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Zirconium and hafnium mono(alkyl) complexes containing a tridentate linked amido-tetramethylcyclopentadienyl ligand. Molecular structure of $Hf(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OCH_3)Cl_2$

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Abstract

Zirconium and hafnium complexes $M(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Cl_2$ (M = Zr, Hf) containing the tridentate 2-methoxyethylamido-functionalized tetramethylcyclopentadienyl ligand $C_5Me_4SiMe_2NCH_2CH_2OMe$ have been synthesized by the reaction of the dilithium derivative $Li_2[C_5Me_4SiMe_2NCH_2CH_2OMe]$ with $MCl_4(THF)_2$. Selective monoalkylation of the dichloro complexes gave complexes of the type $M(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)(R)Cl$ ($R = CH_2Ph$, $o\text{-}C_6H_4CH_2NMe_2$). The crystal structure of the hafnium dichloro complex $Hf(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Cl_2$ has been determined by X-ray crystal diffraction and shows a trigonal bipyramidal structure in which the five-membered ring and the methoxy function adopt the apical positions. Crystal data: monoclininc $P2_1/c$, $a = 12.069(2)$ Å, $b = 15.362(3)$ Å, $c = 9.949(2)$ Å, $\beta = 92.04(1)°$, $V = 1843.4(6)$ Å^3, $Z = 4$, $R = 0.0471$, $R_w = 0.0952$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Zirconium; Hafnium; Linked amido-cyclopentadienyl ligand; Alkyl complex

1. Introduction

Since Bercaw et al. utilized the linked amido-cyclopentadienyl ligand $C_5Me_4SiMe_2NtBu$ in scandium chemistry to successfully develop the first single-component α-olefin polymerization catalysts with living characteristics [1], extensive efforts have recently been devoted to the synthesis and study of group 4 metal complexes of general formula $M(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NR')X_2$ (M = Ti, Zr, Hf; X = halide, amido, alkyl) [2,3]. A major technological breakthrough was the commercial introduction of ethylene polymerization catalysts on the basis of such complexes resulting in novel types of polyethylene materials [4]. In contrast to the conventional 14-electron metallocene catalysts $[M(\eta^5\text{-}C_5R_5)_2R']^+$ [5], the surmised active species $[M(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NR')R'']^+$ with 12 valence electrons are expected to be even more electrophilic and their generation by the alkyl abstraction from dialkyls $M(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NR')R''_2$ are currently under intense scrutiny [6]. One possible route would be the halide abstraction from mono(alkyl) complexes of the type $M(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NR')(R)X$. Here we describe the preparation and characterization of zirconium and hafnium complexes containing the 2-methoxyethylamido-functionalized tetramethylcyclopentadienyl ligand $C_5Me_4SiMe_2NCH_2CH_2OMe$. This tridentate ligand was developed to attenuate the strong electrophilic metal centers through the presence of an additional 2-electron donor function attached to the amido-nitrogen atom [2]c, [7].

2. Results and discussion

When (chlorodimethylsilyl)tetramethylcyclopenta-diene is treated with lithium 2-methoxyethylamide in

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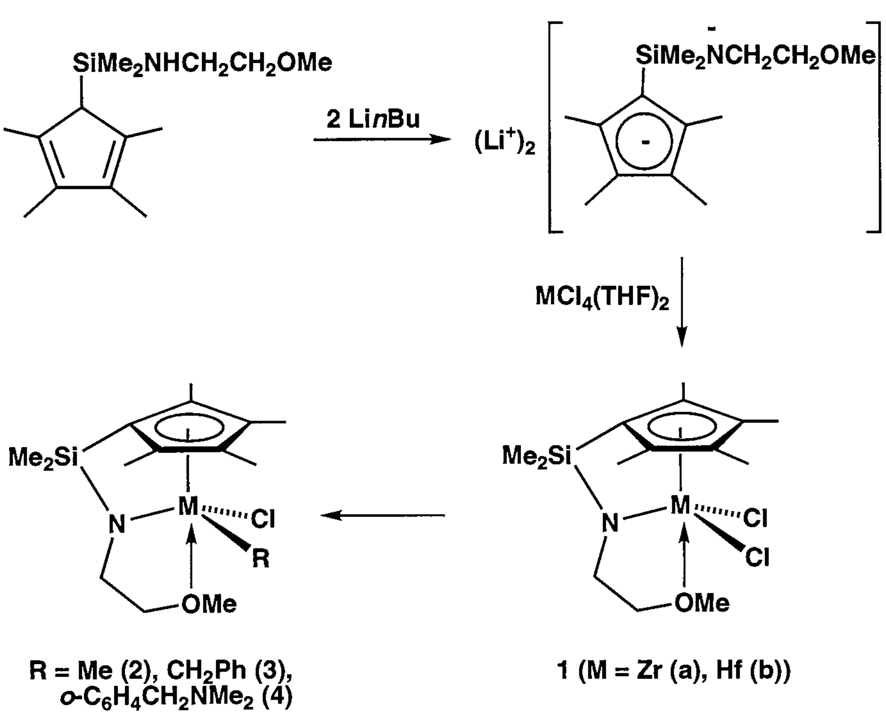


Scheme 1.

hexane, $(C_5Me_4H)SiMe_2NHCH_2CH_2OMe$ is obtained as a yellow, distillable oil in good yield (Scheme 1). The ^1H NMR spectrum of $(C_5Me_4H)SiMe_2NHCH_2CH_2OMe$ shows a singlet for the methyl groups of the silicon bridge at -0.01 ppm and the methyl groups of the cyclopentadienyl ring appear as two singlets at 1.84 and 1.99 ppm. The CH_2 protons of the side chain are recorded as two AA′XX′ multiplets centered at 2.91 and 3.34 ppm and the methoxy group as a singlet at 3.37 ppm. Thus, the molecule appears to contain a mirror plane at room temperature.

Double deprotonation of $(C_5Me_4H)SiMe_2NHCH_2CH_2OMe$ with two equivalents of *n*-butyl lithium in hexane gives crystalline $Li_2(C_5Me_4SiMe_2NCH_2CH_2OMe)$, which reacts with $MCl_4(THF)_2$ (M = Zr, Hf) in toluene at low temperatures to afford colorless, crystalline $Zr(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Cl_2$ (**1a**) and $Hf(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Cl_2$ (**1b**) in 78% and 58% yield, respectively (Scheme 1).

The ^1H NMR spectra of the complexes **1a** and **b** show a pattern similar to that described for the ^1H NMR spectrum of the ligand precursor $(C_5Me_4H)SiMe_2NHCH_2CH_2OMe$. For **1a** the methyl groups of the silicon bridge appear as a singlet at 0.35 ppm and the methyl groups of the cyclopentadienyl ring appear as singlets at 2.12 and 2.13 ppm. The protons of the lateral chain are recorded as two pseudotriplets of a typical AA′XX′ system at 2.88 and 3.36 ppm. The signal of the methoxy group is recorded at 3.60 ppm as a singlet. The resonances of the hafnium complex **1b** are located at lower field, the difference to the corresponding groups in the zirconium homologue **1a** being between 0.01 and 0.09 ppm. These data are in agreement with a trigonal bipyramidal molecular structure possessing a mirror plane or with a three-legged piano-stool structure in which the ether donor is bonded in a flexible manner on the NMR time scale [2]c,d. From the crystallographic study of the hafnium complex **1b** (vide infra) and of the related $Zr(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2NMe_2)Cl_2$ [2]c, we believe that the latter scenario is less likely for the more Lewis-acidic zirconium and hafnium centers.

Attempts to prepare mono(alkyl) complexes starting from the dichloro complexes **1a** and **b** using a variety of alkylating reagents such as the THF adduct of dibenzylmagnesium or phenyl lithium in the appropriate stoichiometry has failed so far, leading to mixtures consisting of di- and mono(alkyl) complexes besides the starting material. The reaction of **1a** with MeMgCl resulted in an inseparable 4:1 mixture consisting of the mono(methyl) zirconium derivative **2a** and the unreacted starting dichloro complex. **2a** can be easily recognized by the lack of a mirror plane in the NMR spectra. Thus, in the ^1H NMR spectrum the methyl group at Zr gives rise to a signal at -0.06 ppm, by 0.3 ppm lower field than that in the dimethyl complex $Zr(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Me_2$ [2]c. The ^{13}C NMR resonance is recorded at 31.5 ppm which is in the expected range for related chloro(methyl)zirconocenes $Zr(\eta^5\text{-}C_5R_5)_2(Me)Cl$ [8]. Similar to the zirconocene analogs, no fast scrambling between the dichloro **1a**, mono(methyl) **2a**, and di(methyl) [2]h seems to occur both on the NMR and laboratory time scale.

The reaction of $PhCH_2MgCl$ with the dichlorides **1a** and **1b** at 0°C gave the mono(benzyl) complexes **3a** and **3b** as pentane-soluble, colorless crystals in 80 and 66% yield, respectively. In agreement with the presence of a configurationally stable chiral metal center, two singlets for the methyl groups at the silicon atom, and four singlets for the five-membered ring methyl groups are detected in the ^1H NMR spectrum of **3**. Each proton of the lateral chain appears as a well separated six-line multiplet of an ABCD spin system. The diastereotopic methylene protons of the benzyl ligand in **3a** appear in the ^1H NMR spectrum as an AB spin system at 1.81 and 2.04 ppm with $^2J_{HH} = 12$ Hz. In the ^{13}C NMR spectrum, the resonance at 58.5 ppm can be assigned to the methylene carbon of the benzyl group. None of these data support any agostic bonding of the benzylic group, as was suggested in the similar mono(benzyl) complex $M\{\eta^5{:}\eta^1{:}\eta^1\text{-}C_5H_4(CH_2)_3NMe\}(CH_2Ph)Cl$ [9].

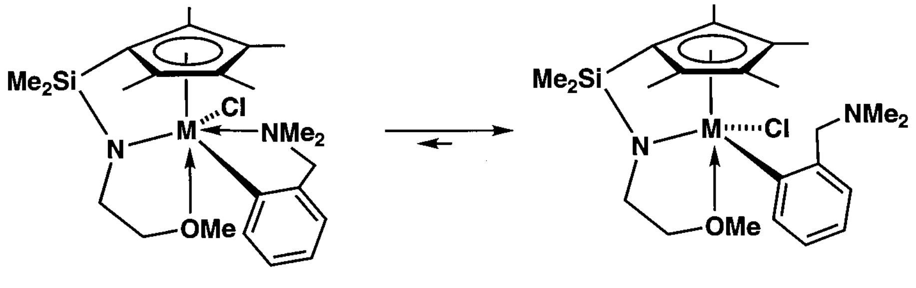
Reaction of **1a** and **1b** with $Li(o\text{-}C_6H_4CH_2NMe_2)$ [10] at −78°C gave the mono(aryl) complexes $M(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)(o\text{-}C_6H_4CH_2NMe_2)Cl$ (M = Zr (**4a**), M = Hf (**4b**)) as colorless crystals in good yields. As was observed for **3a** and **3b**, the ^1H and ^{13}C NMR spectra of the complexes **4a** and **4b** suggest a molecular structure devoid of a mirror plane. Complete assignment was achieved using 1D and 2D NMR spectroscopy. At room temperature, the resonance of the NMe_2 group of the *N*,*N′*-dimethylamino function to the metal center appears as a singlet at 2.27 ppm, suggesting a rapid inversion at the amino nitrogen atom on the NMR time scale. Likewise, the ^{13}C NMR spectrum shows a singlet at 49.6 ppm for the two methyl carbon atoms. The signal of the methylene protons of the $o\text{-}C_6H_4CH_2NMe_2$ ligand are observed as two AB doublets with $^3J_{HH} = 14$ Hz at 2.73 and 3.83 ppm for **4a** and the ^{13}C NMR signal is observed at 70.7 ppm. For **4b** the corresponding resonances are found in a similar region.

As an indication for the tridentate bonding mode of the $C_5Me_4SiMe_2NCH_2CH_2OMe$ ligand in **4a**, the methoxy signal is shifted to higher field to 2.85 as compared to the dichloro complex **1a** with 3.54 ppm. Similar high field shift for this signal is observed in the diphenyl or dibenzyl complexes $M(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)X_2$ (M = Zr, Hf; X = Ph, CH_2Ph) [2]h, indicating the close proximity of the methoxy group to the anisotropy region of the $o\text{-}C_6H_4CH_2NMe_2$ group. Thus the linked amido-cyclopentadienyl ligand $C_5Me_4SiMe_2NCH_2CH_2OMe$ preferably acts as a tridentate ligand and appears to exhibit a stronger chelate effect than the $o\text{-}C_6H_4CH_2NMe_2$ ligand.

3. X-ray crystal structure determination for 1b

An X-ray crystal structure determination of the hafnium dichloro complex **1b** was carried out. Crystallographic details are summarized in Table 1. Fractional coordinates and equivalent isotropic temperature factors are listed in Table 2, selected bond distances and angles in Table 3.

The molecular structure is depicted in Fig. 1. The compound adopts a distorted trigonal bipyramidal configuration with the tetramethylcyclopentadienyl ligand and the methoxy groups occupying the apical positions, as is now established for a series of zirconium and hafnium complexes with the $C_5Me_4SiMe_2NCH_2CH_2X$ ligand [2]c,d,h. The tetramethylcyclopentadienyl ligand is bonded in a slightly distorted pentahapto fashion as judged by the sum of the angles at the ring (540°) and the metal ring-carbon distances ranging from 2.428(7) to 2.585(8) Å. The hafnium-nitrogen bond length of 2.038(6) Å is in the range for an amido ligand bonded to a d^0-hafnium center such as $Hf\{N(SiMe_3)_2\}_3Cl$ (2.04(1) Å) [11]a, $Hf(\eta^5\text{-}C_5Me_5)_2(H)NHMe_2$ (2.027(8) Å) [11]b, $Hf(\eta^5\text{-}C_5Me_5)(N\textit{i}Pr)_3$ (2.041(4), 2.065(3) Å) [11]c or that observed in related hafnium complexes containing a linked amido-cyclopentadienyl ligand [2]h, [3]g. The nitrogen atom is trigonal planar implying a three-electron ligand, the



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sum of the angles at the nitrogen atom amounting to 360°. The hafnium–oxygen bond length of 2.324(5) Å is slightly larger than those found in hafnium complexes with a donor ligand such as THF ([Hf(η^5-C_5Me_5)$_2$$CH_2CHMe_2$(THF)][B($C_6H_5$)$_4$] [12], 2.221(6) Å; Hf($\eta^5$-$C_8H_8$)$Cl_2$(THF) [13], 2.233(9) Å). The averaged Hf–Cl distance in **1b** of 2.4 Å is within the range expected for (dichloro)hafnocene derivatives [14], suggesting an electronically relatively saturated metal center due to the presence of the strongly π-donating amido ligand. However, the angle between the chlorine atoms is 109.2(1)° and is significantly larger than in hafnocene complexes with about 97° [14].

4. Experimental section

All experiments were performed under argon using standard schlenk or glove box techniques. Pentane and hexane were purified by distillation from sodium/triglyme/benzophenone ketyl. Toluene was distilled over sodium sand. $C_5Me_4HSiMe_2Cl$ [1], $MCl_4(THF)_2$ (M = Zr, Hf) [15] Li(*o*-$C_6H_4CH_2NMe_2$) were synthesized according to published procedures [16]. MgMeCl, $MgPhCH_2Cl$, and Li*n*Bu (Aldrich) were titrated prior to use [17]. $H_2NCH_2CH_2OMe$ (Aldrich) was distilled from CaH_2 and stored over molecular sieves. NMR spectra were recorded on a Bruker DRX 400 spectrometer (δ in ppm with respect to $SiMe_4$ as internal reference), mass spectra on a Finigan 8230 spectrometer. Elemental analyses were performed in Analytische Laboratorien, Lindlar (Germany).

Table 1
Crystallographic data for Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OCH_3$)$Cl_2$ (**1b**)

Crystal data	
Empirical formula	$C_{14}H_{25}Cl_2HfNOSi$
Formula weight	500.83
Crystal color	Colorless
Crystal size, mm	0.40 × 0.30 × 0.30
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a, Å	12.069(2)
b, Å	15.362(3)
c, Å	9.949(2)
β (°)	92.04(1)
Volume, Å^3	1843.4(6)
Z	4
D_{calc}, Mg m^{-3}	1.805
Abs. coeff., mm^{-1}	6.009
F(000)	976
Data collection	
Temperature, K	296(2)
Radiation	MoK_α ($\lambda = 0.71070$ Å)
2θ range	3.01–29.96°
Reflns. measd.	$-16 \le h \le 16$; $-21 \le k \le 0$; $0 \le l \le 13$
Refinement	
No. reflns. measd.	5675
No. indep. reflns.	5346 [$R_{int} = 0.0242$]
No. obsd. reflns.	3813 ($I > 2\sigma(I)$)
Goodness-of-fit	1.143
R	0.0471
wR_2	0.0952
Extinction coefficient	0.0005(2)
Largest e-max, e-min, e Å^{-3}	+1.671, −1.943

Table 2
Fractional coordinates (× 10^4) and equivalent isotopic temperature factors [Å^2 × 10^3] for Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OCH_3$)$Cl_2$ (**1b**)

Atom	*x*	*y*	*z*	*U*(eq)
Hf	1948.5(2)	223.4(2)	7856.8(1)	36(1)
Cl(1)	447(2)	−818(2)	7860(3)	73(1)
Cl(2)	2291(2)	632(2)	5580(2)	70(1)
Si	3120(2)	1185(2)	10 217(2)	47(1)
O	387(4)	1073(3)	7398(5)	48(1)
N	1987(5)	1272(4)	9113(6)	42(1)
C(1)	3526(6)	128(4)	9434(7)	38(1)
C(2)	2906(7)	−660(5)	9611(9)	53(2)
C(3)	3026(8)	−1176(6)	8457(11)	66(3)
C(4)	3679(7)	−740(6)	7565(10)	62(2)
C(5)	3999(7)	70(5)	8160(8)	48(2)
C(6)	2245(9)	−903(8)	10 804(11)	90(4)
C(7)	2610(11)	−2103(6)	8278(16)	121(6)
C(8)	4037(11)	−1084(9)	6244(13)	115(5)
C(9)	4756(7)	727(7)	7532(10)	70(3)
C(10)	2776(10)	1147(10)	12027(9)	91(4)
C(11)	4131(9)	2089(7)	10 057(13)	88(4)
C(12)	1144(7)	1952(5)	9122(8)	49(2)
C(13)	551(8)	1960(5)	7783(9)	58(2)
C(14)	−348(8)	993(6)	6239(9)	61(2)

Table 3
Selected bond lengths [Å] and angles [°] for Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OCH_3$)$Cl_2$ (**1b**)

Bond lengths		Angles	
Hf–N	2.038(6)	N–Hf–Cl(1)	121.5(2)
Hf–Cl(1)	2.417(2)	N–Hf–Cl(2)	111.8(2)
Hf–Cl(2)	2.401(2)	Cl(2)–Hf–Cl(1)	109.2(1)
Hf–O	2.324(5)	N–Hf–O	71.2(2)
Hf–C(1)	2.428(7)	O–Hf–Cl(1)	76.7(2)
Hf–C(2)	2.466(8)	O–Hf–Cl(2)	80.4(2)
Hf–C(5)	2.494(8)	N–Si–C(10)	114.7(4)
Hf–C(3)	2.572(9)	N–Si–C(11)	113.2(4)
Hf–C(4)	2.585(8)	N–Si–C(1)	90.8(3)
Si–N	1.728(6)	C(11)–Si–C(10)	106.0(6)
Si–C(1)	1.874(7)	C(13)–O–C(14)	112.0(6)
O–C(13)	1.426(9)	C(13)–O–Hf	112.3(4)
O–C(14)	1.435(9)	C(14)–O–Hf	125.7(5)
N–C(12)	1.459(9)	C(12)–N–Si	126.0(5)
C(12)–C(13)	1.49(1)	C(12)–N–Hf	124.7(5)
		Si–N–Hf	109.2(3)
		O–C(13)–C(12)	106.9(6)
		N–C(12)–C(13)	108.3(6)

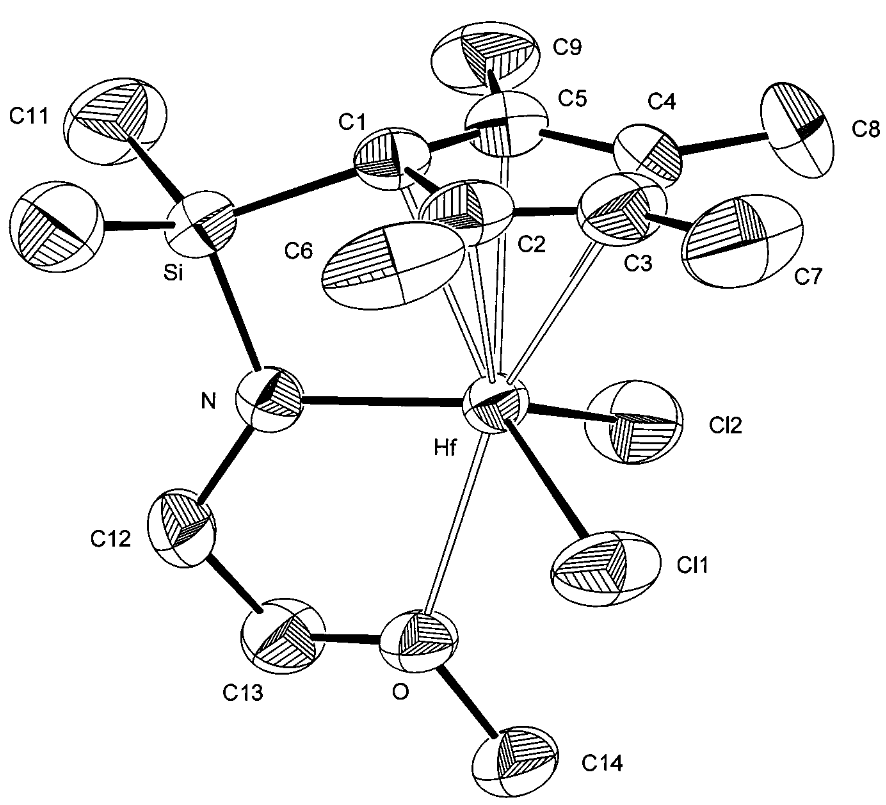

Fig. 1. ORTEP diagram of the molecular structure of Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OCH_3$)$Cl_2$ (**1b**). Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for the sake of clarity.

4.1. $C_5Me_4HSiMe_2NHCH_2CH_2OMe$

A hexane solution of (C_5Me_4H)$SiMe_2Cl$ (17.5 g, 81.9 mmol) was added to a suspension of Li($NHCH_2CH_2OMe$) (8.1 g, 100 mmol) in hexane (100 ml) at −78°C. The reaction mixture was allowed to warm to room temperature and stirred for 14 h. Filtration of the resulting solution and removal of the solvent in vacuo gave crude (C_5Me_4H)$SiMe_2NHCH_2CH_2OMe$ as a yellow oil which was distilled at 75°C and 10^{-2} mbar; yield: 11.4 g (55%). ^1H NMR ($CDCl_3$): δ −0.01 (s, 6 H, $SiCH_3$), 1.84, 1.99 (s, 6 H, CCH_3), 2.91 (m, 2 H, NCH_2), 3.34 (m, 2 H, CH_2O), 3.37 (m, 3 H, OCH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −2.8 ($SiCH_3$), 11.1, 14.2 (C_5CH_3), 41.4 (NCH_2), 56.6 (ring-C at Si), 58.5 (OCH_3), 75.5 (CH_2O), 132.5, 135.4 (CCH_3). EI MS: *m*/*z* (%) 253 (20) [M^+], 194 (15) [$M^+ - CH_2CH_2OMe$]. Anal. Calcd. for $C_{14}H_{27}NOSi$: C, 66.34; H, 10.74; N, 5.53. Found: C, 65.74; H, 10.78; N, 5.64.

4.2. Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)$Cl_2$ (**1a**)

To a cooled at 0°C solution of (C_5Me_4H)$SiMe_2NHCH_2CH_2OMe$ (3.14 g, 12.44 mmol) in hexane (20 ml) was added Li*n*Bu (10.8 ml of a 2.3 M solution in hexane) using a syringe to form $Li_2(C_5Me_4SiMe_2NCH_2CH_2OMe)$ (3.00 g, 91%) as a white precipitate which was filtered. Toluene (40 ml) was added at −78°C to a solid mixture of the dilithium salt (1.00 g, 3.7 mmol) and the THF adduct of zirconium tetrachloride (1.42 g, 3.7 mmol). The mixture was stirred at room temperature and the yellow solution was filtered and concentrated. Cooling the filtrate to −30°C overnight gave **1a** (1.19 g, 78%) as colorless crystals in two crops. ^1H NMR (C_6D_6): δ 0.35 (s, 6 H, $SiCH_3$), 2.12, 2.13 (s, 6 H, CCH_3), 2.88 (t, 2 H, NCH_2), 3.36 (t, 2 H, CH_2O), 3.54 (s, 3 H, OCH_3); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 2.4 ($SiCH_3$), 12.2, 14.7 (CCH_3), 46.9 (NCH_2), 62.5 (OCH_3), 77.1 (CH_2O), 101.1 (ring-C at Si), 130.3, 130.9 (CCH_3). EI MS: *m*/*z* (%) 413 (46) [M^+], 366 (100) [$M^+ - C_2H_5O$], 339 (38) [$M^+ - C_3H_6NO$]. Anal. Calcd. for $C_{14}H_{25}Cl_2NOSiZr$: C, 40.60; H, 6.09; N, 3.38. Found: C, 40.37; H, 6.13; N, 3.29.

4.3. Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)MeCl (**2a**)

MeMgCl (0.62 ml of a 1.6 M solution in THF) were added to a cooled at −78°C suspension of **1a** (0.41 g, 0.99 mmol) and the mixture was stirred to room temperature for 3 h. All solvents were removed and a pale yellow solution was extracted in pentane (15 ml). This solution was concentrated and cooled overnight to −30°C to precipitate white crystals identified as a 4:1

mixture consisting of $Zr(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)MeCl$ and **1a**. ^1H NMR (C_6D_6): δ −0.06 (s, 3 H, $ZrCH_3$), 0.35, 0.37 (s, 3 H, $SiCH_3$), 2.00, 2.08, 2.11, 2.17 (s, 3 H, CCH_3), 2.88, 3.0, 3.3, 3.4 (m, 1 H, NCH_2 and CH_2O), 3.54 (s, 3 H, OCH_3); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 2.5, 2.9 ($SiCH_3$), 11.5, 12.4, 13.8, 14.8 (CCH_3), 31.5 ($ZrCH_3$), 46.2 (NCH_2), 62.1 (OCH_3), 78.1 (CH_2O), 98.76 (ring-C at Si), 126.6, 126.9, 127.7, 127.9 (CCH_3). EI MS: *m/z* (%) 393 (5) [M^+], 377 (100) [$M^+ - CH_3$], 357 (25) [$M^+ - Cl$], 342 (46) [$M^+ - CH_3{-}Cl$].

4.4. $Zr(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)(CH_2Ph)Cl$ (*3a*)

A suspension of **1a** (0.27 g, 0.65 mmol) in hexane (30 ml) was cooled at 0°C and then benzylmagnesium chloride (0.45 ml of a 1.6 M solution in THF) was added via syringe. The mixture was stirred and allowed to warm to room temperature. After removing all volatiles, pentane (15 ml) was added, the solution filtered, and the filtrate concentrated to give **3a** (0.24 g, 80%) as, colorless crystals upon cooling to −30°C. ^1H NMR (C_6D_6): δ 0.36, 0.43 (s, 3 H, $SiCH_3$), 1.81 (d, 1 H, $^2J_{HH} = 12$ Hz, $ZrCH_2C_6H_5$), 1.96 (s, 3 H, CCH_3), 2.04 (d, $^2J_{HH} = 12$ Hz, 1 H, $ZrCH_2C_6H_5$), 2.04, 2.16, 2.23 (s, 3 H, CCH_3), 2.91, 2.99, 3.12 (m, 1 H, NCH_2, CH_2O), 3.17 (s, 3 H, OCH_3), 3.24 (m, 1 H, NCH_2 or CH_2O), 6.87–7.19 (m, 5 H, $CH_2C_6H_5$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 2.2, 2.9 ($SiCH_3$), 11.2, 12.8, 13.6, 14.8 (CCH_3), 46.5 (NCH_2), 58.5 ($ZrCH_2C_6H_5$), 63.5 (OCH_3), 78.3 (CH_2O), 100.2 (ring-C at Si), 121.4 (*para*-C_6H_5), 125.6, 126.9 (CCH_3), 127.3 (*meta*-C_6H_5), 127.6 (*ortho*-C_6H_5), 129.0, 129.3 (CCH_3), 150.1 (*ipso*-C_6H_5). EI MS: *m/z* (%) 377 (24) [$M^+ - CH_2Ph$], 342 (41) [$M^+ - CH_2Ph{-}Cl$]. Anal. Calcd. for $C_{21}H_{32}ClNOSiZr$: C, 53.76; H, 6.82; N, 2.96. Found: C, 46.30; H, 7.26; N, 2.57.

4.5. $Zr(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)(o\text{-}C_6H_4CH_2NMe_2)Cl$ (*4a*)

Hexane (40 ml) was added at −78°C to a mixture of **1a** (0.26 g, 0.62 mmol) and $Li(o\text{-}C_6H_4CH_2NMe_2)$ (0.1 g, 0.70 mmol). The mixture was stirred at room temperature overnight and then all volatiles were removed in vacuo. The residue was extracted with pentane (3 × 15 ml), the yellow extracts were filtered and concentrated. Cooling to −30°C overnight afforded **4a** (0.20 g, 63%) as colorless crystals. ^1H NMR (C_6D_6): δ 0.54, 0.63 (s, 3 H, $SiCH_3$), 1.61, 1.82, 2.03 (s, 3 H, CCH_3), 2.27 (s, 6 H, $N(CH_3)_2$), 2.53 (s, 3 H, CCH_3), 2.73 (d, 1 H, $C_6H_4CH_2NMe$, $^2J_{HH} = 14$ Hz), 2.85 (s, 3 H, OCH_3), 3.21 (m, 2 H, NCH_2 and CH_2O), 3.67 (m, 1 H, NCH_2 or CH_2O), 3.83 (d, 1 H, $C_6H_4CH_2N(CH_3)_2$, $^2J_{HH} = 14$ Hz), 3.88 (m, 1 H, NCH_2 or CH_2O), 6.87 (d, 1 H, H-2 or H-5 in C_6H_4, $^3J_{HH} = 7$ Hz), 7.08 (dt, 1 H, H-3 or H-4 in C_6H_4, $^2J_{HH} = 1.5$ Hz, $^3J_{HH} = 7$ Hz), 7.12 (d, 1 H, H-5 or H-2 in C_6H_4, $^3J_{HH} = 7$ Hz), 7.67 (dd, 1 H, H-4 or H-3 in C_6H_4, $^2J_{HH} = 1.5$ Hz, $^3J_{HH} = 7$ Hz); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 2.4, 3.0 ($SiCH_3$), 12.6, 12.7, 16.2, 16.6 (CCH_3), 46.7 (NCH_2), 49.6 (NCH_3), 61.1 (OCH_3), 70.9 ($C_6H_4CH_2NMe_2$) 76.2 (CH_2O), 102.9 (ring-C at Si), 123.1, 125.5, 125.7 (C-2–C-4 $C_6H_4CH_2NMe_2$), 125.9, 126.9, 128.0, 130.6 (CCH_3), 142.6 (C-5 $C_6H_4CH_2NMe_2$), 145.9 (C-6 $C_6H_4CH_2NMe_2$), 189.3 (C-1 $C_6H_4CH_2NMe_2$). EI MS: *m/z* (%) 513 (84) [M^+], 469 (25) [$M^+ - NMe_2$], 455 (22) [$M^+ - CH_2NMe_2$], 379 (23) [$M^+ - C_6H_4CH_2NMe_2$]. Anal. Calcd. for $C_{23}H_{37}ClN_2OSiZr$: C, 53.94; H, 7.23; N, 5.47. Found: C, 48.52; H, 7.51; N, 4.69.

4.6. $Hf(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Cl_2$ (*1b*)

Following a procedure analogous to that described for **1a**, $Li_2[C_5Me_4SiMe_2NCH_2CH_2OMe]$ (1.20 g, 4.52 mmol) was reacted with the THF adduct of hafnium tetrachloride (2.10 g, 4.52 mmol) to give **1b** as colorless crystals in two crops; yield 1.31 g (58%). ^1H NMR (C_6D_6): δ 0.35 (s, 6 H, $SiCH_3$), 2.19, 2.2 (s, 6 H, CCH_3), 2.97 (t, 2 H, NCH_2), 3.28 (t, 2 H, CH_2O), 3.54 (s, 3 H, OCH_3); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 2.4 ($SiCH_3$), 11.9, 14.3 (CCH_3), 45.7 (NCH_2), 62.3 (OCH_3), 77.5 (CH_2O), 92.9 (ring-C at Si), 128.3, 129.3 (CCH_3). EI MS: *m/z* (%) 501 (1) [M^+], 429 (1) [$M^+ - 2Cl$]. Anal. Calcd. for $C_{14}H_{25}Cl_2HfNOSi$: C, 33.57; H, 4.99; N, 2.79. Found: C, 33.82; H, 4.91; N, 2.71.

4.7. $Hf(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)(CH_2Ph)Cl$ (*3b*)

Following a procedure analogous to that described for the preparation of **3a**, **1b** (0.35 g, 0.69 mmol) was reacted with benzylmagnesium chloride(0.42 ml of a 1.6 M solution in THF) to give **3b** (0.25 g, 66%) as colorless crystals. ^1H NMR (C_6D_6): δ 0.35, 0.42 (s, 3 H, $SiCH_3$), 1.50, 1.87 (d, 1 H, $HfCH_2C_6H_5$, $^2J_{HH} = 13$ Hz), 1.96, 2.09, 2.19, 2.24 (s, 3 H, CCH_3), 2.87–3.10 (m, 4 H, NCH_2 and CH_2O), 3.08 (s, 3 H, OCH_3), 6.8–7.2 (m, 5 H, $CH_2C_6H_5$); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 2.2, 2.9 ($SiCH_3$), 11.1, 12.5, 13.5, 14.7 (CCH_3), 45.6 (NCH_2), 62.7 ($HfCH_2C_6H_5$), 63.4 (OCH_3), 78.6 (CH_2O), 99.8 (ring-C at Si), 121.7 (*para*-C_6H_5), 124.8, 125.5, 126.0, 128.5 (CCH_3), 128.8 (*meta*-C_6H_5), 129.0 (*ortho*-C_6H_5), 150.5 (*ipso*-C_6H_5). EI MS: *m/z* (%) 557 (19) [M^+], 467 (50) [$M^+ - C_7H_7$], 431 (56) [$M^+ - C_7H_7{-}Cl$]. Anal. Calcd. for $C_{21}H_{32}ClHfNOSi$: C, 45.32; H, 5.75; N, 2.52. Found: C, 42.32; H, 6.09; N, 2.39.

4.8. $Hf(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)(\eta^1\text{-}C_6H_4CH_2NMe_2)Cl$ (*4b*)

Following a procedure analogous to that described for the preparation of **4a**, **1b** (0.30 g, 0.59 mmol) was reacted with Li(o-$C_6H_4CH_2NMe_2$) (0.1 g, 0.70 mmol) to give **4b** (0.24 g, 69%) as colorless crystals from pentane solution. ^{1}H NMR (C_6D_6): δ 0.57, 0.65 (s, 3 H, SiCH_3), 1.63, 1.85, 2.01 (s, 3 H, CCH_3), 2.27 (s, 6 H, NCH_3), 2.58 (s, 3 H, CCH_3), 2.79 (s, 3 H, OCH_3), 2.81 (d, 1 H, $C_6H_4CH_2N$, $^2J_{HH} = 14$ Hz), 3.33–3.53 (m, 3 H, NCH_2 and CH_2O), 3.83 (d, 1 H, $C_6H_4CH_2N$, $^2J_{HH} = 14$ Hz), 3.87–3.93 (m, 1 H, NCH_2 or CH_2O), 6.93 (d, 1 H, H-2 or H-5 in C_6H_4, $^3J_{HH} = 7$ Hz), 7.11 (td, 1 H, H-3 or H-4 in C_6H_4, $^2J_{HH} = 1.6$ Hz, $^3J_{HH} = 7$ Hz), 7.19 (t, 1 H, H-4 or H-3 in C_6H_4, $^3J_{HH} = 7$ Hz), 7.79 (d, 1H, H-5 or H-2 in C_6H_4, $^3J_{HH} = 7$ Hz); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 2.5, 3.1 (SiCH_3), 12.4, 12.5, 15.8, 16.5 (CCH_3), 46.6 (NCH_2), 49.6 (N$(CH_3)_2$), 59.9 (OCH_3), 70.7 ($C_6H_4CH_2N$), 75.9 (CH_2O), 102.5 (ring-C at Si), 123.4 (C-2 or C-5 $C_6H_4CH_2N$), 124.7, 125.7 (CCH$_3$), 125.8, 126.0 (C-3, C-4 $C_6H_4CH_2N$), 127.1 (CCH$_3$), 127.8 (C-5 or C-2 $C_6H_4CH_2N$), 129.1 (CCH$_3$, 143.7 (C-6 $C_6H_4CH_2N$), 146.7 (C-1 $C_6H_4CH_2$). EI MS: m/z (%) 600 (66) [M^+], 565 (35) [$M^+ - Cl$], 468 (74) [$M^+ - C_6H_4CH_2NMe_2$], 435 (7) [$M^+ - Cl$, $-C_6H_4CH_2NMe_2$]. Anal. Calcd. for $C_{23}H_{37}ClHfN_2OSi$: C, 46.00; H, 6.17; N, 4.67. Found: C, 45.93; H, 6.30; N, 4.52.

*4.9. X-ray crystal structure analysis of **1b***

Crystal data for **1b** are summarized in Table 1. The compound, obtained as colorless crystals by cooling a concentrated toluene solution, crystallizes in the monoclinic space group $P21/c$. Data collection in the range $3.01 < 2\theta < 29.96°$ was performed using ω-scans on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated MoK_α ratiation. Data correction for Lorentz polarization and absorption (empirically using Ψ-scans) was carried out using the program system MOLEN [18]a. From 5675 measured reflections, all 5346 independent reflections were used and 189 parameters were refined by full-matrix least-squares against all F_o^2 data (SHELXL-93) [18]b. The structure was solved using direct methods (SHELXS-86) [18]c and difference Fourier syntheses and refined with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were calculated at their idealized positions. The refinement converged with $R = 0.0471$, $wR_2 = 0.0952$ for all observed F_o data, goodness of fit 1.143.

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD408459, the names of the authors and the journal citation.

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