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Synthesis and characterization of sterically expanded $ansa-\eta^1$ -fluorenyl-amido complexes

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Abstract

The octamethyloctahydrodibenzofluorenyl (Oct) ligand has been incorporated into twelve *ansa*-Oct-amido complexes having the general structures $Me_2Si(\eta^1-C_{29}H_{36})(\eta^1-N-'Bu)MX_2 \cdot L$ or $Me_2Si(\eta^5-C_{29}H_{36})(\eta^1-N-'Bu)MX_2$ (M = Zr or Hf): 2 (X = Cl, L = Et₂O); 3 (X = Br, L = Et₂O); 4 (X = Me, L = Et₂O); 5 (X = Me, L = THF); 6 (X = CH₂Ph); and 7 (X = CH₂SiMe₃). The solid-state structures have been determined for seven of these complexes by X-ray crystallography, revealing $\eta^5-C_{29}H_{36}$ coordination for the ether-free, pseudotetrahedral species 6-Zr, 6-Hf, and 7-Zr, but $\eta^1-C_{29}H_{36}$ coordination for the ether-bound, trigonal bipyramidal species 2-Zr, 3-Zr, 3-Hf, and 5-Zr. The unusual $\eta^1-C_{29}H_{36}$ coordination was assigned because only one metal–carbon bond in each structure was in the range of 2.281–2.330 Å; a second metal–carbon distance was found between 2.731 and 2.847 Å; the remaining metal–carbon distances were found between 3.130 and 4.029 Å. An increase in the hapticity of these and other Oct- and fluorenyl-containing compounds was correlated to a convergence in the carbon–carbon bond lengths within the relevant five-membered rings. © 2005 Elsevier Ltd. All rights reserved.

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1. Introduction

The world demand for linear low density polyethylene (LLDPE) grew from 12 billion kg in 2000 to 18 billion kg in 2004 – an annualized growth rate of about 10% [1]. Despite the numerous advantages associated with single-site catalyst technology [2–5], only about 5% of the current demand of LLDPE is met with such discrete, organometallic catalysts. Nonetheless, this is a rapidly growing percentage that has spawned considerable research in the area of *ansa*cyclopentadienyl-amido complexes, commonly known as "constrained geometry catalysts" (CGCs) [6]. Fig. 1 depicts the prototypical titanium CGC, Me₂- Si(η^5 -C₅Me₄)(η^1 -N-^{*t*}Bu)TiCl₂ (1) [7–10], which relies on a silicon-linked tetramethylcyclopentadienyl-amido ligand [11,12].

Synthetic modification of **1** has led to indenyl-[13–17] and fluorenyl-containing [18–24] variants, some of which exhibit enhanced polymerization activity or increased α -olefin incorporation rates. All structural characterizations of existing group IV cyclopentadienyl-, indenyl-, and fluorenyl-amido complexes reveal the expected hapticities: η^1 to nitrogen and η^5 to the carbon-based ligand. Very recently, we reported the sole exception to this rule and found that inclusion of a sterically expanded fluorenyl ligand, octamethyloctahydrodibenzofluorenyl (Oct) [25], resulted in η^1 ligation to the Oct moiety; see Me₂Si(η^1 -C₂₉H₃₆)(η^1 -N-^{*t*}Bu)ZrCl₂ · OEt₂ (**2-Zr**) in Fig. 2 [26]. Herein, we report the synthesis and structural characterization of several additional *ansa*-Oct-amido complexes that

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Fig. 1. The titanium *ansa*-tetramethylcyclopentadienyl-amido precatalyst 1, upon activation with methylaluminoxane (MAO), readily copolymerizes ethylene and α -olefins to form linear low density polyethylene (LLDPE).



Fig. 2. The first CGC with η^1 ligation to the carbon-based fivemembered ring [26]. X-ray structure of **2-Zr** with thermal ellipsoids drawn at 50% probability and hydrogen atoms omitted.

contain the η^1 -Oct motif. These structures are compared to alkylated derivates with normal η^5 -Oct binding in the context of quantifying and understanding this variable hapticity, which may be related to the unusual preference toward α -olefins over ethylene that **2-Zr**/MAO can exhibit.

2. Results and discussion

2.1. Synthesis of Zr and Hf complexes

The synthesis of zirconium and hafnium Oct-amido complexes (Scheme 1) parallels that of Okuda for the synthesis of zirconium fluorenyl-amido complexes [18]. Octamethyloctahydrodibenzofluorene [27] is deprotonated with *n*-butyllithium [25,28] and transferred into a hexane solution containing excess dimethyldichlorosilane. Subsequent reaction with Me₃CNHLi, followed by double deprotonation with *n*-butyllithium and combination with ZrCl₄ or HfCl₄ provides 2-Zr or 2-Hf. Interestingly, these five steps can be performed in two flasks (OctLi must be added to excess SiMe₂Cl₂), without isolation of the intermediates or their separation from salts, to yield 17 g of 2-Zr as yellow microcrystals in 31.6% overall yield. The dibromide 3-Zr was obtained from ZrBr₄. Additionally, we have shown that 3-Zr and 3-Hf can be synthesized from the dichlorides 2-Zr and 2-Hf via direct halide exchange with an excess of LiBr in diethyl ether.

2-Zr and 2-Hf are readily derivatized with alkylating agents. The use of methyllithium with diethyl ether as solvent provides diethyl ether adducts 4-Zr and 4-Hf, whereas with methylmagnesium chloride in the presence of tetrahydrofuran, THF adducts 5-Zr and 5-Hf are obtained. The use of larger alkylating agents does not afford ethereal adducts. The dibenzyl species 6-Zr and 6-Hf are made from benzyl potassium and the bis(trimethylsilylmethyl) species 7-Zr and 7-Hf are made from trimethylsilylmethyllithium.



Scheme 1. Synthetic route to zirconium and hafnium ansa-Oct-amido complexes 2-7.

2.2. X-ray crystallography of Zr and Hf complexes

Crystals suitable for X-ray crystallography were obtained for complexes **3-Zr**, **3-Hf**, and **5-Zr** by cooling saturated diethyl ether solutions. Crystals of **6-Zr** and **6-Hf** were grown by vapor diffusion of diethyl ether into saturated dichloromethane solutions, while crystals of **7-Zr** were obtained by cooling a saturated pentane solution. Fig. 3 depicts the structural results of the X-ray crystallography.

It is readily apparent that ethereal solvents remain bound to the metal in **3-Zr**, **3-Hf**, and **5-Zr**, resulting in a trigonal bipyramid with oxygen and nitrogen in the apical positions. This trigonal bipyramid structure is unprecedented for fluorenyl-amido complexes; even the remarkably similar Me₂Si(η^{5} -2,7-^{*t*}Bu₂-C₁₃H₆)(η^{1} -N-^{*t*}Bu)ZrCl₂ [29,30] and Me₂Si(η^{5} -3,6-^{*t*}Bu₂-C₁₃H₆)(η^{1} -N-^{*t*}Bu)ZrCl₂ [23,31] adopt the η^{5} , pseudotetrahedral geometry. Apparently there is an important difference between a 2,3,6,7-*tetra*-substituted fluorenyl ligand (Oct) and a *di*-substituted fluorenyl ligand. **3-Zr** and **3-Hf** are isomorphic, and only **5-Zr** cocrystallizes with solvent, packing one diethyl ether molecule into the cleft of each Oct ligand. In this case, note the selectivity of the metal to bind THF despite the use of diethyl ether as the crystallization solvent.

6-Zr, **6-Hf**, and **7-Zr**, which bear the larger benzyl or trimethylsilylmethyl groups, crystallize as ether-free species with a pseudotetrahedral coordination sphere and η^5 ligation to Oct. **6-Zr** and **6-Hf** are isomorphic and each of these structures contains one benzyl group that is arguably η^2 . The M–CH₂Ph bond length is 2.295 Å for **6-Zr** (2.299 Å for **6-Hf**) and the M–(C_{ipso}) distance is 2.793 Å for **6-Zr** (2.871 Å for **6-Hf**). The structure of **7-Zr** is quite similar to that published for the parent fluorenyl-containing compound, Me₂Si(η^5 -C₁₃H₈)(η^1 -N-^{*t*}Bu)Zr(CH₂SiMe₃)₂ [18].

Table 1 lists selected bond lengths and angles for 2-Zr [26], 3-Zr, 3-Hf, 5-Zr, 6-Zr, 6-Hf, and 7-Zr. In the η^1



Fig. 3. X-ray structures of 3-Zr, 3-Hf, 5-Zr, 6-Zr, 6-Hf, and 7-Zr with thermal ellipsoids drawn at 50% probability and hydrogen atoms omitted.

Table 1 Selected bond lengths (Å) and angles (°)

Complex	M–C(1)	M–N	M-X(1)	M-X(2)	М–О	cent-C(1)–Si ^a	Si-N-M	X-M-X	N–M–O
2-Zr ($Cl_2 \cdot Et_2O$)	2.299(7)	2.013(5)	2.4155(19)	2.3918(18)	2.330(5)	203.67	99.1(2)	112.92(7)	169.87(19)
3-Zr ($Br_2 \cdot Et_2O$)	2.300(8)	2.019(6)	2.5427(13)	2.5387(13)	2.322(6)	202.78	99.0(3)	112.31(5)	169.6(2)
3-Hf ($Br_2 \cdot Et_2O$)	2.281(8)	2.022(7)	2.5112(14)	2.4974(15)	2.297(6)	204.90	98.8(3)	111.93(5)	167.1(3)
5-Zr (Me ₂ \cdot THF)	2.330(5)	2.068(4)	2.240(6)	2.274(5)	2.280(4)	197.86	99.3(2)	111.8(2)	167.05(16)
6-Zr ((CH ₂ Ph) ₂)	2.397(2)	2.052(2)	2.295(2)	2.316(2)		156.80	103.47(9)	116.20(9)	
6-Hf ((CH ₂ Ph) ₂)	2.373(1)	2.087(8)	2.299(9)	2.305(11)		155.80	99.9(4)	111.6(4)	
7-Zr ((CH ₂ SiMe ₃) ₂)	2.390(2)	2.0648(18)	2.249(2)	2.265(2)		156.46	102.85(9)	107.30(8)	

^a cent is defined as the centroid of the five-membered ring of the Oct ligand.

trigonal bipyramidal structures, the metal-C(1) bond lengths are consistently shorter (2.281–2.330 Å) than the corresponding bond lengths in the η^5 pseudotetrahedral structures (2.373-2.397 Å). The shortening of the remaining M–C bond upon η^5 to η^1 ring-slip is typical for cyclopentadienyl [32] and indenyl ligands [33]. In ansa-metallocenes and cyclopentadienyl-amido complexes, the C_{5centroid}-C(1)-Si angle is always less than 180°; examples are rac-Me₂Si(η^{5} -C₉H₆)₂ZrCl₂ (163.7°) [34] and Me₂Si(η^{5} -C₅Me₄)(η^{1} -N-^{*t*}Bu)TiCl₂ (152.3°) [35]. For the η^5 complexes in Table 1, this angle is ~156°, a typical value. Strikingly, the C_{5centroid}–C(1)– Si angles for the η^1 complexes are considerably larger than 180° and range from 197.9° to 204.9°. Thus, the silicon atom and the metal are on opposite sides of the Oct *ligand.* This results in the most sterically open class of CGCs reported.

2.3. Hapticity analysis of Zr and Hf complexes by X-ray crystallography

While η^5 -fluorenyl ligands are the most common [36–40], a number of η^3 -fluorenyl examples have also been documented [41–46]. In contrast, η^1 -fluorenyl ligands are quite rare. The first definitive examples were found with octahedral mid-transition metal species such as $Mn(\eta^1-C_{13}H_9)(CO)_3(P(n-Bu)_3)_2$ [47], $Mn(\eta^1-C_{13}H_9)(CO)_3(PEt_3)_2$ [48], and $Re(\eta^1-C_{13}H_9)(CO)_5$ [49,50]. Later, examples were found with early transition metal species such as pseudotetrahedral $(\eta^5-C_5H_4Me)_2Zr(\eta^1-C_{13}H_9)Cl, (\eta^5-C_5H_5)_2Zr(\eta^1-C_{13}H_9)_2$ [51], and pseudotrigonal bipyramidal $Me_2C(\eta^5-C_5H_4)(\eta^1-C_{13}H_8)TaMe_3$ [52].

The assignment of hapticity can sometimes be arbitrary [53], but the metrical parameters cataloged in



Fig. 4. Structures of 2-Zr, 3-Zr, 3-Hf, 5-Zr, 6-Zr, 6-Hf, and 7-Zr with the Oct ligand truncated to the five-membered ring. Bond lengths and interatomic distances (Å) correspond to the metal–Oct interaction, moving clockwise from the C(1) carbon.

Fig. 4 largely support the conclusion that 2-Zr, 3-Zr, **3-Hf**, and **5-Zr** are η^1 , while **6-Zr**, **6-Hf**, and **7-Zr** are η^5 . Assignments from the literature place the threshold for zirconium-carbon bonding between 2.65 and 2.81 A [41,54]. For example, the two "non-bonded" carbons in $(\eta^5-C_{13}H_9)(\eta^3-C_{13}H_9)ZrCl_2$ are 2.801 and 2.807 Å from the metal while the remaining eight "bonded" carbons are between 2.395 and 2.645 Å away [42]. In Re(η^1 -C₁₃H₉)(CO)₅ the bonded carbon is 2.307 Å from rhenium while the four unequivocally non-bonded carbons are between 3.193 and 4.149 Å from the metal [50]. In structures 2-Zr, 3-Zr, 3-Hf, and 5-Zr, the bonded carbon is between 2.281 and 2.330 Å from the metal. Each structure has one metalcarbon interatomic distance between 2.731 and 2.847 Å, which is at the upper limit of the bonding range. The remaining three distances for each structure are at least 3.130 Å, considerably beyond normal zirconium-carbon or hafnium-carbon bond lengths.

An alternative method for assessing hapticity is by measurement of the carbon-carbon bond lengths of the five-membered ring. In octamethyloctahydrodibenzofluorene, long bonds are found connecting the sp^3 carbon to the aromatic rings (1.515 Å) and short bonds are found as part of the aromatic rings (1.401 Å) [26]. The parameter δ can be defined as the difference between these bond lengths – or average difference for non-symmetrical species – as defined in Fig. 5. Table 2 lists carbon-carbon bond lengths and the calculated parameter δ for a variety of fluorenyl- and Octcontaining compounds. The entries are listed in order of *decreasing* δ , which corresponds to *increasing* hapticity since the carbon-carbon bond lengths are predicted to



Fig. 5. The bond length difference parameter δ is 0.114 Å for octamethyloctahydrodibenzofluorene and is predicted to decrease with increasing hapticity.

become more similar as an η^5 , aromatic cyclopentadienide core is approached.

The largest value of δ (0.095 Å) is found for Re(η^{1} - $C_{13}H_9$ (CO)₅, an electronically (18e⁻) and coordinatively (octahedral) saturated compound that cannot increase its η^1 hapticity with the fluorenyl ligand. Although $(\eta^5 - C_5 H_4 Me)_2 Zr(\eta^1 - C_{13}H_9)Cl$ and $Me_2 C(\eta^5 - C_5 H_4 Me)_2 Zr(\eta^5 - C_5 H_4 Me)_2 Zr(\eta$ C_5H_4)(η^1 - $C_{13}H_8$)TaMe₃ are not electronically saturated, sterics probably dissuade a greater hapticity, resulting in a high δ value (0.081 for both). The next three species are 3-Hf, 3-Zr, and 5-Zr, which have δ values of 0.069, 0.066, and 0.047 Å, respectively, which still indicate significant carbon-carbon bond length differences. This last value is also found for a complex reported as η^3 , Mo(η^3 -C₁₃H₉)(η^3 -C₃H₅)₃. The remaining twelve compounds, including 6-Zr, 7-Zr, and 6-Hf, have δ values of 0.030 Å or less and are predicted to be η^5 . Three anomalies exist in this range: $(\eta^5-C_{13}H_9)(\eta^3 C_{13}H_9$ /ZrCl₂ ($\delta = 0.025$), which is reported as η^3 ; 2-Zr $(\delta = 0.021)$, which is reported as η^1 ; and fluorenylLi(Et₂O)₂ ($\delta = -0.018$), which is reported as η^2 . It

Table 2

Carbon–carbon bond lengths of the fluorenyl or Oct five-membered ring along with the bond length difference parameter $\delta = (a + e - b - d)/2$ in Å

Compound	а	b	с	d	е	δ	References
OctH (C ₂₉ H ₃₈)	1.515(2)	1.401(2)	1.471(2)	1.401(2)	1.515(2)	0.114	[26]
Fluorene ($C_{13}H_{10}$)	1.504(2)	1.397(2)	1.472(3)	1.397(2)	1.504(2)	0.107	[55]
$Re(\eta^{1}-C_{13}H_{9})(CO)_{5}$	1.506	1.405	1.451	1.417	1.505	0.095	[50]
$(\eta^{5}-C_{5}H_{4}Me)_{2}Zr(\eta^{1}-C_{13}H_{9})Cl$	1.505(5)	1.415(5)	1.461(5)	1.405(5)	1.477(5)	0.081	[51]
$Me_2C(\eta^5-C_5H_4)(\eta^1-C_{13}H_8)TaMe_3$	1.502(4)	1.417(5)	1.448(4)	1.417(4)	1.493(4)	0.081	[52]
3-Hf $(Br_2 \cdot Et_2O)$	1.485(10)	1.410(10)	1.479(11)	1.409(10)	1.472(12)	0.069	this work
3-Zr ($Br_2 \cdot Et_2O$)	1.474(11)	1.439(10)	1.449(11)	1.383(11)	1.479(12)	0.066	this work
5-Zr (Me ₂ · THF)	1.459(8)	1.428(7)	1.445(8)	1.417(8)	1.480(7)	0.047	this work
$Mo(\eta^{3}-C_{13}H_{9})(\eta^{3}-C_{3}H_{5})_{3}$	1.476(3)	1.407(3)	1.465(4)	1.433(3)	1.458(3)	0.047	[43]
$Me_2Si(\eta^5-3,6^{-t}Bu_2-C_{13}H_6)(\eta^1-N-tBu)ZrCl_2$	1.46(1)	1.43(1)	1.46(1)	1.42(1)	1.45(1)	0.030	[23]
6-Zr ((CH ₂ Ph) ₂)	1.455(3)	1.426(3)	1.447(3)	1.430(3)	1.459(3)	0.029	this work
7-Zr ($(CH_2SiMe_3)_2$)	1.453(3)	1.426(3)	1.454(3)	1.421(3)	1.448(3)	0.027	this work
6-Hf ((CH ₂ Ph) ₂)	1.454(14)	1.416(12)	1.447(14)	1.445(14)	1.459(13)	0.026	this work
$(\eta^{5}-C_{13}H_{9})(\eta^{3}-C_{13}H_{9})ZrCl_{2}$	1.50	1.41	1.47	1.43	1.39	0.025	[42]
2-Zr ($Cl_2 \cdot Et_2O$)	1.468(9)	1.431(8)	1.434(8)	1.437(9)	1.441(9)	0.021	[26]
$Me_2Si(\eta^5-C_{13}H_8)(\eta^1-N-'Bu)Zr(CH_2SiMe_3)_2$	1.450(4)	1.426(4)	1.442(4)	1.431(4)	1.442(4)	0.018	[18]
$Me_2C(\eta^5-C_5H_4)(\eta^5-C_{29}H_{36})ZrCl_2$	1.449(5)	1.431(5)	1.434(5)	1.440(5)	1.443(5)	0.011	[56]
$Ph_2C(\eta^5-C_5H_4)(\eta^5-C_{29}H_{36})ZrCl_2$	1.457(6)	1.430(6)	1.443(6)	1.458(6)	1.447(6)	0.008	[25]
$(\eta^{5}-C_{13}H_{9})(\eta^{3}-C_{13}H_{9})ZrCl_{2}$	1.44	1.42	1.44	1.44	1.43	0.005	[42]
$Me_2C(\eta^5-C_5H_4)(\eta^5-C_{13}H_8)ZrCl_2$	1.45(1)	1.44(1)	1.43(1)	1.44(1)	1.43(1)	0.000	[57]
FluorenylLi(Et ₂ O) ₂	1.424(4)	1.443(4)	1.434(4)	1.443(5)	1.426(5)	-0.018	[40]

Table 3

Selected ¹H NMR and ¹³C NMR chemical shifts (ppm) for Oct–Zr species: aromatic C–H in the 1 and 4 positions; M-C(1); and aromatic C (in C₆D₆ except **7-Zr**, recorded in CDCl₃)

References
13.6 this work
and work
18.9 [26]
48.8 this work
46.7 this work
41.9 this work
47.0 this work
46.1 this work
43.0 this work
42.8 this work

should be noted that δ is an *indirect* measure of hapticity. It only measures carbon–carbon bond length distortions that occur in response to a metal's location and bonding. Thus, δ and hapticity are reasonably correlative, but the exceptions remind us that hapticity is best determined by measuring metal–carbon interatomic distances.

2.4. Hapticity analysis of Zr complexes in solution by NMR

The solution ¹H NMR spectra of the diethyl ether complexes (2-Zr, 2-Hf, 3-Zr, 3-Hf, 4-Zr, and 4-Hf) show sharp resonances for the ethereal protons, a trait usually attributed to unbound ether species. Thus suggests solution species with η^5 -Oct ligation. The THF adducts, however, provide somewhat broad resonances for the ethereal protons, indicating that THF coordination and low Oct hapticity are maintained in solution. Careful inspection of the ¹H and ¹³C NMR chemical shifts of compounds 2-Zr through 7-Zr indeed reveals unusual chemical shifts for only the THF adduct 5-Zr (Table 3). The aromatic C-H protons in the 1 and 4 positions of the Oct moiety are the most upfield of this group at 7.82 and 8.15 ppm. The M-C(1) carbon is the most downfield (86.3 ppm) and, of the aromatic carbons, two have comparatively high chemical shifts (133.6 and 137.6 ppm) and four have comparatively low chemical shifts (117.4, 118.5, 139.7 and 141.9 ppm). These unusual chemical shifts for 5-Zr are mirrored in Me₂Si(η^1 -C₂₉H₃₆)(η^1 -N-^tBu)ZrCl₂. THF and Me₂Si(η^1 -C₂₉H₃₆)(η^1 -N-^{*t*}Bu)ZrBr₂ · NCMe (see Table 3), suggesting that each of these also maintains η^1 -Oct ligation in solution.

3. Conclusions

A series of sterically expanded *ansa*-fluorenyl-amido zirconium and hafnium complexes with the general formula $Me_2Si(\eta^n-C_{29}H_{36})(\eta^1-N-{}^tBu)MX_2 \cdot L_m$ was synthesized and characterized. Incorporation of the octamethyloctahydrodibenzofluorenyl (Oct) ligand effected ethereal binding in the solid-state when the remaining ligands were small (X = Cl, Br, or Me). Ether-free species were observed when larger ligands (X = benzyl or trimethylsilylmethyl) were present. X-ray crystallography established that an unusual trigonal bipyramidal η^1 -Oct structure accompanied ethereal binding (n = 1, m = 1), while the ether-free species adopted the anticipated pseudotetrahedral η^5 -Oct structure (n = 5, m = 0). The hapticity assignments were made largely by analyzing the relevant metal–carbon distances, but a correlation between hapticity and converging carbon–carbon bond lengths of the five-membered ring was also identified.

4. Experimental

4.1. General remarks

All air sensitive procedures were carried out under a purified atmosphere of nitrogen in a glove box equipped with a -35 °C freezer, or by using standard Schlenk line techniques. Solvents were dried and distilled under nitrogen into Straus flasks and stored until needed. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone; *n*-heptane and dichloromethane were distilled from calcium hydride; and toluene was distilled from elemental sodium.

The commercially available reagents *n*-butyllithium (Acros, 2.5 M in hexanes or Alfa Aesar, 2.87 M in hexanes), LiCH₂SiMe₃ (Aldrich, 1.0 M in pentane), MeLi (Aldrich, 1.6 M in diethyl ether), MeMgCl (Aldrich, 3.0 M in tetrahydrofuran), zirconium tetrachloride (Strem, 99.5+%), hafnium tetrachloride (Strem, 99.9+%), zirconium tetrabromide (Strem, 98%), and lithium bromide (Aldrich, 99.995+%) were used as received, unless otherwise noted. Both KCH₂Ph [58] and the ligand Me₃CNHSiMe₂(C₂₉H₃₇) [26] were prepared according to literature procedures.

All NMR chemical shifts are given in ppm and were recorded on a Mercury-300BB spectrometer (1 H, 299.91 MHz; 13 C { 1 H}, 75.41 MHz) using the residual

protonated solvent peak as an internal standard (CDCl₃: 1 H, 7.27 ppm; 13 C, 77.0 ppm. C₆D₆: 1 H, 7.15 ppm; 13 C, 128.0 ppm).

4.2. Syntheses

4.2.1. Synthesis of $Me_2Si(\eta^{l}-C_{29}H_{36})(\eta^{l}-N^{-t}Bu)ZrCl_2 \cdot OEt_2 (2-Zr)$

In the glove box $Me_3CNHSiMe_2(C_{29}H_{37})$ (3.00 g, 6.26 mmol) was charged into a 100 ml pear-shaped round bottom and then attached to a 3 cm swivel frit. The frit was then evacuated and diethyl ether (50 ml) was vacuum transferred in. Next, n-butyllithium (5.51 ml, 13.77 mmol, 2.5 M in hexanes) was syringed in. The orange slurry was stirred for 20 h and then the diethyl ether was removed under vacuum. ZrCl₄ (1.46 g, 6.26 mmol) was added in the glove box and diethyl ether (40 ml) was vacuum transferred in on the line. After slowly warming to room temperature and stirring the light brown slurry for 48 h, the LiCl was filtered off and the cake was extracted until colorless. The slurry was concentrated to about 10 ml and the precipitated solid was collected by filtration. The cake was washed once to remove a brown oil and then evacuated until dry. This yielded 1.42 g (31.8%) of product as a neon yellow solid. Large rod-shaped crystals can be grown by cooling a saturated diethyl ether solution to -35 °C. ¹H NMR (C₆D₆): δ 0.86 (s, 6H, (CH₃)₂Si), 1.10 (t, ³J_{HH} = 7.0 Hz, 6H, ether-CH₃), 1.26 (s, 9H, -C(CH₃)₃), 1.28, 1.35, 1.38, 1.39 (s, 24H, Oct-CH₃), 1.62 (m, 8H, Oct– CH_2), 3.25 (q, ${}^{3}J_{HH} = 7.0$ Hz, 4H, ether- CH_2), 8.01, 8.24 (s, 4H, Oct- CH_1). ¹³C {¹H} NMR (C₆D₆): δ 5.9, 15.5, 32.3, 32.6, 32.8, 32.9, 33.4, 34.95, 35.02, 35.3, 35.4, 56.4, 66.0, 71.9, 121.5, 123.2, 125.3, 134.8, 145.6, 148.9. Elemental analysis: Anal. Calc.: C, 62.44; H, 8.13; N, 1.87; Cl, 9.45. Found: C, 61.40; H, 8.24; N, 1.81; Cl, 9.45%.

4.2.2. Synthesis of $Me_2Si(\eta^1 - C_{29}H_{36})(\eta^1 - N^{-t}Bu)HfCl_2 \cdot OEt_2$ (**2-Hf**)

2-Hf was prepared in a manner analogous to **2-Zr** except that HfCl₄ (3.34 g, 10.43 mmol) was utilized yielding 3.30 g (39.5%) of **2-Hf** as a yellow solid. ¹H NMR (C₆D₆): δ 0.84 (s, 6H, (CH₃)₂Si), 0.99 (t, ³J_{HH} = 6.0 Hz, 6H, ether–CH₃), 1.31, 1.34, 1.39, 1.42 (s, 24H, Oct–CH₃), 1.37 (s, 9H, –C(CH₃)₃), 1.65 (app. s, 8H, Oct–CH₂), 3.19 (q, ³J_{HH} = 6.0 Hz, 4H, ether–CH₂), 7.99, 8.22 (s, 4H, Oct–CH₁).

4.2.3. Synthesis of $Me_2Si(\eta^1-C_{29}H_{36})(\eta^1-N^{-t}Bu)ZrBr_2 \cdot OEt_2$ (**3-Zr**)

3-Zr was prepared in a manner analogous to **2-Zr** except that ZrBr₄ (2.57 g, 6.26 mmol) was utilized yielding 1.30 g (24.8%) of **3-Zr** as a bright yellow powder. Large rod-shaped crystals can be grown by cooling a saturated diethyl ether solution to $-35 \,^{\circ}$ C. ¹H NMR (C₆D₆): δ

0.86 (s, 6H, (CH₃)₂Si), 1.11 (t, ${}^{3}J_{HH} = 7.0$ Hz, 6H, ether–CH₃), 1.27, 1.34, 1.39, 1.41 (s, 24H, Oct–CH₃), 1.31 (s, 9H, –C(CH₃)₃), 1.61 (m, 8H, Oct–CH₂), 3.26 (q, ${}^{3}J_{HH} = 7.0$ Hz, 4H, ether–CH₂), 8.01, 8.27 (s, 4H, Oct–CH₁). ${}^{13}C$ {¹H} NMR (C₆D₆): δ 5.8, 15.5, 32.1, 32.7, 33.0, 34.98, 35.0, 35.3, 35.4, 56.9, 65.9, 72.0, 122.0, 124.0, 126.0, 134.6, 146.0, 148.8.

4.2.4. Synthesis of $Me_2Si(\eta^1-C_{29}H_{36})(\eta^1-N^{-t}Bu)HfBr_2 \cdot OEt_2$ (**3-Hf**)

In the glove box, 2-Hf (0.13 g, 0.16 mmol) was charged into a 100 ml pear-shaped round bottom flask followed by the addition of anhydrous LiBr (4.90 g, 56.42 mmol). Next, the flask was attached to a 3 cm swivel frit and brought out to the line where diethyl ether (60 ml) was vacuum transferred in. The slurry was then stirred for 2 days after which time the solvent was removed under vacuum and pentane (30 ml) was vacuum transferred in. All insoluble material was removed via filtration and the cake was extracted until colorless. Concentration of the filtrate to 5 ml followed by filtration yielded 0.07 g (69.0%) of 3-Hf as an orange-yellow powder. Large rod-shaped crystals can be grown by cooling a saturated diethyl ether solution to -35 °C. X-ray crystallography suggested that complete salt metathesis of the Hf-Cl bonds had been achieved. This was further supported by ¹H NMR via a characteristic shift of the aromatic Oct– CH_1 protons from 8.22 ppm (2-Hf) to 8.26 ppm (3-Hf). A similar shift is observed between **2-Zr** and **3-Zr**. ¹H NMR (C_6D_6): $\delta 0.89$ (s, 6H, (CH_3)₂Si), 1.03 (t, ${}^{3}J_{\text{HH}} = 6.0$ Hz, 6H, ether–CH₃), 1.28, 1.31, 1.35, 1.36 (s, 24H, Oct-CH₃), 1.32 (s, 9H, -C(CH₃)₃), 1.63 (m, 8H, Oct– CH_2), 3.19 (q, ${}^{3}J_{HH} = 6.0$ Hz, 4H, ether– CH₂), 8.00, 8.26 (s, 4H, Oct-CH₁).

4.2.5. Synthesis of $Me_2Si(\eta^1 - C_{29}H_{36})(\eta^1 - N^{-t}Bu)$ Zr $Me_2 \cdot OEt_2$ (4-Zr)

In the glove box 2-Zr (0.50 g, 0.67 mmol) was charged into a 100 ml pear-shaped round bottom flask, which was then attached to a 3 cm swivel frit. The frit was evacuated on the vacuum line and diethyl ether (50 ml) was then vacuum transferred in. Next, a LiBrfree diethyl ether solution of CH₃Li (0.83 ml, 1.33 mmol, 1.6 M in diethyl ether) was slowly syringed into the yellow solution while vigorously stirring. The solution began to bleach and acquire a very pale fluorescent yellow color. (Note: Extended exposure to excess CH₃Li leads to a dark brown/black solution and complete decomposition of the product in a matter of hours.) After 2 h the precipitated LiCl was removed via filtration and extracted until colorless. Concentration of the filtrate to 10 ml and collection of the precipitated product on the frit led to 0.42 g (89.0%) of product as a pale yellow solid. ¹H NMR (C_6D_6): δ -0.59 (s, 6H, $Zr(CH_3)_2$), 0.89 (s, 6H, $(CH_3)_2Si$), 1.10 (t, ${}^{3}J_{\text{HH}} = 7.0 \text{ Hz}$, 6H, ether-CH₃), 1.32, 1.37 (s, 24H, Oct– CH_3), 1.33 (s, 9H, – $C(CH_3)_3$), 1.64 (m, 8H, Oct– CH_2), 3.24 (q, ${}^{3}J_{HH} = 7.0$ Hz, 4H, ether– CH_2), 7.93, 8.23 (s, 4H, Oct– CH_1). ${}^{13}C$ { ${}^{1}H$ } NMR (C₆D₆): δ 6.6, 15.5, 32.6, 32.8, 32.9, 33.2, 34.5, 34.8, 35.2, 35.55, 35.57, 39.4, 55.0, 65.9, 70.8, 120.6, 122.7, 123.7, 135.0, 142.6, 146.7.

4.2.6. Synthesis of $Me_2Si(\eta^1-C_{29}H_{36})(\eta^1-N^{-t}Bu)$ $HfMe_2 \cdot OEt_2$ (4-Hf)

4-Hf was prepared in a manner analogous to **4-Zr** except that **2-Hf** (0.40 g, 0.49 mmol) was utilized yielding 0.23 g (60.5%) of **4-Hf** as a pale yellow powder. ¹H NMR (C₆D₆): δ -0.16 (s, 6H, Hf(CH₃)₂), 0.84 (s, 6H, (CH₃)₂Si), 1.02 (t, ³J_{HH} = 6.0 Hz, 6H, ether-CH₃), 1.34, 1.35, 1.36, 1.38 (s, 24H, Oct-CH₃), 1.37 (s, 9H, -C(CH₃)₃), 1.66 (app. s, 8H, Oct-CH₂), 3.17 (q, ³J_{HH} = 6.0 Hz, 4H, ether-CH₂), 7.84, 8.21 (s, 4H, Oct-CH₁).

4.2.7. Synthesis of $Me_2Si(\eta^1-C_{29}H_{36})(\eta^1-N^{-t}Bu)$ Zr $Me_2 \cdot THF$ (**5-Zr**)

In the glove box, 2-Zr (5.00 g, 6.67 mmol) was charged into a 100 ml pear-shaped round bottom flask. The flask was then attached to a 3 cm swivel frit and diethyl ether (80 ml) was vacuum transferred in on the line. Next, while the flask was still cold, MeMgCl (4.44 ml, 13.33 mmol, 3.0 M in THF) was slowly added via syringe. A large quantity of white precipitate immediately formed. The contents of the flask were stirred for 2 h before the precipitated salt was removed by filtration. The cake was extracted until the eluent was colorless. The solvent was then removed under vacuum and the frit was brought into the box where the off-white product was recrystallized by cooling a saturated diethyl ether solution to -35 °C, yielding 2.98 g (63.0%) of product as nearly white crystals which were suitable for X-ray diffraction. ¹H NMR (C₆D₆): δ 0.02 (s, 6H, $Zr(CH_3)_2$, 0.77 (s, 6H, (CH₃)₂Si), 1.14 (br, 4H, THF-CH₂), 1.34, 1.37, 1.40, 1.43 (s, 24H, Oct-CH₃), 1.52 (s, 9H, -C(CH₃)₃), 1.69 (m, 8H, Oct-CH₂), 2.81 (br, 4H, THF-C H_2), 7.82, 8.15 (s, 4H, Oct-C H_1). ¹³C {¹H} NMR (C_6D_6): δ 3.9, 15.5, 32.6, 32.7, 32.9, 33.3, 34.5, 34.8, 35.0, 35.9, 36.0, 39.7, 57.2, 65.8, 86.3, 117.4, 118.5, 133.6, 137.6, 139.7, 141.9.

4.2.8. Synthesis of $Me_2Si(\eta^1-C_{29}H_{36})(\eta^1-N^{-t}Bu)$ $HfMe_2 \cdot THF (5-Hf)$

5-Hf was prepared in a manner analogous to **5-Zr** except that **2-Hf** (0.43 g, 0.54 mmol) was utilized yielding 0.43 g of **5-Hf** as an off-white solid (>95% yield, some persistent THF). ¹H NMR (C_6D_6): δ 0.29 (s, 6H, Hf(CH_3)₂), 0.70 (s, 6H, (CH_3)₂Si), 1.01 (br, 4H, THF- CH_2), 1.33, 1.40, 1.45, 1.48 (s, 24H, Oct- CH_3), 1.67 (s, 9H, $-C(CH_3)_3$), 1.73 (m, 8H, Oct- CH_2), 2.41 (br, 4H, THF- CH_2), 7.67, 8.13 (s, 4H, Oct- CH_1). ¹³C {¹H} NMR (C_6D_6): δ 3.8, 15.9, 25.8, 33.0, 33.03, 33.3, 33.7,

34.9, 35.4, 35.5, 36.2, 36.4, 51.4, 66.2, 71.6, 117.5, 118.8, 126.6, 133.8, 137.9, 142.0.

4.2.9. Synthesis of $Me_2Si(\eta^5-C_{29}H_{36})(\eta^1-N^{-t}Bu)Zr$ (CH₂Ph)₂ (**6-Zr**)

In the glove box, 2-Zr (4.00 g, 5.33 mmol) was charged into a 100 ml pear-shaped round bottom flask followed by the addition of KCH_2Ph (1.39 g, 10.66 mmol). The flask was then attached to a 3 cm swivel frit and brought out onto the line where diethyl ether (60 ml) was vacuum transferred in. The contents were allowed to slowly warm to room temperature and then stir for 2 h before the salt was removed by filtration and the cake extracted until colorless. Concentration of the slurry to 20 ml, followed by filtration, led to the desired product as a yellow solid (3.21 g, 76.5%). Large blocklike crystals were grown by the vapor diffusion of diethyl ether into dichloromethane saturated with 6-Zr. ¹H NMR (C₆D₆): δ -0.48, 0.86 (d, ²J_{HH} = 10.5 Hz, 4H, $Zr-CH_2$, 0.99 (s, 9H, $-C(CH_3)_3$), 1.01 (s, 6H, $(CH_3)_2Si$), 1.34, 1.38, 1.39, 1.42 (s, 24H, Oct-CH₃), 1.62 (m, 8H, Oct- CH_2), 6.69 (m, 4H, Zr- $CH_2C_6H_5$), 6.89 (m, 2H, Zr-CH₂C₆H₅), 7.16 (m, 4H, Zr-CH₂C₆H₅), 8.15, 8.16 (s, 4H, Oct–CH₁). ¹³C {¹H} NMR (CDCl₃): δ 6.2, 32.4, 32.6, 32.8, 33.0, 33.5, 34.8, 35.06, 35.08, 35.09, 56.9, 61.3, 73.1, 119.8, 121.2, 122.2, 123.1, 127.5, 128.8, 133.4, 143.5, 145.5, 146.8. ¹³C {¹H} NMR (C₆D₆): δ 6.4, 32.57, 32.6, 33.06, 33.1, 33.6, 34.9, 35.2, 35.26, 35.3, 57.2, 61.9, 73.9, 120.1, 122.0, 122.7, 123.6, 128.3, 129.3, 134.1, 143.7, 145.7, 147.0

4.2.10. Synthesis of $Me_2Si(\eta^5-C_{29}H_{36})(\eta^1-N-{}^tBu)Hf$ (CH₂Ph)₂ (**6-Hf**)

6-Hf was prepared in a manner analogous to **6-Zr** except that **2-Hf** (1.50 g, 1.87 mmol) was utilized yielding 0.42 g (25.8%) of **6-Hf** as a yellow-orange solid. Large block-like crystals were grown by the vapor diffusion of diethyl ether into dichlormethane saturated with **6-Hf**. ¹H NMR (C₆D₆): δ -0.30, 0.66 (d, ²J_{HH} = 7.2 Hz, 4H, Hf-CH₂), 0.95 (s, 6H, (CH₃)₂Si), 1.01 (s, 9H, -C(CH₃)₃), 1.33, 1.34, 1.35, 1.36 (s, 24H, Oct-CH₃), 1.57 (m, 8H, Oct-CH₂), 6.65 (m, 4H, Hf-CH₂C₆H₅), 8.04, 8.26 (s, 4H, Oct-CH₁). ¹³C {¹H} NMR (CDCl₃): δ 6.2, 32.5, 32.6, 33.0, 33.6, 33.7, 34.9, 35.0, 35.08, 35.1, 55.9, 70.4, 71.4, 120.0, 121.1, 122.4, 122.7, 127.5, 128.0, 134.1, 143.5, 146.5, 147.4.

4.2.11. Synthesis of $Me_2Si(\eta^5-C_{29}H_{36})(\eta^1-N^-tBu)Zr$ (CH₂SiMe₃)₂ (7-Zr)

In the glove box, 2-Zr (0.50 g, 0.67 mmol) was charged into a 100 ml pear-shaped round bottom flask. The flask was then attached to a 3 cm swivel frit and brought out to the vacuum line where pentane (50 ml) was vacuum transferred in. Next, LiCH₂SiMe₃ (1.40 ml, 1.40 mmol, 1.0 M in pentane) was slowly

Table 4Crystallographic data summary

Compound	3-Zr ($Br_2 \cdot Et_2O$)	3-Hf $(Br_2 \cdot Et_2O)$	5-Zr (Me ₂ \cdot THF)	6-Zr ((CH ₂ Ph) ₂)	6-Hf ((CH ₂ Ph) ₂)	7-Zr ((CH ₂ SiMe ₃) ₂)
Empirical formula	C ₃₉ H ₆₁ Br ₂ NOSiZr	C ₃₉ H ₆₁ Br ₂ NOSiHf	C45H75NO2SiZr	C49H65NSiZr	C ₄₉ H ₆₅ NSiHf	C43H73NSi3Zr
Formula weight	839.02	926.29	781.36	787.33	874.60	779.53
Temperature (K)	110(2)	110(2)	110(2)	110(2)	110(2)	110(2)
Wavelength (Å)	1.54184	0.71073	1.54184	0.71073	1.54184	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	Cc	Cc	$P2_1/c$	$P2_1/n$	P_1/n	$P2_1$
a (Å)	24.122(3)	24.094(10)	12.564(7)	14.6594(14)	14.630(3)	12.980(4)
b (Å)	11.7263(11)	11.765(5)	25.347(8)	16.0990(15)	16.103(3)	20.326(5)
<i>c</i> (Å)	15.0453(16)	15.069(7)	14.555(6)	18.1773(17)	18.162(4)	17.152(5)
α (°)	90	90	90	90	90	90
β (°)	109.000(6)	108.847(7)	107.60(3)	95.952(2)	95.410(9)	93.840(4)
γ (°)	90	90	90	90	90	90
Volume (Å ³)	4023.9(7)	4042(3)	4418(3)	4271.9(7)	4259.6(14)	4515(2)
Ζ	4	4	8	4	4	5
$D_{\rm calc}~({\rm g~cm^{-3}})$	1.385	1.522	1.175	1.224	1.364	1.147
$\mu (\text{mm}^{-1})$	5.059	4.616	2.548	0.319	5.033	0.351
Crystal size (mm ³)	$0.50 \times 0.01 \times 0.01$	$0.22 \times 0.21 \times 0.08$	$0.10\times0.05\times0.05$	$0.42 \times 0.39 \times 0.27$	$0.20 \times 0.20 \times 0.05$	$0.60 \times 0.40 \times 0.20$
Reflections	22767	15407	41117	48123	31312	42757
Independent reflections	5158	6476	6237	9745	6016	19672
Data/restraints/ parameters	5158/314/445	6476/17/434	6237/1/461	9745/0/491	6016/349/470	19672/1/866
$GOF(F^2)$	1.005	1.078	1.037	1.215	1.020	1.066
$R_1 [I > 2\sigma(I)]$	0.0489	0.0381	0.0592	0.0540	0.0595	0.0310
$wR_2 [I > 2\sigma(I)]$	0.1192	0.0990	0.1262	0.1312	0.1148	0.0790
R_1 (all data)	0.0620	0.0409	0.1078	0.0645	0.1594	0.0325
wR_2 (all data)	0.1257	0.1009	0.1425	0.1498	0.1381	0.0800
Largest differential peak hole ($e \text{\AA}^{-3}$)	0.676, -0.0943	1.792, -1.381	0.819, -1.428	2.320, -0.655	1.634, -1.517	0.713, -0.356

syringed into the still cold solution in the flask. The contents were allowed to stir for 1 h before the LiCl was removed by filtration and the salt was extracted until colorless. The solvent was removed under vacuum yielding a yellow foam. This was brought into the box where 5 ml of pentane was added causing the precipitation of a neon yellow powder. The solvent was decanted and the powder collected and dried under vacuum yielding 0.35 g (67.0%) of 7-Zr. Pentane (5 ml) was then saturated with 7-Zr and stored in a -35 °C freezer for one month, resulting in the formation of large block-like crystals. ¹H NMR (C₆D₆): δ -1.32, -0.77 (d, ${}^{2}J_{\text{HH}} = 12.3 \text{ Hz}, 4\text{H}, \text{Zr}-\text{C}H_{2}), 0.17 \text{ (s, 18H, -Si(CH_{3})_{3})},$ 0.89 (s, 6H, (CH₃)₂Si), 1.31 (s, 9H, -C(CH₃)₃), 1.39, 1.41, 1.41, 1.49 (s, 24H, Oct-CH₃), 1.68 (m, 8H, Oct- CH_2), 7.92, 8.17 (s, 4H, Oct– CH_1). ¹³C {¹H} NMR (CDCl₃): δ 3.3, 6.3, 32.2, 32.9, 33.1, 33.3, 34.3, 34.9, 35.08, 35.1, 35.3, 55.0, 55.9, 71.1, 120.1, 122.5, 123.2, 133.9, 142.7, 146.1.

4.2.12. Synthesis of $Me_2Si(\eta^5-C_{29}H_{36})(\eta^1-N^{-1}Bu)Hf$ (CH₂SiMe₃)₂ (7-**Hf**)

7-Hf was prepared in a manner analogous to **7-Zr** except that **2-Hf** (0.40 g, 0.49 mmol) was utilized yielding 0.24 g (54.5%) of **7-Hf** as a yellow powder. ¹H NMR (CDCl₃): δ -2.09, -1.38 (d, ²J_{HH} = 12.0 Hz, 4H, Hf–

 CH_2), -0.11 (s, 18H, $-Si(CH_3)_3$), 0.89 (s, 6H, $(CH_3)_2Si$), 1.33, 1.35, 1.46, 1.49 (s, 24H, Oct– CH_3), 1.37 (s, 9H, $-C(CH_3)_3$), 1.79 (app. s, 8H, Oct– CH_2), 7.72, 8.02 (s, 4H, Oct– CH_1).

4.3. Crystallographic studies

Crystals were mounted at room temperature in mineral oil, and affixed to a glass fiber. X-ray crystallographic data were obtained using a Bruker SMART 1000 three-circle diffractometer operating at 50 kV and 40 mA, Mo K α ($\lambda = 0.71073$ Å) with a graphite monochromator and a CCD-PXL-KAF2 detector or a Bruker GADPS instrument operating at 40 kV and 40 mA, Cu K α ($\lambda = 1.54578$ Å) with a graphite monochromator and a CCD-PXL-KAF2 detector. Details of the crystallographic data collection and refinement are summarized in Table 4. The molecular structures were solved by direct methods and were refined employing the SHELXS-97 [59] and SHELXL-97 programs [60].

5. Supplementary material

Crystallographic data for **3-Zr** (CCDC 260056), **3-Hf** (CCDC 260057), **5-Zr** (CCDC 260058), **6-Zr** (CCDC

260055), **6-Hf** (CCDC 260059), and **7-Zr** (CCDC 260060) have been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/ cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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