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Formation of sp^3-C$_1$-Bridged Cp/Amido Titanium and Zirconium “CpCN” Constrained-Geometry Ziegler−Natta Catalyst Systems

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Addition of methyllithium or *p*-tolyllithium to the C-6 carbon atom of the lithium (*N*-phenylformimidoyl)cyclopentadienide reagent **5** resulted in the formation of the dianionic sp^3-C$_1$-alkylidene-bridged Cp/amido ligand systems $[C_5H_4{-}CHR{-}NPh]^{2-}$ (**6a**, R = CH$_3$; **6b**, R = *p*-tolyl; each with Li$^+$ cations). Transmetalation of **6a** from lithium to zirconium was achieved by treatment with ZrCl$_4$(THF)$_2$ (**7a**) to yield the metallacyclic sp^3-C$_1$-linked spiro constrained geometry complex (η^5-C$_5$H$_4$−CHMe−NPh-κN)$_2$Zr (**2a**). Treatment of **6a** with Cl$_2$-Ti(NMe$_2$)$_2$ (**7c**) gave the alkylidene-bridged Cp/amido titanium complex (η^5-C$_5$H$_4$−CHMe−NPh-κN)Zr(NMe$_2$)$_2$ (**2b**). Analogous treatment of Cl$_2$Zr(NEt$_2$)$_2$(THF)$_2$ (**7b**) with **6a** or **6b** furnished the related (CpCN)Zr complexes (C$_5$H$_4$−CHR−NPh)Zr(NEt$_2$)$_2$ (**2c**, R = CH$_3$; **2d**, R = *p*-tolyl) each in ≥70% yield. The complexes **2a** and **2b** were both characterized by X-ray crystal structure analyses. The observation that both exhibit Cp(centroid)−M−N angles that are by ca. 10° *smaller* than those of their respective dimethylsilanediyl-bridged analogues renders the CpCN group metal complexes as more constrained than their conventional (Cp*SiN)M analogues. Lithium 4-methylanilide adds to the C-6 carbon atom of the non-CH-acidic pentafulvene (C$_5$H$_4$)═CHCMe$_3$ (**13a**) to yield Li[C$_5$H$_4$−CH(CMe$_3$)(NH-*p*-tolyl)] (**14a**), which was subsequently NH-deprotonated by treatment with LDA to yield the dianionic reagent [C$_5$H$_4$−CH(CMe$_3$)(N-*p*-tolyl)]$^{2-}$ (**6c**, as the dilithium compound). Analogous addition of lithium *tert*-butylamide to **13a**, followed by NH-deprotonation by treatment with *tert*-butyllithium, yielded Li$_2$[C$_5$H$_4$−CH(NCMe$_3$)CMe$_3$] (**6d**). Lithium *tert*-butylamide added to 1,2,3,4-tetramethylpentafulvene (**13b**) to yield Li[C$_5$Me$_4$−CH$_2$−NH(CMe$_3$)] (**14c**), which was subsequently NH-deprotonated by treatment with *tert*-butyllithium to yield Li$_2$[C$_5$Me$_4$−CH$_2$N(CMe$_3$)] (**6e**). Transmetalation of **6c** by treatment with Cl$_2$Ti(NMe$_2$)$_2$ (**7c**) or Cl$_2$Zr-(NEt$_2$)$_2$(THF)$_2$ (**7b**) cleanly gave the respective CpCN group 4 metal complexes [C$_5$H$_4$−CH(CMe$_3$)(N−p-tolyl)]M(NR$_2$)$_2$ (**2e**, M = Ti; **2f**, M = Zr). Similarly, the sp^3-C$_1$-bridged “constrained geometry” system [C$_5$H$_4$−CH(CMe$_3$)(NCMe$_3$)]Zr(NEt$_2$)$_2$ (**2g**) was obtained in good yield (70%) from the reaction of **6d** with **7b**, and treatment of **6e** with **7b** furnished the (Cp*CN)Zr complex [C$_5$Me$_4$−CH$_2$−N(CMe$_3$)]Zr(NEt$_2$)$_2$ (**2h**, 65% isolated). Activation of the (CpCN)M(NR$_2$)$_2$ systems by treatment with a large excess of methylalumoxane in toluene solution gave homogeneous Ziegler−Natta catalysts for the polymerization of ethylene (carried out at 60 °C) and the copolymerization of ethene with 1-octene (at 90 °C).

Introduction

Group 4 metallocene systems have attained a considerable importance in homogeneous Ziegler−Natta chemistry.[1] A variety of recent examples have demonstrated the increasing value of nonmetallocene systems for the development of α-olefin polymerization catalysts.[2] The silanediyl-bridged Cp/amido titanium and zirconium systems **1** probably represent the first significant examples of this general development.[3]

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† X-ray crystal structure analyses.

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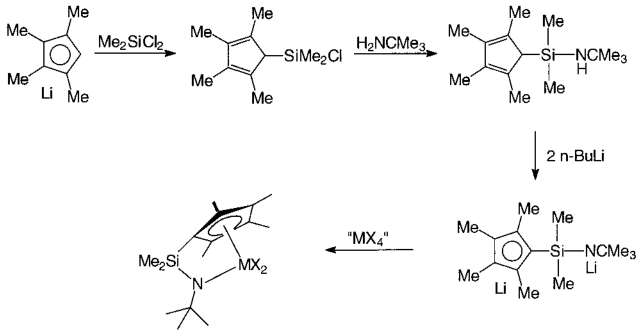
Scheme 1. Synthesis of the Complexes 1



The $[Cp^*SiMe_2NCMe_3]^{2-}$ ligand system was devised and first introduced to scandium chemistry by Shapiro, Bercaw, et al.[4] and shortly thereafter used by groups in industry[5] as well as academic institutions[6] to prepare the corresponding group 4 metal complexes $[(Cp^*SiMe_2NCMe_3)MX_2]$ (**1**; M = Ti, Zr).[7] The synthesis of the $[Cp^*SiMe_2NCMe_3]^{2-}$ ligand system and the complexes **1** is straightforward, starting with silylation of $[Me_4C_5]^-$ followed by base-induced amination at silicon and then double deprotonation (Scheme 1). Activation of **1** with, for example, excess methylalumoxane leads to active homogeneous Ziegler–Natta catalysts for olefin polymerization. The **1**/MAO catalysts have been found to be especially useful for applications in ethene/1-alkene copolymerization reactions.[3–7]

A variety of other bridged Cp/amido group 4 metal systems have become known.[8,9] Especially the C_2 and C_3 hydrocarbyl-bridged systems (Chart 1 shows some representative examples) were shown to exhibit interesting catalytic features.

Chart 1

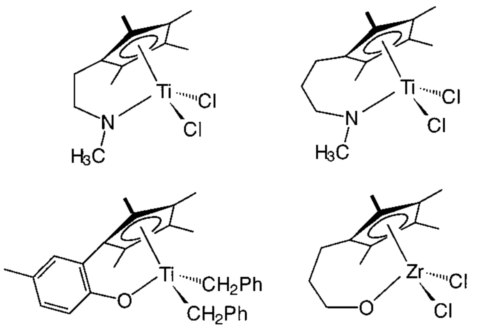
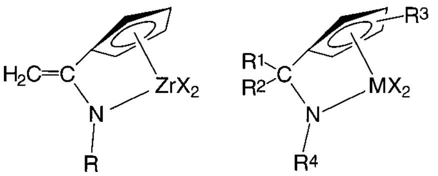


Chart 2



It is surprising that the chemistry of the sp^3-C_1-bridged "CpCN" analogues **2** of the "CpSiN"M systems **1** seems not to have been significantly developed so far.[10] We had previously reported the synthesis and catalytic properties of a few sp^2-C_1-bridged Cp/amido group 4 metal systems (**3**) (see Chart 2).[11] Inspection of the general synthetic scheme of the synthesis of **1** reveals that the sp^3-C_1-linked CpCN complexes **2** cannot be prepared in a simple synthetic analogy. We have now developed two synthetic routes to the new complexes **2**. These are surprisingly simple and straightforward and make such systems available in rather high yields with a number of variations in their substituent pattern. Their preparation, structural features. and first experiments toward a characterization of their catalytic properties are described in this paper.

Results and Discussion

Synthesis of (CpCN)group 4 Metal Complexes Starting From Formimidoylcyclopentadienides. The first synthetic route starts from the formimidoyl-substituted cyclopentadienides **5**. We had recently shown that such systems can readily be prepared by a fulvene route.[12] We had reacted 6-(dimethylamino)fulvene (**4**)[13] with lithium anilide (Scheme 2). In the course of several hours at ambient temperature in THF solution exchange of the $-NMe_2$ unit by $-N(Li)Ph$ took place cleanly with liberation of dimethylamine. The exchange reaction probably takes place by a two-step reaction mechanism, initiated by nucleophilic anilide

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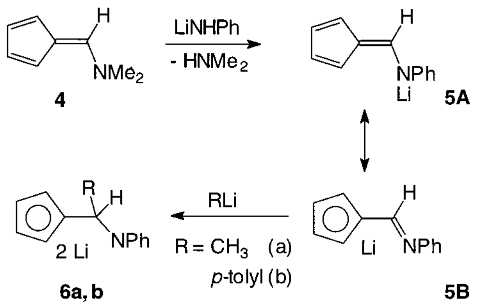
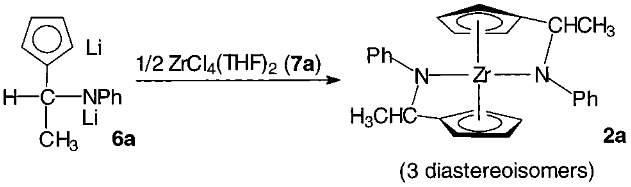
Scheme 2



Scheme 3

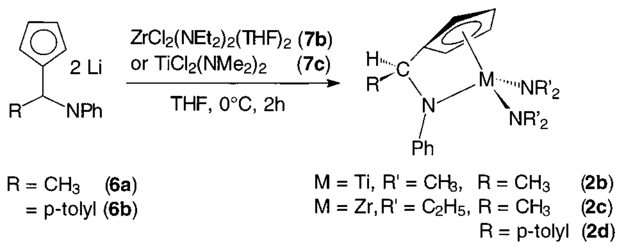


addition to the electrophilic carbon atom C6 of the fulvene followed by subsequent amine elimination.[11,13] The product **5** was shown by X-ray crystal structure analysis and dynamic NMR spectroscopy in solution to exhibit a fully conjugated structure.[12] This can be described by a close to equal participation of the mesomeric resonance hybrid structures **5A** and **5B**, representing residual fulvenoid character (**A**) or imine-functionalized cyclopentadienide properties (**B**) of the product.[14] Both indicate residual electrophilic features of the sp^2-hybridized functionalized C6 carbon atom. Consequently, this is amenable to nucleophilic attack.

Thus treatment of **5** with methyllithium in THF at room temperature proceeded smoothly.[15] The reaction went to completion during 12 h to furnish the "dianionic" CpCN ligand system as the corresponding dilithio compound $[CpCH(CH_3)NPh](Li)_2$ (**6a**). The analogous addition of *p*-tolyllithium cleanly gave the [CpCH(*p*-tolyl)NPh]$(Li)_2$ system **6b**.

Transmetalation of **6a** was achieved by treatment with $ZrCl_4(THF)_2$ (**7a**) in THF at −78 °C (Scheme 3). In each case a complete substitution of all four chloride ligands was observed irrespective of the applied stoichiometry.[16,17] Therefore, treatment of the zirconium tetrachloride reagent with **6a** in a 1:2 molar ratio turned out to be most advantageous. The spiro complex **2a** was isolated in ca. 50% yield. It contains two chiral centers in the sp^3-$CH(CH_3)$ bridging units. Therefore, a mixture of three diastereoisomers is expected. The ^1H NMR spectrum of the isolated product revealed the presence of a mixture of isomers. Crystallization from CH_2Cl_2/pentane by the diffusion method yielded single crystals of one diastereomer (*cis*-**2a**) that was characterized by X-ray diffraction (see below).

Scheme 4



Then we reacted the reagent **6a** with $ZrCl_2(NEt_2)_2$-$(THF)_2$ (**7b**).[18] In a 1:1 stoichiometry a clean reaction takes place in which both chloride ligands are exchanged and the $[CpCH(CH_3)NPh]$ ligand becomes attached to the group 4 transition metal center. Complex **2c** (M = Zr, R = CH_3; see Scheme 4) was obtained in ca. 70% yield. Treatment of **6a** with the related reagent $TiCl_2(NMe_2)_2$ (**7c**)[19] under analogous conditions (THF solution, 0 °C, 2 h reaction time) gave the related "CpCN" titanium complex **2b**. Eventually we treated $ZrCl_2(NEt_2)_2(THF)$ (**7b**) with [CpCH(*p*-tolyl)NPh]$(Li)_2$ (**2b**). The CpCN zirconium complex **2d** was isolated in 75% yield (see Scheme 4).

The complexes **2b**−**d** to our knowledge represent the first examples of simple sp^3-C_1-bridged ("CpCN") analogues of the ubiquitous silanediyl-bridged "CpSiN" constrained-geometry Ziegler−Natta catalyst precursors **1**. The complexes **2b**−**d** each contain a chirality center at the single bridging carbon atoms inside the Cp/amido ligand system. Therefore, the zirconium complex **2c** exhibits two pairs of ^1H NMR signals of the substituted Cp ligand at δ 6.31 (1H), 6.00 (1H), and 6.07 (2H) and two overlapping multiplets of the two separate ABX_3 spin systems of the pair of diastereotopic $-N(C_2H_5)_2$ σ-ligands at the pseudotetrahedral group 4 metal center (δ 3.33, 3.24, 3.19, 3.07).

X-ray Crystal Structure Analyses. The new CpCN group 4 metal complexes *cis*-**2a** and **2b** were characterized by X-ray crystal structure analyses. Single crystals of the spiro-metallocene complex *cis*-**2a** were obtained by diffusion of pentane vapor into a solution of the diastereomeric mixture of the metal complexes **2a** in dichloromethane solution. The complex *cis*-**2a** exhibits a close to C_2-symmetric molecular structure in the crystal. Only one of the three possible diastereomers has crystallized (as a racemate) under these experimental conditions. In the crystal we observed the diastereoisomer that has both the methyl substituents at the symmetry-equivalent bridging sp^3-carbon centers C6A and C6B oriented toward the front side of the bent-metallocene wedge (see Figure 1). Thus one of the two possible cis stereoisomers of complex **2a** is found to be present in the crystal, which will be termed *cis*-**2a**.

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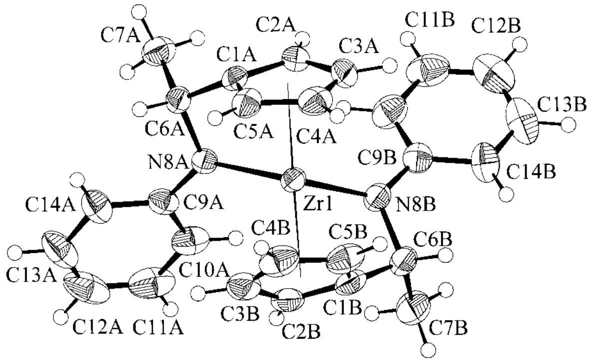


Figure 1. Molecular structure of complex *cis*-**2a**. Selected bond lengths (Å) and angles (deg): Zr−C1A = 2.418(2), Zr−C1B = 2.416(3), Zr−C2A = 2.485(3), Zr−C2B = 2.489(3), Zr−C3A = 2.528(4), Zr−C3B = 2.548(4), Zr−C4A = 2.500(3), Zr−C4B = 2.515(3), Zr−C5A = 2.454(2), Zr−C5B = 2.444(3), Zr−N8A = 2.142(2), Zr−N8B = 2.143(2), C1A−C6A = 1.506(3), C1B−C6B = 1.516(4), C6A−N8A = 1.473(3), C6B−N8B = 1.478(3), N8A−C9A = 1.389(3), N8B−C9B = 1.393(3); C1A−C6A−N8A = 100.1(2) C1B−C6B−N8B = 100.7(2), C6A−N8A−C9A = 118.7(2), C6B−N8B−C9B = 117.6(2), C6A−N8A−Zr = 106.1(1), C6B−N8B−Zr = 105.7(2), C9A−N8A−Zr = 132.0(2), C9B−N8B−Zr = 134.4(2).

The monosubstituted cyclopentadienide ligands in the complex *cis*-**2a** are η^5 coordinated. The Zr−C(Cp) bonding distances show a small but systematic decrease in both rings on going from the periphery toward the ipso carbon center. The Zr−C3/C4 bond lengths amount to 2.528(4)/2.500(3) Å in ring A (2.548(4)/2.515(2) Å in ring B), decreasing to Zr−C2A/C5A values of 2.485(3)/2.454(2) Å (ring B: 2.489(3)/2.444(3) Å) and eventually to even shorter metal−carbon values of 2.418(2) Å for the Zr−C1A bond and 2.416(3) Å for the Zr−C1B linkage. This decrease is likely to be due to the ring strain inside the CpCN framework of the “constrained geometry” complex *cis*-**2a**. The C1A−C6A bond length is 1.506(3) Å (C1B−C6B = 1.516(4) Å), the adjacent C6A−N8A distance amounts to 1.473(3) Å (C6B−N8B = 1.478(3) Å), and the C1A−C6A−N8A angle is rather small at 100.1(2)° (C1B−C6B−N8B = 100.7(2)°). The C1A−C6A vector is oriented out of the plane of the adjacent η^5-Cp ring by 23.3° (C1B−C6B/Cp^B = 23.2°). The nitrogen center in the *cis*-**2a** ligand system is trigonal planar (sum of the bonding angles: at N8A, 356.8°; at N8B, 357.7°), and the N8A−Zr bond length amounts to 2.142(2) Å (N8B−Zr = 2.143(2) Å). The Zr−N distances in *cis*-**2a** are markedly elongated as compared to e.g. the nonbridged complex CpZr(NiPr$_2$)$_3$ (Zr−N = 1.988(4) Å)[20] or the endocyclic Zr−N linkage in [Cp*SiMe$_2$(NCMe$_3$)ZrCl$_2$] at 2.052(2) Å.[21] The averaged Cp(centroid)−Zr−N8 angle in the complex *cis*-**2a** was found at 89.6°. This should be compared with the corresponding Cp*(centroid)−Zr−N angle in the conventional (Cp*SiN)Zr(NR$_2$)$_2$ reference complex **9** (see Chart 3) of 100.2°.[21]

The essential structural features of the (CpCN)-titanium complex **2b** are similar to those of *cis*-**2a**.[10a] In **2b** the η^5-Cp ring is also coordinated slightly unsym-

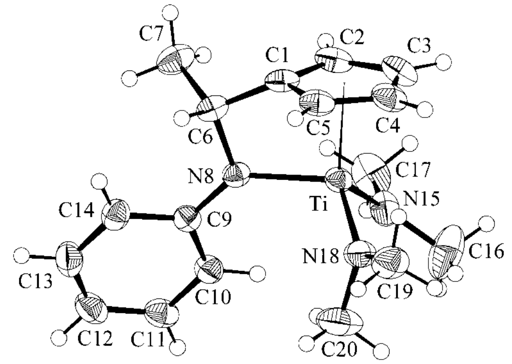
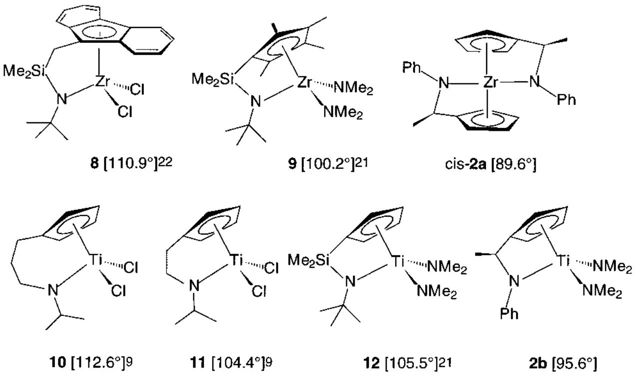


Figure 2. View of the molecular structure of the CpCN titanium complex **2b**. Selected bond lengths (Å) and angles (deg): Ti−C1 = 2.266(2), Ti−C2 = 2.314(2), Ti−C3 = 2.402(2), Ti−C4 = 2.424(2), Ti−C5 = 2.351(2), Ti−N8 = 2.006(1), Ti−N15 = 1.911(2), Ti−N18 = 1.898(1), C1−C6 = 1.505(2), C6−N8 = 1.476(2), N8−C9 = 1.387(2); C1−C6−N8 = 99.1(1), C6−N8−C9 = 119.1(1), C6−N8−Ti = 104.3(1), C9−N8−Ti = 136.2(1).

Chart 3. Comparison of Cp(centroid)−M−N Angles (in Parentheses) of the Complexes *cis*-2a and 2b (This Work) and Selected “Constrained Geometry” Reference Systems from the Literature



metrically to the central group 4 transition metal center with the Ti−C(ipso) linkage (2.266(2) Å) being more than 0.1 Å shorter than the distal Ti−C3/C4 bonds (for details see Figure 2). The endocyclic Ti−N8 bond length is rather long at 2.006(1) Å; the Ti−N15 (1.911(2) Å) and Ti−N(18) (1.898(1) Å) bonds are markedly shorter. The C1−C6−N8 (99.1(1)°) and C6−N−Ti (104.3(1)°) angles in **2b** are even slightly smaller than their counterparts in the zirconium complex *cis*-**2a**. In **2b** the Cp(centroid)−Ti−N angle is 95.6°, which is again ca. 10° smaller as found in the (CpSiN)TiX$_2$ reference molecule **12** (see Chart 3). From a comparison of the typical structural data we must conclude that the (CpCN)Zr and Ti complexes **2** contain a markedly more constrained ligand framework as compared to their (CpSiN)M analogues. One of the most prominent structural features where this shows up is the Cp(centroid)−M−N angle inside the bridged systems. Substituting the Me$_2$Si linker by the RHC moiety consistently results in a reduction of about 10°, which must be considered a large structural effect: the (CpCN)MX$_2$ systems must be regarded as substantially more “constrained” linked Cp/amido group 4 metal complexes as compared to their conventional (CpSiN)MX$_2$ counterparts.

Synthesis of CpCN Group 4 Metal Complexes by a Fulvene Route. Upon treatment with a suitable base

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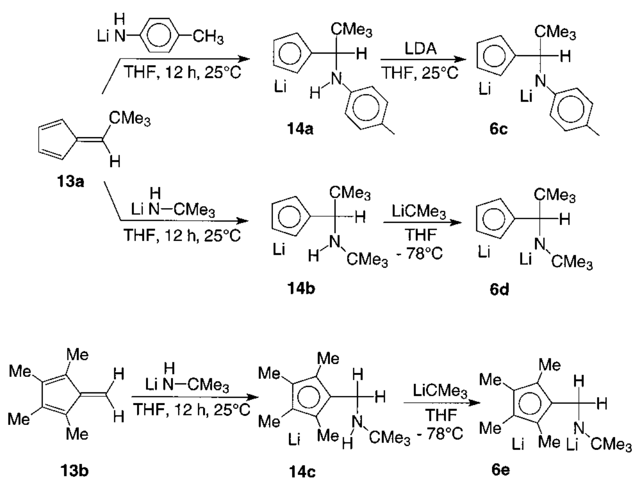
(21) Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572−1581.

Scheme 5



6-alkylfulvenes react by deprotonation at the alkyl substituent α-carbon to yield alkenyl-substituted cyclopentadienide systems. This is one of the most frequently used synthetic entries into bis(alkenylcyclopentadienyl)-group 4 metal complex systems.[23] In the absence of acidic α-hydrogen atoms at the C-6 substituents, alternative addition of a suitable nucleophile to the fulvene C-6 carbon atom becomes feasible[15] even if rather highly basic nucleophilic reagents are used. We have here used the "nonenolizable" fulvene 6-*tert*-butylpentafulvene (**13a**) as a suitable starting material for the synthesis of an sp^3-C_1-bridged Cp/amido ligand system.[24] Treatment of **13a** with in situ generated lithium *p*-methylanilide in THF at room temperature overnight gave the 1-(arylamino)-2,2-dimethylpropyl-substituted lithium cyclopentadienide system **14a**, which was isolated as a solid in ca. 90% yield. Similar treatment of **13a** with lithium *tert*-butylamide gave the corresponding (1-(*tert*-butylamino)-2,2-dimethylpropyl)cyclopentadienide system **14b** as an oil in 91% yield. In **14b** the substituent 1-*H* proton ^{1}H NMR signal is observed as a doublet due to its vicinal $^3J_{HH}$ = 7 Hz coupling with the remaining amino proton (see Scheme 5).

We prepared the tetramethylpentafulvene **13b**[25] by a variation of a literature route[26] via hydride abstraction from pentamethylcyclopentadienide by treatment with triphenylchloromethane.[27] Subsequent addition of lithium *tert*-butylamide[25] cleanly gave the anionic reagent **14c** (75% isolated yield). Compound **14c** shows two Cp−CH_3 ^{1}H NMR singlets at δ 1.86 and 1.82 and a Cp−CH_2− doublet at δ 4.37 ($^3J_{HH}$ = 7 Hz) due to coupling with the adjacent NH proton.

Deprotonation of the NH group in the monoanion equivalent **14a** could be achieved by treatment with the amide base LDA in tetrahydrofuran to yield the dianion equivalent **6c** (as the dilithio compound; see Scheme 5). Deprotonation of the aliphatic amino groups in the alkylamino-substituted cyclopentadienide **14b** required a stronger base. Treatment with *tert*-butyllithium in THF (−78 °C to room temperature) gave the doubly lithiated ligand system (compound **6d**) in almost quantitative yield as a very sensitive solid. The ^{1}H NMR spectrum of **6d** now shows a sharp singlet of the 6-H proton at δ 3.29 (vs a doublet at δ 3.13, $^3J_{HH}$ = 7 Hz for the monoanionic starting material **14b**, see above). NH deprotonation of **14c** was achieved by treatment with *tert*-butyllithium under similar reaction conditions, but the resulting product **6e** was not spectroscopically characterized, due to its very low solubility even in THF-d_8.

Transmetalation of the alkylidene-bridged Cp/amido dianion equivalent **6c** was achieved by treatment with the titanium(IV) reagent $Cl_2Ti(NMe_2)_2$ (**7c**) in THF solution. After a reaction time of 2 h at ambient temperature, workup gave the C_1-alkylidene-linked Cp/amido titanium complex **2e** in ca. 70% yield as a dark red solid. As expected, the chiral complex **2e** exhibits four ^{1}H NMR resonances of the Cp protons at δ 6.16, 6.12, 5.83, and 5.73 (in benzene-d_6; corresponding ^{13}C NMR Cp−methine signals at δ 116.7, 114.8, 114.7, and 111.3), a μ-CH singlet at δ 4.85, and a pair of $-NMe_2$ singlets at δ 3.02 and 2.87.

Analogous treatment of **6c** with $Cl_2Zr(Net_2)_2(THF_2)_2$ (**7b**) gave the CpCN zirconium complex **2f** as a brown oil in >60% yield. Again, the ^{1}H NMR spectrum exhibits four separate Cp−methine resonances (δ 6.38, 6.10, 6.07, 5.93). Due to the chiral ligand framework, the N−CH_2− hydrogens of the $Zr(NEt_2)_2$ moiety are diastereotopic, and the two zirconium-bound $-NEt_2$ ligands are chemically differentiated. Therefore, four distinct multiplets of the [Zr]−NCH_2− protons are observed in the ^{1}H NMR spectrum of complex **2f** (at δ 3.31, 3.28, 3.19, 3.08), and there are two triplets observed originating from the respective $-N(CH_2CH_3)_2$ methyl groups (δ 1.06, 0.65). Treatment of the dianion reagent **6d** with $Cl_2Zr(NEt_2)_2(THF)_2$ (**7b**) furnished the (CpCN)Zr complex **2g** in ca. 70% yield (see Scheme 6). Complex **2g** exhibits a similar NMR behavior.

Eventually, the Cp*-derived dianion reagent **6e** was reacted with the dichloro(diamido)zirconium complex **7b** to give the (Cp*CN)Zr complex **2h**, which was isolated in ca. 65% yield as a colorless oil. The ^{1}H NMR spectrum of complex **2h** shows a μ-CH_2 singlet at δ 4.34 (^{13}C NMR signal at δ 68.6) and a set of two Cp−CH_3 resonances (δ 2.08, 2.06). The two diethylamido ligands at zirconium are symmetry equivalent, but their N−CH_2− hydrogen atoms are each diastereotopic, giving rise to a complex ^{1}H NMR multiplet centered at δ 3.32 (N−CH_2CH_3 triplet at 0.97).

We briefly attempted to convert the bis(diethylamido)-zirconium complex **2h** into the corresponding (Cp*CN)-$ZrCl_2$ complex **2i**. Treatment of **2h** with excess (unpurified) trimethylchlorosilane in dichloromethane-d_2[28] led to a ca. 40% conversion to the zirconium dichloride complex admixed with a complicated mixture of as yet unidentified additional reaction (or decomposition) products. From this mixture single crystals were obtained that were identified by X-ray diffraction as the μ-oxo complex **15**: i.e., the H_2O addition product to two molecules of **2i** (see Scheme 7).[29]

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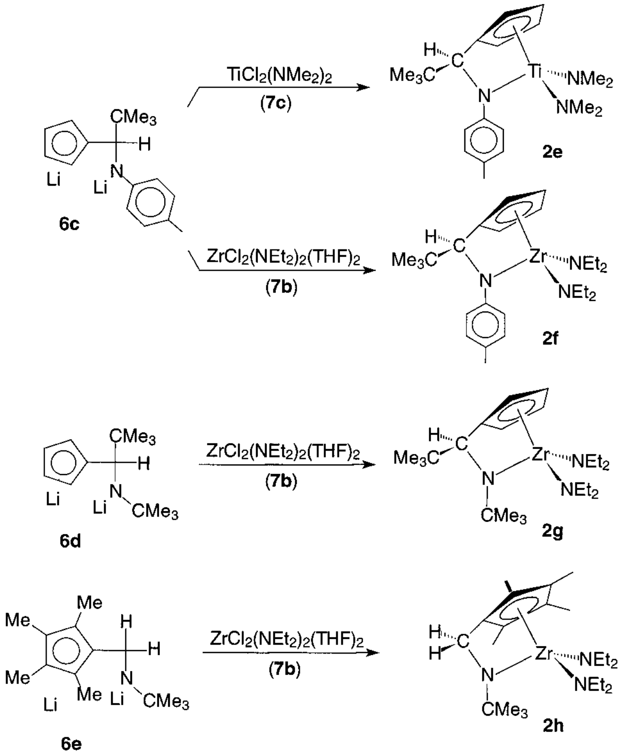
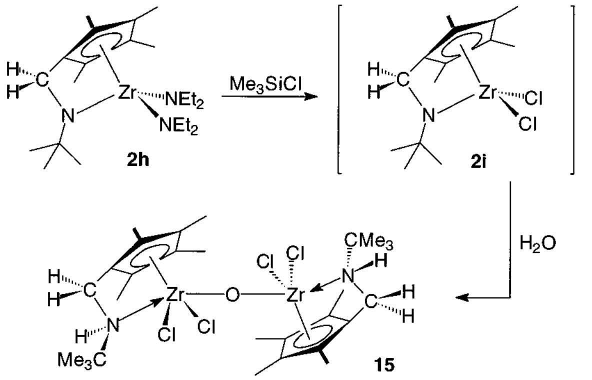
Scheme 6



Scheme 7



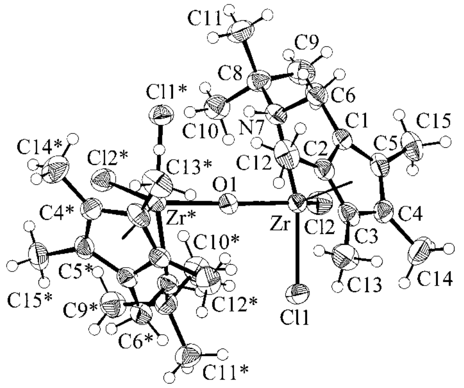


Figure 3. Projection of the molecular structure of complex **15**. Selected bond lengths (Å) and angles (deg): Zr−C1 = 2.419(5), Zr−C2 = 2.460(5), Zr−C3 = 2.543(6), Zr−C4 = 2.559(6), Zr−C5 = 2.502(6), Zr−N7 = 2.500(4), Zr−Cl1 = 2.483(1), Zr−Cl2 = 2.426(2), Zr−O1 = 1.954(1), C1−C6 = 1.504(8), C6−N7 = 1.488(7), N7−C8 = 1.515(7); Zr−O1−Zr* = 168.2(3), C1−C6−N7 = 104.6(4), C6−N7−C8 = 115.3(4), C6−N7−Zr = 97.4(3), C8−N7−Zr = 135.6(3).

The X-ray crystal structure analysis of the crystalline product **15** (Figure 3) revealed that the treatment of the tetramethylfulvene **13b** with lithium *tert*-butylamide had indeed produced the respective Cp*CN ligand system and that it was successfully attached to the group 4 metal. The −NEt$_2$ vs −Cl exchange reaction had apparently taken place, but the resulting product (**2i**) had added 1 equiv of water under the applied reaction conditions to form a [Zr]−μ-O−[Zr] dimer (**15**). In this case, elimination of HCl had not yet taken place, but the doubly N-protonated product was observed. The Zr−O−Zr* angle in complex **15** amounts to 168.2(3)°, which is only by 12° away from the linear arrangement that is often observed in μ-oxo−group 4 metal complex systems. The Zr−O bond in **15** is short at 1.954(1) Å, indicating some oxygen to metal π-back-bonding.[30] The coordination geometry around the two symmetry-equivalent zirconium centers is distorted square-pyramidal, with a pair of cis chloride ligands (Zr−Cl1 = 2.483(1) Å; Zr−Cl2 = 2.426(2) Å), the μ-oxo ligand, and the protonated Cp*CN nitrogen making up the base of the coordination polyhedron. The Zr−N7 distance amounts to 2.500(4) Å, which is much longer than the Zr−N distances observed in the related spiro system **2a** (see above). In **15** the C6−N7−Zr angle amounts to 97.4(3)°. The ammonium nitrogen center in complex **15** is markedly pyramidalized—the sum of the three heavy-atom bond angles around nitrogen in **15** is 348.3°. The N7−C6−C1 angle in **15** amounts to 104.6(4)°. The C$_5$-Me$_4$ ligand is again slightly unsymmetrically η^5-coordinated to zirconium, with the Zr−C1 distance (2.419(5) Å) being markedly shorter than the adjacent Zr−C2/C5 (2.460(5) Å/2.502(6) Å) and the distal Zr−C3/C4 bonds (2.543(6) Å/2.559(6) Å).

Olefin Polymerization Reactions. Ethylene polymerization reactions were carried out with the new CpCN titanium systems **2b,e** and with the CpCN zirconium complexes **2d**,**f**,**g**,**h**. The group 4 metal complexes were in each case activated by treatment with a large excess of methylalumoxane[1,31] (for Al/M ratios and further details see Table 1). For a comparison, ethylene polymerization reactions were carried out under similar conditions, employing the (Cp*SiN)Zr "constrained geometry" systems [(C$_5$Me$_4$)SiMe$_2$CMe$_2$]ZrCl$_2$ (**1**) and [(C$_5$Me$_4$)SiMe$_2$CMe$_3$]Zr(NMe$_2$)$_2$ (**9**). Some of these experiments were repeated several times under similar reaction conditions to check for general reproducibility. Tables 1 and 2 provide representative data of single examples

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Table 1. Ethene Polymerization Reactions Employing CpCN Group 4 Metal/Methylalumoxane Catalysts (at 60 °C and 2 bar of Ethene Pressure in Toluene Solution)[a]

no.	compd	M	amt of cat. (mg)[b]	Al/M	amt of PE (g)	mp (°C)	act[c]
1	**2b**	Ti	21	500	2.0	120	15
2	**2e**	Ti	19	660	4.2	125	42
3	**2d**	Zr	20	820	1.3	123	12
4	**2f**	Zr	20.5	760	1.1	126	13
5	**2g**	Zr	21.5	680	6.3	128	101
6	**2h**	Zr	10	1470	2.2	131	97
7	**1**[d]	Zr	17	800	2.1	123	29
8	**9**[d]	Zr	16	890	2.4	122	27

[a] In most cases typical single examples out of a series of several analogous experiments are reported. [b] Milligrams of group 4 metal component. [c] In (g of PE)/((mmol of group 4 metal catalyst) h (bar of ethene)). The reaction time was in all cases 1 h. [d] **1**, $[(C_5Me_4)SiMe_2NCMe_3]ZrCl_2$; **9**, $[(C_5Me_4)SiMe_2NCMe_3]Zr(NMe_2)_2$.

out of these series. The first experiments showed that the systems **2f**/MAO and **2g**/MAO were close to inactive at 25 °C under the selected standard conditions (2 bar of ethylene in toluene solution). Therefore, the ethene polymerization reactions with the selected examples of the complexes **2** (see Table 1) were carried out at higher temperature. At 60 °C in toluene at a constant ethylene pressure of 2 bar, polyethylene was formed by the **2**/MAO catalyst. Both the CpCN titanium and zirconium systems showed catalyst activities in ethene polymerization under these conditions that were largely in the same range as observed for the Cp*SiN zirconium/MAO reference systems, under our conditions, with the (CpCN)Zr (**2g**)/MAO and the (Cp*CN)Zr (**2h**)/MAO Ziegler−Natta catalysts being the best in this zirconium series (see Table 1).

Ethene/1-octene copolymerization reactions were carried out under slightly optimized reaction conditions. Most of the CpCN group 4 metal complexes give Ziegler−Natta catalysts upon MAO activation that are active in the ethylene/α-olefin copolymerization reaction, and they all produce copolymers that contain reasonable amounts of the extended 1-alkene incorporated (see Table 2). Generally it appears that the (Cp*CN)Zr system (**2h**/MAO) incorporates slightly less 1-octene than the (CpCN)M/MAO systems featuring the smaller C_5H_4 ligand subunit. The latter produced copolymers under these experimental conditions that contained almost as much of the 1-octene component as was incorporated by employing the (Cp*SiN)Zr reference system **9** under these conditions (the copolymer composition was determined by a standard ^{13}C NMR analysis;[32,33] see Figure 4 for a selected example). However, the new (CpCN)M/MAO catalysts seem to be less active ethene/1-octene copolymerization catalysts under the conditions applied here (see Table 2) as compared to the Cp*SiN zirconium (**9**)/MAO catalyst.

Conclusions

In this study we have developed two rather simple routes to alkylidene (sp^3-C_1)-bridged Cp/amido group 4 metal complexes. Both routes are conceptually related, and both make use of the C-6 electrophilicity of pentafulvenes or pentafulvenoid systems. Given the ease of formation of the various (CpCN)group 4 metal complexes, whose syntheses were carried out in the course of our study, it is surprising that the chemistry of such (CpCN)M systems has remained so largely undeveloped as compared to their ubiquitous (Cp*SiN)M relatives.

We were able to show that the CpCN group 4 metal systems can be used for generating active ethylene polymerization catalysts as well as ethylene/α-olefin copolymerization catalysts. 1-Octene incorporation in the resulting copolymers is often quite high in these homogeneous (CpCN)M/MAO Ziegler−Natta catalyst systems, but their activities seem to be somewhat lower as compared to the conventional (Cp*SiN)Zr-derived catalyst systems under the applied specific conditions. This is surprising in view of the markedly decreased Cp(centroid)−M−N angles that we have observed in our X-ray diffraction analysis for the (CpCN)Ti and -Zr examples investigated in the course of this study. The new $(CpCN)M^{IV}$ systems show by ca. 10° smaller such angles at the central group 4 metal as compared to their directly related $(CpSiN)M^{IV}$ analogues, which should render the (CpCN)M systems as *more constrained* than the conventional dimethylsilanediyl-bridged Cp/amido group 4 metal complexes.[34]

There are several possible explanations for our observation, of which the simplest would be that the CpCN catalysts might exhibit different temperature profiles. Our findings could alternatively indicate that the copolymerization activities of such systems, contrary to common belief,[9,34] might not be related to their “constrained geometry” qualities but that steric and electronic effects in Cp/amido group 4 metal catalyst systems in a subtle combination are determining the essential properties of such catalyst systems and their specific action. It could also be that our new catalysts are “too constrained” to allow for a simple extension of the catalytic activities in the general series of such compounds, since they might offer such an open and exposed active catalytic site that toluene solvent (or $[X\text{-}MAO]^-$ anion) interaction begins to effectively compete with monomer about the available coordination space at the active metal center.[35] In that case, alternative pathways of activation[36] and the use of other, less coordinative solvents could be indicated. Investigations

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Table 2. Ethene/1-Octene Copolymerization Reactions Using CpCN Group 4 Metal/MAO Catalysts (in Toluene Solution at 90 °C)[a]

no.	compd	M	amt of cat. (mg)	*t* (h)	Al/M	amt of polym (g)	ethene:octene[b]	mp (°C)	M_w	M_w/M_n	act[c]
					2 bar of Ethene/20% 1-Octene						
1	**2c**	Zr	23	1	600	4.8	21:1	93	25 000	2.8	46
2	**2g**	Zr	20	1	730	7.8	13:1	89	10 000	3.1	86
3	**2h**	Zr	21	1	690	15.4	25:1	98	20 000	*d*	162
					2 bar of Ethene/50% 1-Octene						
4	**2e**	Ti	20	1	630	2.9	4:1	oil			54
5	**2f**	Zr	20.5	1	760	2.1	5:1	oil			25
6	**2g**	Zr	20	1	730	3.6	7:1	oil	3000	2.9	40
7	**2h**	Zr	19	1	770	4.2	13:1	96	29 000	2.8	47
8	**9**[e]	Zr	16	0.75	870	27.0	4:1	oil			480
					1 bar of Ethene/50% 1-Octene						
9	**2e**	Ti	15	0.75	820	5.1	3:1	oil			170
10	**2f**	Zr	25	1	640	1.8	4.5:1	oil			34
11	**2g**	Zr	30	1	490	3.3	5.5:1	oil	15 000	2.4	37
12	**9**[e]	Zr	20	1	660	20.8	3:1	oil			400

[a] In most cases typical examples of a series of several analogous experiments are reported. [b] The ethene:1-octene ratio in the copolymer was determined by ^{13}C NMR spectroscopy.[32] [c] Catalyst activities in (g of copolymer)/((mmol of group 4 metal cat.) h (bar of ethene)). [d] Not determined. [e] [(C_5Me_4)$SiMe_2NCMe_3$]Zr(NMe_2)$_2$.

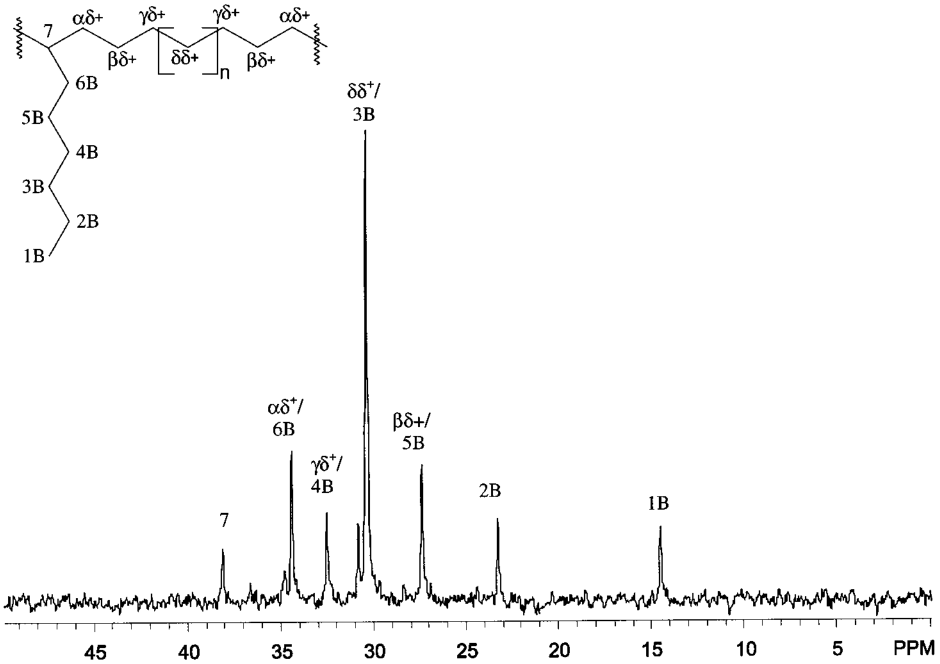

Figure 4. ^{13}C NMR spectrum of the ethene/1-octene copolymer (Table 2, entry 11) in benzene-d_6 solution (with signal assignment according to ref 32).

aimed at clarifying these points are currently being carried out in our laboratory.

Experimental Section

All reactions were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled prior to use. NMR spectra were measured using a Bruker AC 200 P or Varian Unity Plus 600 NMR spectrometer. Most assignments were based on a series of 2D NMR experiments.[37] Pentafulvenes **4** and **13a** and the reagents $ZrCl_4$-(THF)$_2$ (**7a**), $Cl_2Zr(NEt_2)_2(THF)_2$ (**7b**),[18] and $Cl_2Ti(NMe_2)_2$ (**7c**)[19] were prepared according to literature procedures. Lithium (*N*-phenylimidoyl)cyclopentadienide (**5**)[12] and 1,2,3,4-tetramethylpentafulvene (**13b**)[27] were synthesized as described in recent publications.

Preparation of Lithium [1-(*p*-Tolylamino)-2,2-dimethylpropyl]cyclopentadienide (14a). Samples of 800 mg (7.46 mmol) of LDA and 800 mg (7.46 mmol) of 4-methylaniline were dissolved in 100 mL of THF, and the mixture was stirred for 2 h. The in situ generated lithium 4-methylanilide solution was then added to 1.00 g (7.46 mmol) of 6-*tert*-butylpentafulvene (**13a**), dissolved in 50 mL of THF, and the mixture was stirred for 12 h at room temperature. Solvent was removed in vacuo to give a brown viscous oil. A 50 mL portion of pentane was added and subsequently removed to solidify the product. A total of 2.12 g (7.00 mmol, 89%) of a pale brown solid was isolated. ^{1}H NMR (200.13 MHz, THF-d_8, 298 K): δ 6.90 (m, 2H, tol H), 6.56 (m, 2H, tol H), 5.68 (b, 4H, Cp H), 4.09 (b, 1H, CH), 2.23 (s, 3H, tol CH_3), 1.02 (s, 9H, C(CH_3)$_3$), NH not observed.

Preparation of Lithium [1-(*tert*-Butylamino)-2,2-dimethylpropyl]cyclopentadienide (14b). Lithium *tert*-butylamide was formed in situ by reaction of 545 mg (7.46 mmol) of *tert*-butylamine with 800 mg (7.46 mmol) of LDA in 80 mL of THF. A 1.00 g (7.46 mmol) amount of 6-*tert*-butylfulvene

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(37) Braun, S.; Kalinowski, H. O.; Berger, S. *150 and More Basic NMR Experiments*, VCH: Weinheim, Germany, 1998, and references therein.

(**13a**) in 50 mL of THF was added and the reaction mixture stirred for 12 h. A 1.44 g amount (6.79 mmol, 91%) of the oily product was isolated after evaporation of the solvent. ^{1}H NMR (200.13 MHz, THF-d_8, 298 K): δ 5.56 (m, 2H, Cp H), 5.52 (m, 2H, Cp H), 3.18 (d, ^3J = 7.0 Hz, 1H, CH), 0.95 (s, 9H, C(CH$_3$)$_3$), 0.83 (s, 9H, C(CH$_3$)$_3$), NH not observed. ^{13}C{^{1}H} NMR (50.3 MHz, THF-d_8, 298 K): δ 125.4 (ipso Cp), 103.1 (Cp), 101.1 (Cp), 62.4 (CH), 50.9 (N(*C*(CH$_3$)$_3$), 36.2 (C(*C*(CH$_3$)$_3$), 30.5 (C(*C*H$_3$)$_3$), 27.9 (C(*C*H$_3$)$_3$). ^{7}Li NMR (232.8 MHz, THF-d_8, 298 K): δ −7.5.

Synthesis of Lithium 1-[(*tert*-Butylamino)methyl]-2,3,4,5-tetramethylcyclopentadienide (14c). Lithium *tert*-butylamide (200 mg, 2.53 mmol) was dissolved in 50 mL of pentane and 2 mL of THF and reacted with 2.5 g of a 9:1 mixture of toluene and 1,2,3,4-tetramethylpentafulvene (**13b**) at room temperature. Over 12 h a white solid precipitated. The solid was collected by filtration, washed with 20 mL of pentane twice, and dried in vacuo to give 440 mg (1.90 mmol, 75%) of **14c**. ^{1}H NMR (200.13 MHz, THF-d_8, 298 K): δ 4.37 (d, ^3J = 7.0 Hz, 2H, CH$_2$), 1.86 (s, 6H, Cp CH$_3$), 1.82 (s, 6H, Cp CH$_3$), 1.19 (s, 9H, C(CH$_3$)$_3$), NH not observed. ^{13}C{^{1}H} NMR (50.3 MHz, THF-d_8, 298 K): δ 111.0 (ipso Cp), 107.3 (Cp), 107.2 (Cp), 50.6 (*C*(CH$_3$)$_3$), 38.5 (CH$_2$), 29.7 (C(*C*H$_3$)$_3$), 10.8 (Cp CH$_3$), 10.6 (Cp CH$_3$).

Preparation of Dilithium 1-[(Phenylamido)ethyl]cyclopentadienide (6a). A sample of 3.00 g (12.10 mmol) of lithium (*N*-phenylimidoyl)cyclopentadienide (**5**) in 50 mL of diethyl ether was treated with 7.40 mL of a 1.63 M solution of methyllithium in diethyl ether at room temperature, and the mixture was stirred for 12 h. After evaporation of the solvent, 2.93 g (11.60 mmol, 96%) of a pale brown solid was isolated in acceptable purity, containing 0.75 equiv of THF. ^{1}H NMR (200.13 MHz, THF-d_8, 298 K): δ 6.69 (m, 2H, *m*-Ph), 6.29 (m, 2H, *o*-Ph), 5.80 (m, 1H, *p*-Ph), 5.66 (bm, 4H, Cp), 4.25 (q, $^3J_{\mathrm{H-H}}$ = 6.0 Hz, 1H, 6-H), 1.26 (d, ^3J = 6.0 Hz, 3H, 7-H). ^{13}C{^{1}H} NMR (50.3 MHz, THF-d_8, 298 K): δ 161.2 (*ipso*-Ph), 129.6 (Ph), 128.7 (Ph), 114.1 (Ph), 107.9 (C-1), 102.7 (Cp), 102.6 (Cp), 50.6 (C-6), 19.8 (C-7). ^{7}Li NMR (232.8 MHz, THF-d_8, 298 K): δ −3.5 (br).

Synthesis of Dilithium 1-(Phenylamido)-1-(*p*-tolylmethyl)cyclopentadienide (6b). A solution of 390 mg (4.00 mmol) of *p*-tolyllithium in 30 mL of THF was added to 990 mg (4.00 mmol) of lithium (N-phenylimidoyl)cyclopentadienide (**5**), dissolved in 50 mL of THF, and stirred overnight. The solvent was removed and the remaining oil solidified by treatment with 50 mL of pentane and subsequent evaporation. A 1.03 g amount (3.76 mmol, 94%) of a brown solid was isolated. ^{1}H NMR (200.13 MHz, THF-d_8, 298 K): δ 7.25 (m, 2H, tol H), 6.88 (m, 2H, tol H), 5.80 (m, 2H, *m*-Ph H), 6.00 (b, 3H, *o*- and *p*-Ph H), 5.67 (m, 2H, Cp H), 5.53 (b, 2H, Cp H), 5.12 (s, 1H, CH), 2.22 (s, 3H, tol C*H*$_3$).

Formation of Dilithium [1-(*p*-Tolylamido)-2,2-dimethylpropyl]cyclopentadienide (6c). A sample of 2.12 g (7.00 mmol) of lithium [1-(*p*-tolylamino)-2,2-dimethylpropyl]cyclopentadienide (**14a**) was dissolved in 50 mL of THF and treated with 756 mg (7.00 mmol) of LDA in 30 mL of THF at 0 °C for 3 h. The solvent was removed, and the product was solidified by several treatments of the remaining oil with 20 mL of pentane and subsequent evaporation to give 1.34 g (87%, 6.10 mmol) of **6c**. ^{1}H NMR (200.13 MHz, THF-d_8, 298 K): δ 6.38 (m, 2H, tol H), 6.05 (b, 2H, tol H), 5.63 (b, 4H, Cp H), 4.05 (s, 1H, CH), 2.01 (s, 3H, tol CH$_3$), 0.98 (s, 9H, C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (50.3 MHz, THF-d_8/benzene-d_6 1:1, 298 K): δ 161.2 (*ipso* tol), 129.9, 129.3, 115.7 (tol), 102.7, 101.8 (Cp), (C-6), 37.5 (C-7), 28.8 (C-8), 20.2 (tol CH$_3$). ^{7}Li NMR (232.8 MHz, THF-d_8, 298 K): δ −3.5 (br).

Preparation of Dilithium [1-(*tert*-Butylamido)-2,2-dimethylpropyl]cyclopentadienide (6d). A sample of 1.20 g (5.64 mmol) of lithium [1-(*tert*-butylamino)-2,2-dimethylpropyl]cyclopentadienide (**14b**) in 30 mL of THF was treated with 3.70 mL of a 1.52 M solution of *tert*-butyllithium in hexane at −78 °C. The solvent was removed after 12 h reaction time, and 30 mL of pentane was added. The mixture was stirred for 15 min, and the pale solid was collected by filtration and dried in vacuo to yield 1.21 g (5.53 mmol, 98%) of **6d**. ^{1}H NMR (200.13 MHz, THF-d_8, 298 K): δ 5.7−5.5 (b, 4H, Cp H), 3.29 (s, 1H, CH), 1.13 (s, 9H, C(CH$_3$)$_3$), 0.95 (s, 9H, C(CH$_3$)$_3$).

Preparation of Dilithium 1-[(*tert*-Butylamido)methyl]-2,3,4,5-tetramethylcyclopentadienide (6e). A 1.56 M solution of *tert*-butyllithium in hexane (0.63 mL) was added dropwise to a solution of 200 mg (0.98 mmol) of lithium 1-[(*tert*-butylamino)methyl]-2,3,4,5-tetramethylcyclopentadienide (**14c**) in 50 mL of THF at −78 °C. The reaction mixture was stirred for 12 h and the precipitated product collected by filtration, washed with 10 mL of pentane, and dried in vacuo. A 130 mg amount (0.61 mmol, 62%) of a white solid was isolated which was insoluble even in THF.

Preparation of Bis[η^5-[1-(phenylamido)ethyl]cyclopentadienyl-κN]zirconium (2a). A solution of 750 mg (2.8 mmol) of dilithium [1-(phenylamido)ethyl]cyclopentadienide (**6a**) in 50 mL of THF was added slowly to a solution of 1.06 g (2.8 mmol) of ZrCl$_4$(THF)$_2$ (**7a**) in 50 mL of THF at −78 °C. The mixture was warmed to 0 °C, and the solvent was removed subsequently. A 40 mL amount of dichloromethane was added, and the precipitated LiCl was filtered off. The solvent was evaporated and the brown solid dried in vacuo to yield 652 mg (1.42 mmol, 51%) of **2a**. Single crystals for X-ray diffraction were obtained by slow diffusion of pentane into a concentrated solution of **2a** in dichloromethane. ^{1}H NMR (200.13 MHz, THF-d_8, 298 K): δ 7.08 (m, Ph), 6.90−6.70 (m, Ph), 6.59, 6.52, 6.03, 5.69 (each m, Cp), 5.16−5.11 (m, 6-H), 1.50−1.38 (m, 7-H). Anal. Calcd for $C_{26}H_{26}N_2Zr$ (457.7): C, 68.23; H, 5.73; N, 6.12. Found: C, 68.56; H, 6.20; N, 6.28.

X-ray Crystal Structure Analysis of *cis*-2a. Crystal data are as follows: formula $C_{26}H_{26}N_2Zr$, M_r = 457.71, yellow crystal, 0.35 × 0.30 × 0.30 mm, a = 12.346(1) Å, b = 20.442(1) Å, c = 8.422(1) Å, V = 2125.5(3) Å^3, ρ_{calcd} = 1.430 g cm^{-3}, μ = 5.32 cm^{-1}, empirical absorption correction via SORTAV (0.836 ≤ T ≤ 0.857), Z = 4, orthorhombic, space group $Pna2_1$ (No. 33), λ = 0.710 73 Å, T = 198 K, ω and φ scans, 11 065 reflections collected (±h, ±k, ±l), (sin θ)/λ = 0.65 Å^{-1}, 3745 independent (R_{int} = 0.029) and 3429 observed reflections ($I \geq 2\sigma(I)$), 264 refined parameters, R1 = 0.026, wR2 = 0.061, maximum residual electron density 0.22 (−0.33) e Å^{-3}, Flack parameter −0.04(3), hydrogens calculated and refined as riding atoms.

Preparation of Bis(dimethylamido)[η^5-[1-(phenylamido)ethyl]cyclopentadienyl-κN]titanium (2b). A solution of 300 mg (1.12 mmol) of dilithium 1-[(phenylamido)ethyl]-cyclopentadienide (**6a**) in 50 mL of THF was added dropwise to 231 mg (1.12 mmol) of Cl$_2$Ti(NMe$_2$)$_2$ (**7c**) in 50 mL of THF at 0 °C. Over 2 h the reaction mixture was warmed to room temperature. The solvent was removed in vacuo, and the oily residue was treated with 40 mL of pentane. After filtration of LiCl and evaporation of the solvent 246 mg (77 mmol, 69%) of **2b** was obtained as a red solid. Single crystals were obtained from a concentrated solution of **2b** in dichloromethane at −20 °C after several days. ^{1}H NMR (200.13 MHz, THF-d_8, 298 K): δ 7.04 (m, 2H, *m*-Ph H), 6.77 (m, 2H, o-Ph H), 6.52 (m, 1H, *p*-Ph H), 6.42, 6.03 (each m, each 1H, Cp H), 6.20 (m, 2H, Cp H), 4.97 (q, ^3J = 6.2 Hz, 1H, CH), 3.08, 3.06 (each s, each 6H, NCH$_3$), 1.45 (d, ^3J = 6.2 Hz, 3H, CCH$_3$). ^{13}C{^{1}H} NMR (50.3 MHz, THF-d_8, 298 K): δ 152.6 (ipso Ph), 129.3 (Ph), 118.2, 116.1, 115.4, 115.1, 113.6, 113.4, 113.2 (Ph and Cp), 53.0 (CH), 49.1, 47.4 (both NCH$_3$), 17.1 (C*C*H$_3$). Anal. Calcd for $C_{17}H_{25}N_3Ti$ (319.3): C, 63.95; H, 7.89; N, 13.16. Found: C, 63.88; H, 8.18; N, 13.52.

X-ray Crystal Structure Analysis of 2b. Crystal data are as follows: formula $C_{17}H_{25}N_3Ti$, M_r = 319.30, orange crystal, 0.35 × 0.20 × 0.10 mm, a = 8.164(1) Å, b = 22.073(1) Å, c = 10.037(1) Å, β = 113.41(1)°, V = 1659.8(3) Å^3, ρ_{calcd} = 1.278 g cm^{-3}, μ = 5.13 cm^{-1}, empirical absorption correction via SORTAV (0.841 ≤ T ≤ 0.951), Z = 4, monoclinic, space group

$P2_1/c$ (No. 14), $\lambda = 0.710\,73$ Å, $T = 198$ K, ω and φ scans, 6561 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin \theta)/\lambda = 0.65$ Å^{-1}, 3754 independent ($R_{int} = 0.021$) and 3220 observed reflections ($I \geq 2\sigma(I)$), 195 refined parameters, R1 = 0.036, wR2 = 0.087, maximum residual electron density 0.25 (−0.25) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Preparation of Bis(diethylamido)[η^5-[1-(phenylamido)ethyl]cyclopentadienyl-κN]zirconium (2c). A solution of 2.50 g (5.6 mmol) of $Cl_2Zr(NEt_2)_2(THF)_2$ (**7b**) in 100 mL of THF was treated with 1.50 g (5.6 mmol) of dilithium [1-(phenylamido)ethyl]cyclopentadienide (**6a**), dissolved in 60 mL of THF at 0 °C. The mixture was stirred for 2 h, and the solvent was removed subsequently. A 60 mL portion of pentane was added to the oily residue, and LiCl was filtered by means of a frit. The solvent was evaporated, and the remaining brown oil was dried in vacuo to yield 1.60 g (3.84 mmol, 69%) of **2c**. ^{1}H NMR (599.8 MHz, benzene-d_6, 298 K): δ 7.26 (m, 2H, *m*-Ph), 6.87 (m, 2H, *o*-Ph), 6.74 (m, 1H, *p*-Ph), 6.31, 6.00 (m, each 1H, Cp), 6.07 (m, 2H, Cp), 5.00 (q, $^3J_{HH} = 6.6$ Hz, 1H, 6-H), 3.33, 3.24, 3.19, 3.07 (each m, each 2H, NCH_2), 1.52 (d, $^3J_{HH} = 6.6$ Hz, 3H, 7-H), 1.00 (t, $^3J_{HH} = 6.6$ Hz, 6H, NCH_2CH_3), 0.77 (t, $^3J_{HH} = 6.6$ Hz, 6H, NCH_2CH_3). $^{13}C\{^1H\}$ NMR (150.8 MHz, benzene-d_6, 298 K): δ 152.0 (*ipso*-Ph), 129.2 (*m*-Ph), 117.1 (*p*-Ph), 115.1 (*o*-Ph), 114.3, 111.6, 111.2, 109.6 (Cp), 51.4 (C-6), 43.8, 43.0 (NCH_2), 17.8 (C-7), 16.1, 15.9 (NCH_2CH_3). Anal. Calcd for $C_{21}H_{33}N_3Zr$ (418.7): C, 60.23; H, 7.94; N, 10.04. Found: C, 59.28; H, 8.32; N, 9.41.

Preparation of Bis(diethylamido)[η^5-[1-[(phenylamido)-*p*-tolylmethyl]cyclopentadienyl-κN]zirconium (2d). To a stirred solution of 900 mg (2 mmol) of $Cl_2Zr(NEt_2)_2(THF)_2$ (**7b**) in 50 mL of THF was added a solution of 548 mg of dilithium [1-[(phenylamido)-*p*-tolylmethyl]cyclopentadienide (**6b**) in 50 mL of THF at 0 °C. The solvent was removed after 2 h reaction time, and the oily residue was treated with 50 mL of pentane. After filtration of LiCl and evaporation of the solvent, 741 mg (1.5 mmol, 75%) of the brown oily product was obtained. ^{1}H NMR (599.8 MHz, benzene-d_6, 298 K): δ 7.37 (m, 2H, *o*-tol H), 7.18 (m, 2H, *m*-Ph H), 7.02 (m, 2H, *m*-tol H), 6.91 (m, 2H, o-Ph H), 6.70 (m, 1H, *p*-Ph H), 6.14, 5.90 (each m, each 1H, Cp H), 6.00, 5.96 (each m, each 1H, Cp H), 6.03 (s, 1H, CH), 3.38, 3.37, 3.28, 3.16 (m, each 2H, NCH_2), 2.12 (s, 3H, tol CH_3), 1.01 (t, $^3J = 6.6$ Hz, 6H, NCH_2CH_3), 0.87 (t, $^3J = 6.6$ Hz, 6H, NCH_2CH_3).$^{13}C\{^1H\}$ NMR (150.8 MHz, benzene-d_6, 298 K): δ 152.2 (ipso Ph), 139.7 (*p*-tol), 136.2 (ipso tol), 129.4 (*m*-tol), 129.1 (*m*-Ph), 127.0 (*o*-tol), 117.2 (*p*-Ph), 115.4 (*o*-Ph), 114.4 (ipso Cp), 114.3, 114.0 (both Cp), 111.0, 110.5 (both Cp), 60.2 (CH), 43.7, 43.1 (both NCH_2), 21.1 (tol-CH_3), 16.0 (NCH_2CH_3). Anal. Calcd for $C_{27}H_{37}N_3Zr$ (494.8): C, 65.54; H, 7.53; N, 8.49. Found: C, 65.85; H, 7.97; N, 8.52.

Synthesis of Bis(dimethylamido)[η^5-[1-(*p*-tolylamido)-2,2-dimethylpropyl]cyclopentadienyl-κN]titanium (2e). A solution of 231 mg (1.12 mmol) of $Cl_2Ti(NMe_2)_2$ (**7c**) in 50 mL of THF was treated with a solution of 370 mg (1.12 mmol) of dilithium [1-(*p*-tolylamido)-2,2-dimethylpropyl]cyclopentadienide (**6c**) in 40 mL of THF at 0 °C. After 2 h the solvent was removed, 40 mL of pentane was added, and LiCl was removed by filtration. After evaporation of the solvent, the residue was dried in vacuo to obtain 276 mg (0.80 mmol, 71%) of a dark red powder. ^{1}H NMR (599.8 MHz, benzene-d_6, 298 K): δ 7.02 (m, 2H, *m*-tol), 6.99 (m, 2H, *o*-tol), 6.16, 5.73 (each m, each 1H, 2-H and 5-H), 6.12, 5.83 (each m, each 1H, 3-H and 4-H), 4.85 (s, 1H, 6-H), 3.02, 2.87 (each s, each 6H, NCH_3), 2.19 (s, 3H, tol CH_3), 1.14 (s, 9H, 8-H). $^{13}C\{^1H\}$ NMR (150.8 MHz, benzene-d_6, 298 K): δ 154.0 (ipso tol), 129.1 (*m*-tol), 128.5 (*p*-tol), 119.2 (*o*-tol), 116.7, 114.8 (C-2 and C-5), 114.8 (C-1), 114.7, 111.3 (C-3 and C-4), 68.1 (C-6), 48.9, 47.0 (NCH_3), 38.0 (C-7), 28.6 (C-8), 20.8 (tol CH_3). Anal. Calcd for $C_{21}H_{33}N_3Ti$ (375.4): C, 67.19; H, 8.86; N, 11.19. Found: C, 67.90; H, 8.24; N, 10.99.

Preparation of Bis(diethylamido)[η^5-[1-(tolylamido)-2,2-dimethylpropyl]cyclopentadienyl-κN]zirconium (2f). $Cl_2Zr(NEt_2)_2(THF)_2$ (**7b**; 450 mg, 1 mmol) was dissolved in 50 mL of THF and treated with a solution of 325 mg (1 mmol) of dilithium [1-(*p*-tolylamido)-2,2-dimethylpropyl]cyclopentadienide (**6c**) in 30 mL of tetrahydrofuran for 2 h. Evaporation of the solvent, addition of 40 mL of pentane, and filtration of LiCl, followed by removal of pentane, led to a brown oily product, which was dried in vacuo to give 313 mg (0.66 mmol, 66%) of **2f**. ^{1}H NMR (599.8 MHz, benzene-d_6, 298 K): δ 6.98 (m, 2H, *m*-tol H), 6.94 (m, 2H, *o*-tol H), 6.38, 5.93 (each m, each 1H, Cp H), 6.10, 6.07 (each m, each 1H, Cp H), 4.96 (s, 1H, CH), 3.31, 3.28, 3.19, 3.08 (each m, each 2H, NCH_2), 2.19 (s, 3H, tol CH_3), 1.19 (s, 9H, $C(CH_3)_3$), 1.06 (t, $^3J = 4.8$ Hz, 6H, NCH_2CH_3), 0.65 (t, $^3J = 4.8$ Hz, 6H, NCH_2CH_3). $^{13}C\{^1H\}$ NMR (150.8 MHz, benzene-d_6, 298 K): δ 152.3 (ipso tol), 129.7 (*m*-tol), 127.4 (*p*-tol), 119.0 (*o*-tol), 115.5 (Cp), 113.0 (Cp), 112.8 (ipso Cp), 111.6 (Cp), 109.7 (Cp), 66.2 (CH), 43.6, 43.2 (both NCH_2), 38.7 ($C(CH_3)_3$), 28.8 ($C(CH_3)_3$), 20.8 (tol CH_3), 15.7, 15.3 (both NCH_2CH_3). Anal. Calcd for $C_{25}H_{41}N_3Zr$ (474.9): C, 63.23; H, 8.70; N, 8.85. Found: C, 63.03; H, 8.01; N, 8.34.

Preparation of Bis(diethylamido)[η^5-[1-(*tert*-butylamido)-2,2-dimethylpropyl]cyclopentadienyl-κN]zirconium (2g). A solution containing 219 mg (1 mmol) of dilithium [1-(*tert*-butylamido)-2,2-dimethylpropyl]cyclopentadienide (**6d**) in 50 mL of THF was added to a solution of 450 mg (1 mmol) of $Cl_2Zr(NEt_2)_2(THF)_2$ (**7b**) in 50 mL of THF at 0 °C and stirred for 2 h. The solvent was evaporated, 50 mL of pentane was added, and LiCl was removed by filtration. The product was isolated as a pale green oil (313 mg, 0.71 mmol, 71%) after evaporation of the solvent. ^{1}H NMR (599.8 MHz, dichloromethane-d_2, 298 K): δ 6.30, 5.73 (each m, each 1H, Cp H), 6.13, 5.99 (each m, each 1H, Cp H), 4.40 (s, 1H, CH), 3.40, 3.19, 3.14, 3.07 (each m, each 2H, NCH_2), 1.30 (s, 9H, $NC(CH_3)_3$), 1.19 (s, 9H, $CC(CH_3)_3$), 0.96 (t, $^3J = 4.8$ Hz, 6H, NCH_2CH_3), 0.92 (t, $^3J = 4.8$ Hz, 6H, NCH_2CH_3). $^{13}C\{^1H\}$ NMR (150.8 MHz, dichloromethane-d_2, 298 K): δ 113.8 (Cp), 112.6 (Cp) 110.6 (Cp), 107.6 (Cp), 68.6 (CH), 55.2 ($NC(CH_3)_3$), 45.2, 42.1 (both NCH_2), 35.6 ($CC(CH_3)_3$), 31.1 ($NC(CH_3)_3$), 29.7 ($CC(CH_3)_3$), 15.4, 13.9 (both NCH_2CH_3), ipso Cp not observed. Anal. Calcd for $C_{22}H_{43}N_3Zr$ (440.8): C, 59.94; H, 9.83; N, 9.53. Found: C, 60.01; H, 10.11; N, 10.15.

Preparation of Bis(diethylamido)[η^5-1-[(*tert*-butylamido)methyl]-2,3,4,5-tetramethylcyclopentadienyl-κN]zirconium (2h). A sample of 219 mg (1 mmol) of dilithium 1-[(*tert*-butylamido)methyl]-2,3,4,5-tetramethylcyclopentadienide (**6e**) was suspended in 50 mL of THF and added to a solution of 450 mg (1 mmol) of $Cl_2Zr(NEt_2)_2(THF)_2$ (**7b**) in 50 mL of THF at 0 °C. A clear, colorless solution was obtained after 30 min. The mixture was stirred for 90 min before the solvent was removed. Addition of 40 mL of pentane followed by filtration and evaporation of the solvent gave 290 mg (0.66 mol, 66%) of the colorless, oily product. ^{1}H NMR (200.13 MHz, THF-d_8, 298 K): δ 4.34 (s, 2H, CH), 3.52−3.20 (m, 8H, NCH_2), 2.08 (s, 6H, Cp−CH_3), 2.06 (s, 6H, Cp−CH_3), 1.15 (s, 9H, $C(CH_3)_3$), 0.97 (t, $^3J = 4.8$ Hz, 12H, NCH_2CH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, THF-d_8, 298 K): δ 119.5 (ipso Cp), 55.6 ($NC(CH_3)_3$), 43.5 (NCH_2CH_3), 41.9 (NCH_2), 29.4 ($NC(CH_3)_3$), 15.2 (NCH_2CH_3), 11.2, 10.5 (both Cp−CH_3). Anal. Calcd for $C_{22}H_{43}N_3Zr$ (440.8): C, 59.94; H, 9.83; N, 9.53. Found: C, 59.10; H, 10.54; N, 9.67.

Reaction of Bis(diethylamido)[η^5-1-[(*tert*-butylamido)methyl]-2,3,4,5-tetramethylcyclopentadienyl-κN]zirconium (2h) with Me_3SiCl: Formation of 15. A sample of 500 mg (1.13 mmol) of bis(diethylamido)[η^5-1-{(*tert*-butylamido)methyl]-2,3,4,5-tetramethylcyclopentadienyl-κN]zirconium (**2h**) was dissolved in 50 mL of THF and treated with 8 equiv (980 mg, 9.02 mmol) of Me_3SiCl at room temperature. The mixture was stirred for 12 h, the solvent was removed in vacuo, and the pale yellow residue was analyzed by NMR spectroscopy. As determined by integration, only ca. 40% of product had been formed. ^{1}H NMR (200.13 MHz, THF-d_8, 298

K): δ 4.45 (s, 2H, CH_2), 2.12, 2.06 (each s, each 6H, Cp−CH_3), 1.10 (s, 9H, $C(CH_3)_3$).

X-ray Crystal Structure Analysis of 15. After several days single crystals were obtained in the NMR tube, which were analyzed by X-ray diffraction as the hydrolyzed product **15**. Crystal data are as follows: formula $C_{28}H_{48}N_2OCl_4Zr_2\cdot 2CH_2Cl_2$, $M_r = 922.78$, light yellow crystal, 0.10 × 0.10 × 0.05 mm, $a = 20.865(1)$ Å $b = 9.373(1)$ Å, $c = 20.754(1)$ Å, $V = 4058.8(5)$ Å^3, $\rho_{calcd} = 1.510$ g cm^{-3}, $\mu = 10.66$ cm^{-1}, empirical absorption correction via SORTAV ($0.901 \le T \le 0.949$), $Z = 4$, orthorhombic, space group *Pbcn* (No. 60), $\lambda = 0.710\,73$ Å, $T = 198$ K, ω and φ scans, 7715 reflections collected ($\pm h$, $\pm k$, $\pm l$), ($\sin\theta)/\lambda = 0.62$ Å^{-1}, 4103 independent ($R_{int} = 0.065$) and 2655 observed reflections ($I \ge 2\sigma(I)$), 202 refined parameters, R1 = 0.061, wR2 = 0.139, maximum residual electron density 0.80 (−0.65) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a Nonius FR591 rotating anode generator. Programs used: data collection, COLLECT (Nonius BV, 1998); data reduction, Denzo-SMN;[38] absorption correction, SORTAV;[39] structure solution, SHELXS-97;[40] structure refinement, SHELXL-97;[41] graphics, DIAMOND.[42]

Polymerization Reactions. (a) Ethene Polymerization. A glass autoclave was charged with 200 mL of toluene and 20 mL of a 10% solution of MAO in toluene and then thermostated for 1 h and the solution saturated with ethene (at 1 bar) for 30 min. The catalyst was dissolved in toluene and directly injected in the autoclave. The polymerization reaction was stopped by quenching with 20 mL of aqueous HCl/methanol (1:1 v/v). The resulting polymer was collected by filtration, washed subsequently with HCl and water, and dried at 80 °C in vacuo overnight.

(b) Ethene−1-Octene Copolymerization. A glass autoclave was charged with 30 mL of toluene, 50 mL of 1-octene, and 20 mL of a 10% solution of MAO in toluene and then thermostated for 1 h and the solution saturated with ethene (at 1 bar) for 30 min. The catalyst was dissolved in toluene and directly injected in the autoclave. The polymerization reaction was stopped by quenching with 20 mL of aqueous HCl/methanol (1:1 v/v). The reaction mixture was poured into HCl (100 mL) and stirred overnight. The mixture was filtered, washed with water, and dried at 80 °C in vacuo overnight.

Polymer Characterizations. ^{13}C NMR spectra of copolymer samples (100 mg) were obtained in benzene-d_6 (0.5 mL) at 25 °C (oils) or tetrachloroethane-d_2 (0.5 mL) at 80 °C (solids). Melting point analysis of the polyethylene samples was carried out on a DSC. The ethene:1-octene ratio was determined by integration of ^{13}C NMR signals (see Figure 4):

$$a = I(C_{\delta\delta+}, C_{3B})/I(C_{\alpha\delta+}, C_{6B}) = I(C_{\delta\delta+}, C_{3B})/I(C_{\beta\delta+}, C_{5B}) \quad (1)$$

$$\text{ethene/1-octene} = [(3a - 1)/2] + 2 \quad (2)$$

Selected ^{13}C NMR data (for polymer number, see Table 2) for sample 3 (solid) (50.3 MHz, tetrachlorethane-d_2, 353 K): δ 37.6 (C_7), 34.0 ($C_{\alpha\delta+}$, C_{6B}), 31.8 ($C_{\gamma\delta+}$, C_{4B}), 29.6 ($C_{\delta\delta+}$, C_{3B}), 26.9 ($C_{\beta\delta+}$, C_{5B}), 22.5 (C_{2B}), 13.9 (C_{1B}). Integration of signals ($C_{\delta\delta+}$, C_{3B}), ($C_{\alpha\delta+}$, C_{6B}), and ($C_{\beta\delta+}$, C_{5B}) leads to an ethene:1-octene ratio of 13:1. $^{13}C\{^1H\}$ NMR for sample 13 (oil) (50.3 MHz, benzene-d_6, 298 K): δ 38.0 (C_7), 34.3 ($C_{\alpha\delta+}$, C_{6B}), 32.4 ($C_{\gamma\delta+}$, C_{4B}), 30.3 ($C_{\delta\delta+}$, C_{3B}), 27.3 ($C_{\beta\delta+}$, C_{5B}), 23.1 (C_{2B}), 14.4 (C_{1B}). Integration of signals ($C_{\delta\delta+}$, C_{3B}), ($C_{\alpha\delta+}$, C_{6B}), and ($C_{\beta\delta+}$, C_{5B}) leads to an ethene:1-octene ratio of 5.5:1.

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Supporting Information Available: Details of the X-ray crystal structure analyses of the complexes *cis*-**2a**, **2b**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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