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Journal of Organometallic Chemistry 591 (1999) 71–77

Journal of Organometallic Chemistry

The tendency of tripodal amidozirconium and hafnium complexes to form hexacoordinate structures: alkali metal halide cages versus solvent adducts

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Received 5 July 1999; accepted 6 August 1999

Abstract

Reaction of the tripodal lithium amide $[HC\{SiMe_2N(Li)(4\text{-}CH_3C_6H_4)\}_3]$ with $ZrCl_4$ in diethylether gave the chlorozirconium–lithum chloride complex $[HC\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3Zr\{Cl_4(Li\text{–}OEt_2)_3\}]$ (**3**). This contains a metal halide heterocubane unit fused to the tripodal amido cage through the hexacoordinate zirconium atom as established by an X-ray diffraction study. Recrystallisation of the compound in THF gives the hexacoordinate solvent adduct $[HC\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3ZrCl(THF)_2]$ (**4**) which was also characterized by X-ray crystallography. Alkylation of the chloro complex $[HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3Zr((\text{-}Cl)_2Li(OEt_2)_2]$ (**2a**) with methyllithium or *t*-butyllithium yields the alkylcomplexes $[HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3ZrCH_3]$ (**6**) and $[HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3ZrC(CH_3)_3]$ (**7**) for which the JFH and JFC coupling with the metal-bound alkyl groups indicates involvement of the peripheral fluoro functions in the coordination to the metal centre. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Zirconium; Hafnium; Tripodal amide; Heterocubane; Alkyl

1. Introduction

Triamidochloro complexes of the Ti-triad metals coordinated by tripodal triamido ligands have been found to be versatile organometallic reagents and molecular building blocks [1–4]. Whereas the titanium complexes usually adopt a four-coordinate distorted tetrahedral geometry, the greater ionic radius of its heavier congeners, zirconium and hafnium, render them more susceptible to an increase in the coordination number by addition of one or two further ligands. This was for instance observed in the reaction of the lithium amide $[MeSi\{SiMe_2N(Li)(4\text{-}MeOC_6H_4)\}_3]$ with $ZrCl_4$ in diethyl ether, which yielded the pentacoordinate complex $[MeSi\{SiMe_2N(4\text{-}MeOC_6H_4)\}_3Zr((-Cl)_2Li(OEt_2)_2]$ (**1**) (Fig. 1) [5].

The more exposed nature of the central atom in these species, compared with the Ti analogues, generally implies an increased sensitivity towards hydrolysis or degradation by other protic species. The latter can be partially suppressed by incorporation of weakly coordinating functionalities into the ligand periphery, such as achieved in the tripodal amides containing a 1-fluorophenyl periphery [6]. Their effect has been evident in the synthesis of the analogues of compound **1** which yielded products of the same composition $[E\{SiMe_2N\text{-}(2\text{-}FC_6H_4)\}_3Zr(\mu\text{-}Cl)_2Li(OEt_2)_2]$ (E = HC: **2a**, MeSi: **2b**) [5,6]. Single-crystal X-ray structure analyses of both compounds established hexacoordinate structures in which one of the fluorophenyl groups is weakly coordinated to the metal centre.

In this paper we report further studies concerning the tendency towards an expansion of the coordination sphere in the heavier Ti-group metal complexes. In particular, we show how the presence of the alkali

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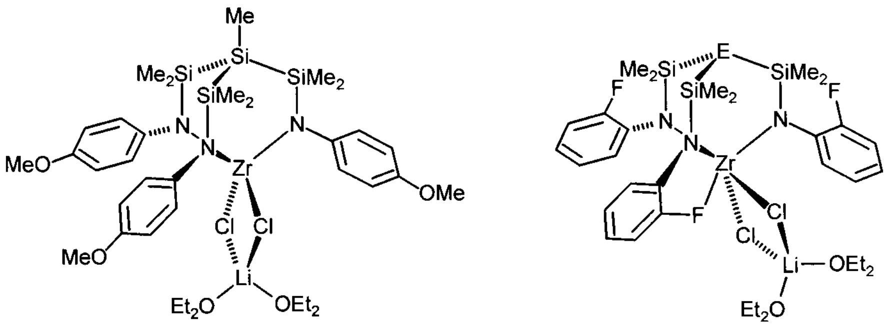
PII: S0022-328X(99)00486-6



1

E = HC : **2a**

MeSi : **2b**

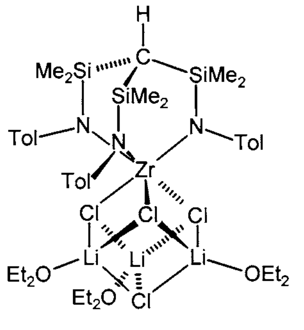
Fig. 1. Molecular structures of the pentacoordinate complex **1** and the hexacoordinate complexes **2a/b**.

metal salt generated in the salt methathesis of the lithium amide with the metal halide as well as the presence of a donor solvent affects the structure of the isolated product.

2. Results and discussion

2.1. Synthesis and single-crystal X-ray structure analyses of [HC{SiMe$_2$N(4-CH$_3$C$_6$H$_4$)}$_3$Zr-{Cl$_4$(Li–OEt$_2$)$_3$}] (3) and [HC{SiMe$_2$N(4-CH$_3$-C$_6$H$_4$)}$_3$ZrCl(THF)$_2$] (4)

Reaction of the lithium amide [HC{SiMe$_2$N(Li)(4-CH$_3$C$_6$H$_4$)}$_3$] [1c] with one molar equivalent of ZrCl$_4$ in diethylether yielded a zirconium amide derivative which remained dissolved along with more than 90% of the theoretical amount of LiCl to be formed in this conversion. From this solution a highly crystalline, colourless solid could be isolated by crystallization. The analytical data were consistent with its formulation as [HC{SiMe$_2$N(4-CH$_3$C$_6$H$_4$)}$_3$ZrCl{ClLi–OEt$_2$)$_3$}] (**3**), i.e. the adduct of the triamidochlorozirconium complex with three units of ether-solvated lithium chloride. The ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra of the compound, recorded at 295 K in C$_6$D$_6$ indicate an effective threefold molecular symmetry in solution. In order to establish its structure unambiguously, a single-crystal X-ray structure analysis was carried out. The molecular structure of the complex is displayed in Fig. 2 while the principal bond lengths and interbond angles are listed in Table 1.



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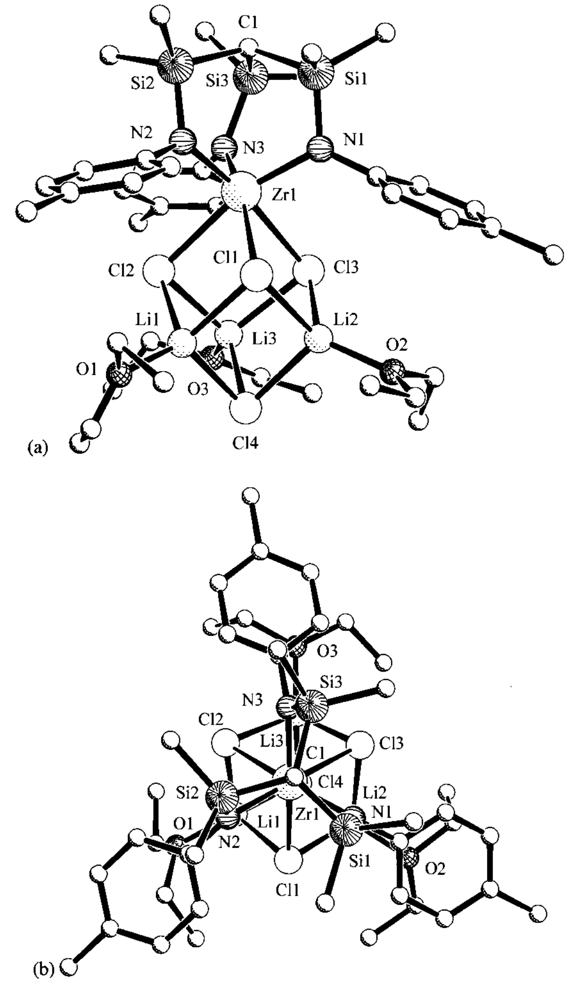


Fig. 2. View of the molecular structure of **3** perpendicular (a) and along (b) the threefold molecular axis.

Table 1
Selected bond lengths (Å) and interbond angles (°) of **3**

Bond lengths			
Zr(1)–N(1)	2.082(2)	Zr(1)–Cl(3)	2.6921(12)
Zr(1)–N(2)	2.080(2)	Li(l)–Cl(2)	2.373(5)
Zr(l)–N(3)	2.081(2)	Li(1)–Cl(l)	2.396(5)
Zr(1)–Cl(l)	2.6553(11)	Li(1)–Cl(4)	2.351(6)
Zr(1)–Cl(2)	2.6581(15)	Li(1)–O(1)	1.885(6)
Bond angles			
N(1)–Zr(1)–N(2)	97.61 (9)	Cl(2)–Zr(1)–Cl(3)	80.73(4)
N(1)–Zr(1)–N(3)	99.79(9)	Li(1)–Cl(4)–Li(3)	80.57(19)
N(2)–Zr(1)–N(3)	97.09(9)	Li(1)–Cl(4)–Li(2)	81.60(19)
Cl(1)–Zr(1)–Cl(2)	79.28(4)	Li(2)–Cl(4)–Li(3)	82.77(18)
Cl(1)–Zr(1)–Cl(3)	80.72(4)		

The main structural feature established for compound **3** is the combination of two cage units that are fused through a joint vertex occupied by the zirconium atom, the [2,2,2]-bicyclooctane-related tripodal triamidozirconium moiety and a distorted metallacubane cage comprising three LiCl and one ZrCl units (Fig. 2(a)). The tripodal amido ligand shows a helical twist that may be envisaged as a rotation of the N_3 triangle of the ligand with respect to an Si_3 triangle described by the three $SiMe_2$ units of each tripod arm (Fig. 2(b)). This situation is thought to be a consequence of the steric repulsions of the methyl groups in the $SiMe_2$ units. The three peripheral tolyl groups are twisted in relation to the Si–N vectors in the amido cage and thus adopt the lamp shade arrangement also noted for the previously reported trisilylsilane derivatives [3b,3f]. The zirconium atom is hexacoordinated in a highly distorted octahedral arrangement generated by the facial coordination of the tripod ligand and the coordination of three chloro ligands. The steric constraints of the ligand backbone enforce an increase in the N–Zr–N′ bond angles with respect to the value of 90° in an octahedral structure [N(1)–Zr(1)–N(2) 97.61(9), N(1)–Zr(1)–N(3) 99.79(9), N(2)–Zr(1)–N(3) 97.09(9)°]. This situation in turn induces smaller Cl–Zr–Cl′ bond angles than 90° [Cl(1)–Zr(1)–Cl(2) 79.28(4), Cl(1)–Zr(1)–Cl(3) 80.72(4), Cl(2)–Zr(1)–Cl(3) 80.73(4)°] and, as a consequence an elongation of the cubic cage along the diagonal threefold axis going through Zr(1) and Cl(4). The interbond angles around the Cl(4) atom are in fact very similar to the values at the zirconium vertex quoted above [Li(1)–Cl(4)–Li(3) 80.57(19), Li(1)–Cl(4)–Li(2) 81.60 (19), Li(2)–Cl(4)–Li(3) 82.77(18)°], while there is a considerable variation of the angles at the other vertices ranging from 80 to 101°. The three lithium atoms attain their fourfold coordination geometry by coordination of one molecule of diethylether per metal atom.

The heterocubane is a fairly common structural motif in alkalimetal chemistry [7] although we are unaware of derivatives incorporating a transition metal. The most prominent examples are the alkyllithium tetramers such as $(LiEt)_4$ and $(LiR)_4(L)_2$ (e.g. R = Me, L = tetramethylethylenediamine) [8,9], imidolithium complexes such as $[Ph_2=NLi{\cdot}NC_5H_5]_4$ [10] as well as lithium enolates [11], e.g. the tetrahydofuran complex $[Li(THF)O^tBuC{=}CH_2]_4$ [12]. The structurally most closely related compound is the tetrameric $[ClLi{\cdot}O{=}P(NMe_2)_3]_4$ reported by Snaith and co-workers, which contains a central $(LiCl)_4$ cube [10]. While the Li–Cl distances lie in the same range as for compound **3** (2.35–2.44 Å), the cuboidal core is somewhat less distorted than observed upon incorporation of an early transition metal.

If the recrystallization of complex **3** is carried out in THF, the increased polarity and donor properties of the solvent lead to a disintegration of the alkali metal halide cube. The compound isolated upon crystallization is the bis(THF) adduct of the triamidomonohalide, $[HC\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3ZrCl(THF)_2]$ (**4**) as established by elemental analysis. The observation of resonance patterns in the NMR spectra of the compound which are consistent with an effective threefold molecular symmetry indicate configurational instability of the complex. This is thought to exchange the THF and Cl ligand positions via dissociation of a THF molecule and rearrangement of the pentacoordinate intermediate. While considerable resonance broadening is observed upon lowering the temperature of a sample in toluene-d_8, the dynamic process could not be frozen out.

The hexacoordinate structure of complex **4**, deduced from the analytical and spectroscopic data, could be established by an X-ray diffraction study. Two views of the molecular structure are given in Fig. 3 while the principal bond lengths and interbond angles are listed in Table 2.

The overall structure of the tripod ligand cage is very similar to that of **3**, however, there is a marked difference between the three amido–N–Zr distances. Whereas the bond lengths Zr(1)–N(1) and Zr–N(3) lie in the same range as those observed in the structure of

Table 2
Selected bond lengths (Å) and interbond angles (°) of **4**

Bond lengths			
Zr(1)–N(1)	2.097(2)	Zr(1)–Cl(1)	2.4991 (8)
Zr(1)–N(2)	2.124(2)	Zr(1)–O(l)	2.356(2)
Zr(1)–N(3)	2.096(3)	Zr(1)–O(2)	2.343(2)
Bond angles			
N(1)–Zr(l)–N(2)	97.68(10)	0(2)–Zr(1)–O(1)	82.36(9)
N(1)–Zr(l)–N(3)	96.80(10)	Cl(1)–Zr(1)–O(2)	76.49(6)
N(2)–Zr(l)–N(3)	96.29(10)	Cl(l)–Zr(l)–O(1)	80.93(6)

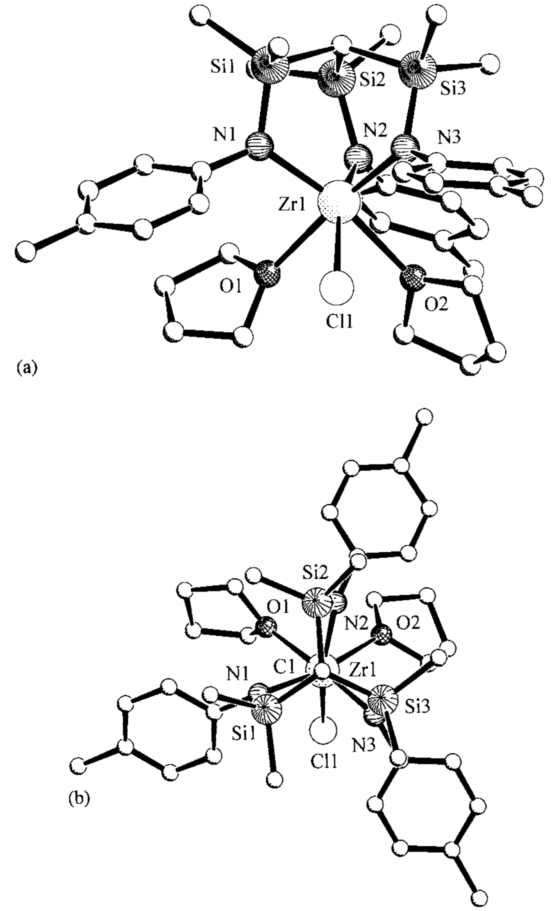


Fig. 3. View of the molecular structure of **4** perpendicular (a) and along (b) the molecular axis of the metal-tripod cage.

complex **3** [Zr(1)–N(1) 2.097(2) and Zr(1)–N(3) 2.096(3) Å] the value of Zr(1)–N(1) of 2.124(2) Å is significantly greater and probably a consequence of the stronger *trans* influence of the chloro ligand in comparison to the two THF ligands. This observation is complemented by the shorter Zr(1)–Cl(1) distance of 2.4991(8) compared to the corresponding values in the formally dianionic Cl_3Zr(tripod) unit of **3**.

The structural unit containing two donor molecules coordinated to the triamidochloro–zirconium complex established for **4** by X-ray crystallography is also thought to be present in the reaction product of $[HC\{SiMe_2N(Li)(2\text{-}FC_6H_4)\}_3]$ [6] with $HfCl_4$ in diethyl ether. While the synthesis of the corresponding zirconium complex yielded the hexacoordinate LiCl-adduct **2a** [5], the reaction with hafnium tetrachloride gave the bis(diethylether)complex **5** (Scheme 1).

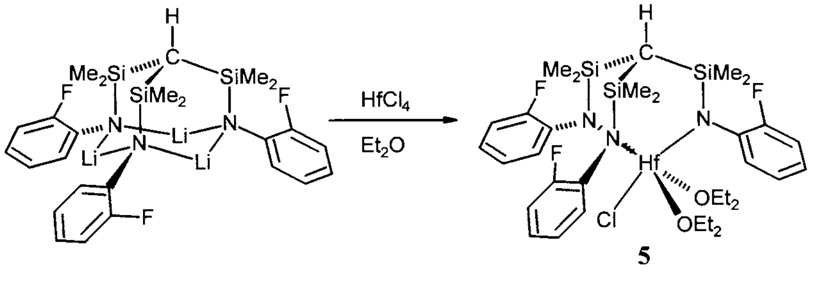
*2.2. Synthesis $[HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3ZrCH_3]$ (**6**) and $[HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3ZrC(CH_3)_3]$ (**7**)*

Reaction of $[HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3Zr(\mu\text{-}Cl)_2Li(OEt_2)_2]$ (**2a**) [5] with one molar equivalent of methyllithium or *t*-butyllithium gave the alkylzirconium complexes $[HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3ZrCH_3]$ (**6**) and $[HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3ZrC(CH_3)_3]$ (**7**), respectively (Scheme 2). Both compounds are thermally very stable and do not decompose in solution at temperatures up to 80°C.

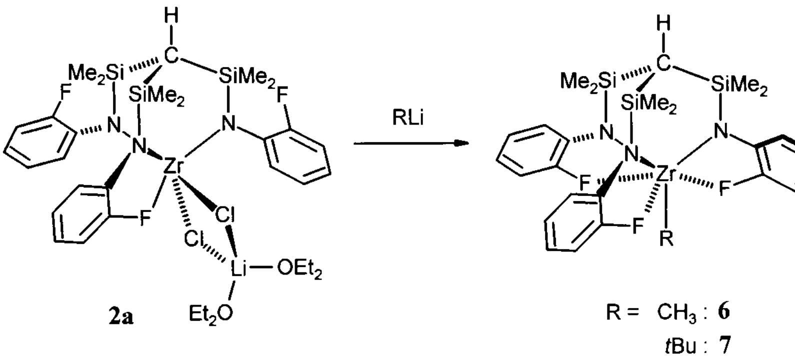
The ^{1}H- and ^{13}C-NMR spectra support the proposed threefold symmetrical molecular structure displayed in Scheme 2. In particular, the signal assigned to the protons of the metal-bonded methyl group in **6**, observed at (0.65 is split as a quartet resonance due to coupling with the three fluorine nuclei ($^3J_{FH} = 8.4$ Hz). This observation may be interpreted as providing evidence for the involvement of the three peripheral fluorine atoms to the metal centre. Coupling with the fluorine nuclei is also observed in the ^{13}C-NMR spectra of **6** and **7**. In both cases a quartet splitting is observed for the resonance due to the ^{13}C nucleus bound to the zirconium atom (**6**: (47.3, $^2J_{FC} = 4.6$ Hz; **7**: (67.2, $^2J_{FC} = 3.0$ Hz). In both cases, this is consistent with the involvement of the peripheral fluorine atoms in the first coordination sphere of the central metal atoms, reflecting the tendency of zirconium to adopt coordination numbers higher than four.

3. Experimental

All manipulations were performed under an inert gas atmosphere of dried argon in standard (Schlenk) glassware, which was flame dried with a Bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with Ar. The deuterated sol-



Scheme 1. Synthesis of the bis(diethylether) complex **5**.



Scheme 2. Synthesis of the alkylzirconium complexes **6** and **7**.

vents used for the NMR spectroscopic measurements were degassed by three successive ‘freeze–pump–thaw’ cycles and dried over 4 Å molecular sieves.

The ^{1}H-, ^{13}C-, ^{29}Si- and ^{19}F-NMR spectra were recorded on a Bruker AC 200 spectrometer equipped with a B-VT-2000 variable temperature unit (at 200.13, 50.32, 39.76, and 188.31 MHz, respectively) with tetramethylsilane and $CFCl_3$ as references.

Elemental analyses were carried out in the Microanalytical Laboratory of the Chemistry Department at Würzburg. The ligand precursors $HC\{SiMe_2NH(4\text{-}CH_3C_6H_4)\}_3$ and $HC\{SiMe_2NH(2\text{-}FC_6H_4)\}_3$ were prepared as reported previously [1c,6].

3.1. Preparation of [$HC\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3Zr\{Cl_4(Li\text{-}OEt_2)_3\}$] (**3**)

To a solution of $HC\{SiMe_2NH(4\text{-}CH_3C_6H_4)\}_3$ (5.63 g = 11.13 mmol) in diethyl ether (40 ml) which was cooled at −78°C were added 14.69 ml of BuLi (2.5 M solution in *N*-hexanes = 36.73 mmol). After stirring for 5 h, the solution was concentrated to ca. 4 ml and the lithium amide, which precipitated almost quantitatively, was isolated by centrifugation. The solid lithium amide was re-dissolved in ca. 30 ml of diethyl ether, the solution thus obtained cooled at −78°C and solid $ZrCl_4$ (2.59 g = 11.13 mmol) was subsequently added to the reaction mixture. After warming to room temperature (r.t.) and stirring for 14 days, the solution was concentrated, and a small amount of precipitated LiCl separated by centrifugation. Storage of the solution at −25°C yielded colourless crystals of **3**. Yield: 5.72 g (82%). ^{1}H-NMR (200.13 MHz, C_6D_6, 295 K): δ −0.26 (s, 1 H, $HC(Si\ldots)_3$), 0.45 (s, 18 H, $Si(CH_3)_2$), 0.80 (t, $(CH_3CH_2)_2O$), 2.15 (s, 9 H, $CH_3C_6H_4$), 3.21 (q, $(CH_3CH_2)_2O$), 6.95–7.13 (m, 12 H, C_6H_4). $\{^1H\}^{13}$C-NMR (50.32 MHz, C_6D_6, 295 K): δ 4.5 ($Si(CH_3)_2$), 5.3 ($HC(Si\ldots)_3$), 14.6 ($(CH_3CH_2)_2O$), 20.9 ($CH_3C_6H_4$), 66.2 ($(CH_3CH_2)_2O$), 124.8 ($C^{2,6}$ of C_6H_4), 130.3 ($C^{3,5}$ of C_6H_4), 130.9 (C^1 of C_6H_4), 149.3 (C^1 of C_6H_4). $\{^1H\}^{29}$Si-NMR (39.76 MHz, C_6D_6, 295 K): δ 1.1. $\{^1H\}^{7}$Li-NMR (77.77 MHz, C_6D_6, 295 K): δ −2.4. IR (benzene): 3016 (w) cm^{-1}, 2975 (vs), 2922 (s), 2866 (s), 1606 (m), 1512 (vs), 1499 (vs), 1444 (w), 1381 (w), 1368 (w), 1288 (m), 1252 (vs), 1222 (vs), 1118 (s), 1016 (s), 970 (s), 848 (br.vs), 808 (vs), 704 (m), 521 (m). $C_{40}H_{70}N_3Cl_4Li_3O_3Si_3Zr$ (979.13): Anal. Calc. C, 49.07; H, 7.21; N, 4.29; Found C, 48.58; H, 6.85; N, 4.53.

3.2. Preparation of [$HC\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3ZrCl(THF)_2$] (**4**)

Preparation as for **3**. However, recrystallization occured from THF. Yield: 72%. ^{1}H-NMR (400.14 MHz, C_6D_6, 295 K): δ −0.32 (s, 1 H, $HC(Si\ldots)_3$), 0.45 (s, 18 H, $Si(CH_3)_2$), 1.17 (THF), 2.12 (s, 9 H, $CH_3C_6H_4$), 3.58 (THF), 7.00 (d, 6 H, $^3J_{HH}$ = 7.8 Hz, $H^{2,6}$ of C_6H_4), 7.09 (d, 6 H, $H^{3,5}$ of C_6H_4). $\{^1H\}^{13}$C-NMR (100.62 MHz, C_6D_6, 295 K): δ 4.5 ($Si(CH_3)_2$), 4.9 ($HC(Si\ldots)_3$), 20.7 ($CH_3C_6H_4$), 25.5 (THF), 69.8 (THF), 124.2 ($C^{2,6}$ of C_6H_4), 130.2 ($C^{3,5}$ of C_6H_4), 130.8 (C^4 of C_6H_4), 148.9 (C^1 of C_6H_4). $\{^1H\}^{29}$Si-NMR (79.50 MHz, C_6D_6, 295 K): δ 1.1. $C_{36}H_{56}ClN_3O_2Si_3Zr$ (773.79): Anal. Calc. C, 55.88; H, 7.29; N, 5.43. Found C, 55.45; H, 7.03; N, 5.49.

3.3. Preparation of [$HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3HfCl(OEt_2)_2$] (**5**)

To a stirred solution of $HC\{SiMe_2NH(2\text{-}FC_6H_4)\}_3$ (2.81 g = 5.44 mmol) in 100 ml of diethyl ether, which was cooled at −78°C, were added dropwise 6.6 ml of an *N*-BuLi solution (2.5 M in *n*-hexane). The reaction mixture was subsequently warmed to r.t. and stirred for a further 60 min. The solution obtained was then re-cooled to −78°C and solid $HfCl_4$ (1.74 mg = 5.50 mmol) was added. The reaction mixture was warmed to ambient temperature over a period of ca 8 h and stirred for another 2 days. The solid lithium chloride formed in the reaction was removed by centrifugation. Upon slowly evaporating the solvent of the centrifugate, colourless crystals of compound **5** formed, which were isolated by filtration and dried in vacuo. Yield: 2.52 g

Table 3
Crystal data and structure refinement for **3** and **4**

	3	**4**
Empirical formula	$C_4OH_7OCl_4Li_3N_3O_3Si_3Zr \cdot C_4H_{10}O$	$C_{36}H_{56}ClN_3O_2Si_3Zr$
Formula weight	1053.22	773.78
Temperature (K)	153(2)	193(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions		
a (Å)	12.339(5)	16.743(2)
b (Å)	13.579(5)	17.0148(11)
c (Å)	19.585(8)	13.8937(17)
α (°)	78.09(3)	
β (°)	81.69(3)	97.388(6)
γ (°)	64.01(4)	
Volume (Å^3), Z	2880.8(19), 2	3925.0(8), 4
D_{calc} (g cm^{-3})	1.214	1.309
Absorption coefficient (mm^{-1})	0.476	0.474
F(000)	1112	1632
Crystal size (mm)	0.6 × 0.5 × 0.5	0.8 × 0.8 × 0.6
θ range for data collection	2.07–24.99	2.16–24.99
Limiting indices	$-14 \leq h \leq 1$, $-16 \leq k \leq 14$, $-23 \leq l < 23$	$-2 \leq h \leq 19$, $-3 \leq k \leq 20$, $-16 \leq l \leq 16$
Reflections collected	10664	9386
Independent reflections	10118 ($R_{int} = 0.0229$)	6892 ($R_{int} = 0.0338$)
Refinement method	Full-matrix least-squares on F_2	Full-matrix least-squares on F_2
Data/restraints/parameters	10118/662/728	6892/0/424
Goodness-of-fit on F^2	1.024	1.035
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0395$, $wR_2 = 0.0966$	$R_1 = 0.0393$, $wR_2 = 0.0905$
R indices (all data)	$R_1 = 0.0473$, $wR_2 = 0.1036$	$R_1 = 0.0539$, $wR_2 = 0.0996$
Largest diff. peak and hole (e Å^{-3})	0.619 and −0.616	0.539 and −0.581

(53%). M.p.: 75°C (dec.). ^{1}H-NMR (C_6D_6, 295 K):δ −0.54 (s, HC(Si…)$_3$), 0.37 (s, Si(CH$_3$)$_2$), 1.01 (t, $^3J_{HH} = 6.8$ Hz, OCH$_2$*C*H$_3$), 3.30 (q, OC*H*$_2$CH$_3$), 6.46–6.86 (m, 2-FC$_6$H$_4$). {^{1}H}^{13}C-NMR (C_6D_6, 295 K):δ 4.2 (Si(CH$_3$)$_2$), 5.3 (HC(Si…)$_3$), 15.3 (OCH$_2$*C*H$_3$), 66.0 (O*C*H$_2$CH$_3$), 114.7 (d, $^2J_{FC} = 22.2$ Hz, C^3 of 2-F*C*$_6$H$_4$), 120.8, 123.7, 125.6 (C$^{4-6}$ of 2-F*C*$_6$H$_4$), 139.7 (d, $^2J_{FC} = 13.9$ Hz, C^1 of 2-F*C*$_6$H$_4$), 159.6 (d, $^1J_{FC} = 232.7$ Hz, C^2 of 2-F*C*$_6$H$_4$). {^{1}H}^{19}F-NMR (C_6D_6, 295 K): δ −121.3. {^{1}H}^{29}Si-NMR (C_6D_6, 295 K): δ 3.3. IR (toluene): 1614 (s) cm^{-1}, 1310 (vs), 1260 (m), 1243 (m), 1184 (w), 1120 (w), 1093 (w), 1028 (m), 1004 (m), 898 (m), 847 (s). $C_{33}H_{51}ClF_3HfN_3Si_3O_2$ (877.98): Anal. Calc. C, 45.15; H, 5.86; N, 4.79. Found C, 45.19; H, 5.65; N, 4.57.

3.4. Preparation of [HC{SiMe$_2$N(2-FC$_6$H$_4$)}$_3$ZrCH$_3$] (**6**)

To a stirred solution of HC{SiMe$_2$N(2-FC$_6$H$_4$)}$_3$-ZrCl$_2$Li(OEt$_2$)$_2$ (**2a**) (500 mg = 0.601 mmol) in 20 ml of diethyl ether, which was cooled at −78°C, were added dropwise 0.4 ml of a solution of MeLi (1.7 M in diethylether). Over a period of 3 h, the reaction mixture was warmed to r.t. and the LiCl that precipitated during the course of this process was removed by centrifugation. Upon slowly evaporating the solvent of the centrifugate, colourless crystals of compound **6** formed, which were isolated by filtration and dried in vacuo. Yield: 330 mg (88%). M.p.: 82°C (dec.). ^{1}H-NMR (C_6D_6, 295 K): δ −0.46 (s, HC(Si…)$_3$), 0.37 (s, Si(CH$_3$)$_2$), 0.65 (q, $^3J_{FH} = 8.4$ Hz, H$_3$C–Zr), 6.44–6.85 (m, 2-FC$_6$H$_4$). {^{1}H}^{13}C-NMR (C_6D_6, 295 K): δ 4.3 (Si(CH$_3$)$_2$), 6.3 (HC(Si…)$_3$), 47.3 (q, $^2J_{FC} = 4.6$ Hz, H$_3$C–Zr), 114.6 (d, $^2J_{FC} = 22.0$ Hz, C^3 of 2-F*C*$_6$H$_4$), 120.0, 122.0, 125.9 (C$^{4-6}$ of 2-F*C*$_6$H$_4$), 139.8 (d, $^2J_{FC} = 14.0$ Hz, C^1 of 2-F*C*$_6$H$_4$), 158.7 (d, $^1J_{FC} = 224.8$ Hz, C^2 of 2-FC$_6$H$_4$). {^{1}H}^{19}F-NMR (C_6D_6, 295 K): δ −121.3. IR (Nujol): 1621 (m) cm^{-1}, 1500 (s), 1476 (vs), 1310 (s), 1285 (s), 1266 (s), 1253 (s), 1246 (s) 1062 (m), 1036 (m), 968 (w), 937 (m), 823 (vs), 739 (s), 727 (m). $C_{26}H_{34}F_3N_3Si_3Zr$ (621.05): Anal. Calc. C, 50.28; H, 5.52; N, 6.77. Found C, 50.11; H, 5.73; N 6.62.

3.5. Preparation of [HC{SiMe$_2$N(2-FC$_6$H$_4$)}$_3$ZrC(CH$_3$)$_3$] (*7*)

To a stirred solution of HC{SiMe$_2$N(2-FC$_6$H$_4$)}$_3$ZrCl$_2$Li(OEt$_2$)$_2$ (**2a**) (500 mg = 0.601 mmol) 20 ml of toluene, which was cooled at −78°C, were added dropwise 0.5 ml of a solution of *t*-BuLi (1.5 M in pentane). Over a period of 3 h, the reaction mixture was warmed to r.t. and the LiCl which precipitated during the course of this process was removed by centrifugation. The centrifugate was concentrated to 5 ml and stored at r.t. for several days. During this period compound **7** crystallized as a colourless solid, which was isolated by decanting the supernatant solution and drying in vacuo. Yield: 302 mg (76%). M.p.: 85°C (dec.). ^{1}H-NMR (C_6D_6, 295 K): δ -0.38 (s, HC(Si...)$_3$), 0.37 (s, Si(CH$_3$)$_2$), 0.97 (d, $J = 2.1$ Hz, ZrC(CH$_3$)$_3$), 6.85–7.09 (m, 2-FC$_6$H$_4$). {^{1}H}^{13}C-NMR (C_6D_6, 295 K): δ 4.3 (Si(CH$_3$)$_2$), 8.5 (HC(Si...)$_3$), 26.8 (C(CH$_3$)$_3$), 67.2 (q, $^2J_{FC} = 3.0$ Hz, ZrC(CH$_3$)$_3$), 115.2 (d, $^2J_{FC} = 21.7$ Hz, C^3 of 2-FC_6H$_4$), 120.0 (d, $^3J_{FC} = 7.9$ Hz, C^4 of 2-FC_6H$_4$), 122.0, 125.9 (C^{5,6} of 2-FC_6H$_4$), 140.6 (d, $^2J_{FC} = 13.8$ Hz, C^1 of 2-FC_6H$_4$), 158.7 (d, $^1J_{FC} = 229.2$ Hz, C^2 of 2-FC_6H$_4$). {^{1}H}^{19}F-NMR (C_6D_6, 295 K): δ -123.5. {^{1}H}^{29}Si-NMR (C_6D_6, 295 K): δ 3.2. $C_{29}H_{40}F_3N_3Si_3Zr$ (663.13): Anal. Calc. C, 52.53; H, 6.08; N, 6.34. Found C, 52.31; H, 5.99; N, 6.30.

*3.6. X-ray crystallographic studies of **3** and **4***

Data were collected using an Enraf–Nonius CAD4 diffractometer at a temperature of 153(2) K (3) and 193(2) K (4) with oil-coated shock-cooled crystals [13] mounted on the top of a glass pin under nitrogen. Crystal data and experimental details for the crystals of **3** and **4** are given in Table 3. All data for the two structures were corrected for absorption (Ψ-scans). Structure **3** was solved by direct methods, structure **4** by Patterson methods (SHELXS-97) and both were refined on F^2 (SHELXL-97) [14]. In the case of **3**, disorder of all diethylether molecules was found. In the final cycles of refinement, all non-hydrogen atoms of **3** and **4** were assigned anisotropic displacement parameters. Hydrogen atoms were included in idealized positions riding on the parent atoms and were assigned isotropic displacement parameters of $1.2U_{eq}$ (=CH, CH, CH$_2$) and $1.5U_{eq}$ (CH$_3$) of the parent atom.

The structure of the chlorozirconium–lithum chloride complex [HC{SiMe$_2$N(4-CH$_3$C$_6$H$_4$)}$_3$Zr{Cl$_4$-(Li–OEt$_2$)$_3$}] (**3**) was refined (SHELXL-97) by application of a rigid-bond restraint to U_{ij} values (DELU) with low ESDs and assumption of 'similar' U_{ij} values (SIMU) with large ESDs due to the high disorder of all four diethylether molecules. For one carbon atom (C60) approximation of isotropic behaviour of its U_{ij} values (ISOR) with large ESDs was used.

4. Supplememtary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Database Centre, CCDC no. 130257 for compound **3** and 130258 for compound **4**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk].

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