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Zirconium, hafnium and yttrium complexes containing two linked amido–tetramethylcyclopentadienyl ligands: Synthesis, reactivity and molecular structure of $Hf(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\textit{i}Pr)_2$†

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Abstract—Zirconium and hafnium complexes $M(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NR')_xCl_{(4-2x)}$ (M = Zr, Hf; x = 1, 2; R′ = *i*Pr, *t*Bu) containing one or two linked amido–tetramethylcyclopentadienyl ligands $C_5Me_4SiMe_2NR'$ have been synthesized by the reaction of the dilithium derivative $Li_2(C_5Me_4SiMe_2NR')$ with $MCl_4(THF)_2$. The crystal structure of the hafnium complex $Hf(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\textit{i}Pr)_2$ has been determined by a single-crystal X-ray diffraction study and shows a C_2-symmetric helical metallocene, in which the amido ligands are bonded as π-donor ligands with Hf—N bond lengths of 2.115(2) Å. The isoelectronic heterobimetallic yttrium complex $Li[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)_2]$ reacts with phenylacetylene to give the bis(phenylacetylide) derivative $Li[Y\{\eta^5\text{-}C_5Me_4SiMe_2NH(CH_2CH_2OMe)\}_2(C{\equiv}CPh)_2]$. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: zirconium; hafnium; yttrium; amido–cyclopentadienyl; alkynyl complex.

Homogeneous α-olefin polymerization catalysts based on titanium complexes that contain the linked amido–cyclopentadienyl ligand $C_5Me_4SiMe_2NR'$ (R′ = alkyl, aryl) have recently gained considerable technological importance through the efficient synthesis of new types of polyethylenes and copolymers with comonomers such as 1-octene and styrene [1]. The linked amido–cyclopentadienyl ligand was introduced by Bercaw and Shapiro to successfully develop the first single-component catalysts $[Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\textit{t}Bu)R'']$ (R″ = H, alkyl) for the living polymerization of propylene [2]. Compared with Brintzinger-type *ansa*-metallocenes, the increased Lewis acidity together with a sterically open ligand sphere [3,4] appear to accommodate the bulkier comonomers better. In the course of synthetic and structural studies on 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) [3,4] we have isolated and characterized several complexes containing two linked amido–cyclopentadienyl ligands with different amido and cyclopentadienyl substituents $M(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NR')_2$ [3c,d]. Such compounds have attracted some attention as C_2-symmetric metallocenes and were also shown to form by aminolysis reactions [5], sometimes more reproducibly than by the salt metathesis reactions using the dianion of the ligand [6]. More recently, we have discovered that isoelectronic heterobimetallics of the general type $Li[Ln(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NCH_2CH_2X)_2]$ (Ln = Y, Lu; C_5R_4 = C_5Me_4, C_5H_4, $C_5H_3\textit{t}Bu$; X = OMe, NMe_2) can be obtained when a tridentate linked amido–cyclopentadienyl ligand is used [7]. Here we describe the preparation and characterization of zirconium, hafnium, and yttrium complexes containing two amido-functionalized tetramethylcyclopentadienyl ligands $C_5Me_4SiMe_2NR'$ along with some reactivity studies.

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† Dedicated to Prof. Dr. W. A. Herrmann on the occasion of his 50th birthday.

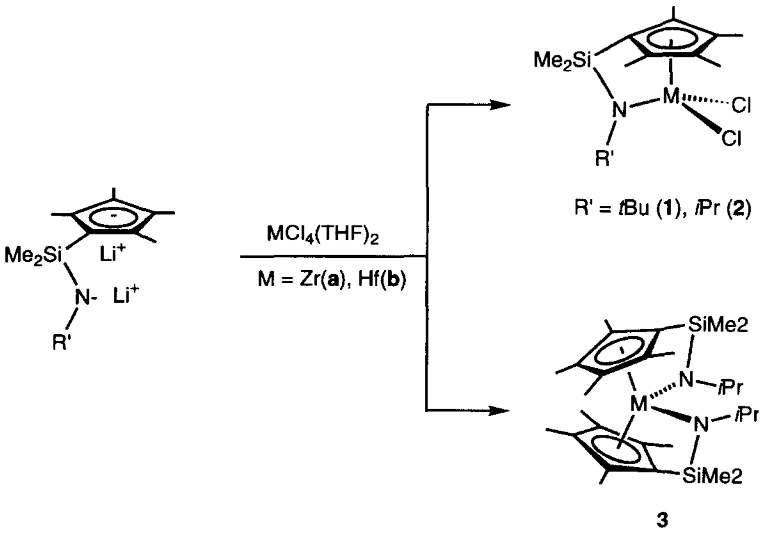
RESULTS AND DISCUSSION

As was independently noted by other authors [4–6], we too have occasionally observed the formation of group 4 metal complexes of the type $M(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NR')_2$ containing two amido-functionalized cyclopentadienyl ligands $C_5Me_4SiMe_2NR'$. Generally, the larger metals, zirconium and hafnium, have a greater tendency to form such complexes than titanium. For example, for R′ = allyl and M = Zr the metallocene derivative $Zr(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH{=}CH_2)_2$ is exclusively formed in the reaction of $Li(C_5Me_4SiMe_2NCH_2CH{=}CH_2)$ with $ZrCl_4(THF)_2$, whilst the reaction with $TiCl_3(THF)_3$, followed by oxidative chlorination with $PbCl_2$ results in the expected formation of the mono(ligand) complex $Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH{=}CH_2)Cl_2$ [3c,d]. We suspected that the nature of the amido substituent R′ may play a decisive role, and in fact, we observe no formation of the metallocene for R′ = *t*Bu, even when an excess of the dilithium salt is employed. Thus in the reaction of $Li_2(C_5Me_4SiMe_2N\textit{t}Bu)$ under various conditions and independently of the solvent only the mono(ligand) complexes $M(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\textit{t}Bu)Cl_2$ (**1**) (**a** = Zr, **b** = Hf) are detected and isolated as colourless crystals in good to moderate yields. The synthesis of the zirconium complex **1a** was previously described by Petersen *et al.* [4c]. These findings may suggest that the complexation of the amido group precedes that of the cyclopentadienyl moiety.

On the other hand, when the *iso*-propylamido ligand $Li_2(C_5Me_4SiMe_2N\textit{i}Pr)$ is employed in the complexation reaction with $MCl_4(THF)_2$, a mixture of the mono(ligand) and metallocene are formed under a variety of conditions for M = Zr. For M = Hf, the mono(ligand) complex $Hf(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\textit{i}Pr)Cl_2$ (**2b**) can be prepared only in toluene, whereas in THF, the metallocene $Hf(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\textit{i}Pr)_2$ (**3b**) is formed in moderate yields. We suspected therefore that the higher solubility of the dilithium derivative would cause higher local concentrations of the dianion leading to the preferred formation of the bis(ligand) complex. In fact, reactions in THF tend to increase the yield of the metallocene over that of the mono(ligand) complex. However, it is remarkable that the latter does not react with an excess of the dilithium derivative to give the metallocene complex, suggesting different intermediates on the way to both products. Evidently, the situation is more complicated and no conclusive explanation can be given at this time.

The significantly more soluble, C_2-symmetric metallocenes $M(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NR')_2$ are easily distinguished from the C_s-symmetric mono(ligand) complexes $M(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NR')Cl_2$ by the chirality which results in pairs of diastereotopic methyl resonances. One remarkable feature is the low-field shift for the methine proton that is recorded as a multiplet at $\delta = 4.13$ and 3.99 for **3a** and **3b**, respectively. Preliminary studies reveal that the formally 20-electron metallocene $M(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NR')_2$ **3a** and **b** are capable of initiating the polymerization of ε-caprolactone, albeit at much slower rates than the isolelectronic rare earth complexes $Li[Ln(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NCH_2CH_2X)_2]$ also mentioned below [7].

An ORTEP diagram of the molecular structure of complex **3b** is depicted in Fig. 1. Crystallographic data are compiled in Table 1, selected bond distances and angles are listed in Table 2. The compound residing on a crystallographic C_2-axis adopts the typical bent metallocene configuration in agreement with the solution structure. The angle between the two cyclopentadienyl rings is 127.9°, similar to the values found in the literature for non-linked hafnocenes such as



Scheme 1.

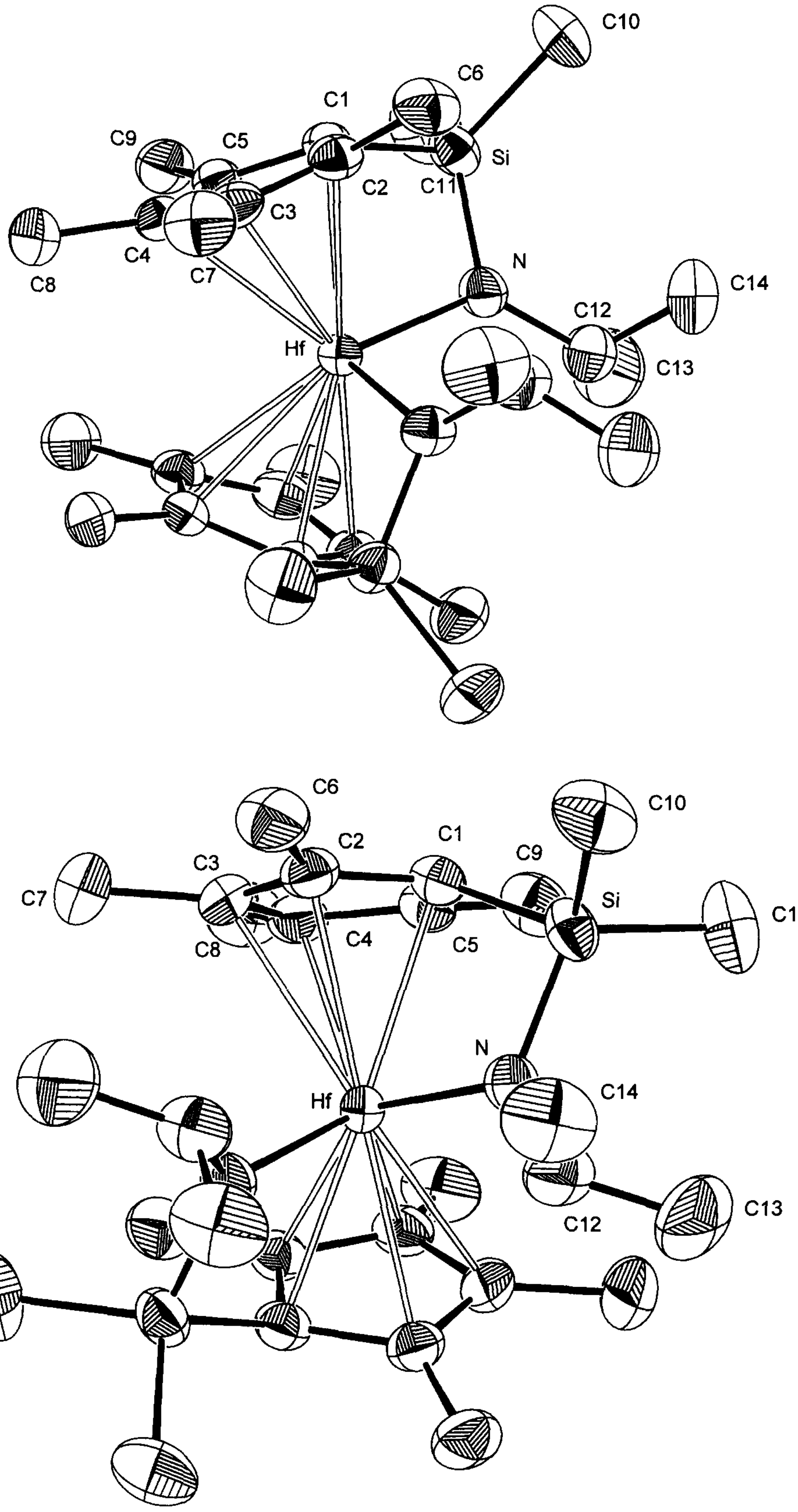


Fig. 1. (a) ORTEP diagram of the molecular structure of Hf($\eta^5:\eta^1$-$C_5Me_4SiMe_2N$*i*Pr$)_2$ (**3b**). (b) Alternative view from the front. Thermal ellipsoids are drawn at a 50% probability level. Hydrogen atoms are omitted for the sake of clarity.

Table 1. Crystallographic data for $Hf(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\mathit{i}Pr)_2$ (**3b**)

Empirical formula	$C_{28}H_{50}HfN_2Si_2$
Formula weight	649.37
Crystal colour	Colourless
Crystal size mm	0.50 × 0.28 × 0.23
Crystal system	Monoclinic
Space group	$C2/c$ (No. 15)
a (Å)	17.456(2)
b (Å)	12.128(2)
c (Å)	14.272(1)
β (°)	100.245(8)
Volume (Å^3)	2973.3(6)
Z	8/2
D_{calc}, Mg/m^3	1.451
Abs. coeff. (mm^{-1})	3.607
F(000)	1328
Temperature (K)	296(2)
Radiation	Mo–K_α ($\lambda = 0.71070$ Å)
θ range	3.4°–29.9°
Reflns measd	$-21 \leqslant h \leqslant 24$; $0 \leqslant k \leqslant 17; -20 \leqslant l \leqslant 19$
Refinement	
No. reflns measd	7235
No. indep. reflns	4310 [$R_{int} = 0.0192$]
No. obsd reflns	3854 ($I > 2\sigma(I)$)
Goodness-of-fit	1.097
R	0.0182
wR_2	0.0360
Extinction coefficient	0.00051(8)
Largest e-max, e-min (e Å^{-3})	0.703, −0.513

Table 2. Selected bond lengths (Å) and angles (°) for $Hf(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\mathit{i}Pr)_2$ (**3b**)

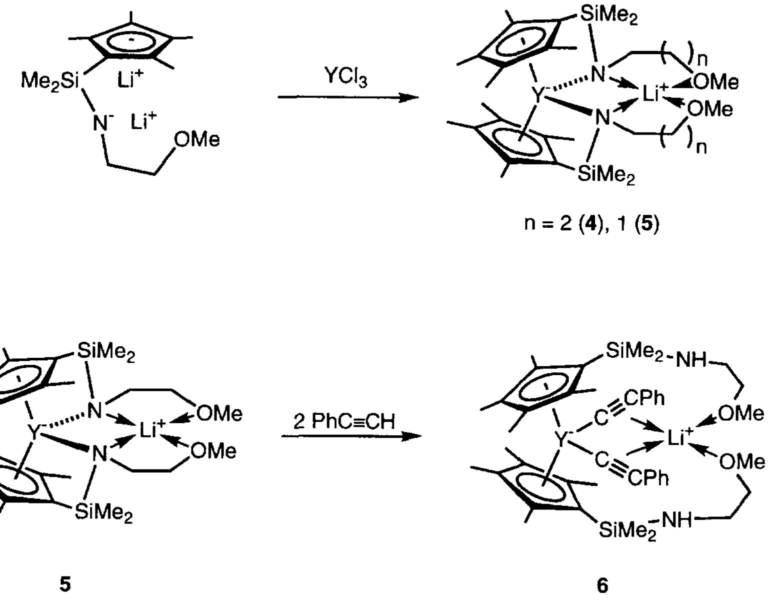
Hf—N	2.115(2)	Cp_{cent}—Hf—N	97.9
Hf—C(1)	2.476(2)	Cp_{cent}—Hf—N′	116.7
Hf—C(2)	2.535(2)	Cp_{cent}—Hf—Cp_{cent}'	127.9
Hf—C(3)	2.644(2)	Cp_{cent}'—Hf—N	116.7
Hf—C(4)	2.698(2)	N—Hf—N′	96.2(1)
Hf—C(5)	2.595(2)	N—Si—C(10)	118.7(1)
Si—N	1.721(2)	N—Si—C(11)	114.6(2)
Si—C(1)	1.864(2)	N—Si—C(1)	93.60(9)
N—C(12)	1.483(3)	C(10)—Si—C(11)	103.4(2)
		Hf—N—C(12)	128.8(2)
		Si—N—C(12)	124.8(2)
		Hf—N—Si	106.47(9)
		N—C(12)—C(13)	112.8(3)
		N—C(12)—C(14)	113.0(2)
		C(13)—C(12)—C(14)	109.4(3)

$Hf(\eta^5\text{-}C_5H_5)_2(CH_2Ph)_2$ (128.2°) [8a] and $Hf(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)Cl_2$ (130.6°) [8b], but significantly smaller than in the decamethylhafnocene derivative $Hf(\eta^5\text{-}C_5Me_5)_2(H)(NMe_2)$ (139.1°) [9]. The distances between the hafnium center and the centroid of each five-membered ring of 2.29 Å are somewhat longer than those observed in comparable hafnocene complexes (about 2.2 Å) [8,9]. The tetramethylcyclopentadienyl ligands are bonded in a pentahapto fashion as judged by the sum of the angles at the ring (540°) and the metal to ring-carbon distances ranging from 2.476(2) to 2.698(2) Å. The angle at hafnium N—Hf—N′ is 96.2(1)°, significantly smaller than that found in $Zr(\eta^5:\eta^1\text{-}C_5H_4SiMe_2NPh)_2$ (106.5(8)°) [5a]. This can be accounted for by the presence of the bulkier phenyl rings on the amido nitrogen atoms and the possibility of gear meshing of the two *iso*-propyl groups in **3b**.

The Hf—N bond length of 2.115(2) Å is slightly longer than the Hf—N distances observed in amido complexes where the amido ligand acts as a 3-electron ligand (2.027(8) Å in $Hf(\eta^5\text{-}C_5Me_5)_2(H)(NMe_2)$ [9], 2.041(4), 2.065(3) in $Hf(\eta^5\text{-}C_5Me_5)(N\mathit{i}Pr_2)_3$ [10a], 2.065(3) in $Hf(\eta^5:\eta^1\text{-}C_{13}Me_8SiMe_2CH_2N\mathit{t}Bu)Cl_2$ [10b]). However, the nitrogen atom is trigonal planar, the sum of the angles at the nitrogen atom being 360°. These observations support the view that the π-electrons are delocalized over both nitrogen atoms, a feature found in the only other structurally authenticated derivative $Zr(\eta^5:\eta^1\text{-}C_5H_4SiMe_2NPh)_2$ (Zr—N bond length 2.137(2), 2.127(2) Å) [5a]. In the isoelectronic yttrium complex $Li[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)_2]$ (**5**) pyramidalization of the amido nitrogen atoms are detectable, but not particularly pronounced [7a]. According to the theoretical model by Lauher and Hoffmann for d^0-metallocenes Cp_2MX_2 containing two potential π-donors such as amido or alkoxo ligands [11], only one lone pair of electrons can be accommodated in the empty a_1 orbital of the Cp_2MX_2 unit. In some d^0-Cp_2MX_2 complexes, structural evidence for the localization of a single and double bond can be found [11,12].

Reaction of two equivalents of $Li_2(C_5R_4SiMe_2NCH_2CH_2X)$ ($C_5R_4 = C_5Me_4$, C_5H_4, $C_5H_3\mathit{t}Bu$; X = OMe, NMe_2) with anhydrous $LnCl_3$ (Ln = Y, Lu) has been shown to give the C_2-symmetric heterobimetallic lanthanocenes $Li[Ln(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NCH_2CH_2X)_2]$ in high yield, whereas in the presence of one equivalent of the dilithium salt, inseparable product mixtures are formed [7]. In order to investigate the influence of the length of the amido side chain, an additional methylene carbon was introduced. The reaction of anhydrous YCl_3 with $Li_2(C_5Me_4SiMe_2NCH_2CH_2CH_2OMe)$ gives colourless crystals of $Li[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2CH_2OMe)_2]$ (**4**) for which a C_2-symmetric heterobimetallic structure analogous to that of $Li[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)_2]$ (**5**) can be assumed based on the NMR spectroscopic data and elemental analysis.

The electronically "oversaturated" metallocene unit $[Ln(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NCH_2CH_2X)_2]^-$ incorporates two π-donating amido ligands and can be assumed to show nucleophilic behaviour toward electrophiles. All heterobimetallic complexes have been



Scheme 2.

shown to be active catalysts for the polymerization of ε-caprolactone [7]. In order to prove the nucleophilicity of the amido substituents, the reaction with a weak Brönsted acid has been studied. Thus, the reaction of Li[Y(η^5:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)$_2$] with two equivalents of phenylacetylene leads to the formation of colourless crystals of the bis (acetylide) complex Li[Y{η^5-$C_5Me_4SiMe_2NH(CH_2CH_2OMe)$}$_2$(C≡CPh)$_2$] (**6**) with the structure proposed in Scheme 2. The ^{1}H NMR and ^{13}C NMR spectrum of **6** consists of only one signal for the methyl groups on the silicon and two signals for the methyl groups on the cyclopentadienyl ring. Additional evidence for the loss of the helical chiral structure of the starting material is the observation of an AA′XX′ instead of the ABCD pattern for the four methylene protons of the ligand side-chain. The methylene protons next to the oxygen of the side chain give rise to a triplet, whereas a doublet of triplets are observed for the methylene protons attached to the $NHSiMe_2$ group due to the coupling to the amine proton. The latter is recorded at δ 1.40 as a triplet with $^3J_{HH}$ = 7.8 Hz. The coordination of the acetylide ligand to both yttrium and lithium in solution is obvious from the ^{13}C NMR spectrum that shows a doublet of a quartet for the α-carbon of the acetylide ligand at δ 141.2 ($^1J_{YC}$ = 49.9 Hz, $I(^{89}Y) = \frac{1}{2}$; $^1J_{LiC}$ = 7.3 Hz, $I(^7Li) = \frac{3}{2}$) (Fig. 2), whereas a doublet at δ 114.9 ($^2J_{YC}$ = 10.1 Hz) is found for the β-carbon. A similar bridging coordination of the acetylide ligands to yttrium and lithium atom was found in the crystallographically confirmed structure of Cp$^{‡}_{2}$Y(μ-C≡CCMe$_3$)$_2$ Li(THF) [13]. However no coupling of lithium to carbon was observed in the ^{13}C NMR spectrum of this complex. A bridging mode of two acetylide ligands are quite common in dimeric lanthanocenes of the type [Ln(η^5-C_5R_5)$_2$(μ-C≡CR′)$_2$] [14]. The chemical shifts and coupling constants for the sp-hybridized α-carbon atom of the acetylide ligand are in the normal range for terminal acetylide complexes, such as Cp$^{‡}_{2}$Y(μ-C≡CCMe$_3$)$_2$Li(THF) (δ 127.0, $^1J_{YC}$ = 46 Hz) [13], Cp$^{‡}_{2}$Y(C≡CPh)(OEt$_2$) (δ 146.95, $^1J_{YC}$ = 70.9 Hz) [15], (DAC)Y(C≡CPh)(THF) (DAC = 4,13-Diaza-18-crown-6; δ 149.1, $^1J_{YC}$ = 46.9 Hz) [16]. The ^{13}C–^{7}Li coupling constant is slightly smaller than that observed in LiC≡C*t*Bu ($^1J_{LiC}$ = 16 Hz in THF at −90°C) [17a] and Li*t*Bu ($^1J_{LiC}$ = ca 10 Hz in toluene at room temperature) [17b].

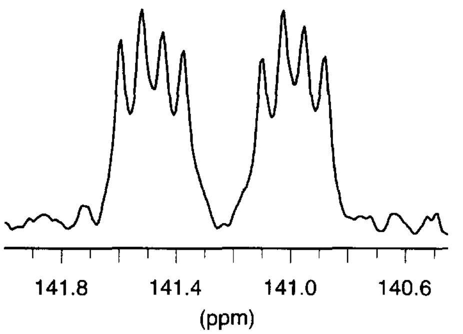


Fig. 2. ^{13}C NMR signal for the acetylide α-carbon atom in Li[Y{η^5-$C_5Me_4SiMe_2NH(CH_2CH_2OMe)$}$_2$(C≡CPh)$_2$] (**6**).

In conclusion, we have shown that the apparent 20-electron configuration in the metallocenes of the type [M(η^5:η^1-$C_5R_4SiMe_2NR'$)$_2$] (M = Zr, Hf, Ln^-) results in some nucleophilic behaviour, the polymerization activity toward ε-caprolactone being one example. It will be interesting to see whether this type of metallocene complexes exhibits further novel reactivities. One principal drawback, however, would be the loss of the helical chirality upon modification of the amido function.

EXPERIMENTAL

General considerations

All operations were performed under an inert atmosphere of argon using standard Schlenk or glovebox techniques. THF, toluene and hexane were purified by distillation from sodium/benzophenone ketyl. $MCl_4(THF)_2$ (M = Zr, Hf) [18], $Li_2(C_5Me_4SiMe_2N\textit{i}Pr)$ [3j], $Li_2(C_5Me_4SiMe_2N\textit{t}Bu)$ [2a] and $Li_2(C_5Me_4SiMe_2NCH_2CH_2CH_2OMe)$ [7c] were synthesized according to published procedures. YCl_3 (ALFA) was used as received. Li*n*Bu was used as received and titrated prior to use [19]. NMR spectra were recorded on a Bruker DRX 400 spectrometer at 25°C, mass spectra on a Finnigan 8230 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of this department.

$Zr(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\textit{t}Bu)Cl_2$ (**1a**) [4c]

A mixture of $ZrCl_4(THF)_2$ (2.61 g, 6.92 mmol) and $Li_2(C_5Me_4SiMe_2N\textit{t}Bu)$ (1.82 g, 6.92 mmol), obtained by double deprotonation of $(C_5Me_4H)SiMe_2NH\textit{t}Bu$ using Li*n*Bu in hexane, was treated dropwise with 35 ml of toluene at −60°C and stirred for 3 days at room temperature. Filtration of the reaction mixture through glass fibre, followed by concentrating the filtrate and recrystallization at −20°C afforded 2.11 g (74% yield) of colourless crystals. ^1H NMR (C_6D_6): δ 0.53 (s, 6 H, $SiCH_3$), 1.44 (s, 9 H, $C(CH_3)_3$), 2.07 (s, 6 H, ring CH_3), 2.13 (s, 6 H, ring CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 6.0 ($SiCH_3$), 11.9, 14.7 (ring CH_3), 33.1 ($C(\textit{C}H_3)_3$), 56.6 ($\textit{C}(CH_3)_3$), 101.2 (ring C attached to Si), 131.5, 134.2 (ring C). EI MS: *m*/*z* 410 (3%, M^+), 395 (51%, M^+-CH_3), 340 (5%, M^+-2Cl). Anal. calc. for $C_{15}H_{27}Cl_2NSiZr$: C, 43.77; H, 6.61; N, 3.40. Found C, 43.33, H, 6.84, N, 3.54.

$Hf(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\textit{t}Bu)Cl_2$ (**1b**)

Following a procedure analogous to that described for the preparation of **1a**, $Li_2(C_5Me_4SiMe_2N\textit{t}Bu)$ (1.00 g, 3.80 mmol) was reacted with $HfCl_4(THF)_2$ (1.76 g, 3.80 mmol) to give **1b** (0.50 g, 38% yield) as colourless microcrystals. ^1H NMR (C_6D_6): δ 0.44 (s, 6 H, $SiCH_3$), 1.29 (s, 9 H, $C(CH_3)_3$), 1.98, 2.08 (s, 6 H, ring CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 6.2 ($SiCH_3$), 11.5, 14.4 (ring CH_3), 33.9 ($C(\textit{C}H_3)_3$), 55.3 ($\textit{C}(CH_3)_3$), 100.7 (ring C attached to Si), 130.1, 131.8 (ring C). EI MS: *m*/*z* 500 (9%, M^+), 464 (18%, M^+-Cl), 429 (7%, $M^+-2\,Cl$). Anal. calc. for $C_{15}H_{27}NSiCl_2Hf$: C, 36.12; H, 5.41; N, 2.80. Found: C, 36.68; H, 6.97; N, 3.05.

$Zr(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\textit{i}Pr)Cl_2$ (**2a**)

This compound can only be prepared as an inseparable mixture with $Zr(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\textit{i}Pr)_2$ (**3a**) (*vide infra*). ^1H NMR (C_6D_6): δ 0.15 (s, 6 H, $SiCH_3$), 1.08 (d, $^3J_{HH}$ = 6.3 Hz, 6 H, $CH(C\textit{H}_3)_2$), 1.97, 2.12 (s, 6 H, ring CH_3), 3.03 (sept, $^3J_{HH}$ = 6.6 Hz, 1 H, $C\textit{H}(CH_3)_2$).

$Hf(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\textit{i}Pr)Cl_2$ (**2b**)

Toluene (30 ml) was added to a solid mixture of $Li_2(C_5Me_4SiMe_2N\textit{i}Pr)$ (1.50 g, 6.02 mmol) and $HfCl_4(THF)_2$ (2.80 g, 6.02 mmol) at −78°C. The mixture was stirred overnight, the solution was filtered, concentrated and cooled to −30°C to give a white solid. Extraction with hexane (2 × 10 ml) followed by filtration and cooling afforded 0.58 g (20% yield) of **2b** as colourless microcrystals. ^1H NMR (C_6D_6): δ 0.26 (s, 6 H, $SiCH_3$), 0.85 (d, $^3J_{HH}$ = 6.6 Hz, 6 H, $CH(C\textit{H}_3)_2$), 2.14, 2.19 (s, 6 H, ring CH_3), 3.05 (sept, $^3J_{HH}$ = 6.6 Hz, 1 H, $C\textit{H}(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 1.0 ($SiCH_3$), 12.3, 15.9 (ring CH_3), 26.1 ($CH(\textit{C}H_3)_2$), 48.8 ($\textit{C}H(CH_3)_2$), 107.9 (ring C attached to Si), 131.4, 133.4 (ring C). EI MS: *m*/*z* (%) 450 (3%, M^+-Cl), 415 (6%, $M^+-2\,Cl$).

$Zr(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\textit{i}Pr)_2$ (**3a**)

A mixture of $ZrCl_4(THF)_2$ (0.62 g, 1.64 mmol) and $Li_2(C_5Me_4SiMe_2N\textit{i}Pr)$ (0.82 g, 3.29 mmol) was treated dropwise with 35 ml of toluene at −60°C and stirred for 2 days at room temperature. Filtration of the extracts, followed by concentrating the filtrate and cooling to −50°C afforded 0.30 g of pale yellow crystals, yield: 33%. ^1H NMR (C_6D_6): δ 0.65, 0.78 (s, 3 H, $SiCH_3$), 1.29 (d, $^3J_{HH}$ = 6.3 Hz, 3 H, $CH(C\textit{H}_3)_2$), 1.35 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, $CH(C\textit{H}_3)_2$), 1.96 (s, 6H, ring CH_3), 2.09, 2.42 (s, 3 H, ring CH_3), 4.13 (m, 1 H, $C\textit{H}(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 8.6, 8.9 ($SiCH_3$), 11.4, 12.1, 13.6, 15.3 (ring CH_3), 28.8, 29.6 ($CH(\textit{C}H_3)_2$), 52.7 ($\textit{C}H(CH_3)_2$), 107.3 (ring C attached to Si), 122.9, 124.5, 125.9, 128.6 (ring C). EI MS: *m*/*z* 560 (24%, M^+), 545 (39%, M^+-CH_3) 517 (17%, M^+-CHMe_2), 501 (100%, $M^+-NH_2CHMe_2$), 460 (25%, $M^+-CHMe_2-NCHMe_2$), 387 (27%, $M^+-Me_2SiNHCHMe_2-NCHMe_2$). Anal. calc. for $C_{28}H_{50}N_2Si_2Zr$: C, 59.83; H, 8.83; N, 4.98. Found: C, 62.37; H, 9.34; N, 6.10.

$Hf(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\textit{i}Pr)_2$ (**3b**)

Following a similar procedure described for the preparation of **2b**, $Li_2(C_5Me_4SiMe_2N\textit{i}Pr)$ (1.00 g, 4.01 mmol) was reacted with $HfCl_4(THF)_2$ (1.86 g, 4.01

mmol) in THF to obtain $Hf(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NiPr)_2$ (**3b**) (0.65 g, 25% yield) as colourless crystals, suitable for X-ray diffraction studies. ^1H NMR (C_6D_6) : δ 0.53, 0.64 (s, 3 H, $SiCH_3$), 1.18, 1.23 (d, $^3J_{HH}$ = 6.4 Hz, 3 H, $CH(CH_3)_2$), 1.88, 1.90, 2.02, 2.30 (s, 3 H, ring CH_3), 3.99 (m, 1 H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6) : δ 8.6, 8.7 ($SiCH_3$), 11.5, 12.2, 13.6, 15.3 (ring CH_3), 28.9, 30.0 ($CH(CH_3)_2$), 52.1 ($CH(CH_3)_2$), 106.4 (ring C attached to Si), 121.6, 124.6, 125.0, 127.2 (ring C). EI MS: m/z 650 (52%, M^+), 591 (13%, $M^+ - NH_2CHMe_2$), 534 (20%, $M^+ - Me_2SiNHCHMe_2$), 505 (97%, $M^+ - Me_2SiNHCHMe_2 - 2\,CH_3$). Anal. calc. for $C_{28}H_{50}N_2Si_2Hf$: C, 51.81; H, 7.82; N, 4.31. Found: C, 47.80; H, 7.82; N, 3.79.

$Li[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2CH_2OMe)_2]$ (4)

YCl_3 (223 mg, 1.14 mmol) and $Li_2(C_5Me_4SiMe_2NCH_2CH_2CH_2OMe)$ (638 mg, 2.28 mmol) were combined in a flask and pre-cooled THF (15 ml) was added at —78°C with stirring. The resulting mixture was allowed to warm to room temperature and stirred for 13 h. The solvent was removed *in vacuo* and the crude product extracted with 2×10 ml of toluene. LiCl was filtered off and the clear solution was concentrated to 2 ml. After crystallization at -25°C for 24 h, the mother liquor was decanted off and the crystals were dried *in vacuo* to yield 605 mg (85%) of **4** as pale yellow microcrystals. ^1H NMR (C_6D_6): δ 0.52, 0.64 (s, 6 H, $SiCH_3$), 1.50 (m, 4 H, $NCH_2CH_2CH_2O$), 2.08, 2.17, 2.21, 2.32 (s, 6 H, ring CH_3), 2.81 (s, 6 H, OCH_3), 2.92, 3.09 (m, 2 H, CH_2O), 3.38 (m, 4 H, NCH_2); ^{13}C NMR (C_6D_6) : δ 2.3, 9.3 ($SiCH_3$), 10.8, 12.0, 13.4, 15.7 (ring CH_3), 37.2 ($NCH_2CH_2CH_2O$), 46.9 (NCH_2), 58.9 (OCH_3), 74.8 (CH_2O), 105.8 (ring C attached to Si), 120.0, 121.3, 121.4, 124.3 (ring C). Anal. calc. for $C_{30}H_{54}LiN_2O_2Si_2Y$: C, 57.49; H, 8.68; N, 4.47. Found: C, 51.06; H, 8.28; N, 4.42.

$Li[Y\{\eta^5\text{-}C_5Me_4SiMe_2NH(CH_2CH_2OMe)\}_2(C{\equiv}CPh)_2]$ (6)

$Li[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)_2]$ (**5**) (57 mg, 95 μmol) was dissolved in C_6D_6 (0.5 ml) and phenylacetylene (20 mg, 196 μmol) was added at room temperature. The solution was kept at 5°C overnight, before the NMR spectra were recorded. The compound was isolated by removal of the solvent *in vacuo* and the crude product recrystallized from hexane at -30°C to yield 63 mg (83%) of **6** as colourless microcrystals. ^1H NMR (C_6D_6) : δ 0.54 (s, 12 H, $SiCH_3$), 1.40 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, NH), 2.21, 2.52 (s, 12 H, ring CH_3), 2.67 (dt, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 5.5 Hz, 4 H, NCH_2), 2.83 (s, 6 H, OCH_3), 2.89 (t, 4 H, $^3J_{HH}$ = 5.5 Hz, CH_2O), 6.99 (m, 2 H, 4-C_6H_5), 7.07 (m, 4 H, 3-C_6H_5), 7.49 (m, 4 H, 2-C_6H_5); ^{13}C NMR (C_6D_6): δ 1.8 ($SiCH_3$), 11.9, 15.6 (ring CH_3), 41.5 (NCH_2), 58.3 (OCH_3), 75.0 (CH_2O), 111.7 (ring C attached to Si), 114.9 (d, $^2J_{YC}$ = 10.1 Hz, $C{\equiv}CPh$), 121.4, 125.3 (ring C), 126.5 (*ipso*-C_6H_5), 126.9 (*para*-C_6H_5), 128.4 (*meta*-C_6H_5), 131.7 (*ortho*-C_6H_5), 141.2 (dq, $^1J_{YC}$ = 49.9 Hz, $^1J_{LiC}$ = 7.3 Hz, $C{\equiv}CPh$). Anal. calc. for $C_{44}H_{62}LiN_2O_2Si_2Y$: C, 65.81; H, 7.78; N, 3.49. Found: C, 65.86; H, 8.50; N, 4.56.

X-ray crystal structure analysis of **3b**

Crystal data for **3b** are summarized in Table 1. The compound, obtained as colourless crystals by cooling a concentrated pentane solution, crystallizes in the monoclinic space group $C2/c$ (No. 15). Data collection in the range $3.4° < \theta < 29.9°$ was performed using ω-scans on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo-K_α radiation. Data correction for Lorentz polarization and absorption (empirically using PSI-scans) was carried out using the program system MolEN [20a]. From 7235 measured reflections, all 4310 independent reflections were used and 251 parameters were refined by full-matrix least-squares against all F_o^2 data (SHELXL-93) [20b]. The structure was solved using direct methods (SHELXS-86) [20c] and difference Fourier syntheses and refined with anisotropic thermal parameters for non-hydrogen atoms. All hydrogen atoms were refined with isotropic thermal parameters. The refinement converged with $R = 0.0182$, $wR_2 = 0.0360$ for all observed F_o data, goodness-of-fit 1.097. Listings of all crystal data and refinement parameters, atomic parameters including hydrogen atoms, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Centre.

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