li–O = 1.889(7) Å), nitrogen (Li–N = 2.147(7) Å, and to the fluorenyl group in an  $\eta^2$ -fashion (Li–C distances of 2.279(7) and 2.325(7) Å). The remaining Li–C(fluorenyl) distances are relatively long (2.51, 2.56, 2.68 Å), and are not indicative of any significant interaction. The four-coordinate amino nitrogen center adopts a pyramidal geometry. Overall structural features of **1** are similar (consistent with the solution data) to those of the *t*-butyl analog [27].

The dilithium salt  $[Pr^iNSiMe_2CH_2(C_{13}H_8)]Li_2$  was prepared by the addition of one equivalent of *n*-BuLi to **1** in diethyl ether and used directly in the preparation of Group 4 metal complexes (Scheme 1). The treatment of this deep red compound  $[Pr^iNSiMe_2CH_2(C_{13}H_8)]Li_2$  with an equivalent of  $ZrCl_4$  or  $HfCl_4$  in diethyl ether gave  $[(\eta^1-NPr^i)SiMe_2CH_2(\eta^5-C_{13}H_8)]ZrCl_2$  (**2**) and  $[(\eta^1-NPr^i)SiMe_2CH_2(\eta^5-C_{13}H_8)]HfCl_2$  (**3**) in 65% and 75% yields respectively. In contrast to the *N*-*t*-butyl analog, compounds **2** and **3** show some tendency to retain solvent molecules such as  $Et_2O$  in the solid materials. However, drying under vacuum at room temperature leads to solvent free metal complexes. These solvent free adducts show good solubility in aromatic

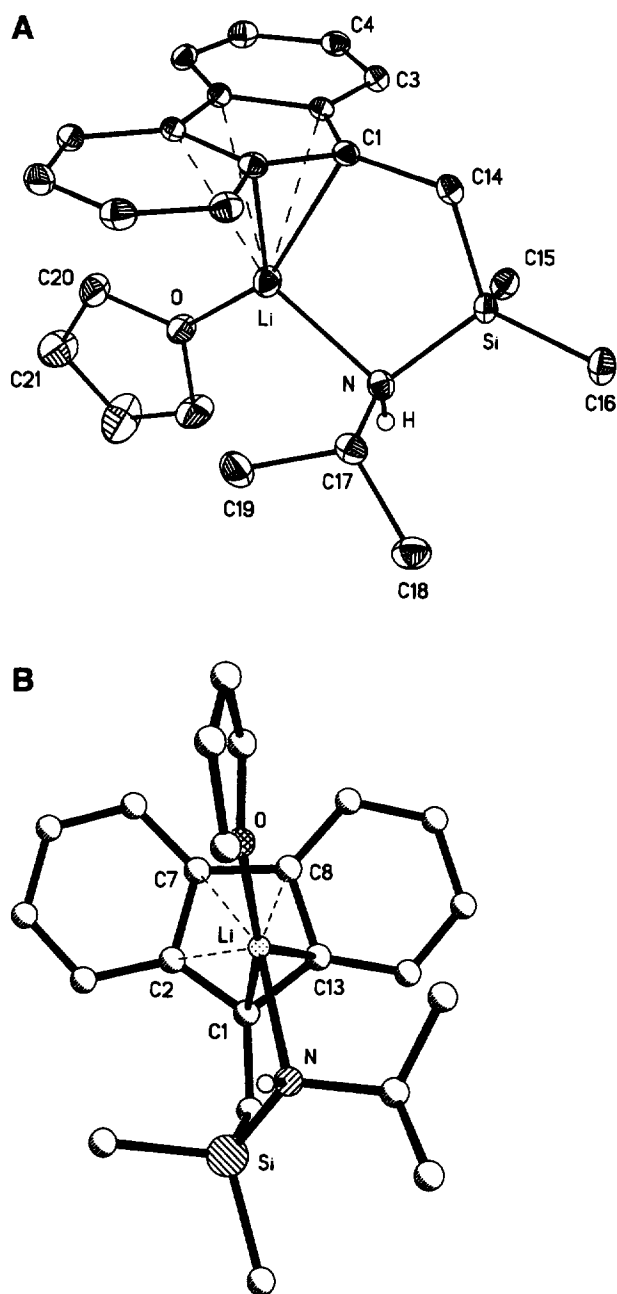


Fig. 1. Structure and atom numbering scheme for **1**. Hydrogen atoms (except the one on N) have been omitted for clarity: (A) ORTEP diagram; (B) a view perpendicular to the fluorene ring plane.

hydrocarbons or ether solvents. Interestingly, the  $-\text{SiMe}_2-$  bridged analog  $[(\eta^1\text{-NBu}^i)\text{SiMe}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{ZrCl}_2$  shows strong affinity towards ethers, and the removal of ethers leads to a solid material with poor solubility even in hot THF (presumably due formation of chloride-bridged aggregates) [26].

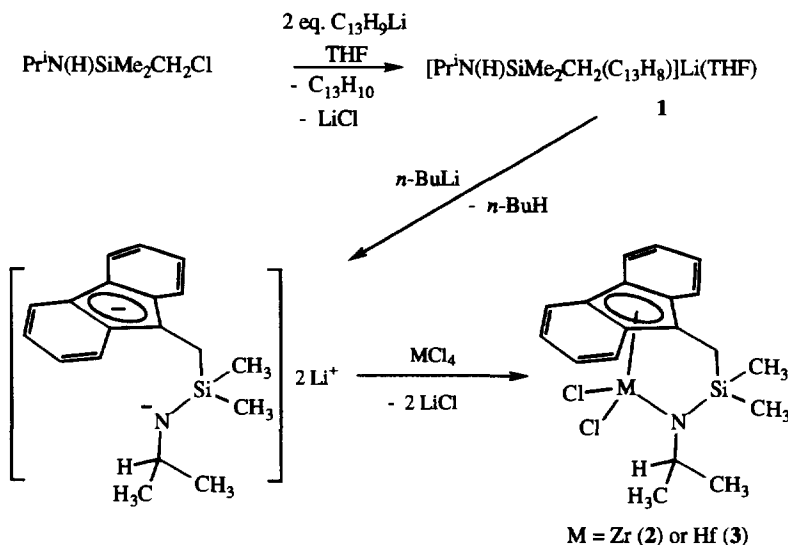
Compounds **2** and **3** were characterized by elemental analyses,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectroscopy. The two complexes show similar spectra with only minor

differences in the chemical shift values, suggesting closely related structures in solution. The  $^1\text{H}$  NMR signals due to the fluorenyl hydrogens of **2** and **3** are spread over a relatively narrow region of about 0.6 ppm, whereas in **1** the spread is much wider (1.3 ppm). The resonances due to the isopropyl group in the Zr and Hf adducts appear at about 1.0 and 4.0 ppm. The corresponding signals in the lithium salt **1** were observed at 0.3 and 2.5 ppm. The NMR chemical shift data of **2** and **3** are not affected by the presence or absence of  $\text{Et}_2\text{O}$  in the sample. This suggests a very weak interaction between the metal ion and the donor solvent.

We have obtained pale yellow crystals of **3** and characterized using X-ray crystallography. The ORTEP diagram [49] of  $[(\eta^1\text{-NPr}^i)\text{SiMe}_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{HfCl}_2$  is illustrated in Fig. 2. Compound **3** adopts a monomeric structure in which the hafnium atom is coordinated to the fluorenyl group in an  $\eta^5$ -fashion (Hf–C distances range from 2.423(11) to 2.557(11) Å) [50,51], the nitrogen and two chlorine atoms. The relatively large variation in the metal to ring carbon distances is believed to be the result of molecular orbital structure of the fluorenyl anion [52]. The  $\text{Fl(c)}\text{-Hf-N}$  (where  $\text{Fl(c)}$  is the centroid of the  $\eta^5\text{-C}_{13}\text{H}_8$  group) angle is  $108.4^\circ$ . This is slightly smaller than the corresponding angle in the *N*-*t*-butyl analog ( $112.4^\circ$ ).

The most notable feature in **3** is the weak interaction between Hf and the carbon ( $\text{C(H)Me}_2$ :  $\text{Hf}\cdots\text{C}$  2.797(12) Å) and hydrogen atom ( $\text{C(H)Me}_2$ :  $\text{Hf}\cdots\text{H}$  2.35 Å) of the isopropyl group. The hydrogen atom on this carbon was located from the difference map during the data refinement. The  $\text{Hf}\cdots\text{C(17)}$  distance is longer than the normal Hf–C single bond distance of 2.275 Å [53]. Nevertheless, this  $\text{Hf}\cdots\text{C}$  contact significantly distorts the angles around the amido nitrogen center. As evident from the data in Table 3, the Hf–N–C angle of the  $[(\eta^1\text{-NPr}^i)\text{SiMe}_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{HfCl}_2$  is  $104.8(8)^\circ$  whereas the corresponding parameter in  $[(\eta^1\text{-NBu}^i)\text{SiMe}_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{HfCl}_2$  is  $120.2(3)^\circ$ . The Si–N–C angles in the two systems are  $125.8(8)^\circ$  and  $118.2(2)^\circ$  respectively. Interestingly, this Si–N–C angle in **3** is closer to that observed for the  $-\text{SiMe}_2-$  bridged complexes  $[(\eta^1\text{-NBu}^i)\text{SiMe}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{Zr}(\text{CH}_2\text{SiMe}_3)_2$  ( $126.3(2)^\circ$ ) [26] or  $[(\eta^1\text{-NBu}^i)\text{SiMe}_2(\eta^5\text{-C}_5\text{Me}_4)]\text{Zr}(\text{NMe}_2)_2$  ( $126.1(3)^\circ$ ) [36]. Although, the metal/H–C separation is relatively small in the solid state, the NMR data provide no indication for a significant agostic interaction in solution [54]. The  $^1J_{\text{C-H}}$  coupling constant value of 126 Hz for the corresponding carbon in the  $^{13}\text{C}$  NMR spectrum is in the normal region [54–56].

The nitrogen atom in **3** adopts a planar geometry. The Hf–N bond distance is 2.013(9) Å. This separation can be compared to the corresponding distances found in  $[(\eta^1\text{-NBu}^i)\text{SiMe}_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{HfCl}_2$  (2.065(3) Å) [27],  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Hf(H)NHMe}]$  (2.027(8) Å) [57],



Scheme 1.

$[(\eta^5\text{-C}_5\text{Me}_5)\text{Hf}\{\text{NH}(2,6\text{-i-Pr}_2\text{C}_6\text{H}_3)\}_3]$  (2.041(4), 3.048(4), and 2.065(3) Å) [58] or  $[\text{HfCl}\{\text{N}(\text{SiMe}_3)_2\}_3]$  (2.040(10) Å) [59]. The decrease in the Hf–N distance from 2.065(3) Å to 2.013(9) Å upon replacement of *t*-Bu with *i*-Pr may be a direct result of steric effects. The Hf–Cl distances (2.376(3), 2.386(3) Å) are very similar to those of the related *N*-*t*-butyl analog. However, they are much shorter than those of 2.510(1) Å in  $[\text{Me}_2\text{C}(\eta^5\text{-C}_5\text{H}_4)_2\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$  [60], 2.42 Å in  $[(\text{CH}_2)_3(\eta^5\text{-C}_5\text{H}_4)_2\text{HfCl}_2]$  [61] and 2.436(5) Å in  $[\text{HfCl}\{\text{N}(\text{SiMe}_3)_2\}_3]$  [59].

In order to evaluate the steric crowding endowed by the  $[(\text{NBu}^t)\text{SiMe}_2\text{CH}_2(\text{C}_{13}\text{H}_8)]^{2-}$  ligand on a zirconium (or hafnium) center, we investigated the reaction

between  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  and  $[(\eta^1\text{-NBu}^t)\text{SiMe}_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{ZrCl}_2$ . This reaction proceeds smoothly to give  $[(\eta^1\text{-NBu}^t)\text{SiMe}_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{Zr}(\text{CH}_2\text{SiMe}_3)_2$  (**4**) in 68% yield. In the  $^1\text{H}$  NMR spectrum, the Zr–CH<sub>2</sub> resonances appear as two sets of doublets at a fairly upfield region (–1.18 and –0.40 ppm). The high-field shift may be due to the shielding effects of the fluorenyl ligand [26]. The geminal coupling constant of the diastereotopic CH<sub>2</sub> group is 11.7 Hz. Similar values for geminal coupling have been observed in various Zr, Mo and W complexes containing –CH<sub>2</sub>SiMe<sub>3</sub> groups [26,62–64]. This  $^2J_{\text{HH}}$  value is not indicative of any strong agostic interaction [29].

The crystal structure of **4** is illustrated in Fig. 3. The zirconium to fluorenyl ring carbon distances range from 2.474(4) to 2.669(4) Å. These values are slightly longer than the distances in the corresponding dichloro analog  $[(\eta^1\text{-NBu}^t)\text{SiMe}_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{ZrCl}_2$  (2.430(5)–2.587(4) Å) [27]. This may be due to the increased steric crowding around the zirconium center in **4**. The Zr–N distance of 2.075(3) Å is normal for this type of Zr(IV) complex. The F1(c)–Zr–N angle is 110.9°. This is several degrees larger than the Cp(c)–Zr–N angle of  $[(\eta^1\text{-NBu}^t)\text{SiMe}_2(\eta^5\text{-C}_5\text{Me}_4)]\text{ZrCl}_2$  (102.0°).

The orientation of the two –CH<sub>2</sub>SiMe<sub>3</sub> groups, and the angles at the methylene carbons (Zr–C–Si: 126.4(2)° and 133.4(2)°) of  $[(\eta^1\text{-NBu}^t)\text{SiMe}_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{Zr}(\text{CH}_2\text{SiMe}_3)_2$  are remarkably similar to those of the –SiMe<sub>2</sub>– bridged zirconium complex  $[(\eta^1\text{-NBu}^t)\text{SiMe}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{Zr}(\text{CH}_2\text{SiMe}_3)_2$  (see Table 3) [26]. However, in contrast to the –SiMe<sub>2</sub>– bridged analog, the bond angles of **4** at the nitrogen are much closer to the ideal trigonal planar values. This suggests

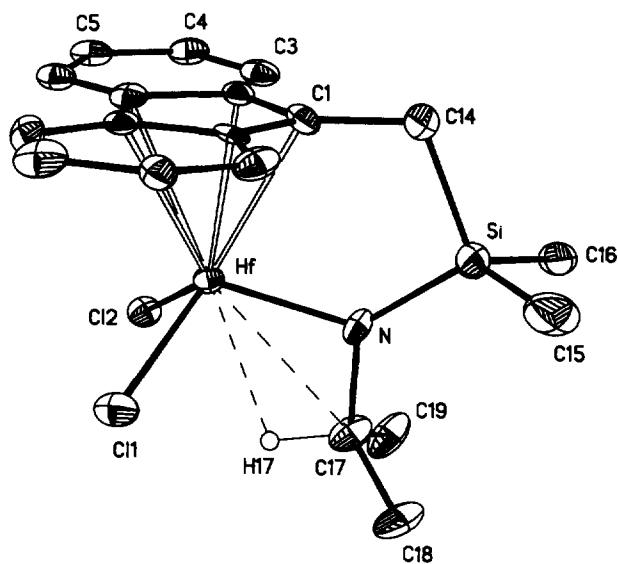


Fig. 2. Structure and atom numbering scheme for **3**. Hydrogen atoms (except H17) have been omitted for clarity.

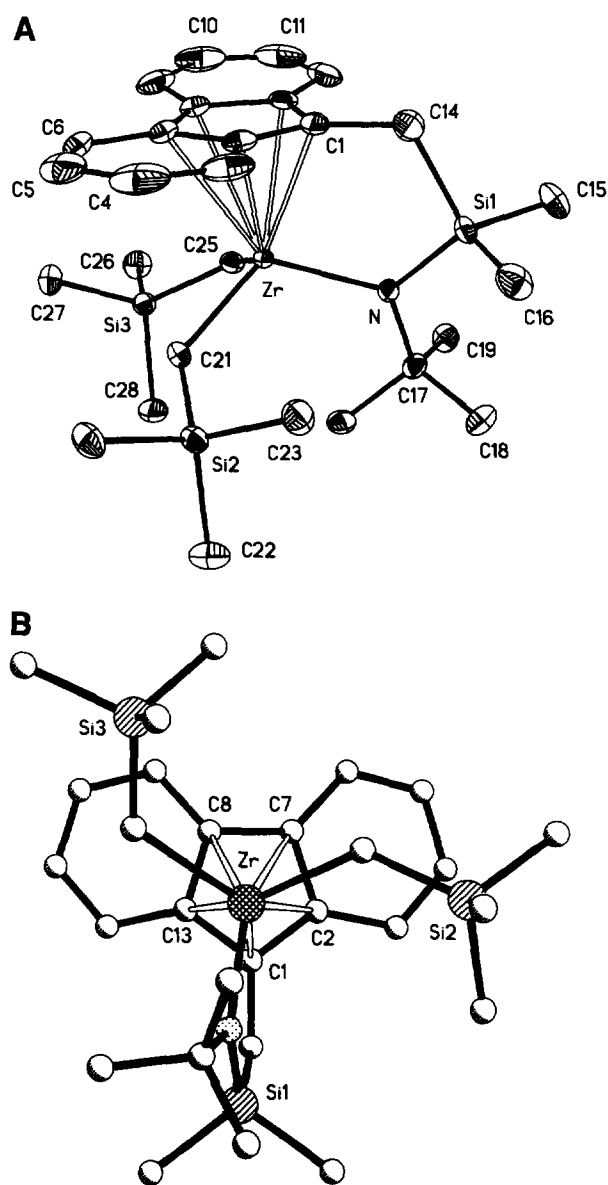


Fig. 3. Structure and atom numbering scheme for 4. Hydrogen atoms have been omitted for clarity: (A) ORTEP diagram; (B) a view perpendicular to the fluorene ring plane.

the presence of a fairly relaxed ligand backbone in 4. The corresponding Zr and Hf dichloro analogs also exhibit very similar angles at the nitrogen center [27].

## 5. Summary and conclusion

We have reported the synthesis of an amido-fluorenyl ligand system and its utility in the preparation of Group 4 metal complexes. The mono lithium salt  $[\text{Pr}^i\text{N}(\text{H})\text{SiMe}_2\text{CH}_2(\text{C}_{13}\text{H}_8)]\text{Li}(\text{THF})$  (1) is monomeric in the solid state. The fluorenyl group coordinates to Li in an  $\eta^2$ -fashion. Lithiated derivative of 1 was used in the preparation of solvent-free, monomeric, Zr and Hf adducts, 2 and 3 in good yield. The hafnium adduct

$[(\eta^1\text{-NPr}^i)\text{SiMe}_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{HfCl}_2$  (3) which has a hydrogen atom in  $\beta$  position to the metal center shows close  $\text{Hf} \cdots \text{H}-\text{C}$  interaction in the solid state, whereas the *N*-*t*-butyl analog  $[(\eta^1\text{-NBu}^t)\text{SiMe}_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{HfCl}_2$  shows no unusual contacts. The angles around the nitrogen of 3 show large distortions from the ideal trigonal planar values, but the stability resulting from the interaction between the formally 14 electron Hf center and the H-C moiety seems to outweigh the unfavorable strain energy (at least in the solid state).

Despite the presence of the sterically demanding  $[(\text{NBu}^t)\text{SiMe}_2\text{CH}_2(\text{C}_{13}\text{H}_8)]^{2-}$  ligand on the metal ion, chlorides of the  $[(\eta^1\text{-NBu}^t)\text{SiMe}_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{ZrCl}_2$  can be substituted easily with alkyl groups such as  $\text{CH}_2\text{SiMe}_3$ . Compounds 3 and 4 represent rare examples of structurally authenticated mono(fluorenyl) complexes of Group 4 metal ions [26,27]. The Group 4 metal complexes based on this amido-fluorenyl ligand could be useful as catalyst precursors in the olefin polymerization reactions [21,37,38,41–43]. We are currently studying the chemistry of 2 and 3, and the reactions of 1 with various other metal ions.

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