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Alkyl Complexes of Group 4 Metals Containing a Tridentate-Linked Amido−Cyclopentadienyl Ligand: Synthesis, Structure, and Reactivity Including Ethylene Polymerization Catalysis

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A series of group 4 metal complexes $M(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2X)R_2$ (M = Ti; R = Me, CH_2Ph; M = Zr, Hf; R = Me, Et, ^{n}Pr, ^{n}Bu, CH_2Ph, CH_2SiMe_3, Ph) containing the tridentate-linked amido−tetramethylcyclopentadienyl ligand $C_5Me_4SiMe_2NCH_2CH_2X$ (X = OMe, NMe_2) were synthesized by alkylation of the dichloro complexes $M(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2X)Cl_2$. The complexes were characterized by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. Nuclear Overhauser effect measurements of the dimethyl complexes show that, in solution, the side chains of the zirconium derivatives coordinate intramolecularly, in contrast to the titanium complexes. The crystal structures of the zirconium alkyls $Zr(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)R_2$ (R = Me, Ph) were determined by X-ray diffraction studies. Both complexes adopt a trigonal-bipyramidal structure, with the five-membered ring and the methoxy group in the apical positions. Insertion of carbon monoxide into the hafnium dimethyl and di(*n*-butyl) complexes led to the η^2-acyl derivatives $Hf(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)(\eta^2\text{-}COR)R$ (R = Me, ^{n}Bu). Chloro mono(ethyl) complexes underwent insertion of *tert*-butyl isonitrile to give η^2-iminoacyl derivatives $M(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2X)\{\eta^2\text{-}C(=N^tBu)Et\}Cl$. The X-ray diffraction structure of the titanium complex $Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)\{\eta^2\text{-}C(=N^tBu)Et\}Cl$ showed a square-pyramidal configuration with the imino nitrogen trans to the amido nitrogen. The zirconium dimethyl complexes $Zr(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2X)Me_2$ reacted with $B(C_6F_5)_3$ to form the contact ion pairs $[Zr(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2X)Me]^+[MeB(C_6F_5)_3]^-$. Reaction between the titanium dibenzyl $Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2X)(CH_2Ph)_2$ and $B(C_6F_5)_3$ resulted in the clean formation of the solvent-separated ion pair $[Ti(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2X)(CH_2Ph)]^+[(PhCH_2)B(C_6F_5)_3]^-$. When activated with methylaluminoxane, the complexes $Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Cl_2$ and $M(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)R_2$ (M = Zr, Hf; R = Me, ^{n}Bu) are active in the polymerization of ethylene.

Introduction

Complexes of early transition metals and lanthanides containing a linked amido−cyclopentadienyl ligand $C_5R'_4ZNR''$ (Z = $SiMe_2$, $SiMe_2CH_2$, CH_2CH_2, $CH_2CH_2CH_2$)$^{1-5}$ occupy a position halfway between the ubiquitous metallocene derivatives $M(C_5R'_5)_2L_mX_n$ and the half-sandwich complexes $M(C_5R'_5)L_mX_n$. These linked amido−cyclopentadienyl transition-metal complexes can also be regarded as hybrids of metallocenes and the

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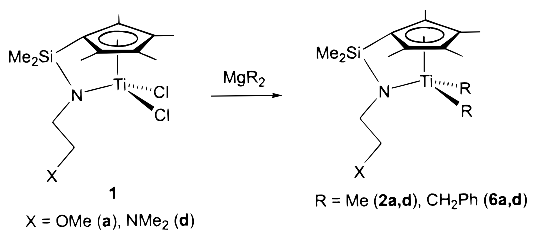
electronically even more unsaturated and sterically more open bis(amido) chelate complexes.[6]

Whereas the active species in group 4 metallocene-catalyzed α-olefin polymerization has been established as the 14-electron alkyl cation $[M(C_5R'_5)_2R]^+$,[7] the active species of group 4 metal catalysts containing a linked amido−cyclopentadienyl ligand, presently being commercialized to produce novel copolymers of ethylene with α-olefin and styrene,[3] is presumed to be the 12-electron alkyl cation $[Ti(\eta^5{:}\eta^1\text{-}C_5R'_4ZNR'')R]^+$.[4c,8] Isoelectronic to this are scandium hydride and alkyls of the type $[Sc(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)X]$ (X = H, ^{n}Pr, ^{n}Bu) that were demonstrated by Bercaw et al. to effect the living polymerization of α-olefins.[1a,b] In contrast to this, 10-electron cations $[Ti(C_5R'_5)R_2]^+$ or 9-electron cations $[Ti(C_5R'_5)R]^+$ are generated when half-sandwich alkyl complexes $Ti(C_5R'_5)R_3$ are activated with cocatalysts.[9] Although the former is capable of polymerizing α-olefins[9a−c] and the latter is active in the syndiospecific polymerization of styrene,[9d,e] such extremely electron-deficient species often defy structural characterization.

We recently introduced a potentially tridentate variation of the linked amido−cyclopentadienyl ligand, $C_5R'_4SiMe_2NCH_2CH_2X$, which was designed to mimic the bis(cyclopentadienyl) ligand set in the d^0-metallocene fragment.[2c,d] The additional two-electron donor function X = OMe and NMe_2 was hypothesized to act as a semilabile ligand that would stabilize highly electrophilic metal centers temporarily and allow an unsaturated substrate molecule to approach the metal more readily.[10] We report here the synthesis and characterization of an extensive series of group 4 metal dialkyl complexes containing such tridentate-linked amido−cyclopentadienyl ligands. The insertion chemistry of unsaturated molecules such as *tert*-butyl isonitrile and ethylene was explored, and attempts at the generation of alkyl cations supported by these tridentate-linked amido−cyclopentadienyl ligands are presented here. Preliminary results have been published earlier.[2c,h]

Results and Discussion

Synthesis of Dialkyl Complexes. The dichlorotitanium complexes $Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2X)Cl_2$ (**1a**,**d**) can be alkylated with Grignard reagents MgRCl or dialkylmagnesium MgR_2 to give the dialkyl derivatives $Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2X)R_2$, R = Me (**2a**,**d**) and CH_2Ph (**6a**,**d**), in reproducibly good yields as pentane-soluble, pale yellow and red crystals, respectively (eq 1). Although detectable in most instances, other dialkyl complexes could not be isolated in pure state. When more than 1 equiv of an alkylating reagent containing β-hydrogens was employed, rapid reduction even at −78 °C ensued, resulting in the formation of intractable dark products.



(1)

The red dibenzyl complexes **6a** and **6d** proved to be particularly robust. This is probably due to the presence of agostic bonding of one of the benzyl groups in the solid state, as was found in the crystallographically characterized $Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2Ph)(CH_2Ph)_2$[2g] and related mono(cyclopentadienyl)titanium benzyl complexes.[11] No unusual features were observed in the ^{1}H NMR spectra of **6a** and **6d**: the methylene protons of the benzyl groups were recorded as AB spin systems at around δ 2.0 (**6a**: δ 2.08, 2.19 with $^2J_{HH} = 10.6$ Hz; **6d**: δ 2.05, 2.18 with $^2J_{HH} = 10.9$ Hz).

It appears that the additional donor group X on the amido substituent has no direct influence on the stability of the titanium dialkyl complexes. NOESY spectra (C_6D_6, 25 °C, $t_{mix} = 2.0$ s) of the dimethyl complexes **2a** and **2d** indicated no interaction between the methyl groups on titanium and the additional donor; thus intramolecular coordination of the side chain at the tetravalent titanium center is at most fluxional. Since only small chemical shift differences for the OMe and NMe_2 groups were recorded in the temperature range −80 to +80 °C, we assume that the equilibrium between the bidentate and tridentate form of the ligands lies on the side of the open form where the third donor is not intramolecularly coordinated.[12]

The double alkylation of the four dichloro complexes of zirconium and hafnium **1b**,**c**,**e**,**f** using the appropriate alkylating reagent was general and straightforward. Even alkyl complexes containing β-hydrogens such as ethyl, *n*-propyl, and *n*-butyl were formed in good to

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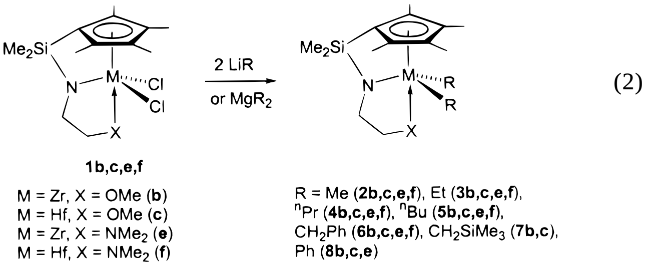
excellent yields, resulting in the isolation in most cases of unexpectedly thermally stable, pentane-soluble, colorless crystals (eq 2). NMR spectra consistently showed the presence of a mirror plane bisecting the molecule. Thus for all complexes, enantiotopic pairs of methyl signals were recorded as singlets for the C_5Me_4, $SiMe_2$, and NMe_2 groups in the temperature range −80 to +80 °C. The amido substituent CH_2CH_2X gives rise to an AA′XX′ spin system with tripletlike features. The chemical shifts for the methyl groups of X did not change significantly with changing temperature. For instance, for the zirconium diphenyl **8b**, expected to be sterically fairly strained, the ^1H NMR spectroscopic shift in C_6D_6 varied merely from δ 2.15 at 25 °C to δ 2.24 at 80 °C. NOESY spectra clearly showed that the additional coordination of X in the dimethyl complexes **2b** and **2e** is fairly rigid on the NMR time scale. In contrast to the titanium analogues **2a** and **2d**, there were NOE cross-peaks between the resonance for $ZrMe_2$ and those for OMe and NMe_2 in **2b** and **2e**. We assume that for the series of zirconium and hafnium dialkyl complexes the tridentate coordination mode is the dominant one on the NMR time scale.



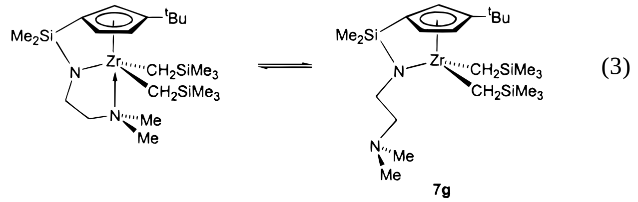
(2)

1b,c,e,f

M = Zr, X = OMe (**b**)
M = Hf, X = OMe (**c**)
M = Zr, X = NMe$_2$ (**e**)
M = Hf, X = NMe$_2$ (**f**)

R = Me (**2b,c,e,f**), Et (**3b,c,e,f**), ^{n}Pr (**4b,c,e,f**), ^{n}Bu (**5b,c,e,f**), CH$_2$Ph (**6b,c,e,f**), CH$_2$SiMe$_3$ (**7b,c**), Ph (**8b,c,e**)

The planar chiral dichloro complex $Zr(\eta^5:\eta^1:\eta^1\text{-}C_5H_3\text{-}tBuSiMe_2NCH_2CH_2NMe_2)Cl_2$ (**1g**) was found to possess a rigidly coordinated NMe_2 group up to +80 °C, as evidenced by the two well-separated signals of the NMe_2 group in both the ^1H and ^{13}C NMR spectra. On the other hand, the NMR spectrum of the analogous titanium derivative, with only one peak for the two rapidly interconverting NMe_2 methyls, confirms that the titanium complex is fluxional.[2c] When the less Lewis-acidic, planar chiral dialkyl derivative $Zr(\eta^5:\eta^1:\eta^1\text{-}C_5H_3tBuSiMe_2\text{-}NCH_2CH_2NMe_2)(CH_2SiMe_3)_2$ (**7g**) was studied by variable-temperature ^1H NMR spectroscopy, a decoalescence of the NMe_2 signals was observed at 7 °C. Above this coalescence temperature nitrogen inversion renders the two diastereotopic NMe_2 groups equivalent. A value for the activation barrier of $\Delta G^{\ddagger} = 13.1(1)$ kcal mol^{-1} was obtained for the reversible dissociation/association of the amino nitrogen (eq 3).



7g

(3)

An X-ray diffraction study verified the pseudo-trigonal-bipyramidal configuration of the dimethyl derivative **2b** (Figure 1, Tables 1 and 2). The η^5-bonded five-membered ring and the OMe group approximately occupy the apical positions. The two methyl groups and the doubly bonded amido nitrogen atom (Zr−N distance 2.099(3) Å, sum of angles at N 360°) occupy the equatorial sites. All three ligands are turned away from the C_5Me_4 ligand. The Zr−O bond length of 2.375(2) Å lies within the range of distances usually observed for a bond between tetravalent zirconium and an ether oxygen atom.[13] The five-membered chelate ring is slightly puckered, with the methyl group of the methoxy function out of the mirror plane that bisects the molecule.

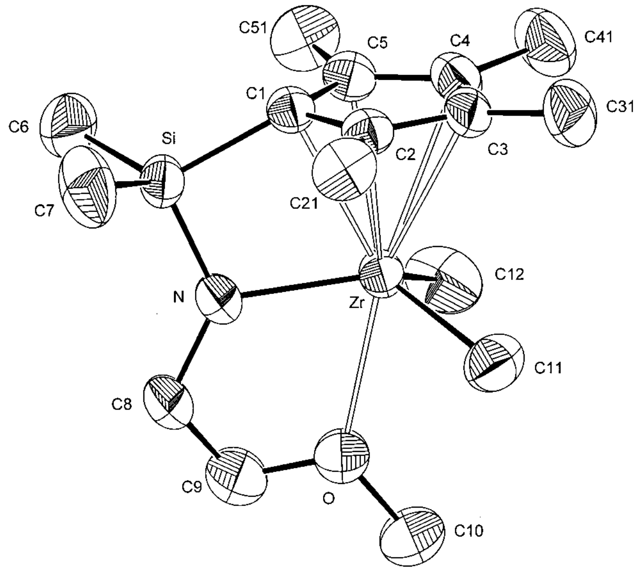


Figure 1. ORTEP diagram of the molecular structure of the complex $Zr(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Me_2$ (**2b**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity.

Somewhat surprising was the observation of this structural type for the sterically more congested diphenyl derivative $Zr(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Ph_2$ (**8b**) (Figure 2 and Tables 1 and 3). Evidently, through propeller-like torsion, the two phenyl groups are accommodated within the coordination sphere of the $Zr(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)$ fragment. Diphenyl complexes of group 4 metallocenes are well-known.[14] Previously reported single-crystal X-ray structure analyses of the dichloro complexes $Hf(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2\text{-}NCH_2CH_2OMe)Cl_2$ (**1c**)[2i] and $Zr(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2\text{-}NCH_2CH_2NMe_2)Cl_2$ (**1e**)[2c] as well as of di(*n*-butyl) $Hf(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)^nBu_2$ (**5c**)[2h] all revealed an analogous configuration. Five-coordinate half-sandwich complexes of transition metals most commonly adopt a square-pyramidal configuration;[15] hence only a limited number of trigonal bipyramidal structures have been reported in the literature.[16] The coordination of

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Table 1. Experimental Data for the Crystal Structure Determination of $Zr(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Me_2$ (2b), $Zr(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Ph_2$ (8b), and $Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)\{\eta^2\text{-}C(N^tBu)Et\}Cl$ (12a)

	2b	**8b**	**12a**
	Crystal Data		
empirical formula	$C_{16}H_{30}NOSiZr$	$C_{26}H_{35}NOSiZr$	$C_{21}H_{39}ClN_2OSiTi$
fw	371.72	496.86	446.98
cryst color	colorless	colorless	yellow
cryst size, mm	0.3 × 0.3 × 0.3	0.4 × 0.4 × 0.7	0.6 × 0.3 × 0.3
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1$ (no. 4)
a, Å	8.416(3)	8.800(2)	8.180(9)
b, Å	14.667(2)	15.903(2)	12.026(7)
c, Å	15.769(2)	18.273(2)	13.004(5)
β, deg	102.61(2)	91.32(1)	95.32(8)
V, Å^3	1899.5(8)	2556.6(7)	1274(3)
Z	4	4	2
$\rho_{calc.}$, g cm^{-3}	1.300	1.291	1.165
μ(Mo Kα), mm^{-1}	0.639	0.493	0.500
F(000)	780	1040	480
	Data Collection		
wavelength	Mo Kα (0.710 70 Å)	Mo Kα (0.710 70 Å)	Mo Kα (0.710 70 Å)
T, K	293(2)	296(2)	296(2)
θ-range, deg	3−28	3−27	3−26
index ranges	h, 0 to 11; k, 0 to 19; l, −20 to 20	h, 0 to 11; k, 0 to 20; l, −23 to 23	h, 0 to 10; k, 0 to 14; l, −16 to 15
	Solution and Refinement		
no. of rflns measd	4860	5890	2789
no. of indep rflns	4564 [$R_{int} = 0.0190$]	5533 [$R_{int} = 0.0392$]	2606 [$R_{int} = 0.0423$]
no. of obsd rflns	3246 [$I > 2\sigma(I)$]	3405 [$I > 2\sigma(I)$]	1972 [$I > 2\sigma(I)$]]
ext coeff			0.0058(5)
GOF	1.161	1.167	1.144
R	0.0368	0.0549	0.0611
wR_2 [$I > 2\sigma(I)$]	0.0687	0.1117	0.1403
largest e-max, e-min, e·Å^{-3}	0.419 and −0.320	0.372 and −0.364	0.563 and −0.400

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Zr(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Me_2$ (2b)

bond lengths		bond angles	
Zr−N	2.099(3)	N−Zr−C(11)	120.6(2)
Zr−C(11)	2.272(4)	N−Zr−C(12)	114.3(2)
Zr−C(12)	2.266(5)	C(12)−Zr−C(11)	108.5(2)
Zr−O	2.375(2)	N−Zr−O	70.18(9)
Zr−C(1)	2.450(3)	O−Zr−C(11)	77.7(1)
Zr−C(2)	2.484(3)	O−Zr−C(12)	81.7(1)
Zr−C(5)	2.524(3)	N−Si−C(6)	113.9(2)
Zr−C(3)	2.602(3)	N−Si−C(7)	114.9(2)
Zr−C(4)	2.616(3)	N−Si−C(1)	93.0(1)
Si−N	1.704(3)	C(6)−Si−C(7)	105.2(3)
Si−C(1)	1.869(3)	C(9)−O−C(10)	114.3(3)
O−C(9)	1.393(5)	C(9)−O−Zr	114.8(2)
O−C(10)	1.429(5)	C(10)−O−Zr	126.8(3)
N−C(8)	1.451(4)	C(8)−N−Si	127.8(2)
C(8)−C(9)	1.461(6)	C(8)−N−Zr	124.2(2)
Cp_{cent}−Zr	2.23	Si−N−Zr	107.9(1)
		N−C(8)−C(9)	111.1(3)
		O−C(9)−C(8)	110.8(4)
		Cp_{cent}−Zr−N	98.9

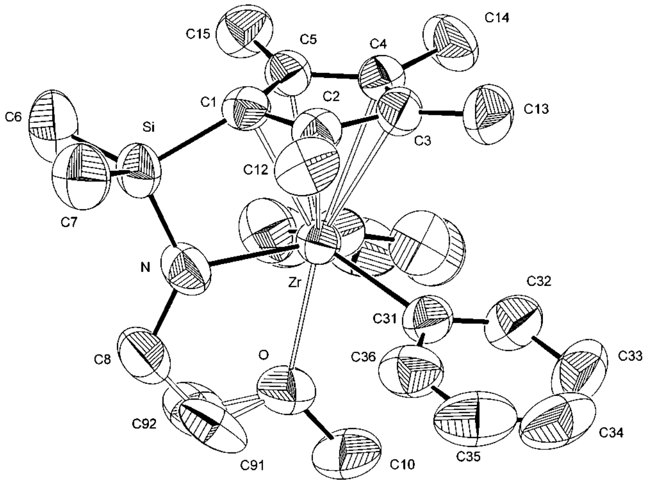

Figure 2. ORTEP diagram of the molecular structure of the complex $Zr(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Ph_2$ (**8b**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity.

the oxygen atom does not result in any distortion when compared to bidentate chelates such as $Zr(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)Me_2$.[5c]

The thermal stability of the dialkyl complexes qualitatively follows the general order Ti ≪ Zr < Hf and Et < ^{n}Pr < ^{n}Bu < CH_2SiMe_3 < Me < Ph < CH_2Ph. The zirconium diphenyl complex did not undergo any decomposition reaction during prolonged heating (100 °C for 1 week). A representative member of the series containing two higher alkyls, $Hf(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)^nBu_2$ (**5c**), decomposed in the solid state only above 90 °C, giving 1-butene as the sole volatile product detectable by GC MS. Complexes **3**−**5** are more thermally sensitive in solution, however, although no clear decomposition pathway has been identified so far by NMR spectroscopy.[17] Iodinolysis of **5c** afforded in quantitative yield 1-iodobutane along with the dark yellow diiodo homologue of **1c**, $Hf(\eta^5:\eta^1:\eta^1\text{-}C_5Me_4SiMe_2$-

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(16) (a) Liu, A. H.; Murray, R. C.; Dewan, J. C.; Santarsiero, B. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 4282. (b) Nadasdi, T. T.; Huang, Y.; Stephan, D. W. *Inorg. Chem.* **1993**, *32*, 347.

(17) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529.

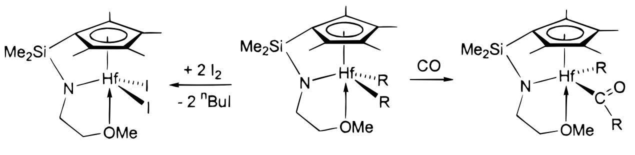
Table 3. Selected Bond Lengths (Å) and Angles (deg) for Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)$Ph_2$ (8b)

bond lengths		bond angles	
Zr−N	2.095(5)	N−Zr−C(21)	110.6(2)
Zr−C(21)	2.284(6)	N−Zr−C(31)	119.1(2)
Zr−C(31)	2.288(6)	C(21)−Zr−C(31)	114.6(2)
Zr−O	2.330(4)	N−Zr−O	71.4(2)
Zr−C(1)	2.450(5)	C(21)−Zr−O	79.3(2)
Zr−C(2)	2.489(5)	C(31)−Zr−O	79.1(2)
Zr−C(5)	2.534(5)	N−Si−C(6)	113.4(3)
Zr−C(4)	2.598(6)	N−Si−C(7)	115.3(3)
Zr−C(3)	2.607(6)	C(6)−Si−C(7)	104.9(3)
Si−N	1.704(5)	N−Si−C(1)	92.7(2)
Si−C(1)	1.874(6)	C(91)−O−Zr	113.3(9)
O−C(91)	1.39(2)	C(92)−O−Zr	115.3(8)
O−C(92)	1.41(2)	C(10)−O−Zr	126.0(4)
O−C(10)	1.414(7)	C(8)−N−Si	128.8(4)
N−C(8)	1.462(8)	C(8)−N−Zr	122.7(4)
C(8)−C(92)	1.47(2)	Si−N−Zr	107.9(2)
C(8)−C(91)	1.48(2)	N−C(8)−C(92)	112.1(9)
Cp_{cent}−Zr	2.23	N−C(8)−C(91)	108.8(9)
		O−C(91)−C(8)	110(1)
		O−C(92)−C(8)	110(1)
		Cp_{cent}−Zr−N	98.8

$NCH_2CH_2OMe)I_2$ (**11c**). The robustness of dialkyl complexes containing β-hydrogens is remarkable. When Zr(η^5:η^1-$C_5Me_4SiMe_2N^tBu$)Cl_2 was treated with 2 equiv of an alkyllithium reagent, no clean reaction was observed and no dialkyls isolated, indicating the critical role of the third donor group. Few metallocene derivatives that contain two alkyl groups with β-hydrogen atoms have been mentioned in the literature.[18] This is even more scarce in half-sandwich complexes.[19] Recently, a series of group 4 diamido complexes containing higher alkyls were reported,[6a−c] after Andersen had recognized some time ago that amido ligands support higher alkyls at d^0 metal centers.[20]

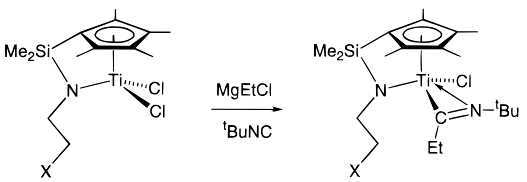
Insertion Reactions. Since insertion of carbon monoxide into the alkyl bond of group 4 metallocene dialkyls constitutes a well-studied important type of reaction,[21] we briefly examined the reaction of carbon monoxide with the hafnium dimethyl **2c** and di(n-butyl) **5c**. As followed by ^1H NMR spectroscopy, a slow reaction of the dialkyl with carbon monoxide (1 bar) occurred over a period of 12 h to give the mono(insertion) product Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)(COR)R (R = Me (**9c**); R = ^{n}Bu (**10c**)) (Scheme 1). The unsymmetrical η^2-acyl derivatives are easily identified by the low-field shift of the acyl carbon in the ^{13}C NMR spectrum. Thus a signal at δ 342.3 and at δ 343.0 for the acetyl **9c** and valeroyl **10c**, respectively, was found. Curiously only one of the possible diastereomers (exo or endo isomer) was found in each case, even at −80 °C. In contrast to the zirconocene monoacyl complexes[21] the exo and endo diastereomers are fluxional, the acyl group rotating freely about the metal carbon bond via a monohapto-bound acyl group.

Scheme 1



11c R = Me (**2c**), ^{n}Bu (**5c**) R = Me (**9c**), ^{n}Bu (**10c**)

When the titanium dimethyl complexes **2a** and **2d** were reacted with *tert*-butyl isonitrile, mixtures of several compounds were obtained from very sluggish reactions. Originally when we attempted to isolate the diethyl derivatives of titanium, we obtained evidence for the formation of a chloro mono(ethyl) compound Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2CH_2X$)(Et)Cl, although it could not be isolated. Upon addition of *tert*-butyl isonitrile to the reaction mixture of ethylmagnesium chloride and the dichloro complexes **1a** and **1d**, we were able to isolate the chloro(*tert*-butylimino)propionyl complexes Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2CH_2X$){η^2-C(=N^tBu)Et}Cl (**12a**,**d**) as air-stable, yellow crystals in excellent yields (eq 4).



(4)

1
X = OMe (**a**), NMe$_2$ (**d**)

12a,d

The chirality at the metal was evident from the lack of a mirror plane, rendering all enantiotopic groups inequivalent in the NMR spectra. Most strikingly, for **12a** the ^1H NMR resonances for the four ring methyl groups were spread over a range δ 1.32−2.63. The resonances of the ethyl group appeared as a triplet at δ 1.00 for the methyl and as a high-order ABX_3 multiplet at 2.28 and 2.60.

A single-crystal X-ray diffraction study confirmed the structure (Figure 3, Tables 1 and 4). The pseudo-square-pyramidal configuration consists of cyclopentadienyl, amido, chloro, and the dihapto-bonded (imino)propionyl group. The methoxy group of the side chain does not interact with the titanium center, similar to the structure of Ti(η^5:η^1-$C_5H_4SiMe_2NCH_2CH_2OMe$)Cl_2.[2d] The imino nitrogen (Ti−N(2) 2.061(7) Å) is coordinated trans to the doubly bonded amido nitrogen (Ti−N(1) 1.957(8) Å), in agreement with the former being a weak σ-donor ligand. The geometry of the (imino)propionyl group (Ti−C(11) 2.050(9), C(11)−N(2) 1.24(1) Å, Ti−C(11)−N(2) 72.9(5)°) is comparable to that reported in other tetravalent titanium complexes that contain a similar ligand unit.[22]

Following an analogous procedure, it was possible to prepare the heavier homologues of **12a** and **12d** M(η^5:

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[22] (a) Chamberlain, L.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P. *J. Am. Chem. Soc.* **1987**, *109*, 390. (b) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Short, R. L. *Organometallics* **1987**, *6*, 2556. (c) Campora, J.; Buchwald, S. L.; Gutierrez-Puebla, D. E.; Monge, A. *Organometallics* **1995**, *14*, 2039. (d) Fandos, R.; Lanfranchi, M.; Otero, A.; Pellinghelli, M. A.; Ruiz, M. J.; Teuben, J. H. *Organometallics* **1997**, *16*, 5283.

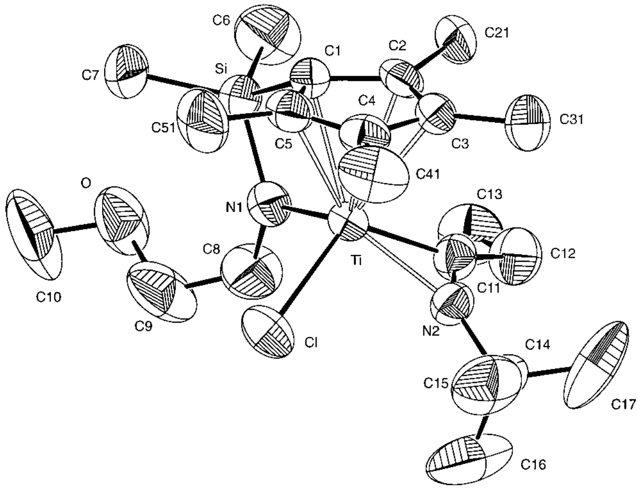


Figure 3. ORTEP diagram of the molecular structure of the complex $Ti(\eta^5:\eta^1-C_5Me_4SiMe_2NCH_2CH_2OMe)\{\eta^2-C(=N^tBu)Et\}Cl$ (**12a**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Ti(\eta^5:\eta^1:\eta^1-C_5Me_4SiMe_2NCH_2CH_2OMe)\{\eta^2-C(=N^tBu)Et\}Cl$ (12a)

bond lengths		bond angles	
Ti−N(1)	1.957(8)	N(1)−Ti−C(11)	99.4(3)
Ti−N(2)	2.061(7)	N(1)−Ti−Cl	96.3(2)
Ti−C(11)	2.050(9)	C(11)−Ti−N(2)	35.2(3)
Ti−Cl	2.377(3)	N(2)−Ti−Cl	89.4(2)
Ti−C(1)	2.270(8)	Ti−C(11)−N(2)	72.9(5)
Ti−C(2)	2.341(8)	C(11)−N(2)−Ti	71.9(5)
Ti−C(5)	2.341(8)	C(11)−N(2)−C(14)	135.9(9)
Ti−C(3)	2.442(7)	C(12)−C(11)−N(2)	131.9(9)
Ti−C(4)	2.411(7)	C(11)−C(12)−C(13)	112.4(9)
Si−N(1)	1.696(8)	N(1)−Si−C(6)	113.5(6)
Si−C(1)	1.872(9)	N(1)−Si−C(7)	117.6(5)
N(2)−C(11)	1.24(1)	N(1)−Si−C(1)	91.7(4)
N(2)−C(14)	1.48(1)	C(6)−Si−C(7)	104.9(7)
C(11)−C(12)	1.52(1)	C(8)−N(1)−Si	131.2(8)
C(12)−C(13)	1.50(2)	C(8)−N(1)−Ti	123.1(7)
O−C(9)	1.41(2)	Si−N(1)−Ti	105.4(4)
O−C(10)	1.40(2)	N(1)−C(8)−C(9)	115(1)
N(1)−C(8)	1.467(12)	C(8)−C(9)−O	109(1)
C(8)−C(9)	1.45(2)	C(9)−O−C(10)	111(1)
Cp_{cent}−Ti	2.03	Cp_{cent}−Ti−N	106

$\eta^1-C_5Me_4SiMe_2NCH_2CH_2X)\{\eta^2-C(=N^tBu)Et\}Cl$ (**12b**,**c**,**e**,**f**). Again, even in cases where the isolation of the diethyl proved to be difficult (**3b**), the chloro (imino)propionyl derivatives were obtained as colorless, analytically pure crystals in high yields. While the metal-centered chirality was obvious from the NMR spectra, the variable-temperature ^1H NMR spectra of the NMe_2-functionalized derivatives $M(\eta^5:\eta^1-C_5Me_4SiMe_2NCH_2CH_2NMe_2)\{\eta^2-C(=N^tBu)Et\}Cl$ (**12e**,**f**) revealed interesting fluxional behavior. As seen in Figure 4, there is only one set of methyl signals for the NMe_2 group of **12e** at higher temperatures, indicating fast inversion at nitrogen because the side chain is not rigidly coordinated. Upon cooling to 0 °C, decoalescence occurs and the signal splits into two. The activation barrier is estimated to be $\Delta G^{\ddagger}$ (301.15 K) = 13.7(1) kcal mol^{-1}. At −30 °C the two resonances again disappear into the baseline, while two C_5Me_4 signals are also broadened. This phenomenon can be interpreted as the freezing-out of the rotation about the zirconium-iminoacyl carbon (Scheme 2). In agreement with this suggestion, the two eight-line multiplets of the ethyl group undergo an upfield shift of about 0.5 ppm upon cooling. On the basis of the structure of the titanium complex **12a**, we assume a pseudo-octahedral structure for the zirconium and hafnium complexes with the imino nitrogen arranged trans to the amido-nitrogen atom and the NMe_2 group adopting the site trans to the C_5Me_4 ligand.

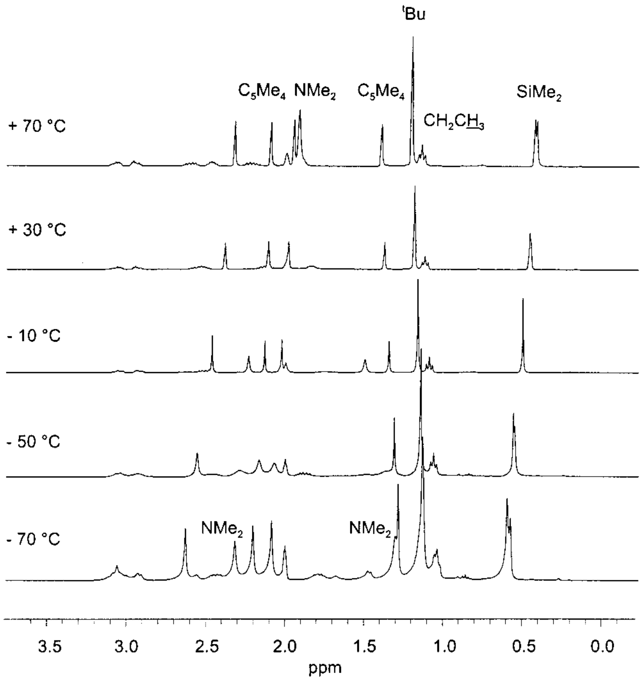
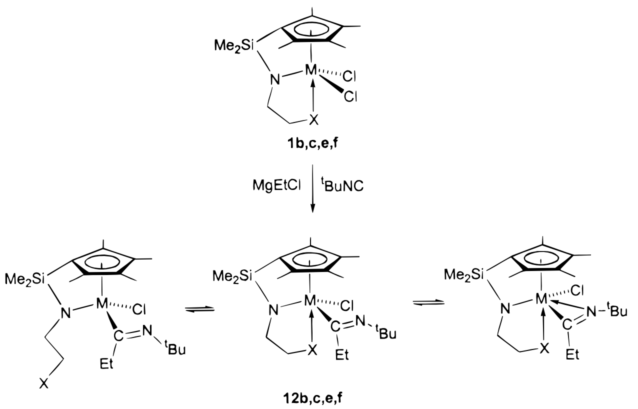


Figure 4. Variable-temperature ^1H NMR spectra (400 MHz) of $Zr(\eta^5:\eta^1-C_5Me_4SiMe_2NCH_2CH_2NMe_2)\{\eta^2-C(=N^tBu)Et\}Cl$ (**12e**) in toluene-d_8.

Scheme 2



Alkyl Cation Formation and Ethylene Polymerization. Alkyl cations supported by the tridentate-linked amido−cyclopentadienyl ligands were expected to be more amenable to study than those containing the original bidentate amido−cyclopentadienyl ligands. However, the generation, detection, and isolation of alkyl cations, in most cases, were severely hampered by what appeared to be high thermal sensitivity leading to rapid decomposition and complicated fluxional behavior. Unfortunately the usual methods for the generation of metallocene alkyl cations such as protonolytic and oxidative cleavage failed.[23] When the zirconium dimethyl complexes **2b** and **2e** were treated with 1 equiv of $B(C_6F_5)_3$ in bromobenzene (eq 5), the formation of the corresponding methyl cation $[Zr(\eta^5:\eta^1-C_5Me_4SiMe_2NCH_2-$

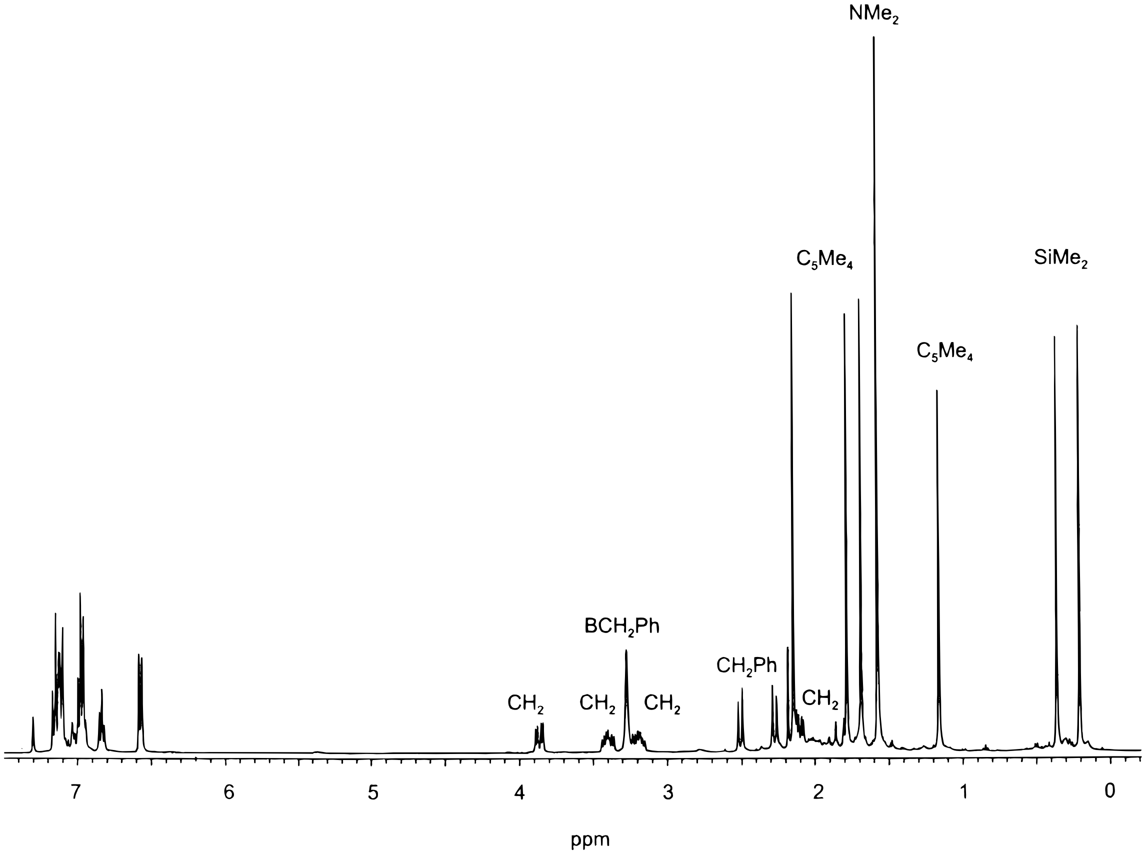
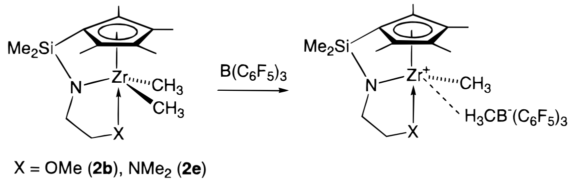


Figure 5. ^{1}H NMR spectrum (400 MHz, 25 °C) of $[Ti(\eta^5:\eta^1:\eta^x\text{-}C_5Me_4SiMe_2NCH_2CH_2NMe_2)(CH_2Ph)]^+[PhCH_2B(C_6F_5)_3]^-$ in bromobenzene-d_5.

$CH_2X)Me]^+$ with the familiar anion $[MeB(C_6F_5)_3]^-$ [24] could be detected by NMR spectroscopy. The signals



(5)

were somewhat broad in the observed temperature range 0−25 °C. The cation lacks a mirror plane with two and four signals for the $SiMe_2$ and C_5Me_4 methyl groups, respectively. In addition, in **2e**/$B(C_6F_5)_3$ the signals for the diastereotopic methyl groups of the NMe_2 function are well separated at −25 °C, indicating a slowed dissociation of the additional donor function. The resonances for the zirconium methyl signals appear at δ −0.21 (**2b**/$B(C_6F_5)_3$) and −0.14 ppm (**2e**/$B(C_6F_5)_3$) in the ^{1}H NMR spectrum and at δ 34.8 (**2b**/$B(C_6F_5)_3$) and 35.3 ppm (**2e**/$B(C_6F_5)_3$) in the ^{13}C NMR spectrum. These values are comparable to those reported for $[Zr(\eta^5\text{-}C_5Me_5)Me_2(toluene)]^+[MeB(C_6F_5)_3]^-$ (δ −0.11 and 45.5, respectively)[9a] and $[Zr(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)Me(toluene)]^+[B(C_6F_5)_4]^-$ (δ −0.45 and 32.2, respectively).[8b] Judged from the values of $\Delta\delta(m\text{-}, p\text{-}F)$, 3.7 and 5.9 ppm for **2b**/$B(C_6F_5)_3$ and **2e**/$B(C_6F_5)_3$, respectively, the anion $[MeB(C_6F_5)_3]^-$ appears to be coordinating.[25] We believe that an equilibrium between the contact ion pair and the solvent-separated ion pair exists.

When the titanium dibenzyl complexes **6a** and **6d** were reacted with equimolar amounts of $B(C_6F_5)_3$ in bromobenzene at room temperature, clean formation of the corresponding benzyl cations was observed. Attempts at isolating these compounds have failed so far, although a dark red powder precipitates upon addition of pentane. As Figure 5 shows for **6d**, it is quite obvious that the reaction according to Scheme 3 results in the formation of $[Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2NMe_2)(CH_2Ph)]^+[PhCH_2B(C_6F_5)_3]^-$, stable for a period of several hours. On the basis of the NMR spectroscopic evidence, we believe it to be a solvent-separated ion pair rather than a contact ion pair (**B** favored over **A** in Scheme 3). The anion shows ^{19}F NMR spectroscopic features that are indicative of a free $[PhCH_2B(C_6F_5)_3]^-$ ion ($\Delta\delta(m\text{-}, p\text{-}F) = 2.8$ ppm).[25] The methylene protons of the benzyl group bonded to the boron appear at δ 3.27 as a broad singlet and all aromatic protons are recorded well below δ 6.5, excluding the possibility of any strong interaction of the aromatic ring with the cationic metal center.

The methylene protons of the benzyl group at the cationic titanium center give rise to an AB spin pattern at δ 2.51 and 2.27 ppm with $^2J_{HH} = 11.4$ Hz. The coupling constant is similar to that observed in the parent neutral dibenzyl **6d** (10.6 Hz), indicating that there is no agostic or dihapto bonding of the benzyl group.[23,26] The diastereotopic methyls of the NMe_2 group

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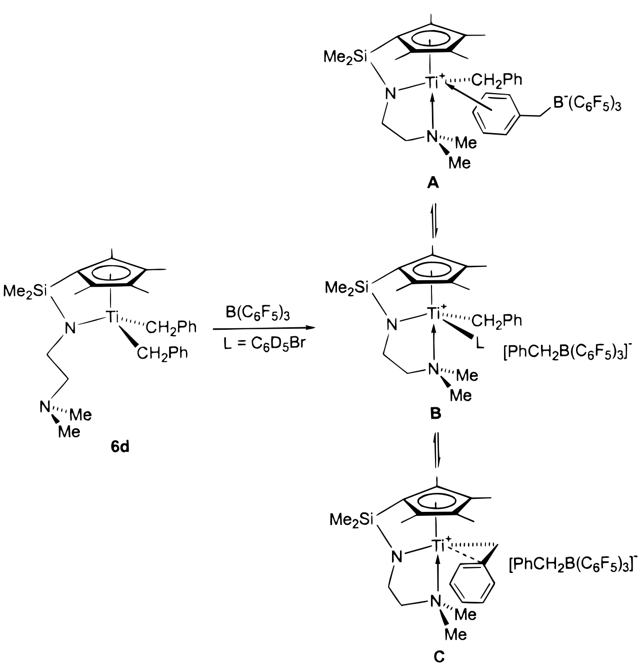
(23) Mono(ring) alkyl zirconium cations seem to be thermally less robust: Crowther, D. J.; Jordan, R. F.; Baenziger, N. C.; Verma, A. *Organometallics* **1990**, *9*, 2574.

(24) (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623. (b) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015.

(25) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672.

Scheme 3



give rise to one signal in the ^{1}H NMR spectrum, whereas in the ^{13}C NMR spectrum two signals are recorded, suggesting a fluxional coordination of the side chain. As a matter of fact, the signal of the NMe_2 group decoalesces below −20 °C into two resonances. We assume that at room temperature the side chain is engaged in a fluxional ("weak") bonding without halting the nitrogen inversion. Rigid coordination of the NMe_2 group would probably cause stronger inequivalency of the methyl signals. Thus, the strongly electrophilic, formally 12-electron cation appears to be sufficiently stabilized by this mode of fluxional coordination.

Polymerization of ethylene and 1-hexene was observed with the above cations, but with erratic results. Therefore study of ethylene polymerization was conducted with the dichloro titanium **1a** and the zirconium and hafnium dialkyl derivatives **2b**, **5b**, **2c**, and **5c** containing the methoxy-functionalized ligand. Upon activation with methylaluminoxane (metal-to-aluminum ratio 1:500), ethylene is readily polymerized to give high molecular weight polyethylene of melting temperatures in the range 130−135 °C. The results are summarized in Table 5. The polymerization generally proceeded significantly faster at 70 °C. As often observed in metallocene catalysis,[7] the activity of zirconium catalysts is higher than that of the titanium and hafnium homologues at a given metal-to-aluminum ratio. Compared to similar complexes containing the bidentate ligand such as $Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)Cl_2$ under identical conditions,[2j] it is evident that side chain modification results in significantly lower activities (12 vs 950 kg polyethylene/(mol Ti h)).[27] We tentatively ascribe this to the occupation of one additional site at the metal site that blocks the π-complex formation of the ethylene.[28]

Table 5. Polymerization of Ethylene with Methylaluminoxane-Activated $M(\eta^5{:}\eta^1{:}\eta^x\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)R_2$ Complexes[a]

precat	temp (°C)	yield (g)	activity[b]	T_m[c]
1a	25	0.08[d]	12	132.3
1a	70	1.55	239	131.3
2b	25	0.08	13	136.5
2b	70	3.80	586	129.7
2c	25	0.06	9	134.8
2c	70	0.66	102	127.5
5b	25	0.20[e]	31	131.1
5b	70	1.12	173	129.5
5c	25	0.21	32	130.7
5c	70	0.08	12	125.3

[a] Ethylene pressure 3 bar, precatalyst 5.0 μmol, 2.5 mmol of methylalumoxane, metal-to-aluminum ratio: 1:500, 200 mL of toluene, 1.5 h reaction time. [b] Activity: kg of polyethylene/mol of metal·h·ethylene concentration. [c] The melting temperatures were measured by DSC (DSC-7 Perkin-Elmer) from the second scan with a heating ratio of 10 °C/min. [d] Molecular weight (GPC, vs polystyrene): $M_n = 13\,000$, $M_w = 4\,660\,000$. [e] Molecular weight (GPC, vs polystyrene): $M_n = 970\,000$, $M_w = 9\,310\,000$.

Conclusion

The linked amido−cyclopentadienyl ligand is an ancillary ligand set that is comparable to the linked bis(cyclopentadienyl) ligand system in *ansa*-metallocenes.[2k] Although donating two π-electrons less to a d^0-metal center, the pronounced donor property of the amido group imparts resistance to reduction at the metal center comparable to that of the metallocene unit. When the formal electron count at the metal is identical with that of the metallocene as a result of additional σ-donors such as OMe and NMe_2, as in the tridentate ligands discussed above, one starts seeing differences as a result of the relative "electron richness" of the complexes containing the linked amido−cyclopentadienyl ligand. Most prominently, β-hydrogen elimination of higher alkyl groups clearly slows down in the dialkyl complexes, at least for the less reducible metals Zr and Hf. This feature is also prevalent in the group 4 metal bis(amido) complexes recently studied.[6a−c] The metal−carbon bond energy however does not change dramatically, as observed in the ready insertion reaction of CO and *tert*-butyl isonitrile. The additional donor furthermore enabled the observation of a benzyl titanium cation, the presumed active species in the polymerization of α-olefins, when titanium complexes with linked amido−cyclopentadienyl ligands are used.[3,8] Since the additional σ-donor is not bonded rigidly in the kinetic sense and undergoes reversible dissociation and association, polymerization of α-olefins is not completely suppressed. Recent studies confirm the extremely high electrophilicity of the alkyl cation within the coordination sphere of the linked amido−cyclopentadienyl system. It was reported that the reaction of the dibenzyl $Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(CH_2Ph)_2$ with $B(C_6F_5)_3$ results in a C−H activation product, $[Ti\{\eta^5{:}\eta^1{:}\eta^1\text{-}(C_5Me_3CH_2)SiMe_2N^tBu\}]^+[PhCH_2B(C_6F_5)_3]^-$, and that the dimethyl $Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)Me_2$ forms a dimeric cation $[\{Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)Me\}_2(\mu\text{-}Me)]^+$.[8d] In conclusion, we have delineated a "metallocene-like" coordination sphere[29] for group 4 metal centers based on the functionalized

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linked amido−cyclopentadienyl ligands. Coordination properties of such ligands at the even more electrophilic d^0-metal center of the heavier group 3 metals are currently also a focus of our attention.[30]

Experimental Section

General Considerations. All experiments were performed under argon using standard Schlenk or glovebox techniques. THF, pentane, and hexane were purified by distillation from sodium/benzophenone ketyl. Toluene was distilled over sodium sand. $Li_2[C_5Me_4SiMe_2NCH_2CH_2X]$ ($X = OMe, NMe_2$),[2i] $M(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Cl_2$ ($M = Zr$ (**1b**); Hf (**1c**)),[2i] $TiCl_3(THF)_2$,[31] $Mg(CH_2Ph)_2(THF)_2$,[32] LiEt,[33] Li^nPr,[33] and $B(C_6F_5)_3$[34] were synthesized according to published procedures. $PbCl_2$ (Fluka) was dried at 120 °C before use. MgMeCl (Aldrich), MgEtCl (Aldrich), Li^nBu (Aldrich), $Mg(CH_2SiMe_3)Cl$ (Aldrich), LiPh (Aldrich), and ^tBuNC (Fluka) were used as received. Alkyllithium[35] and Grignard[36] solutions were titrated prior to use. NMR spectra were recorded on a Bruker DRX 400 spectrometer (^1H, 400 MHz; ^{13}C, 101 MHz; ^{11}B, 128 MHz; ^{19}F, 376 MHz) in C_6D_6 at 298 K, unless otherwise stated. Chemical shifts for ^1H and ^{13}C spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. ^{11}B spectra were referenced externally to $BF_3(Et_2O)$, ^{19}F spectra to $CFCl_3$. Mass spectra were recorded on a Finnigan 8230 spectrometer. Elemental analyses were performed by the microanalytical laboratory of this department or by the Analytische Laboratorien GmbH, Lindlar, Germany.

$Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Cl_2$ (1a). THF (40 mL) was added at −78 °C to a solid mixture of $Li_2[C_5Me_4SiMe_2NCH_2CH_2OMe]$ (1.00 g, 3.7 mmol) and $TiCl_3(THF)_3$ (1.39 g, 3.7 mmol). After warming to room temperature, solid $PbCl_2$ (1.04 g, 3.7 mmol) was added, and the mixture was stirred for 30 min. All volatiles were removed in vacuo, and the residue was extracted with pentane (3 × 15 mL). Filtration followed by concentrating the filtrate and cooling to −30 °C afforded light-yellow-brown crystals: 67% yield; mp 98 °C; ^1H NMR δ 0.46 (s, 6 H, $SiCH_3$), 2.00, 2.02 (s, 6 H, $C_5(CH_3)_4$), 2.90 (s, 3 H, OCH_3), 3.08 ("t", 2 H, CH_2O), 4.34 ("t", 2 H, NCH_2); $^{13}C\{^1H\}$ NMR δ 2.9 ($SiCH_3$), 12.9, 16.2 ($C_5(\mathit{C}H_3)_4$), 54.9 (NCH_2), 57.9 (OCH_3), 72.5 (CH_2O), 104.6 (ring C at Si), 135.8, 141.0 ($\mathit{C}_5(CH_3)_4$); EI MS *m*/*z* 369 (5, M^+), 324 (100, $M^+ - CH_2OMe$), 295 (33, $M^+ - NHCH_2CH_2OMe$), 178 (52, $C_5Me_4SiMe_2^+$), 45 (50, CH_2OMe^+). Anal. Calcd for $C_{14}H_{25}Cl_2NOSiTi$: C, 45.42; H, 6.81; N, 3.78. Found: C, 45.10; H, 6.71; N, 3.77.

$Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Me_2$ (2a). Methylmagnesium chloride (1.0 mL of a 1.6 M solution in THF) was added to a suspension of **1a** (0.30 g, 0.84 mmol) in hexane (30 mL) at 0 °C. After the mixture was stirred for 3 h at room temperature, all volatiles were removed in vacuo. Extraction of the residue with pentane (20 mL) was followed by filtration through glass fiber, and the volume of the filtrate was reduced. Crystallization from pentane at −30 °C gave yellow needles in 75% yield: mp 35 °C; ^1H NMR δ 0.42 (s, 6 H, $SiCH_3$), 0.45 (s, 6 H, $TiCH_3$), 1.89, 1.99 (s, 6 H, $C_5(CH_3)_4$), 3.11 (s, 3 H, OCH_3), 3.38 ("t", 2 H, CH_2O), 4.33 ("t", 2 H, NCH_2); ^{13}C NMR δ 3.3 (q, $^1J_{CH} = 119$ Hz, $SiCH_3$), 11.9, 15.1 (q, $^1J_{CH} = 126$ Hz, $C_5(\mathit{C}H_3)_4$), 49.7 (q, $^1J_{CH} = 118$ Hz, $TiCH_3$), 50.6 (t, $^1J_{CH} = 134$ Hz, NCH_2), 58.2 (q, $^1J_{CH} = 139$ Hz, OCH_3), 75.3 (t, $^1J_{CH} = 145$ Hz, CH_2O), 97.4 (s, ring C at Si), 128.0, 134.1 (s, $\mathit{C}_5(CH_3)_4$); EI MS: *m*/*z* 330 (3, MH^+), 314 (100, $M^+ - CH_3$), 298 (30, $M^+ - OMe$), 272 (41, $MH_2^+ - CH_2CH_2OMe$), 256 (22, $MH^+ - CH_2CH_2OMe, - CH_3$), 241 (37, $MH^+ - CH_2CH_2OMe, - 2CH_3$). Anal. Calcd for $C_{16}H_{31}NOSiTi$: C, 58.34; H, 9.49; N, 4.25. Found: C, 56.55; H, 9.28; N, 4.42.

$Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)(CH_2Ph)_2$ (6a). Hexane (40 mL) was added to a solid mixture of **1a** (0.39 g, 1.09 mmol) and the THF adduct of dibenzylmagnesium (0.42 g, 1.20 mmol) at −78 °C. The mixture was allowed to warm to room temperature and stirred at room temperature overnight. All volatiles were removed in vacuo, and the residue was extracted with hexane (20 mL). After filtration through glass fiber, the yellow solution was concentrated and cooled to −30 °C overnight to give red crystals: yield 0.35 g (67%); ^1H NMR δ 0.41 (s, 6 H, $SiCH_3$), 1.74, 1.86 (s, 6 H, $C_5(CH_3)_4$), 2.08, 2.19 (d, 2 H, $^2J_{HH} = 10.6$ Hz, $TiCH_2$), 2.92 ("t", 2 H, CH_2O), 2.95 (s, 3 H, OCH_3), 3.82 ("t", 2 H, NCH_2), 6.88−7.17 (m, 10 H, C_6H_5); $^{13}C\{^1H\}$ NMR δ 3.4 ($SiCH_3$), 11.4, 14.9 ($C_5(\mathit{C}H_3)_4$), 52.1 (NCH_2), 57.8 (OCH_3), 74.4 (CH_2O), 79.5 ($TiCH_2$), 98.9 (ring C at Si), 121.9 (*para* C_6H_5), 126.8 (*meta* C_6H_5), 128.5 (*ortho* C_6H_5), 129.2, 135.4 ($\mathit{C}_5(CH_3)_4$), 149.2 (*ipso* C_6H_5); EI MS *m*/*z* 482 (21, M^+), 390 (17, $M^+ - C_7H_7$), 299 (29, $M^+ - 2C_7H_7$). Anal. Calcd for $C_{28}H_{39}NOSiTi$: C, 69.87; H, 8.11; N, 2.91. Found: C, 69.56; H, 8.00; N, 2.81.

Reaction of 6a with $B(C_6F_5)_3$. C_6D_5Br (0.5 mL) was added to an equimolar mixture of **6a** (20 mg, 41 μmol) and $B(C_6F_5)_3$ (21 mg, 41 μmol) in an NMR tube at −78 °C. The color turned dark red at room temperature: ^1H NMR (C_6D_5Br) δ 0.12, 0.35 (s, 3 H, $SiCH_3$), 1.45, 1.69, 1.77, 2.15 (s, 3 H, $C_5(CH_3)_4$), 2.16 (s, 3 H, OCH_3), 2.43, 2.90 (d, 1 H, $^2J_{HH} = 6.8$ Hz, $TiCH_2$), 3.16 (m, 1 H, $C\mathit{H}_2OMe$), 3.31 (br s, 2 H, $CH_2B(C_6F_5)_3$), 3.36 (m, 1 H, $C\mathit{H}_2OMe$), 3.45, 4.64 (m, 1 H, $SiNCH_2$), 6.44 (br, 2 H, $CH_2C_6\mathit{H}_5$), 6.86−7.15 (signals overlap. with solvent signals, 8 H, $CH_2C_6\mathit{H}_5$); $^{13}C\{^1H\}$ NMR (C_6D_5Br) δ 0.4, 2.8 ($SiCH_3$), 11.1, 13.1, 13.8, 15.2 ($C_5(\mathit{C}H_3)_4$), 32.0 (br, $\mathit{C}H_2B(C_6F_5)_3$), 49.1 ($SiNCH_2$), 62.6 ($\mathit{C}H_2OMe$), 74.5 (OCH_3), 88.3 ($TiCH_2$), 108.4 (ring C at Si), 122.0, 122.6, 122.9, 127.2, 128.9, 130.7, 131.9, 134.9, 135.9, 136.4, 142.4 (ring C), 135.6, 137.8, 138.9, 147.5 (C_6F_5), 148.7 (*ipso* $CH_2C_6H_5$) 149.8 (*ipso* C_6F_5); ^{11}B NMR (C_6D_5Br) δ −12.1; ^{19}F NMR (C_6D_5Br) δ −130.2 (d, $^3J_{FF} = 22.9$ Hz, *ortho* C_6F_5), −163.4 (t, $^3J_{FF} = 20.6$ Hz, *para* C_6F_5), −166.3 (t, $^3J_{FF} = 20.6$ Hz, *meta* C_6F_5).

$Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)\{C({=}N^tBu)Et\}Cl$ (12a). Ethylmagnesium chloride (1.30 mL of a 1.7 M solution in THF) was added to a mixture of **1a** (0.82 g, 2.21 mmol) and *tert*-butyl isonitrile (0.25 mL, 2.21 mmol) in hexane (30 mL) at −78 °C. The mixture was allowed to warm to room temperature over a period of 5 h under stirring. All volatiles were removed in vacuo, and the residue was extracted with pentane (15 mL). Filtration was followed by concentrating the filtrate and cooling the concentrated pentane solution to −78 °C to afford yellow needles: yield 0.70 g (71%); ^1H NMR δ 0.59, 0.70 (s, 3 H, $SiCH_3$), 1.00 (t, 3 H, $^3J_{HH} = 7$ Hz, $CH_2C\mathit{H}_3$), 1.32 (s, 3 H, $C_5(CH_3)_4$), 1.34 (s, 9 H, $C(CH_3)_3$), 1.95, 2.10 (s, 3 H, $C_5(CH_3)_4$), 2.28, 2.60 (m, 1 H, $C\mathit{H}_2CH_3$), 2.63 (s, 3 H, $C_5(CH_3)_4$), 3.05 (s, 3 H, OCH_3), 3.28 ("t", 2 H, CH_2O), 3.48, 3.60 (m, 1 H, NCH_2); $^{13}C\{^1H\}$ NMR δ 3.3, 4.8 ($SiCH_3$), 11.7 ($CH_2\mathit{C}H_3$), 11.8, 12.2, 15.5, 16.3 ($C_5(\mathit{C}H_3)_4$), 28.3 ($\mathit{C}H_2CH_3$), 30.2 ($C(\mathit{C}H_3)_3$), 52.6 (NCH_2), 58.0 (OCH_3), 63.3 ($\mathit{C}(CH_3)_3$), 73.9 (CH_2O), 104.2 (ring C at Si), 125.8, 127.5, 128.7, 133.8 ($\mathit{C}_5(CH_3)_4$), 238.8 (CN); EI MS *m*/*z* 446 (4, M^+), 417 (1, $M^+ - Et$), 411 (23, $M^+ - Cl$), 382 (3, $M^+ - C_2H_5 - Cl$), 363 (2, $M^+ - CNCMe_3$), 334 (95, $M^+ - CNCMe_3, - C_2H_5$), 327 (3, $M^+ - CNCMe_3, - Cl$), 298 (14, M^+

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− $CNCMe_3$, − C_2H_5, − Cl). Anal. Calcd for $C_{21}H_{39}N_2ClOSiTi$: C, 56.46; H, 8.73; N, 6.27. Found: C, 56.63; H, 8.72; N, 6.44.

Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)$Me_2$ (2b). Following a procedure similar to that described for the preparation of **2a**, **1b** (0.41 g, 1.0 mmol) was reacted with methylmagnesium chloride (1.05 mL of a 1.9 M solution in THF) to afford colorless crystals: yield 0.23 g (61%); ^{1}H NMR δ −0.35 (s, 6 H, $ZrCH_3$), 0.41 (s, 6 H, $SiCH_3$), 2.06, 2.08 (s, 6 H, $C_5(CH_3)_4$), 3.08 ("t", 2 H, NCH_2), 3.35 (s, 3 H, OCH_3), 3.44 ("t", 2 H, CH_2O); ^{13}C NMR δ 3.2 (q, $^1J_{CH}$ = 120 Hz, $SiCH_3$), 11.7, 14.3 (q, $^1J_{CH}$ = 126 Hz, $C_5(CH_3)_4$), 31.8 (q, $^1J_{CH}$ = 113 Hz, $ZrCH_3$), 45.8 (t, $^1J_{CH}$ = 134 Hz, NCH_2), 61.0 (q, $^1J_{CH}$ = 144 Hz, OCH_3), 79.0 (t, $^1J_{CH}$ = 144 Hz, CH_2O), 96.1 (s, ring C at Si), 124.1, 126.2 (s, $C_5(CH_3)_4$); EI MS *m/z* 372 (9%, M^+), 356 (11%, $M^+ - CH_3$), 340 (8%, $M^+ - OCH_3$). Anal. Calcd for $C_{16}H_{31}NOSiZr$: C, 51.56; H, 8.38; N, 3.76. Found: C, 51.29; H, 8.14; N, 3.62.

Reaction of 2b with $B(C_6F_5)_3$. C_6D_5Br (0.5 mL) was added to an equimolar mixture of **2b** (30 mg, 80.5 μmol) and $B(C_6F_5)_3$ (41 mg, 80.5 μmol) in an NMR tube at −78 °C. The reaction mixture turned yellow at −30 °C: ^{1}H NMR (C_6D_5Br, 253 K) δ −0.21 (br s, 3 H, $ZrCH_3$), 0.21 (br s, 6 H, $SiCH_3$), 0.81 (br s, 3 H, $CH_3B(C_6F_5)_3$), 1.8 (br s, 12 H, $C_5(CH_3)_4$), 3.1 (br, 2 H, NCH_2), 3.19 (br s, 3 H, OCH_3), 3.67 (br, 2 H, CH_2O); ^{13}C{^{1}H} NMR (C_6D_5Br, 253 K) δ 1.9 ($SiCH_3$), 10.0 (br, $C_5(CH_3)_4$), 20.0 ($CH_3B(C_6F_5)_3$), 34.8 ($ZrCH_3$), 47.4 (NCH_2), 62.3 (OCH_3), 80.4 (CH_2O), 102.2 (ring C at Si); ^{11}B NMR (C_6D_5Br, 253 K) δ −15.00; ^{19}F NMR (C_6D_5Br, 253 K) δ −130.3 (*ortho* C_6F_5), −160.0 (*para* C_6F_5), −163.7 (*meta* C_6F_5).

Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)^n$Pr_2$ (4b). Following a procedure similar to that described for the preparation of **2a**, **1b** (0.46 g, 1.11 mmol) was reacted with *n*-propyllithium (6.18 mL of a 0.36 M solution in pentane) to afford a brownish oil: yield 0.36 g (77%); ^{1}H NMR δ −0.14 (td, 2 H, $^2J_{HH}$ = 12 Hz, $^3J_{HH}$ = 5 Hz, $ZrCH_2$), 0.40 (s, 6 H, $SiCH_3$), 0.60 (td, 2 H, $^2J_{HH}$ = 12 Hz, $^3J_{HH}$ = 5 Hz, $ZrCH_2$), 1.14 (t, 6 H, $^3J_{HH}$ = 7 Hz, γ-CH_3), 1.3−1.5 (m, 4 H, β-CH_2), 2.00, 2.09 (s, 6 H, $C_5(CH_3)_4$), 3.08 ("t", 2 H, NCH_2), 3.36 (s, 3 H, OCH_3), 3.47 ("t", 2 H, CH_2O); ^{13}C{^{1}H} NMR δ 2.9 ($SiCH_3$), 11.3, 14.1 ($C_5(CH_3)_4$), 21.9 (β-CH_2, γ-CH_3), 46.0 (NCH_2), 54.8 ($ZrCH_2$), 60.9 (OCH_3), 79.4 (CH_2O), 96.8 (ring C at Si), 123.7, 125.4 ($C_5(CH_3)_4$); EI MS *m/z* 384 (2, $M^+ - C_3H_7$), 340 (3, $M^+ - C_3H_7$, $- C_3H_8$), 342 (6, $M^+ - C_3H_7$, $- C_3H_6$).

Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)^n$Bu_2$ (5b). A suspension of **1b** (0.48 g, 1.16 mmol) in hexane (30 mL) was treated with *n*-butyllithium (1.0 mL of a 2.3 M solution in hexane) at 0 °C. After stirring for 16 h at room temperature, all volatiles were removed in vacuo. The residue was extracted into pentane and filtered. Recrystallization from pentane at −78 °C afforded colorless crystals: yield 0.35 g (67%); mp (dec) 60 °C; ^{1}H NMR δ −0.18 (m, 2 H, $ZrCH_2$), 0.41 (s, 6 H, $SiCH_3$), 0.54 (m, 2 H, $ZrCH_2$), 1.04 (t, 6 H, $^3J_{HH}$ = 7 Hz, δ-CH_3), 1.2−1.5 (overlap. m, 8 H, β-, γ-CH_2), 2.06, 2.14 (s, 6 H, $C_5(CH_3)_4$), 3.1 ("t", 2 H, NCH_2), 3.42 (s, 3 H, OCH_3), 3.49 ("t", 2 H, CH_2O); ^{13}C NMR δ 2.9 (q, $^1J_{CH}$ = 117 Hz, $SiCH_3$), 11.3, 14.1 (q, $^1J_{CH}$ = 125 Hz, $C_5(CH_3)_4$), 14.3 (q, $^1J_{CH}$ = 123 Hz, δ-CH_3), 30.1 (t, $^1J_{CH}$ = 124 Hz, β-CH_2), 30.7 (t, $^1J_{CH}$ = 124 Hz, γ-CH_2), 45.9 (t, $^1J_{CH}$ = 133 Hz, NCH_2), 51.0 (t, $^1J_{CH}$ = 112 Hz, $ZrCH_2$), 60.8 (q, $^1J_{CH}$ = 143 Hz, OCH_3), 79.4 (t, $^1J_{CH}$ = 142 Hz, CH_2O), 96.8 (s, ring C at Si), 123.6, 125.4 (s, $C_5(CH_3)_4$); EI MS *m/z* 398 (10, $M^+ - C_4H_9$), 344 (37, $M^+ - C_4H_9$, $- C_4H_7$), 342 (100, $M^+ - C_4H_9$, $-C_4H_8$), 340 (48, $M^+ - C_4H_9$, $- C_4H_{10}$). Anal. Calcd for $C_{22}H_{43}NOSiZr$: C, 57.86; H, 9.42; N, 3.06. Found: C, 57.60; H, 9.25; N, 3.16.

Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)$(CH_2Ph)_2$ (6b). Following a procedure analogous to that described to prepare **6a**, **1b** (1.0 g, 2.42 mmol) was reacted with dibenzylmagnesium THF adduct (0.84 g, 2.42 mmol) to give colorless crystals: yield 0.83 g (66%); ^{1}H NMR δ 0.37 (s, 6 H, $SiCH_3$), 1.37, 1.85 (d, 2 H, $^2J_{HH}$ = 12 Hz, $ZrCH_2$), 1.97, 1.98 (s, 6 H, $C_5(CH_3)_4$), 2.63 (s, 3 H, OCH_3), 3.02 ("t", 2 H, NCH_2), 3.26 ("t", 2 H, CH_2O), 6.63−7.15 (m, 10 H, C_6H_5); ^{13}C{^{1}H} NMR δ 2.7 ($SiCH_3$), 11.6, 14.4 ($C_5(CH_3)_4$), 46.6 (NCH_2), 58.1 ($ZrCH_2$), 62.4 (OCH_3), 78.9 (CH_2O), 97.9 (ring C at Si), 121.3 (*para* C_6H_5), 125.5, 126.8 ($C_5(CH_3)_4$), 127.8 (*meta* C_6H_5), 128.3 (*ortho* C_6H_5), 150.6 (*ipso* C_6H_5); EI MS *m/z* 433 (100, $M^+ - C_7H_7$), 342 (36, $M^+ - 2C_7H_7$). Anal. Calcd for $C_{28}H_{39}NOSiZr$: C, 64.00; H, 7.43; N, 2.76. Found: C, 63.78; H, 7.31; N, 2.60.

Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)$(CH_2SiMe_3)_2$ (7b). The preparation of this compound is analogous to the preparation of **2a**. The reaction between **1b** (0.50 g, 1.21 mmol) and trimethylsilylmethylmagnesium chloride (2.42 mL of a 1.0 M solution in Et_2O) gave colorless crystals: yield 0.54 g (87%); ^{1}H NMR δ −0.73, 0.13 (d, 2 H, $^2J_{HH}$ = 11 Hz, $ZrCH_2$), 0.15 (s, 18 H, $Si(CH_3)_3$), 0.40 (s, 6 H, $Si(CH_3)_2$), 2.03, 2.09 (s, 6 H, $C_5(CH_3)_4$), 3.11 ("t", 2 H, NCH_2), 3.45 ("t", 2 H, CH_2O), 3.45 (s, 3 H, OCH_3); ^{13}C{^{1}H} NMR δ 2.8 ($Si(CH_3)_2$), 4.6 ($Si(CH_3)_3$), 12.9, 14.9 ($C_5(CH_3)_4$), 42.5 ($ZrCH_2$), 45.9 (NCH_2), 62.8 (OCH_3), 78.8 (CH_2O), 98.0 (ring C at Si), 124.8, 125.9 ($C_5(CH_3)_4$; EI MS *m/z* 501 (3, $M^+ - CH_3$), 428 (76, $M^+ - CH_2SiMe_3$), 340 (16, $M^+ - 2CH_2SiMe_3$). Anal. Calcd for $C_{22}H_{47}NOSi_3Zr$: C, 51.14; H, 9.10; N, 2.71. Found: C, 50.87; H, 9.06; N, 2.82.

Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)$Ph_2$ (8b). Following a procedure analogous to that described for the preparation of **2a**, **1b** (0.54 g, 1.30 mmol) was reacted with phenyllithium (1.5 mL of a 1.8 M solution in cyclohexane/ether) to give colorless crystals: yield 0.45 g (70%); ^{1}H NMR δ 0.53 (s, 6 H, $SiCH_3$), 1.71, 2.01 (s, 6 H, $C_5(CH_3)_4$), 2.17 (s, 3 H, OCH_3), 3.21 ("t", 2 H, NCH_2), 3.34 ("t", 2 H, CH_2O), 7.11−7.44 (m, 10 H, C_6H_5); ^{13}C{^{1}H} NMR δ 3.0 ($SiCH_3$), 12.1, 14.8 ($C_5(CH_3)_4$), 46.8 (NCH_2), 61.3 (OCH_3), 78.3 (CH_2O), 97.7 (ring C at Si), 126.0 (*para* C_6H_5), 126.2 ($C_5(CH_3)_4$), 126.5 (*meta* C_6H_5), 128.7 ($C_5(CH_3)_4$), 134.1 (*ortho* C_6H_5), 191.1 (*ipso* C_6H_5); EI MS *m/z* 341 (1, $M^+ - 2C_6H_5$), 328 (1, $M^+ - 2C_7H_7$). Anal. Calcd for $C_{26}H_{35}NOSiZr$: C, 62.80; H, 7.05; N, 2.82. Found: C, 62.57; H, 7.20; N, 2.73.

Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$){C(=N^{t}Bu)Et}-Cl (12b). Following a procedure analogous to that described for **12a**, ethylmagnesium chloride (0.93 mL of a 1.7 M solution in THF) was added to a mixture of **1b** (0.66 g, 1.59 mmol) and *tert*-butyl isonitrile (0.18 mL, 1.59 mmol) in hexane (30 mL) at −78 °C to give colorless crystals after cooling a concentrated pentane solution: yield 0.50 g (64%); ^{1}H NMR δ 0.58 (s, 6 H, $SiCH_3$), 1.11 (t, 3 H, $^3J_{HH}$ = 7 Hz, CH_2CH_3), 1.26 (s, 9 H, $C(CH_3)_3$), 1.47, 2.18, 2.19 (s, 3 H, $C_5(CH_3)_4$), 2.29 (m, 1 H, CH_2CH_3), 2.58 (s, 3 H, $C_5(CH_3)_4$), 2.67 (m, 1 H, CH_2CH_3), 3.00 (m, 1 H, NCH_2), 3.10 (m, 1 H, CH_2O), 3.19 (s, 3 H, OCH_3), 3.25 (m, 2 H, NCH_2, CH_2O); ^{13}C{^{1}H} NMR δ 3.0, 3.2 ($SiCH_3$), 12.2, 12.5 ($C_5(CH_3)_4$), 12.7 (CH_2CH_3), 15.0, 15.2 ($C_5(CH_3)_4$), 28.9 (CH_2CH_3), 31.4 ($C(CH_3)_3$), 46.8 (NCH_2), 60.4 ($C(CH_3)_3$), 62.0 (OCH_3), 78.3 (CH_2O), 102.8 (ring C at Si), 123.5, 128.6 ($C_5(CH_3)_4$), 247.6 (CN). Anal. Calcd for $C_{21}H_{39}N_2ClOSiZr$: C, 51.46; H, 7.96; N, 5.72. Found: C, 51.22; H, 7.87; N, 5.85.

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)$Me_2$ (2c). Following a procedure analogous to that described to prepare **2a**, **1c** (0.40 g, 0.79 mmol) was treated with methylmagnesium chloride (0.88 mL of a 1.9 M solution in THF) to give **2c** as colorless crystals: yield 0.22 g (60%); ^{1}H NMR δ −0.46 (s, 6 H, $HfCH_3$), 0.42 (s, 6 H, $SiCH_3$), 2.08, 2.12 (s, 6 H, $C_5(CH_3)_4$), 3.12 ("t", 2 H, NCH_2), 3.30 (s, 3 H, OCH_3), 3.39 ("t", 2 H, CH_2O); ^{13}C{^{1}H} NMR δ 2.9 ($SiCH_3$), 11.9, 14.0 ($C_5(CH_3)_4$), 41.8 ($HfCH_3$), 45.3 (NCH_2), 60.8 (OCH_3), 72.9 (CH_2O), 96.7 (ring C at Si), 123.4, 124.7 ($C_5(CH_3)_4$); EI MS *m/z* 446 (100, $M^+ - CH_3$), 431 (21, $M^+ - 2CH_3$). Anal. Calcd for $C_{16}H_{31}NHfOSi$: C, 41.78; H, 6.74; N, 3.04. Found: C, 41.62; H, 6.61; N, 2.91.

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)$Et_2$ (3c). Following a procedure analogous to that described to prepare **2a**, **1c** (0.30 g, 0.59 mmol) was reacted with ethyllithium (11.4 mL of a 0.11 M solution in hexane) to give **3c** as colorless crystals: yield 0.19 g (66%); ^{1}H NMR δ −0.27 (m, 2 H, $HfCH_2$), 0.42 (s, 6 H, $SiCH_3$), 0.48 (m, 2 H, $HfCH_2$), 1.21 (t, $^3J_{HH}$ = 8 Hz, 6 H, CH_2CH_3), 2.04, 2.16 (s, 6 H, $C_5(CH_3)_4$), 3.11 ("t", 2 H, NCH_2), 3.34 (s, 3 H, OCH_3), 3.42 ("t", 2 H, CH_2O); ^{13}C{^{1}H} NMR δ 2.8 ($SiCH_3$), 11.3 ($C_5(CH_3)_4$), 11.6 ($HfCH_2$), 13.9 ($C_5(CH_3)_4$), 45.5

(NCH_2), 49.5 (CH_2CH_3), 60.6 (OCH_3), 79.5 (CH_2O), 97.5 (ring C at Si), 123.1, 124.1 ($C_5(CH_3)_4$); EI MS *m/z* 460 (10, $M^+ - C_2H_6$), 431 (80, $M^+ - 2C_2H_6$). Anal. Calcd for $C_{18}H_{35}NHfOSi$: C, 44.31; H, 7.17; N, 2.87. Found: C, 44.19; H, 7.07; N, 2.76.

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)$^nPr_2$ (4c). Following a procedure analogous to that described to prepare **2a**, **1c** (0.56 g, 1.12 mmol) was reacted with *n*-propyllithium (7.5 mL of a 0.3 M solution in pentane) to give **4c** as pale yellow needles that melt at room temperature: yield 0.36 g (63%); ^1H NMR δ −0.37 (td, 2 H, $^2J_{HH} = 12$ Hz, $^3J_{HH} = 5$ Hz, $HfCH_2$), 0.40 (s, 6 H, $SiCH_3$), 0.49 (td, 2 H, $^2J_{HH} = 12$ Hz, $^3J_{HH} = 5$ Hz, $HfCH_2$), 1.16 (t, 6 H, $^3J_{HH} = 6$ Hz, γ-CH_3), 1.2−1.5 (m, 4 H, β-CH_2), 2.04, 2.13 (s, 6 H, $C_5(CH_3)_4$), 3.10 ("t", 2 H, NCH_2), 3.33 (s, 3 H, OCH_3), 3.42 ("t", 2 H, CH_2O); $^{13}C\{^1H\}$ NMR δ 2.8 ($SiCH_3$), 11.2, 14.0 ($C_5(CH_3)_4$), 22.5 (γ-CH_3), 23.0 (β-CH_2), 45.5 (NCH_2), 60.7 (OCH_3), 64.7 ($HfCH_2$), 79.5 (CH_2O), 98.0 (ring C at Si), 123.3, 124.2 ($C_5(CH_3)_4$); EI MS *m/z* 474 (18, $M^+ - C_3H_7$), 432 (28, $M^+ - C_3H_7, - C_3H_6$), 431 (16, $M^+ - 2C_3H_7$), 430 (29, $M^+ - C_3H_7, - C_3H_8$).

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)$^nBu_2$ (5c). This compound was prepared analagously to **5b**. From **1c** (0.40 g, 0.79 mmol) and *n*-butyllithium (0.62 mL of a 2.7 M solution in hexane), **5c** was obtained as colorless crystals: yield 0.23 g (55%); mp (dec) 90 °C; ^1H NMR δ −0.47 (m, 2 H, $HfCH_2$), 0.42 (s, 6 H, $SiCH_3$), 0.49 (m, 2 H, $HfCH_2$), 1.06 (t, 6 H, $^3J_{HH} = 7$ Hz, δ-CH_3), 1.20 (m, 2 H, β-CH_2), 1.50 (overlap. m, 6 H, β-, γ-CH_2), 2.06, 2.14 (s, 6 H, $C_5(CH_3)_4$), 3.13 ("t", 2 H, NCH_2), 3.39 (s, 3 H, OCH_3), 3.45 ("t", 2 H, CH_2O); ^{13}C NMR δ 2.8 (q, $^1J_{CH} = 117$ Hz, $SiCH_3$), 11.3, 13.9 (q, $^1J_{CH} = 125$ Hz, $C_5(CH_3)_4$), 14.3 (q, $^1J_{CH} = 123$ Hz, δ-CH_3), 31.1 (t, $^1J_{CH} = 124$ Hz, β-CH_2), 31.2 (t, $^1J_{CH} = 124$ Hz, γ-CH_2), 45.9 (t, $^1J_{CH} = 133$ Hz, NCH_2), 60.4 (t, $^1J_{CH} = 110$ Hz, $HfCH_2$), 60.8 (q, $^1J_{CH} = 144$ Hz, OCH_3), 79.6 (t, $^1J_{CH} = 141$ Hz, CH_2O), 97.4 (s, ring C at Si), 123.4, 124.2 (s, $C_5(CH_3)_4$); EI MS *m/z* 488 (26, $M^+ - C_4H_9$), 432 (83, $M^+ - C_4H_8, - C_4H_9$), 430 (100, $M^+ - C_4H_9, - C_4H_{10}$). Anal. Calcd for $C_{22}H_{43}NHfOSi$: C, 48.57; H, 7.91; N, 2.57. Found: C, 48.30; H, 7.75; N, 2.43.

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)($CH_2Ph$)$_2$ (6c). Following a procedure analogous to that described to prepare **6a**, **1c** (0.30 g, 0.59 mmol) was reacted with dibenzylmagnesium THF adduct (0.27 g, 0.77 mmol) to give colorless crystals: yield 0.24 g (67%); ^1H NMR δ 0.40 (s, 6 H, $SiCH_3$), 1.04, 1.73 (d, 2 H, $^2J_{HH} = 13$ Hz, $HfCH_2$), 2.01, 2.07 (s, 6 H, $C_5(CH_3)_4$), 2.58 (s, 3 H, OCH_3), 3.09 ("t", 2 H, NCH_2), 3.18 ("t", 2 H, CH_2O), 6.8−7.1 (m, 10 H, C_6H_5); $^{13}C\{^1H\}$ NMR δ 2.7 ($SiCH_3$), 11.5, 14.3 ($C_5(CH_3)_4$), 45.9 (NCH_2), 62.4 (OCH_3), 66.6 ($HfCH_2$), 79.2 (CH_2O), 98.4 (ring C at Si), 121.7 (*para* C_6H_5), 124.9, 125.3 ($C_5(CH_3)_4$), 127.7 (*meta* C_6H_5), 128.8 (*ortho* C_6H_5), 151.0 (*ipso* C_6H_5); EI MS *m/z* 522 (1, $M^+ - C_7H_7$), 431 (35, $M^+ - 2C_7H_7$). Anal. Calcd for $C_{28}H_{39}NHfOSi$: C, 54.94; H, 6.39; N, 2.28. Found: C, 54.68; H, 6.20; N, 2.14.

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)($CH_2SiMe_3$)$_2$ (7c). Following a procedure analogous to that described to prepare **2a**, **1c** (0.30 g, 0.59 mmol) was reacted with trimethylsilylmethylmagnesium chloride (1.25 mL of a 1 M solution in Et_2O) to give **7c** as colorless crystals: yield 0.25 g (71%); ^1H NMR δ −1.17, −0.20 (d, 2 H, $^2J_{HH} = 12$ Hz, $HfCH_2$), 0.17 (s, 18 H, $Si(CH_3)_3$), 0.41 (s, 6 H, $Si(CH_3)_2$), 2.07, 2.13 (s, 6 H, $C_5(CH_3)_4$), 3.17 ("t", 2 H, NCH_2), 3.41 ("t", 2 H, CH_2O), 3.43 (s, 3 H, OCH_3); $^{13}C\{^1H\}$ NMR δ 2.7 ($Si(CH_3)_2$), 4.9 ($Si(CH_3)_3$), 12.3, 14.7 ($C_5(CH_3)_4$), 45.4 ($HfCH_2$), 48.6 (NCH_2), 62.6 (OCH_3), 78.9 (CH_2O), 98.5 (ring C at Si), 124.1, 124.4 ($C_5(CH_3)_4$); EI MS *m/z* 605 (1, M^+), 518 (4, $M^+ - CH_2SiMe_3$), 431 (21, $M^+ - 2CH_2SiMe_3$). Anal. Calcd for $C_{22}H_{47}NHfOSi_3$: C, 43.74; H, 7.78; N, 2.32. Found: C, 43.64; H, 7.66; N, 2.27.

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)$Ph_2$ (8c). Following a procedure analogous to that described to prepare **2a**, **1c** (0.41 g, 0.82 mmol) was reacted with phenyllithium (0.92 mL of a 1.8 M solution in cyclohexane/ether) to give **8c** as yellow crystals: yield 0.32 g (68%); ^1H NMR δ 0.53 (s, 6 H, $SiCH_3$), 1.76, 2.04 (s, 6 H, $C_5(CH_3)_4$), 2.14 (s, 3 H, OCH_3), 3.25 ("t", 2 H, NCH_2), 3.32 ("t", 2 H, CH_2O), 7.15−7.47 (m, 10 H, C_6H_5); $^{13}C\{^1H\}$ NMR δ 2.9 ($SiCH_3$), 12.0, 14.6 ($C_5(CH_3)_4$), 46.3 (NCH_2), 61.2 (OCH_3), 78.6 (CH_2O), 98.1 (ring C at Si), 125.5 ($C_5(CH_3)_4$), 125.9 (*para* C_6H_5), 126.9 (*meta* C_6H_5), 127.2 ($C_5(CH_3)_4$), 135.4 (*ortho* C_6H_5), 202.6 (*ipso* C_6H_5); EI MS *m/z* 585 (30, M^+), 508 (100, $M^+ - C_7H_7$), 431 (18, $M^+ - 2C_7H_7$). Anal. Calcd for $C_{26}H_{35}NHfOSi$: C, 53.47; H, 5.99; N, 2.39. Found: C, 53.13; H, 6.08; N, 2.25.

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)(COMe)Me (9c). Toluene (15 mL) was added to a 50 mL flask containing **2c** (0.20 g, 0.43 mmol), and the argon atmosphere was replaced by carbon monoxide. The solution was stirred overnight, and toluene was completely removed to give **9c** as a yellow oil: yield 0.17 g (80%); ^1H NMR δ −0.08 (s, 3 H, $HfCH_3$), 0.53, 0.54 (s, 3 H, $SiCH_3$), 1.30 (s, 3 H, $HfCOCH_3$), 1.99, 2.27, 2.45, 2.46 (s, 3 H, $C_5(CH_3)_4$), 2.68 (s, 3 H, OCH_3), 2.9−3.2 (m, 4 H, NCH_2-CH_2O); ^{13}C NMR δ 2.9, 3.3 (q, $^1J_{CH} = 118$ Hz, $SiCH_3$), 10.5, 11.2, 14.4, 14.7 (q, $^1J_{CH} = 126$ Hz, $C_5(CH_3)_4$), 23.8 (q, $^1J_{CH} = 111$ Hz, $HfCOCH_3$), 35.0 (q, $^1J_{CH} = 125$ Hz, $HfCH_3$), 45.1 (t, $^1J_{CH} = 133$ Hz, NCH_2), 58.6 (q, $^1J_{CH} = 144$ Hz, OCH_3), 78.9 (t, $^1J_{CH} = 143$ Hz, CH_2O), 98.5 (s, ring C at Si), 121.1, 121.5, 123.9, 125.3 (s, $C_5(CH_3)_4$), 342.3 (s, $HfCOCH_3$); EI MS *m/z* 489 (11, M^+), 446 (41, $M^+ - COCH_3$), 431 (78, $M^+ - COCH_3, - CH_3$).

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)($CO^nBu$)$^nBu$ (10c). An NMR tube containing a solution of **5c** (27 mg, 0.05 mmol) in C_6D_6 (0.5 mL) was placed into a flask, and the argon atmosphere was replaced by carbon monoxide. The NMR tube was left overnight under carbon monoxide, during which time the color of the solution changed from colorless to slightly yellow. ^1H NMR spectra indicated complete conversion of **5c** into **10c**. Removal of all the volatiles resulted in a yellow oil; ^1H NMR δ 0.35 (m, 2 H, $HfCH_2$), 0.53, 0.55 (s, 3 H, $SiCH_3$), 0.55−1.20 (overlap. m, 10 H, $HfCOCH_2$, β-, γ-CH_2), 0.89, 1.23 (t, 3 H, $^3J_{HH} = 7$ Hz, δ-CH_3), 1.32, 1.99, 2.26, 2.48 (s, 3 H, $C_5(CH_3)_4$), 2.5 (m, 2 H, NCH_2), 2.69 (s, 3 H, OCH_3), 2.7 (m, 2 H, CH_2O); $^{13}C\{^1H\}$ NMR δ 2.8, 3.3 ($SiCH_3$), 10.6, 11.1, 14.2, 14.4 ($C_5(CH_3)_4$), 14.5, 14.6 (δ-CH_3), 23.3, 26.2, 32.1, 33.4 (β- and γ-CH_2), 43.2 ($HfCOCH_2$), 45.1 (NCH_2), 49.1 ($HfCH_2$), 58.8 (OCH_3), 79.1 (CH_2O), 98.6 (ring C at Si), 121.1, 121.2, 123.7, 125.3 ($C_5(CH_3)_4$), 343.0 ($HfCOCH_2$).

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)$I_2$ (11c). C_6D_6 (0.5 mL) was added to an NMR tube containing **5c** (30 mg, 0.05 mmol) and I_2 (28 mg, 0.11 mmol). Complete conversion of **5c** to **11c** with concomitant signals for ^nBuI was observed within 5 min by ^1H NMR spectroscopy. After removing all the volatiles, the dark yellow solid was washed with pentane (2 mL) and dried: yield 32 mg (95%); ^1H NMR δ 0.28 (s, 6 H, $SiCH_3$), 2.19, 2.42 (s, 6 H, $C_5(CH_3)_4$), 2.89 ("t", 2 H, NCH_2), 3.44 ("t", 2 H, CH_2O), 3.72 (s, 3 H, OCH_3); $^{13}C\{^1H\}$ NMR δ 2.2 ($SiCH_3$), 12.9, 15.2 ($C_5(CH_3)_4$), 46.5 (NCH_2), 65.8 (OCH_3), 77.5 (CH_2O), 100.7 (ring C at Si), 129.6, 130.6 ($C_5(CH_3)_4$); EI MS *m/z* 685 (14, M^+), 558 (37, $M^+ - I$). Anal. Calcd for $C_{14}H_{25}NHfI_2OSi$: C, 24.58; H, 3.65; N, 2.04. Found: C, 22.16; H, 3.94; N, 2.78.

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$){$C(=N^tBu)Et$}-Cl (12c). Following a procedure analogous to that described for **12a**, ethylmagnesium chloride (0.42 mL, 0.84 mmol, 2 M in THF) was added to a mixture of **1c** (421 mg, 0.84 mmol) and *tert*-butyl isonitrile (0.09 mL, 0.84 mmol) in hexane (30 mL) at −78 °C to give colorless crystals: yield 247 mg (51%); ^1H NMR δ 0.59 (s, 6 H, $SiCH_3$), 1.15 (t, 3 H, $^3J_{HH} = 7.0$ Hz, CH_2CH_3), 1.25 (s, 9 H, $C(CH_3)_3$), 1.54, 2.22, 2.23 (s, 3 H, $C_5(CH_3)_4$), 2.28 (m, 1 H, CH_2CH_3), 2.63 (s, 3 H, $C_5(CH_3)_4$), 2.80 (m, 1 H, CH_2CH_3), 3.09 (m, 2 H, CH_2O, 1 H, $SiNCH_2$), 3.12 (br s, 3 H, OCH_3), 3.24 (m, 1 H, $SiNCH_2$); $^{13}C\{^1H\}$ NMR δ 3.4, 3.6 ($SiCH_3$), 12.4, 12.8 ($C_5(CH_3)_4$), 13.3 (CH_2CH_3), 15.1, 15.5 ($C_5(CH_3)_4$), 30.3 (CH_2CH_3), 31.6 ($C(CH_3)_3$), 46.5 ($SiNCH_2$), 60.3 ($C(CH_3)_3$), 61.8 (OCH_3), 78.4 (CH_2O), 102.3 (ring C at Si), 121.8, 123.9 ($C_5(CH_3)_4$), 223.9 (CN); EI MS *m/z* 578 (6, M^+), 549 (13, $M^+ - C_2H_5$), 521 (24, $M^+ - CMe_3$), 502 (23, $M^+ - NCH_2CH_2$-OMe), 466 (38, $M^+ - CNCMe_3, - C_2H_5$), 458 (100, $M^+ - C_5$-

Me_4). Anal. Calcd for $C_{21}H_{39}N_2ClHfOSi$: C, 43.66; H, 6.82; N, 4.85. Found: C, 43.62; H, 6.79; N, 4.95.

Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)$Cl_2$ (1d). The same procedure as that described for the preparation of **1a** was followed, to prepare **1d** from $TiCl_3(THF)_3$ and $Li_2[C_5Me_4SiMe_2NCH_2CH_2NMe_2]$: orange crystals; yield 57%; mp 142 °C; ^1H NMR δ 0.34 (s, 6 H, $SiCH_3$), 2.06, 2.14 (s, 6 H, $C_5(CH_3)_4$), 2.31 (s, 6 H, NCH_3), 2.61 ("t", 2 H, CH_2NMe_2), 3.49 ("t", 2 H, CH_2NSi); $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C) δ 2.2 ($SiCH_3$), 13.2, 15.9 ($C_5(CH_3)_4$), 47.1 (NCH_3), 53.4 ($SiNCH_2$), 60.7 (CH_2NMe_2), 105.3 (ring C at Si), 136.7, 137.6 ($C_5(CH_3)_4$); EI MS: *m/z* 382 (1, M^+), 295 (1, $M^+ - NCH_2CH_2NMe_2$), 178 (2, $C_5Me_4SiMe_2$), 119 (1, $C_9H_{11}{}^+$), 58 (100, $C_3H_8N^+$). Anal. Calcd for $C_{15}H_{28}Cl_2N_2SiTi$: C, 47.00; H, 7.36; N, 7.31. Found: C, 47.00; H, 7.32; N, 6.83.

Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)$Me_2$ (2d). The same procedure as that described for the preparation of **2a** was followed, to prepare **2d** from **1d**: pale beige-yellow crystals; yield 43%; mp 45 °C; ^1H NMR δ 0.33 (s, 6 H, $TiCH_3$), 0.40 (s, 6 H, $SiCH_3$), 1.92 (s, 6 H, $C_5(CH_3)_4$), 2.03 (s, 6 H, $C_5(CH_3)_4$), 2.15 (s, 6 H, NCH_3), 2.52 ("t", 2 H, CH_2NMe_2), 4.05 ("t", 2 H, CH_2NSi); ^{13}C NMR δ 3.4 (q, $^1J_{CH}$ = 121 Hz, $SiCH_3$), 12.1 (q, $^1J_{CH}$ = 126 Hz, $C_5(CH_3)_4$), 15.0 (q, $^1J_{CH}$ = 127 Hz, $C_5(CH_3)_4$), 45.8 (q, $^1J_{CH}$ = 133 Hz, NCH_3), 48.8 (q, $^1J_{CH}$ = 118 Hz, $TiCH_3$), 49.1 (t, $^1J_{CH}$ = 134 Hz, $SiNCH_2$), 63.3 (t, $^1J_{CH}$ = 131 Hz, CH_2NMe_2), 98.5 (s, ring C at Si), 128.2, 132.3 (s, $C_5(CH_3)_4$); EI MS *m/z* 340 (5, $M^+ - 2H$), 327 (3, $M^+ - CH_3$), 311 (9, $M^+ - 2CH_3$, $-$ H), 283 (1, $M^+ - NMe_3$), 266 (4, $M^+ - NMe_3$, $- CH_3$, $-$ 2H), 252 (2, $M^+ - NMe_3$, $-$ 2CH_3), 240 (9, $C_{11}H_{18}NSiTi^+$), 58 (100, $C_3H_8N^+$). Anal. Calcd for $C_{17}H_{34}N_2SiTi$: C, 59.62; H, 10.01; N, 8.18. Found: C, 58.33; H, 9.75; N, 8.30.

Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)$(CH_2C_6H_5)_2$ (6d). Following a procedure analogous to that described to prepare **6a**, **1d** (500 mg, 1.3 mmol) was reacted with the THF adduct of dibenzylmagnesium (600 mg, 1.71 mmol) to give orange-red needles: yield 322 mg (50%); ^1H NMR δ 0.39 (s, 6 H, $SiCH_3$), 1.73, 1.83 (s, 6 H, $C_5(CH_3)_4$), 1.89 (s, 6 H, NCH_3), 1.93 ("t", 2 H, CH_2NMe_2), 2.05, 2.18 (d, 2 H, $^2J_{HH}$ = 10.3 Hz, $TiCH_2$), 3.69 ("t", 2 H, $SiNCH_2$), 6.87, 7.14 (m, 5 H, C_6H_5); $^{13}C\{^1H\}$ NMR δ 4.2 ($SiCH_3$), 11.4, 15.0 ($C_5(CH_3)_4$), 45.4 (NCH_3), 49.8 ($SiNCH_2$), 61.9 (CH_2NMe_2), 79.2 ($TiCH_2$), 99.5 (ring C at Si), 121.9 (*para* C_6H_5), 126.8 (*meta* C_6H_5), 128.5 (*ortho* C_6H_5), 129.2, 135.2 ($C_5(CH_3)_4$), 149.3 (*ipso* C_6H_5); EI MS *m/z* 312 (9, $M^+ - 2C_7H_7$), 240 (13, $M^+ - 2C_7H_7$, $- CH_2CH_2NMe_2$), 211 (15, $TiC_5Me_4SiMe_2$). Anal. Calcd for $C_{29}H_{42}N_2SiTi$: C, 70.40; H, 8.57; N, 5.66. Found: C, 69.83; H, 8.45; N, 5.78.

Reaction of 6d with B(C_6F_5)$_3$. C_6D_5Br (0.5 mL) was added to an equimolar mixture of **6d** (20 mg, 40 μmol) and $B(C_6F_5)_3$ (21 mg, 40 μmol) in an NMR tube at -78 °C. The color turned dark red at room temperature: ^1H NMR (C_6D_5Br) δ 0.21, 0.36 (s, 3 H, $SiCH_3$), 1.16 (s, 3 H, $C_5(CH_3)_4$), 1.58 (s, 6 H, NCH_3), 1.69, 1.78 (s, 3 H, $C_5(CH_3)_4$), 2.09 (dd, 1 H, $SiNCH_2$), 2.15 (s, 3 H, $C_5(CH_3)_4$), 2.27, 2.51 (d, 1 H, $^2J_{HH}$ = 11.4 Hz, $TiCH_2$), 3.19 (m, 1 H, CH_2NMe_2), 3.30 (br s, 2 H, $CH_2B(C_6F_5)_3$), 3.40 (m, 1 H, CH_2NMe_2), 3.86 (dd, 1 H, $SiNCH_2$), 6.35 (d, 2 H, $^2J_{HH}$ = 7.2 Hz, $CH_2C_6H_5$), 6.83 (t, $^2J_{HH}$ = 7.2 Hz, 1 H, $CH_2C_6H_5$), 6.80$-$7.12 (signals overlap. with solvent signals, 7 H, $CH_2C_6H_5$); $^{13}C\{^1H\}$ NMR (C_6D_5Br) δ -0.6, 2.2 ($SiCH_3$), 10.5, 12.5, 15.3, 15.8 ($C_5(CH_3)_4$), 31.8 ($CH_2B(C_6F_5)_3$), 45.9, 46.4 (NCH_3), 49.9 ($SiNCH_2$), 59.5 (CH_2NMe_2), 78.7 ($TiCH_2$), 104.7 (ring C at Si), 122.9, 127.2, 128.1, 128.3, 128.9, 129.1, 130.6, 132.6, 134.0, 139.1, 141.6, 143.7 (ring C), 136.0, 137.5, 138.5, 147.0 (C_6F_5), 148.8 (*ipso* $CH_2C_6H_5$), 149.9 (*ipso* C_6F_5); ^{19}F NMR (C_6D_5Br) δ -130.4 (d, $^3J_{FF}$ = 22.2 Hz, *ortho* C_6F_5), -163.7 (t, $^3J_{FF}$ = 20.2 Hz, *para* C_6F_5), -166.5 (t, $^3J_{FF}$ = 20.2 Hz, *meta* C_6F_5).

Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)$\{C(=N^tBu)Et\}$Cl (12d). Following a procedure analogous to that described to prepare **12a**, ethylmagnesium chloride (0.73 mL, 1.44 mmol, 2 M in THF) was added to a mixture of **1d** (553 mg, 1.44 mmol) and *tert*-butyl isonitrile (0.16 mL, 1.44 mmol) in hexane (35 mL) at -78 °C. After cooling a concentrated pentane solution, yellow crystals were obtained: yield 179 mg (27%); ^1H NMR δ 0.60, 0.73 (s, 3 H, $SiCH_3$), 1.03 (t, 3 H, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3), 1.34 (s, 3 H, $C_5(CH_3)_4$), 1.36 (s, 9 H, $C(CH_3)_3$), 1.97 (s, 3 H, $C_5(CH_3)_4$), 2.03 (s, 6 H, NCH_3), 2.12 (s, 3 H, $C_5(CH_3)_4$), 2.26 (m, 2 H, CH_2CH_3, 1 H, CH_2NMe_2), 2.62 (m, 1 H, CH_2NMe_2), 2.64 (s, 3 H, $C_5(CH_3)_4$), 3.37, 3.59 (m, 1 H, $SiNCH_2$); $^{13}C\{^1H\}$ NMR δ 4.3, 5.0 ($SiCH_3$), 11.9, 12.0 ($C_5(CH_3)_4$), 12.4 (CH_2CH_3), 15.8, 16.6 ($C_5(CH_3)_4$), 28.4 (CH_2CH_3), 30.4 ($C(CH_3)_3$), 45.7 (NCH_3), 51.1 ($SiNCH_2$), 61.7 ($C(CH_3)_3$), 63.4 (CH_2NMe_2), 104.7 (ring C at Si), 125.7, 127.4, 128.6, 133.8 ($C_5(CH_3)_4$), 238.8 (CN); EI MS *m/z* 403 (18, $M^+ - C_4H_9$), 385 (5, $M^+ - CH_2CH_2NMe_2$), 348 (28, $M^+ - CNCMe_3$, $- C_2H_5$), 290 (100, $M^+ - CNCMe_3$, $- C_2H_5$, $- SiMe_2$). Anal. Calcd for $C_{22}H_{42}N_3ClSiTi$: C, 57.43; H, 9.22; N, 9.14. Found: C, 57.05; H, 8.85; N, 9.18.

Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)$Cl_2$ (1e). Toluene (55 mL) was added to a solid mixture of $ZrCl_4(THF)_2$ (1.71 g, 4.0 mmol) and $Li_2(C_5Me_4SiMe_2NCH_2CH_2NMe_2)$ (1.26 g, 4.0 mmol) at -78 °C. The mixture was stirred at room temperature overnight and filtered. The product was obtained as colorless crystals after concentrating the filtrate and cooling it to -30 °C: yield 1.08 g (56%); ^1H NMR δ 0.36 (s, 6 H, $SiCH_3$), 2.09, 2.12 (s, 6 H, $C_5(CH_3)_4$), 2.35 (s, 6 H, NCH_3), 2.52 ("t", 2 H, CH_2NMe_2), 2.92 ("t", 2 H, CH_2NSi); $^{13}C\{^1H\}$ NMR δ 2.3 ($SiCH_3$), 12.2, 14.4 ($C_5(CH_3)_4$), 46.9 ($SiNCH_2$), 47.3 (NCH_3), 62.3 (CH_2NMe_2), 102.2 (ring C at Si), 129.1, 131.3 ($C_5(CH_3)_4$); EI MS *m/z* 426 (3, $MH_2{}^+$), 424 (2, M^+), 368 (10, $MH_2{}^+ - CH_2NMe_2$), 366 (10, $M^+ - CH_2NMe_2$), 339 (3, $C_{11}H_{19}Cl_2SiZr^+$), 58 (100, $C_3H_8N^+$). Anal. Calcd for $C_{15}H_{28}Cl_2N_2SiZr$: C, 42.23; H, 6.62; N, 6.57. Found: C, 43.19; H, 6.08; N, 6.16.

Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)$Me_2$ (2e). Following a procedure analogous to that described for **2b**, **1e** (1.07 g, 2.5 mmol) was reacted with methylmagnesium chloride (1.67 mL, 5.0 mmol, 3 M in THF) in hexane (40 mL) at -78 °C to give colorless crystals; mp 58 °C: yield 500 mg (55%); ^1H NMR δ -0.39 (s, 6 H, $ZrCH_3$), 0.42 (s, 6 H, $SiCH_3$), 2.03, 2.06 (s, 6 H, $C_5(CH_3)_4$), 2.19 (s, 6 H, NCH_3), 2.50 ("t", 2 H, CH_2NMe_2), 3.05 ("t", 2 H, $SiNCH_2$); ^{13}C NMR δ 3.0 (q, $^1J_{CH}$ = 118 Hz, $SiCH_3$), 11.7 (q, $^1J_{CH}$ = 126 Hz, $C_5(CH_3)_4$), 14.1 (q, $^1J_{CH}$ = 126 Hz, $C_5(CH_3)_4$), 32.7 (q, $^1J_{CH}$ = 112 Hz, s, 6 H, $ZrCH_3$), 45.4 (t, $SiNCH_2$), 46.2 (q, NCH_3), 64.8 (t, CH_2NMe_2), 97.9 (s, ring C at Si), 124.5, 124.9 (s, $C_5(CH_3)_4$). Anal. Calcd for $C_{17}H_{34}N_2SiZr$: C, 52.93; H, 8.88; N, 7.26. Found: C, 52.55; H, 8.76; N, 7.13.

Reaction of 2e with B(C_6F_5)$_3$. C_6D_5Br (0.5 mL) was added to a equimolar mixture of **2e** (28 mg, 72 μmol) and $B(C_6F_5)_3$ (37 mg, 72 μmol) in a NMR tube at -78 °C and allowed to warm to -20 °C: ^1H NMR (253 K, C_6D_5Br) δ -0.14 (br s, 3 H, $ZrCH_3$), 0.25, 0.32 (s, 3 H, $SiCH_3$), 0.94 (br s, 3 H, $CH_3B(C_6F_5)_3$), 1.45, 1.72, 1.84 (br s, 3 H, $C_5(CH_3)_4$), 1.87, 1.89 (br s, 3 H, NCH_3), 1.99 (br s, 3 H, $C_5(CH_3)_4$), 2.97 (br s, 2 H, CH_2NMe_2), 3.15 (br s, 2 H, $SiNCH_2$); $^{13}C\{^1H\}$ NMR (253 K, C_6D_5Br) δ 1.2, 2.2 ($SiCH_3$), 10.1, 10.9, 12.5, 14.6, ($C_5(CH_3)_4$), 35.3 ($ZrCH_3$), 42.7 ($CH_3B(C_6F_5)_3$), 46.6 ($SiNCH_2$), 47.4 (NCH_3), 62.6 (CH_2NMe_2), 102.4 (ring C at Si); ^{19}F NMR (253 K, C_6D_5Br) δ -133.5 (*ortho* C_6F_5), -160.7 (*para* C_6F_5), -165.9 (*meta* C_6F_5).

Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)$Et_2$ (3e). Ethyllithium (8.13 mL, 2.36 mmol, 0.29 M in pentane) was added to a suspension of **1e** (503 mg, 1.18 mmol) in hexane (30 mL) at -78 °C. The mixture was allowed to warm to 0 °C over a period of 3 h under stirring. All volatiles were removed in vacuo, and the residue was extracted with pentane (30 mL). Filtration, followed by concentrating the yellow filtrate and cooling the concentrated pentane solution to -35 °C, afforded yellow crystals: yield 68 mg (14%); ^1H NMR (C_6D_5Br, 253 K) δ 0.09 (m, 4 H, $ZrCH_2$), 0.38 (s, 6 H, $SiCH_3$), 1.06 (t, 6 H, $^3J_{HH}$ = 7.8 Hz, CH_2CH_3), 2.03 (s, 6 H, $C_5(CH_3)_4$), 2.06 (s, 6 H, NCH_3), 2.31 (s, 6 H, $C_5(CH_3)_4$), 2.59 (br s, 2 H, CH_2NMe_2), 3.09 (br s, 2 H, $SiNCH_2$); $^{13}C\{^1H\}$ NMR (C_6D_5Br, 253 K) δ 2.8 ($SiCH_3$), 11.2 ($C_5(CH_3)_4$), 13.3 ($ZrCH_2$), 14.2 ($C_5(CH_3)_4$), 42.3 (br s, NCH_3), 45.2 (CH_2CH_3), 46.3 ($SiNCH_2$), 64.3 (CH_2NMe_2), 97.7 (ring C at Si), 122.9, 123.8 ($C_5(CH_3)_4$). Anal. Calcd for $C_{17}H_{38}N_2SiZr$: C, 55.13; H, 9.27; N, 6.77. Found: C, 51.58; H, 7.87; N, 6.95.

Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)$^nPr_2$ (4e). Following a procedure analogous to that described to prepare **3e**, **1e** (550 mg, 1.29 mmol) was treated with *n*-propyllithium (10.4 mL, 2.6 mmol, 0.25 M in hexane) in hexane (35 mL) at −78 °C to give a pale yellow solid: yield 140 mg (25%); ^{1}H NMR δ 0.17 (m, 4 H, $ZrCH_2$), 0.40 (s, 6 H, $SiCH_3$), 1.11 (t, 6 H, $^3J_{HH}$ = 7 Hz, γ-CH_3), 1.26, 1.43 (m, 2 H, β-CH_2), 2.04, 2.08, (s, 6 H, $C_5(CH_3)_4$), 2.22 (s, 6 H, NCH_3), 2.50 ("t", 2 H, CH_2NMe_2), 3.05 ("t", 2 H, $SiNCH_2$); $^{13}C\{^1H\}$ NMR δ 2.8 ($SiCH_3$), 11.2, 14.2 ($C_5(CH_3)_4$), 22.7 (γ-CH_3), 23.5 (β-CH_2), 45.6 ($SiNCH_2$), 46.5 (NCH_3), 56.9 ($ZrCH_2$), 64.9 (CH_2NMe_2), 98.6 (ring C at Si), 124.2, 124.5 ($C_5(CH_3)_4$); EI MS *m*/*z* 442 (2, M^+), 398 (15, $M^+ - NMe_2$), 356 (83, $M^+ - NCH_2CH_2NMe_2$). Anal. Calcd for $C_{21}H_{42}N_2SiZr$: C, 57.06; H, 9.60; N, 6.34. Found: C, 55.84; H, 9.29; N, 6.68.

Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)^{n}Bu$_2$ (5e). A suspension of **1e** (436 mg, 1 mmol) in hexane (35 mL) was treated with *n*-butyllithium (1.15 mL, 2 mmol, 1.8 M in hexane) at 0 °C. After stirring for 3 h at this temperature all volatiles were removed in vacuo. The residue was extracted into hexane (20 mL) to afford a yellow-brown oil: yield 268 mg (56%); ^{1}H NMR δ 0.16 (m, 4 H, $ZrCH_2$), 0.39 (s, 6 H, $SiCH_3$), 1.01 (t, 6 H, δ-CH_3), 1.21 (m, 2 H, β-CH_2), 1.38 (m, 2 H, β-CH_2, 4 H γ-CH_2), 2.04, 2.07 (s, 6 H, $C_5(CH_3)_4$), 2.23 (s, 6 H, NCH_3), 2.49 ("t", 2 H, CH_2NMe_2), 3.03 ("t", 2 H, $SiNCH_2$); $^{13}C\{^1H\}$ NMR δ 2.9 ($SiCH_3$), 11.3, 14.3 ($C_5(CH_3)_4$), 14.1 (δ-CH_3), 30.8 (β-CH_2), 32.3 (γ-CH_2), 45.6 ($SiNCH_2$), 46.6 (NCH_3), 53.2 ($ZrCH_2$), 64.9 (CH_2NMe_2), 98.1 (ring C at Si), 124.1, 124.5 ($C_5(CH_3)_4$). Anal. Calcd for $C_{23}H_{46}N_2SiZr$: C, 58.77; H, 9.88; N, 5.96. Found: C, 52.97; H, 8.80; N, 5.69.

Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)($CH_2C_6H_5$)$_2$ (6e). Following a procedure analogous to that described to prepare **6a**, **1e** (427 mg, 1 mmol) was reacted with dibenzylmagnesium THF adduct (560 mg, 1.6 mmol) to give yellow crystals: yield 250 mg (47%); ^{1}H NMR δ 0.40 (s, 6 H, $SiCH_3$), 1.71 (d, 2 H, $^2J_{HH}$ = 11.2 Hz, $ZrCH_2$), 1.80 (s, 6 H, NCH_3), 1.91, 2.01 (s, 6 H, $C_5(CH_3)_4$), 1.92 (d, 2 H, $^2J_{HH}$ = 11.2 Hz, $ZrCH_2$), 2.22 ("t", 2 H, CH_2NMe_2), 2.97 ("t", 2 H, $SiNCH_2$), 6.90−7.18 (m, 10 H, C_6H_5); $^{13}C\{^1H\}$ NMR δ 2.3 ($SiCH_3$), 11.8, 14.2 ($C_5(CH_3)_4$), 45.7 (NCH_3), 45.9 ($SiNCH_2$), 60.9 ($ZrCH_2$), 65.4 (CH_2NMe_2), 101.1 (ring C at Si), 121.3 (*para* C_6H_5), 125.7, 127.3 ($C_5(CH_3)_4$), 127.9 (*meta* C_6H_5), 128.2 (*ortho* C_6H_5), 151.4 (*ipso* C_6H_5); EI MS *m*/*z* 356 (71, $M^+ - 2C_7H_7$), 295 (4, $M^+ - 2C_7H_7, - SiMe_2$). Anal. Calcd for $C_{29}H_{42}N_2SiZr$: C, 64.73; H, 7.88; N, 5.21. Found: C, 63.48; H, 7.96; N, 5.38.

Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)Ph$_2$ (8e). Phenyllithium (2.25 mL, 4.1 mmol, 1.8 M in cyclohexane/Et_2O = 7/3) was added to a suspension of **1e** (866 mg, 2.0 mmol) in diethyl ether (30 mL) at −78 °C. The mixture was allowed to warm to 0 °C over a period of 4.5 h under stirring. All volatiles were removed in vacuo, and the residue was extracted with hexane (25 mL). Filtration followed by concentrating the yellow filtrate and cooling the concentrated hexane solution to −35 °C afforded a colorless microcrystalline solid: yield 470 mg (44%); ^{1}H NMR δ 0.54 (s, 6 H, $SiCH_3$), 1.45 (s, 6 H, $C_5(CH_3)_4$), 1.56 (s, 6 H, NCH_3), 2.08 (s, 6 H, $C_5(CH_3)_4$) 2.52 (br s, 2 H, CH_2NMe_2), 3.19 ("t", 2 H, $SiNCH_2$), 7.17−7.59 (m, 10 H, C_6H_5); $^{13}C\{^1H\}$ NMR δ 2.9 ($SiCH_3$), 11.7, 15.2 ($C_5(CH_3)_4$), 46.5 ($SiNCH_2$), 48.0 (NCH_3), 63.5 (CH_2NMe_2), 97.7 (ring C at Si), 125.8, 126.5, 126.5, 127.9, 128.2 (*o*-, *m*-, *p*-C_6H_5, $C_5(CH_3)_4$), signal for *ipso* C_6H_5 not observed; EI MS *m*/*z* 510 (2, M^+), 433 (98, $M^+ - C_6H_5$), 356 (10, $M^+ - 2C_6H_5$). Anal. Calcd for $C_{27}H_{38}N_2SiZr$: C, 63.58; H, 7.53; N, 5.49. Found: C, 60.15; H, 6.91; N, 5.22.

Zr(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)\{C(=N^{t}Bu)Et\}Cl (12e). Following a procedure analogous to that described for **12a**, ethylmagnesium chloride (1.04 mL, 2.07 mmol, 2 M in THF) was added to a mixture of **1e** (885 mg, 2.07 mmol) and *tert*-butyl isonitrile (0.23 mL, 2.07 mmol) in hexane (50 mL) at −78 °C to give colorless crystals after cooling a concentrated pentane solution: yield 713 mg (68%); ^{1}H NMR δ 0.58 (s, 6 H, $SiCH_3$), 1.18 (t, 3 H, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3), 1.27 (s, 9 H, $C(CH_3)_3$), 1.46 (s, 3 H, $C_5(CH_3)_4$), 1.90 (m, 1 H, CH_2NMe_2), 2.13 (s, 3 H, $C_5(CH_3)_4$), 2.20 (m, 1 H, CH_2CH_3), 2.24, 2.57 (s, 3 H, $C_5(CH_3)_4$), 2.63 (m, 1 H, CH_2CH_3), 2.63 (m, 1 H, CH_2NMe_2), 3.04, 3.14 (m, 1 H, $SiNCH_2$), signal for NMe_2 not observed; $^{13}C\{^1H\}$ NMR δ 2.3, 3.6 ($SiCH_3$), 12.2, 12.5 ($C_5(CH_3)_4$), 13.4 (CH_2CH_3), 15.2, 15.4 ($C_5(CH_3)_4$), 29.6 (CH_2CH_3), 31.5 ($C(CH_3)_3$), 45.9 ($SiNCH_2$), 61.5 ($C(CH_3)_3$), 64.4 (CH_2NMe_2), 103.6 (ring C at Si), 122.9, 123.9, 124.8, 127.1 ($C_5(CH_3)_4$), 246.6 (CN), signal for NMe_2 not observed; ^{1}H NMR ($C_6D_5CD_3$, −70 °C) δ 0.64, 0.66 (s, 3 H, $SiCH_3$), 1.12 (br s, 3 H, CH_2CH_3), 1.19 (s, 9 H, $C(CH_3)_3$), 1.35 (s, 3 H, $C_5(CH_3)_4$), 1.37 (s, 3 H, NCH_3), 1.53 (m, 1 H, CH_2NMe_2), 1.85 (m, 1 H, CH_2CH_3), 2.15, 2.27 (s, 3 H, $C_5(CH_3)_4$), 2.38 (s, 3 H, NCH_3), 2.49 (m, 1 H, CH_2CH_3), 2.60 (m, 1 H, CH_2NMe_2), 2.69 (s, 3 H, $C_5(CH_3)_4$), 2.99, 3.12 (m, 1 H, $SiNCH_2$); ^{1}H NMR ($C_6D_5CD_3$, +30 °C) δ 0.54 (s, 6 H, $SiCH_3$), 1.20 (t, 3 H, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3), 1.27 (s, 9 H, $C(CH_3)_3$), 1.46 (s, 3 H, $C_5(CH_3)_4$), 1.92 (m, 1 H, CH_2NMe_2), 2.07, 2.20 (s, 3 H, $C_5(CH_3)_4$), 2.23 (m, 1 H, CH_2CH_3), 2.47 (s, 3 H, $C_5(CH_3)_4$), 2.60 (m, 1 H, CH_2CH_3), 2.66 (m, 1 H, CH_2NMe_2), 3.04, 3.14 (m, 1 H, $SiNCH_2$), signal for NMe_2 not observed; ^{1}H NMR ($C_6D_5CD_3$, +70 °C) δ 0.50, 0.52 (s, 3 H, $SiCH_3$), 1.23 (t, 3 H, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3), 1.30 (s, 9 H, $C(CH_3)_3$), 1.49 (s, 3 H, $C_5(CH_3)_4$), 2.01 (br s, 7 H, NCH_3, CH_2NMe_2), 2.04, 2.19 (s, 3 H, $C_5(CH_3)_4$), 2.30 (m, 1 H, CH_2CH_3), 2.42 (s, 3 H, $C_5(CH_3)_4$), 2.57 (m, 1 H, CH_2NMe_2), 2.71 (m, 1 H, CH_2CH_3), 3.04, 3.15 (m, 1 H, $SiNCH_2$); EI MS *m*/*z* 446 (22, $M^+ - C_4H_9$), 391 (100, $M^+ - CNCMe_3, - C_2H_5$), 347 (5, $M^+ - CNCMe_3, - C_2H_5, - NMe_2$), 305 (14, $M^+ - CNCMe_3, - C_2H_5, - NCH_2CH_2NMe_2$). Anal. Calcd for $C_{22}H_{42}N_3ClSiZr$: C, 52.48; H, 8.43; N, 8.35. Found: C, 52.41; H, 8.38; N, 8.47.

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)Cl$_2$ (1f). Following a procedure analogous to that described to prepare **1e**, toluene (30 mL) was added to a solid mixture of $HfCl_4(THF)_2$ (1.69 g, 3.64 mmol) and $Li_2(C_5Me_4SiMe_2NCH_2CH_2NMe_2)$ (1.01 g, 3.64 mmol) at −78 °C to afford colorless crystals: yield 1.12 g (60%); ^{1}H NMR δ 0.37 (s, 6 H, $SiCH_3$), 2.18, 2.19 (s, 6 H, $C_5(CH_3)_4$), 2.33 (s, 6 H, NCH_3), 2.46 ("t", 2 H, CH_2NMe_2), 3.03 ("t", 2 H, $SiNCH_2$); $^{13}C\{^1H\}$ NMR δ 2.4 ($SiCH_3$), 12.0, 14.1 ($C_5(CH_3)_4$), 45.5 ($SiNCH_2$), 47.3 (NCH_3), 62.8 (CH_2NMe_2), 102.3 (ring C at Si), 126.1, 129.7 ($C_5(CH_3)_4$); EI MS *m*/*z* 514 (9, M^+), 456 (11, $M^+ - CH_2NMe_2$), 428 (21, $M^+ - NCH_2CH_2NMe_2$). Anal. Calcd for $C_{15}H_{28}N_2Cl_2HfSi$: C, 35.05; H, 5.50; N, 5.45. Found: C, 35.08; H, 5.41; N, 6.19.

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)Me$_2$ (2f). Methylmagnesium chloride (0.83 mL, 1.32 mmol, 1.6 M in THF) was added to a suspension of **1f** (340 mg, 0.66 mmol) in hexane (30 mL) at −78 °C. The mixture was allowed to warm to 0 °C over 3 h under stirring. All volatiles were removed in vacuo, and the residue extracted with pentane (15 mL). The extracts were filtered and concentrated. Cooling to −30 °C gave a colorless microcrystalline powder: yield 150 mg (48%); ^{1}H NMR δ −0.51 (s, 6 H, $HfCH_3$), 0.43 (s, 6 H, $SiCH_3$), 2.06, 2.10 (s, 6 H, $C_5(CH_3)_4$), 2.15 (s, 6 H, NCH_3), 2.46 ("t", 2 H, CH_2NMe_2), 3.11 ("t", 2 H, $SiNCH_2$); $^{13}C\{^1H\}$ NMR δ 2.9 ($SiCH_3$), 11.6, 13.9 ($C_5(CH_3)_4$), 42.5 ($HfCH_3$), 45.0 ($SiNCH_2$), 46.1 (NCH_3), 65.3 (CH_2NMe_2), 98.4 (ring C at Si), 123.4, 123.9 ($C_5(CH_3)_4$); EI MS *m*/*z* 443 (23, $M^+ - 2CH_3$), 300 (52, 443 − $SiMe_2NCH_2CH_2NMe_2$). Anal. Calcd for $C_{17}H_{40}N_2HfSi$: C, 43.15; H, 8.54; N, 5.92. Found: C, 42.92; H, 8.32; N, 6.62.

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)Et$_2$ (3f). Following a procedure analogous to that described to prepare **3e**, ethyllithium (9.36 mL, 2.72 mmol, 0.29 M in pentane) was reacted with a suspension of **1f** (698 mg, 1.36 mmol) in hexane (30 mL) to give colorless crystals: yield 68 mg (26%); ^{1}H NMR δ 0.05 (qq, 4 H, $HfCH_2$), 0.41 (s, 6 H, $SiCH_3$), 1.31 (t, 6 H, $^3J_{HH}$ = 8.0 Hz, CH_2CH_3), 2.11, 2.14, 2.19 (s, 6 H, C_5Me_4, NCH_3), 2.46 ("t", 2 H, CH_2NMe_2), 3.09 ("t", 2 H, $SiNCH_2$); $^{13}C\{^1H\}$ NMR δ 2.7 ($SiCH_3$), 6.9 ($HfCH_2$), 11.3, 14.2 ($C_5(CH_3)_4$), 45.1 ($SiNCH_2$), 45.5 (NCH_3), 46.5 (CH_2CH_3), 65.3 (CH_2NMe_2), 99.75 (ring C at Si), 123.3, 123.7 ($C_5(CH_3)_4$). Anal. Calcd for $C_{17}H_{38}N_2SiHf$: C, 45.53; H, 7.66; N, 5.59. Found: C, 43.70; H, 6.79; N, 5.67.

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)^{n}Pr$_2$ (4f). Following a procedure analogous to that described to prepare **4e**, **1f**

(449 mg, 0.87 mmol) was treated with *n*-propyllithium (7 mL, 1.75 mmol, 0.25 M in pentane) in hexane (30 mL) at −78 °C to give a colorless solid: yield 174 mg (38%); ^{1}H NMR δ −0.01 (m, 4 H, $HfCH_2$), 0.40 (s, 6 H, $SiCH_3$), 1.14 (t, 6 H, $^3J_{HH} = 8.0$ Hz, γ-CH_3), 1.28, 1.43 (m, 2 H, β-CH_2), 2.09, 2.11 (s, 6 H, $C_5(CH_3)_4$), 2.19 (s, 6 H, NCH_3), 2.46 ("t", 2 H, CH_2NMe_2), 3.09 ("t", 2 H, $SiNCH_2$); $^{13}C\{^1H\}$ NMR δ 2.7 ($SiCH_3$), 11.2, 14.1 ($C_5(CH_3)_4$), 23.8 (γ-CH_3), 24.2 (β-CH_2), 45.1 ($SiNCH_2$), 46.4 (NCH_3), 65.3 (CH_2NMe_2), 66.2 ($HfCH_2$), 99.1 (ring C at Si), 123.3, 123.8 ($C_5(CH_3)_4$); EI MS *m/z* 485 (3, $M^+ - NMe_2$), 443 (52, $M^+ - NCH_2CH_2NMe_2$), 357 (12, $M^+ - NCH_2CH_2NMe_2$, $- 2\ C_3H_7$). Anal. Calcd for $C_{21}H_{42}N_2SiHf$: C, 47.66; H, 8.02; N, 5.29. Found: C, 46.16; H, 7.37; N, 5.98.

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)^{n}Bu$_2$ (5f). Following a procedure analogous to that described to prepare **5e**, **1f** (405 mg, 0.79 mmol) was treated with *n*-butyllithium (1.13 mL, 1.58 mmol, 1.38 M in hexane) in hexane (30 mL) at 0 °C to give a yellow oil: yield 101 mg (23%); ^{1}H NMR δ −0.01 (m, 4 H, $HfCH_2$), 0.41 (s, 6 H, $SiCH_3$), 1.02 (t, 6 H, $^3J_{HH} = 7.4$ Hz, δ-CH_3), 1.23 (m, 2 H, β-CH_2), 1.42 (m, 2 H, β-CH_2, 4 H, γ-CH_2), 2.11, 2.13 (s, 6 H, $C_5(CH_3)_4$), 2.24 (s, 6 H, NCH_3), 2.50 ("t", 2 H, CH_2NMe_2), 3.11 ("t", 2 H, $SiNCH_2$); $^{13}C\{^1H\}$ NMR δ 2.7 ($SiCH_3$), 11.3, 14.1 ($C_5(CH_3)_4$), 14.2 (δ-CH_3), 31.8 (γ-CH_2), 32.9 (β-CH_2), 45.2 ($SiNCH_2$), 46.5 (NCH_3), 62.4 ($HfCH_2$), 65.4 (CH_2NMe_2), 99.2 (ring C at Si), 123.3, 123.7 ($C_5(CH_3)_4$).

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$)($CH_2C_6H_5$)$_2$ (6f). Following a procedure analogous to that described to prepare **6a**, **1f** (388 mg, 0.76 mmol) was reacted with dibenzylmagnesium THF adduct (430 mg, 1.23 mmol) to give colorless needles: yield 380 mg (81%); ^{1}H NMR δ 0.42 (s, 6 H, $SiCH_3$), 1.46 (d, 2 H, $^2J_{HH} = 12.0$ Hz, $HfCH_2$), 1.69 (d, 2 H, $^2J_{HH} = 12.0$ Hz, $HfCH_2$), 1.80, 1.97 (s, 6 H, $C_5(CH_3)_4$), 2.08 (s, 6 H, NCH_3), 2.18 ("t", 2 H, CH_2NMe_2), 3.05 ("t", 2 H, $SiNCH_2$), 6.8−7.16 (m, 10 H, C_6H_5); $^{13}C\{^1H\}$ NMR δ 2.3 ($SiCH_3$), 11.8, 14.1 ($C_5(CH_3)_4$), 45.2 ($SiNCH_2$), 45.7 (NCH_3), 65.9 (CH_2NMe_2), 67.9 ($HfCH_2$), 101.1 (ring C at Si), 121.8, (*para* C_6H_5), 124.2, 126.5 ($C_5(CH_3)_4$), 129.2 (*meta* C_6H_5), 129.5 (*ortho* C_6H_5), 151.6 (*ipso* C_6H_5); EI MS *m/z* 539 (15, $M^+ - NCH_2CH_2NMe_2$), 482 (21, $M^+ - NCH_2CH_2NMe_2$, $- SiMe_2$), 443 (7, $M^+ - 2C_7H_7$). Anal. Calcd for $C_{29}H_{42}N_2HfSi$: C, 55.70; H, 6.78; N, 4.48. Found: C, 56.26; H, 6.29; N, 4.69.

Hf(η^5:η^1:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2$){C(=N^{t}Bu)Et}Cl (12f). Following a procedure analogous to that described to prepare **12a**, ethylmagnesium chloride (1.44 mL, 2.88 mmol, 2 M in THF) was added to a mixture of **1f** (1.48 g, 2.88 mmol) and *tert*-butyl isonitrile (0.32 mL, 2.88 mmol) in hexane (50 mL) at −78 °C to give colorless crystals after cooling a concentrated pentane solution: yield 460 mg (27%); ^{1}H NMR δ 0.58 (s, 6 H, $SiCH_3$), 1.20 (t, 3 H, $^3J_{HH} = 7.4$ Hz, CH_2CH_3), 1.26 (s, 9 H, $C(CH_3)_3$), 1.53 (s, 3 H, $C_5(CH_3)_4$), 1.87 (m, 1 H, CH_2CH_3), 2.00 (br s, 6 H, NCH_3), 2.16 (s, 3 H, $C_5(CH_3)_4$), 2.19 (m, 1 H, CH_2CH_3), 2.30, 2.63 (s, 3 H, $C_5(CH_3)_4$), 2.77 (m, 2 H, CH_2NMe_2), 3.19 (m, 2 H, $SiNCH_2$); $^{13}C\{^1H\}$ NMR δ 2.1, 3.6 ($SiCH_3$), 12.0, 12.5 ($C_5(CH_3)_4$), 13.6 (CH_2CH_3), 15.0, 15.4 ($C_5(CH_3)_4$), 30.0 (CH_2CH_3), 31.5 ($C(CH_3)_3$), 45.2 ($SiNCH_2$), 48.3 (br s, NCH_3), 61.2 ($C(CH_3)_3$), 64.8 (CH_2NMe_2), 103.0 (ring C at Si), 121.1, 122.4, 124.1, 125.5 ($C_5(CH_3)_4$), 256.0 (CN); EI MS *m/z* 533 (5, $M^+ - CMe_3$), 477 (100, $M^+ - CNCMe_3$, $- C_2H_5$). Anal. Calcd for $C_{22}H_{42}N_3ClHfSi$: C, 44.73; H, 7.18; N, 7.12. Found: C, 44.87; H, 7.21; N, 7.34.

Zr(η^5:η^1:η^1-$C_5H_3tBuSiMe_2NCH_2CH_2NMe_2$)Cl$_2$ (1g). Following a similar procedure that was used to prepare **1e**, reaction of $ZrCl_4(THF)_2$ with $Li(C_5H_3tBuSiMe_2NCH_2CH_2NMe_2)$ gave **1g** as colorless crystals: yield 67%; ^{1}H NMR δ 0.19, 0.25 (s, 3 H, $SiCH_3$), 1.47 (s, 9 H, $C(CH_3)_3$), 2.08, 2.55 (s, 3 H, NCH_3), 1.87 (m, 1 H, CH_2NMe_2), 3.19 (m, 6.2 Hz, 1 H, CH_2NMe_2), 2.79 (m, 1 H, $SiNCH_2$), 2.90 (m, 1 H, $SiNCH_2$), 6.04 (m, 1 H, C_5H_3), 6.30 (m, 1 H, C_5H_3), 7.03 (m, 1 H, C_5H_3); $^{13}C\{^1H\}$ NMR δ −3.4, −2.1 ($SiCH_3$), 31.3 ($C(CH_3)_3$), 33.2 ($C(CH_3)_3$), 44.8, 48.6 (NCH_3), 47.2 ($SiNCH_2$), 62.5 (CH_2NMe_2), 106.9 (ring C attached to Si), 115.5, 118.0, 126.3 (ring C), 146.8 (ring C attached to ^{t}Bu); EI MS *m/z* 426 (24, $M^+ + 2H$), 424 (18, M^+), 368 (38, $M^+ - C_4H_8$), 366 (32, $M^+ - C_3H_8N$), 58 (100, $C_3H_8N^+$), 42 (44, $C_2H_4N^+$). Anal. Calcd for $C_{15}H_{28}N_2Cl_2SiZr$: C, 42.23; H, 6.62; N, 6.57. Found: C, 41.59; H, 7.36; N, 6.45.

Zr(η^5:η^1:η^1-$C_5H_3tBuSiMe_2NCH_2CH_2NMe_2$)($CH_2SiMe_3$)$_2$ (7g). Following a procedure similar to that to prepare **7b**, **7g** was prepared from **1g** and trimethylsilylmethylmagnesium chloride to give colorless crystals: yield 31%; ^{1}H NMR δ −0.63 (d, $^2J_{HH} = 11.5$ Hz, 1 H, $ZrCH_2$), −0.21 (d, $^2J_{HH} = 11.0$ Hz, 1 H, $ZrCH_2$), −0.14 (d, $^2J_{HH} = 11.0$ Hz, 1 H, $ZrCH_2$), 0.57 (d, $^2J_{HH} = 11.5$ Hz, 1 H, $ZrCH_2$), 0.19, 0.22 (s, 9 H, $SiCH_3$), 0.27, 0.39 (s, 3 H, $SiCH_3$), 1.43 (s, 9 H, $C(CH_3)_3$), 2.17 (br s, 6 H, NCH_3), 1.96, 3.30 (m, 1 H, CH_2NMe_2), 2.91, 3.08 (m, 1 H, $SiNCH_2$), 6.09 (m, 1 H, C_5H_3), 6.31 (m, 1 H, C_5H_3), 7.03 (m, 1 H, C_5H_3); $^{13}C\{^1H\}$ NMR δ −2.3, −1.5 ($Si(CH_3)_2$), 4.5, 4.7 ($Si(CH_3)_3$), 32.0 ($C(CH_3)_3$), 33.1 ($C(CH_3)_3$), 41.5, 42.2 ($ZrCH_2$), signal for $N(CH_3)_2$ not observed, 45.9 ($SiNCH_2$), 64.6 (CH_2NMe_2), 102.7 (ring C attached to Si), 110.7, 116.0, 117.7 (ring C), 144.1 (ring C attached to ^{t}Bu). Anal. Calcd for $C_{23}H_{50}N_2Si_3Zr$: C, 52.11; H, 9.51; N, 5.28. Found: C, 48.63; H, 9.01; N, 5.33.

Ethylene Polymerization. A 0.5 L Büchi reactor was charged with 200 mL of toluene. At a constant ethene pressure of 3 bar ($c = 0.432$ mol/L), a mixture of 5 μmol of catalyst ($c = 25$ μmol/L) and 1.5 mL (2.5 mmol) of MAO ($c \approx 1.658$ mol/L) was added at 3.5 bar pressure, followed by 1.5 h of stirring at 23 °C. After the reaction mixture was drained into 0.5 L of methanol and acidified with 10 mL of concentrated hydrochloric acid, the polymer was collected by filtration, washed with methanol, and dried to constant weight. Melting points were determined by DSC.

X-ray Crystal Structure Analysis of 2b, 8b, and 12a. Relevant crystallographic data for **2b**, **8b**, and **12a** are summarized in Table 1. Single crystals suitable for X-ray crystal structure analysis were obtained by slow cooling of concentrated pentane solutions. Data were performed using ω-scans on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo-Kα radiation. Data correction for Lorentz polarization and absorption (empirically using ψ-scans) was carried out using the program system MolEN.[37a] From the measured reflections, all independent reflections were used and the parameters were refined by full-matrix least-squares against all F_o^2 data (SHELXL-93).[37b] The structure was solved using direct methods (SHELXS-86)[37c] and difference Fourier syntheses and refined with anisotropic thermal parameters for non-hydrogen atoms. For **2b**, hydrogen atoms were refined with isotropic thermal parameters. The hydrogen atoms were calculated at their idealized positions for **8b** and **12a**. For more details see the Supporting Information.

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Supporting Information Available: Listings of all crystal data and refinement parameters, atomic parameters including hydrogen atoms, thermal parameters, and bond lengths and angles for **2b**, **8b**, and **12a** (10 pages). Ordering information is given on any current masthead page.

OM980722N

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