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Titanium and Zirconium Bent-Sandwich Complexes with the New [2-(Diisopropylamino)ethyl]cyclopentadienyl Ligand: Catalysts for the Polymerization of Ethylene and the Dehydrocoupling of Phenylsilane

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Titanium(IV) and zirconium(IV) bent-sandwich complexes containing the new donor substituted [2-(diisopropylamino)ethyl]cyclopentadienyl (Cp^N) ligand are described. Cp^NH (**1**; $C_5H_5CH_2CH_2N^iPr_2$) is prepared from sodium cyclopentadienide and 2-chloro-1-(diisopropylamino)ethane. The highly moisture-sensitive metallocene dichlorides $Cp^N{}_2TiCl_2$ **(2)** and $Cp^N{}_2ZrCl_2$ **(3)** are synthesized by reaction of Cp^NLi with $TiCl_4$ and $ZrCl_4$, respectively. In combination with the cocatalyst methylaluminoxane (MAO) they are precursors for ethylene polymerization catalysts. Compounds **2** and **3** react with 2 equiv of HCl with protonation of the amino groups to give the air- and moisture-stable metallocene dichloride dihydrochlorides $Cp^N{}_2TiCl_2\cdot 2HCl$ **(4)** and $Cp^N{}_2ZrCl_2\cdot 2HCl$ **(5)**, which also are found to be precatalysts for the polymerization of ethylene. The dimethyl compounds $Cp^N{}_2TiMe_2$ **(6)** and $Cp^N{}_2ZrMe_2$ **(7)** can be obtained by reaction of **2** and **3** with 2 equiv of methyllithium. The dibenzyl complexes $Cp^N{}_2TiBz_2$ **(8)** and $Cp^N{}_2ZrBz_2$ **(9)** are formed analogously with a stoichiometric amount of benzylmagnesium bromide. The diphenoxy complex $Cp^N{}_2Ti(OPh)_2$ **(10)** is synthesized by reaction of **2** with 2 equiv of lithium phenoxide. The dialkyl compounds **6**−**8** and the diphenoxy compound **10** show a remarkable activity in the catalytic dehydrocoupling of phenylsilane. $Zr(NMe_2)_4$ reacts with 2 equiv of Cp^NH **(1)** to give the zirconocene derivative $Cp^N{}_2Zr(NMe_2)_2$ **(11)** in quantitative yield. The structure of **2** has been determined by a single-crystal X-ray diffraction study. The effects of the (dialkylamino)- and (dialkylammonio)ethyl substituents in metallocene-type compounds of titanium and zirconium are described.

Introduction

Cyclopentadienyl systems with an additional donor function in the side chain are attracting increased interest in the chemistry of metal complexes.[1−19] Under appropriate conditions, the donor atom can coordinate reversibly to the metal center and temporarily block a vacant coordination site. As a result, it seems possible to stabilize highly reactive intermediates in catalytic reactions and to increase their lifetimes. This could effect the activity of such systems in a variety of catalytic processes. Furthermore, enhanced water solubility may be achieved, for example, by quaternization of an amino group in the side chain.[7,8a,11] Another important feature of the additional donor function is the possibility of fixing catalytically active complexes on surfaces.[9]

Very recently, we have introduced cyclopentadienyl ligands with an additional dimethylamino functionality into the chemistry of s-, p-, d-, and f-block elements.[1−8] Most of this work was concentrated on compounds with [(dimethylamino)ethyl]cyclopentadienyl ligands.

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1996.

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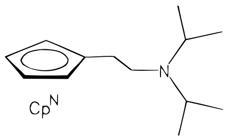
Chart 1

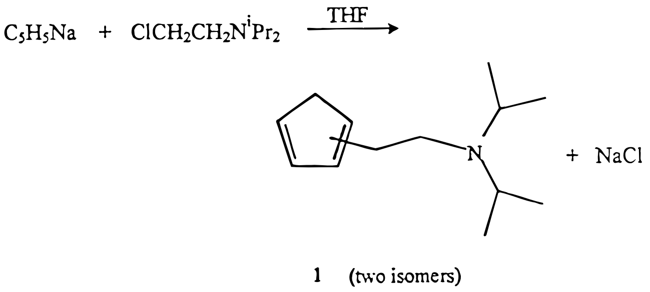


In this work, we describe the synthesis of titanium and zirconium bent-sandwich complexes with the new (diisopropylamino)ethyl-functionalized cyclopentadienyl ligand Cp^N ($\equiv C_5H_4CH_2CH_2N^iPr_2$, Chart 1). Special emphasis is put on the characterization of these complexes and on their suitability as precursors in homogeneous Ziegler–Natta ethylene polymerization reactions[20] and in the dehydrocoupling of phenylsilane.[21]

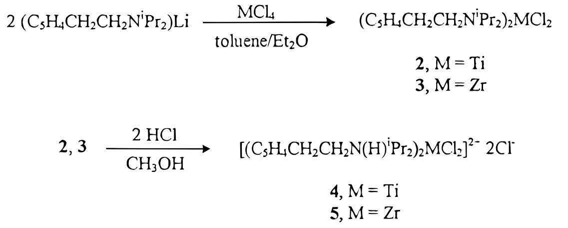
Results

I. Syntheses. The new cyclopentadiene $C_5H_5CH_2CH_2N^iPr_2$ ($\equiv$Cp^{N}H; **1**), with a (diisopropylamino)ethyl side chain, is synthesized from sodium cyclopentadienide and 2-chloro-1-(diisopropylamino)ethane in THF as solvent. After aqueous workup, the monosubstituted cyclopentadiene **1** is obtained in good yield after distillation in the form of a colorless liquid as a mixture of two isomers with the side chain in a vinylic position. Cp^{N}H **(1)** dimerizes at room temperature by a cycloaddition process and must therefore be stored at low temperatures; the dimer can be cracked at 180 °C to give the monomer.

Scheme 1



Scheme 2



Treating a solution of $TiCl_4$ in toluene with a suspension of 2 equiv of Cp^{N}Li in ether leads to the formation of the desired metallocene dichloride $(C_5H_4CH_2CH_2N^iPr_2)_2TiCl_2$ **(2)**, which can be isolated as a red solid in 49% yield. The zirconium complex $(C_5H_4CH_2CH_2N^iPr_2)_2ZrCl_2$ **(3)** can be synthesized in 57% yield in the form of a pale yellow solid by an analogous procedure. Crystallization of **2** and **3** from toluene affords deep red and colorless crystals, respectively.

Complexes **2** and **3** are moderately soluble in polar solvents such as diethyl ether and THF and are remarkably soluble in nonpolar solvents such as benzene and toluene. Over several days an amorphous solid precipitates from a concentrated benzene solution. This solid can only scarcely be redissolved. It is a coordination polymer and not a decomposition product.[22] However, in dilute solution a complete characterization of Cp$^N_2$MCl$_2$ is possible. ^{1}H NMR spectroscopy indicates the presence of monomeric species (vide infra). Furthermore, crystals of monomeric **2** can be obtained from a dilute toluene solution (see section III, X-ray Crystal Structure Analysis of **2**). In contrast to the nonfunctionalized, parent metallocene dichlorides[23] Cp_2TiCl_2 and Cp_2ZrCl_2, the complexes **2** and **3** are extremely moisture-sensitive. Decomposition takes place in protic solvents such as methanol and water, and the N-protonated cyclopentadiene $[C_5H_5CH_2CH_2N(H)^iPr_2]^+[Cl]^-$ is formed.

Compound **2** reacts with 2 equiv of hydrogen chloride in methanolic solution with protonation of the amino

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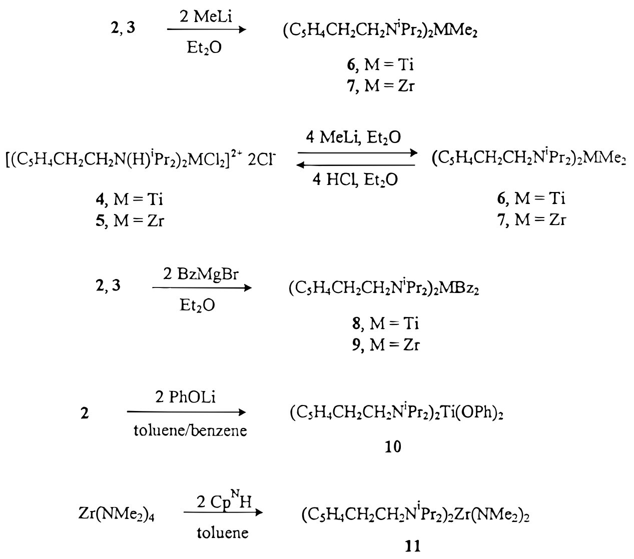
Scheme 3



groups to give the titanocene dichloride dihydrochloride $[(C_5H_4CH_2CH_2N(H)^iPr_2)_2TiCl_2]^{2+}Cl^-{}_2$ **(4)** as a red, amorphous solid in quantitative yield. The analogous reaction of $Cp^N{}_2ZrCl_2$ **(3)** leads to the formation of the zirconocene dichloride dihydrochloride $[(C_5H_4CH_2CH_2N(H)^iPr_2)_2ZrCl_2]^{2+}Cl^-{}_2$ **(5)** as a colorless, amorphous solid (Scheme 2). Crystallization of the dihydrochlorides **4** and **5** from acetonitrile affords deep red and colorless crystals, respectively, which are hygroscopic. The complexes **4** and **5** are excellently soluble in polar solvents such as methanol, dimethyl sulfoxide, and acetonitrile, but they are insoluble in nonpolar solvents. It is remarkable that, in contrast to the metallocene dichlorides **2** and **3**, the dihydrochlorides **4** and **5** are stable to air and moisture. Complex **4** is stable even in water for several hours of exposure.

The dimethyltitanium compound $(C_5H_4CH_2CH_2N^iPr_2)_2TiMe_2$ **(6)** and the analogous zirconium species $(C_5H_4CH_2CH_2N^iPr_2)_2ZrMe_2$ **(7)** are obtained in high yields by the reaction of **2** and **3**, respectively, with 2 equiv of methyllithium in diethyl ether.

Complexes **6** and **7** are highly moisture-sensitive, yellow oils with a characteristic odor; they show a good solubility in polar and nonpolar aprotic solvents such as THF and toluene. The thermal stability of **6** is remarkable. In contrast to the temperature- and light-sensitive complex Cp_2TiMe_2,[24] for which an autocatalytic, "catastrophic" decomposition is reported, no decomposition is observed for **6** even after several weeks under an inert-gas atmosphere at room temperature. The stability of the dimethylzirconium complex **7** is comparable to that of the titanium complex **6**.

The dimethyl compounds **6** and **7** are also formed by the reaction of the metallocene dichloride dihydrochlorides **4** and **5**, respectively, with 4 equiv of methyllithium (Scheme 3). The first 2 equiv of methyllithium deprotonates the N-functions to generate the metallocene dichloride **2** or **3**, which reacts with the further 2 equiv of methyllithium to form the dimethyl compounds **6** and **7**.

Treating the dimethyl complexes **6** and **7** in diethyl ether with 4 equiv of HCl in methanolic solution affords the metallocene dichloride dihydrochlorides **4** and **5** in quantitative yields (Scheme 3). After the evolution of 2 equiv of methane and the intermediate formation of the metallocene dichlorides **2** and **3**, the protonation of the N-functions in the side chain of the Cp^N ligand leads to the formation of the metallocene dichloride dihydrochlorides **4** and **5**. No decomposition products are observed.

The deep red titanium dibenzyl complex $(C_5H_4CH_2CH_2N^iPr_2)_2TiBz_2$ **(8)** and the analogous yellow zirconium complex $(C_5H_4CH_2CH_2N^iPr_2)_2ZrBz_2$ **(9)** are formed in moderate yields by the reaction of **2** and **3** with a stoichiometric amount of benzylmagnesium bromide in diethyl ether (Scheme 3). An alternative synthesis of the dibenzyl compounds **8** and **9** is based on the reaction of the metallocene dichloride dihydrochlorides **4** and **5** with 4 equiv of benzylmagnesium bromide. The isolated compounds **8** and **9** are stable toward air at room temperature for a short period of time. They show a good solubility in all common aprotic organic solvents. Complex **8** decomposes slowly in benzene solution under an inert-gas atmosphere at room temperature over several hours. In contrast, complex **9** is stable under these conditions. At −30 °C, **8** can be stored in solution for several weeks without decomposition. This phenomenon is also described for the parent dibenzyl complex Cp_2TiBz_2.[25]

Treating a toluene solution of $Cp^N{}_2TiCl_2$ **(2)** with 2 equiv of lithium phenoxide leads to the formation of the diphenoxy derivative $(C_5H_4CH_2CH_2N^iPr_2)_2Ti(OPh)_2$ **(10)** in excellent yield (Scheme 3). As for the parent complex $Cp_2Ti(OPh)_2$,[211,26] compound **10** can be isolated as an air-stable yellow solid, which is excellently soluble in aromatic organic solvents. The analogous zirconium complex $(C_5H_4CH_2CH_2N^iPr_2)_2Zr(OPh)_2$ could not be isolated.[27]

Refluxing a toluene solution of $Zr(NMe_2)_4$ with 2 equiv of Cp^NH **(1)** leads to the evolution of 2 equiv of dimethylamine and to the formation of the zirconium complex $(C_5H_4CH_2CH_2N^iPr_2)_2Zr(NMe)_2$ **(11)**, which can be isolated as an extremely air- and moisture-sensitive bright yellow oil (Scheme 3). In contrast to $Cp_2Zr(NMe_2)_2$,[28] **11** can be obtained in quantitative yield without further purification. The solubility of **11** in nonpolar solvents such as pentane and toluene is excellent. The analogous titanium complex $(C_5H_4CH_2CH_2N^iPr_2)_2Ti(NMe_2)_2$ could not be prepared by this route.

The compounds **1**−**11** have been characterized by ^1H and ^{13}C NMR and MS data and by elemental analysis. For compound **9** a correct elemental analysis could not be obtained; this is attributed to the presence of traces of $ZrCl_4$, which could not be separated completely.

II. NMR Analyses. The NMR spectra (Table 1) of **2**−**11** are in agreement with metallocene-type structures

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[27] Treating a toluene solution of $Cp^N{}_2ZrCl_2$ **(3)** with 2 equiv of PhOLi leads to the formation of the diphenoxy compound $Cp^N{}_2Zr(PhO)_2$. The ^1H and ^{13}C NMR spectra show the presence of the N-functionalized cyclopentadiene $C_5H_5CH_2CH_2N^iPr_2$ (Cp^NH) (50%), which could not be removed.

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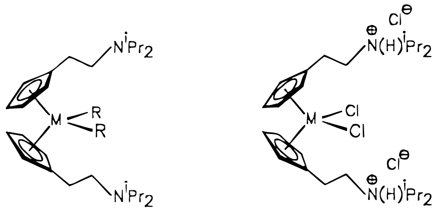
Table 1. ^{1}H NMR Data for the New Complexes 1−11

	C_5H_4	$CpCH_2$	CH_2N	$CHCH_3$	$CHCH_3$	MR
1[a]	6.00−6.52 (m, 3 H)	2.54 (m, 2 H)	2.65 (m, 2 H)	2.92 (m, 2 H)	0.94, 0.99 (2 d, 12 H, ^3J = 4.5 Hz)	
2[a]	5.76, 6.13 (2 t, 8 H, ^3J = 2.6 Hz)	2.60 (m, 4 H)	2.93 (m, 4 H)	2.93 (m, 4 H)	0.90 (d, 24 H, ^3J = 6.6 Hz)	
3[a]	5.77, 6.03 (2 t, 8 H, ^3J = 2.7 Hz)	2.57 (m, 4 H)	2.82 (m, 4 H)	2.90 (m, 4 H)	0.90 (d, 24 H, ^3J = 6.6 Hz)	
4[b]	6.49, 6.61 (2 m, 8 H)	3.32 (m, 4 H)	3.32 (m, 4 H)[c]	3.63 (m, 4 H)	1.36, 1.43 (2 d, 24 H, ^3J = 6.5 Hz)	
5[b]	6.47, 6.50 (2 m, 8 H)	3.24 (m, 4 H)	3.24 (m, 4 H)[c]	3.63 (m, 4 H)	1.36, 1.43 (2 d, 24 H, ^3J = 6.6 Hz)	
6[a]	5.47, 5.80 (2 t, 8 H, ^3J = 2.5 Hz)	2.56 (m, 4 H)	2.74 (m, 4 H)	2.97 (m, 4 H)	0.98 (d, 24 H, ^3J = 6.6 Hz)	0.10 (s, 6 H)[d]
7[a]	5.56, 5.82 (2 t, 8 H, ^3J = 3.4 Hz)	2.63 (m, 4 H)	2.63 (m, 4 H)	2.95 (m, 4 H)	0.96 (d, 24 H, ^3J = 6.5 Hz)	−0.06 (s, 6 H)[d]
8[a]	5.72, 5.77 (2 t, 8 H, ^3J = 2.5 Hz)	2.14 (m, 4 H)	2.53 (m, 4 H)	2.88 (m, 4 H)	0.92 (d, 24 H, ^3J = 6.6 Hz)	2.00 (s, 4 H)[e]
9[a]	5.56, 5.68 (2 t, 8 H, ^3J = 2.7 Hz)	2.30 (m, 4 H)	2.49 (m, 4 H)	2.88 (m, 4 H)	0.92 (d, 24 H, ^3J = 6.6 Hz)	1.95 (s, 4 H)[e]
10[a]	5.80, 5.93 (2 t, 8 H, ^3J = 2.5 Hz)	2.52 (m, 4 H)	2.60 (m, 4 H)	2.87 (m, 4 H)	0.88 (d, 24 H, ^3J = 6.6 Hz)	
11[a]	5.88, 6.00 (2 t, 8 H, ^3J = 2.7 Hz)	2.62 (m, 4 H)	2.62 (m, 4 H)	2.96 (m, 4 H)	0.99 (d, 24 H, ^3J = 6.6 Hz)	2.91 (s, 6 H)[f]

[a] Measured in C_6D_6. [b] Measured in CD_3CN. [c] The proton resonance for the NH groups is observed at 10.90 ppm. [d] R = CH_3. [e] R = $CH_2C_6H_5$. [f] R = NMe_2.

Chart 2



M=Ti,Zr (2, 3, 6 - 11)

R=Cl,Me,Bz,PhO,NMe$_2$

M=Ti,Zr (4, 5)

with two η^5-bonded monosubstituted cyclopentadienyl ligands, as shown in Chart 2.

In the ^{1}H NMR spectra of the complexes **2−11**, a pair of two pseudotriplets (AA′BB′ pattern) is observed for the hydrogen atoms of the two cyclopentadienyl rings. The methylene protons of the side chain appear as two multiplets; the signals of the isopropyl group are observed as a multiplet and a doublet. In the hydrochlorides **4** and **5**, the methyl signals of the isopropyl groups appear as two doublets.

Noncoordination of the additional (diisopropylamino)ethyl function can be assumed for the complexes $Cp^N{}_2TiCl_2$ **(2)**, $Cp^N{}_2ZrCl_2$ **(3)**, and $Cp^N{}_2MR_2$ (M = Ti, Zr; R = Me, Bz, OPh, NMe_2; **6−11**). The signal due to the methyl protons of the diisopropyl group is observed at ca. 0.90 ppm. The two multiplets for the methylene protons appear in the range of 2.1−2.9 ppm. The ring protons are observed in the range of 5.5−6.1 ppm. These values are nearly identical with those of the (diisopropylamino)ethyl-substituted cyclopentadiene $C_5H_5CH_2CH_2N^iPr_2$ **(1)**.

In contrast, the protonation of the N-functions in $[(C_5H_4CH_2CH_2N(H)^iPr_2)_2TiCl_2]^{2+}Cl^-{}_2$ **(4)** and $[(C_5H_4CH_2CH_2N(H)^iPr_2)_2ZrCl_2]^{2+}Cl^-{}_2$ **(5)** causes a significant change of the ^{1}H NMR shifts. All signals in **4** and **5** show a remarkable downfield shift compared to all other complexes (see Table 1). Now the signal of the methyl groups at the isopropyl unit is observed at ca. 1.40 ppm. The two multiplets for the methylene protons appear in the range of 3.3−3.6 ppm. The ring protons are observed in the range of 6.4−6.7 ppm.

The methyl signals of the alkyl complexes $Cp^N{}_2TiMe_2$ **(6)** and $Cp^N{}_2ZrMe_2$ **(7)** are observed as expected as singlets at 0.10 and −0.06 ppm, respectively. These values are very similar to those of the parent complexes Cp_2MMe_2[29] (M = Ti, Zr). Similarly, the signals of the hydrogen atoms of the benzyl groups in the complexes $Cp^N{}_2TiBz_2$ **(8)** and $Cp^N{}_2ZrBz_2$ **(9)** show only small shift differences compared with those of the parent compounds Cp_2MBz_2.[25,30ab]

The data of the ^{13}C NMR spectra of all compounds show features consistent with the proposed structures (see the Experimental Section). The benzyl ipso C atom is a reliable indicator to distinguish the ligation mode (η^x) of the benzyl ligand. There are no decisive differences between **8** and **9** and the structurally characterized complexes $(CpSiMe_3)_2ZrBz_2$[30c] and Cp_2TiBz_2,[25c,d] which show an η^1 binding mode for the benzyl ligand.

III. X-ray Crystal Structure Analysis of 2. Suitable crystals of **2** are obtained by crystallization from dilute toluene solution. A single-crystal X-ray diffraction study established the expected bent-metallocene type structure for $(C_5H_4CH_2CH_2N^iPr_2)_2TiCl_2$ **(2)**. The molecular structure and selected bond lengths and angles are shown in Figure 1; crystallographic data are given in Table 2.

The structure analysis shows that $Cp^N{}_2TiCl_2$ **(2)** forms monomeric molecules. Neither an intramolecular nor an intermolecular coordination of the additional (diisopropylamino)ethyl side chains is observed. The molecule possesses a crystallographic 2-fold axis passing trough the titanium atom. The chlorine atoms together with the centroids of the cyclopentadienyl rings form a considerably distorted pseudotetrahedral coordination geometry around the titanium with angles ranging from 94.4° (Cl−Ti−Cl′) to 132.6° ((Cp centroid)−Ti−(Cp centroid)′, see Table 3). The Cp^N ring is nearly planar. The methylene groups of the (diisopropylamino)ethyl side chains attached to the Cp^N rings lie above the plane defined by the carbon atoms of the Cp^N ring (2.9°). The Cp^N rings are slightly staggered with the (diisopropylamino)ethyl groups arranged at the opened side of the sandwich. This molecular structure is similar to that observed for $(C_5H_4Me)_2TiCl_2$[31a] with two methyl-substituted cyclopentadienyl ligands. The average Ti−C(Cp) and the Ti−(Cp centroid) distances of 2.383(3) and 2.062 Å are similar to those found for the parent complex Cp_2TiCl_2[31b] (2.370(9) and 2.058 Å). As displayed in Table 3, all other bonding parameters for **2** (Ti−Cl = 2.3681(11) Å, (Cp centroid)−Ti−(Cp centroid)′ = 132.60°, (Cp centroid)−Ti−Cl = 105.7°, Cl−Ti−Cl′ = 94.40(5)°) are

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[29] (a) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *33*, 181. (b) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *34*, 155. (c) Samuel, E.; Rausch, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 6263. (d) Jordan, R. F. *J. Organomet. Chem.* **1985**, *294*, 321.

[30] (a) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 1946. (b) Brindley, P. B.; Scotton, M. J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 419. (c) Thiele, K.-H.; Böhme, U. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1951.

[31] (a) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422. (b) Clearfield, A.; Warner, D. K.; Saladarriaga-Molina, C. H.; Ropal, R.; Bernal, I. *Can. J. Chem.* **1975**, *53*, 1622.

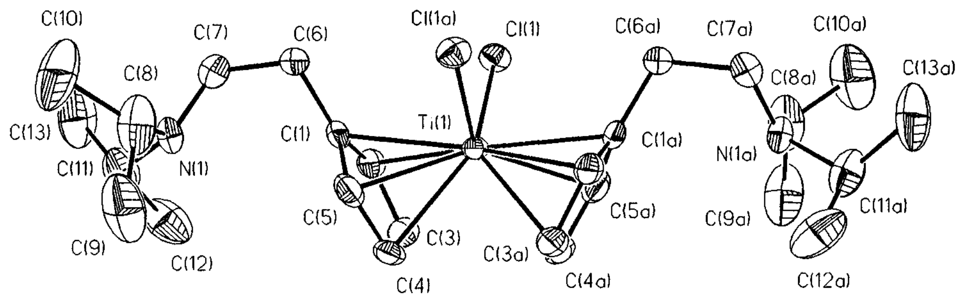

Figure 1. Plot of the molecular structure of **2**, with thermal ellipsoids at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ti(1)−Cl(1), 2.3683(11); Ti(1)−Cp(centroid), 2.062; C(1)−C(6), 1.490(4); Cp(centroid)−Ti−Cp(centroid), 132.60°; Cl(1a)−Ti−Cl(1), 94.40°.

Table 2. Crystallographic Data for Diffraction Studies of 2

empirical formula	$C_{26}H_{44}Cl_2N_2Ti$
cryst size, mm^3	0.40 × 0.40 × 0.20
fw	503.43
cryst syst	monoclinic
space group	*C*2/*c*
lattice params	
a, Å	33.430(13)
b, Å	6.549(2)
c, Å	13.866(3)
β, deg	112.31(3)
V, Å^3	2809(2)
Z	4
d_{calcd}, g/cm^3	1.191
diffractometer	Siemens $P2_1$
programs	Siemens SHELXTLplus/SHELXL-93
F(000)	1080
μ(Mo Kα), mm^{-1}	0.510
temp, °C	−100
$2\theta_{max}$, deg	55
no. of data collected	3268
no. of params refined	145
residuals	$R_F = 0.0547$ for 2050 rflns ($I > 2\sigma(I)$) $R_{wF}{}^2 = 0.1209$ (all data)
largest peak in final diff map, e/Å^3	0.6
abs cor	semiempirical

within the range established for the complexes $(C_5H_5)_2TiCl_2$[31b] and $(C_5H_4Me)_2TiCl_2$.[31a] This demonstrates that the introduction of the two (diisopropylamino)ethyl functions does not significantly affect the basic molecular structure.

IV. Polymerization and Dehydrocoupling Reactions. Ethylene Polymerization Reactions. The metallocene dichlorides and dihydrochlorides of titanium and zirconium **2**−**5** are catalyst precursors for the polymerization of ethylene. In the reaction of the complexes **2** and **3** with 500 equiv of methylaluminoxane in toluene, the color of the solution immediately turns yellow, which corresponds to the color of the dimethyl compounds $Cp^N{}_2MMe_2$ (**6** and **7**) in this solvent. This is in agreement with the assumption that methylaluminoxane acts first as a methylation reagent to form the dimethyl compounds as intermediates. The further equivalents of methylaluminoxane abstract one methyl group by forming cationic species, which are the active catalyst systems. In the case of the metallocene dichloride dihydrochlorides **4** and **5**, 2 equiv of MAO acts first as a deprotonating reagent to form the metallocene dichlorides **2** and **3** as intermediates. The further reaction to active catalytic species is analogous to that described above. The reaction mixture was stirred at ambient temperature, and ethylene (atmospheric pressure) was bubbled through the solution. After 4 h, a HCl−MeOH mixture was added to terminate the polymerization reaction. The productivities of the catalyst systems and the numbers of merit (M_w, M_n) of the polyethylene determined by GPC analysis are summarized in the Experimental Section. The high values for the molecular weight distributions M_w/M_n can be attributed to inhomogeneities in the reaction mixture during the polymerization reaction (high catalyst concentration, precipitation of polyethylene) and not to catalyst decomposition.[32] The differences in the activity of precursors **2**−**5** in comparison to that of the nonsubstituted parent metallocene dichlorides Cp_2MCl_2[20d] must be ascribed to influences of the additional (diisopropylamino)ethyl side chains of the Cp^N ligands. The activities of the titanium compounds **2** and **4** are comparable to those of titanocene complexes with substituted cyclopentadienyl ligands such as $Cp^R{}_2TiCl_2$ (R = ^{i}Pr).[20d] The zirconocene complexes **3** and **5** show rather low polymerization activities compared to other substituted zirconocene catalysts.[20d] This difference may be due to the nonoptimized reaction conditions.

Phenylsilane Dehydrocoupling Reactions. High catalytic activity in the dehydrocoupling of phenylsilane is observed for the complexes $Cp^N{}_2TiMe_2$ **(6)**, $Cp^N{}_2ZrMe_2$ **(7)**, $Cp^N{}_2TiBz_2$ **(8)**, and $Cp^N{}_2Ti(OPh)_2$ **(10)**. Reaction of these complexes with phenylsilane at room temperature under an inert atmosphere over a period of several days leads to the production of poly(phenylsilanes) in excellent yields. The polymer products are recovered by filtration of the reaction solution through a Florisil column, followed by vacuum evaporation of the solvent. The poly(phenylsilanes) thus obtained are extremely viscous oils.

As generally described in the literature,[21] poly(phenylsilanes) synthesized via the dehydrocoupling method with dimethyltitanocene and dimethylzirconocene catalysts are predominantly atactic polymers. They consist of linear, cyclic, and branched species; therefore, their characterization is quite complicated. The ^{1}H and ^{29}Si NMR spectra give only a small amount of information concerning the details of the polymer structure; only broad unresolved resonances are observed in the range of 4−5 ppm and −50 to −70 ppm, respectively. The IR spectra show, in addition to the bands due to the phenyl substituents, characteristic, intense ν_{SiH} bands at ca. 2100 cm^{-1}, typical for trisubstituted Si−H compounds,[33a] and strong δ_{SiH} bands at ca. 910 cm^{-1}, typical for the bending mode of SiH_2 groups.[33b]

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(32) Catalyst decomposition can be excluded. The catalyst precursors can be recycled (Jutzi, P.; Redeker, T., unpublished results).

Table 3. Bonding Parameters for $(C_5H_4CH_2CH_2N^iPr_2)_2TiCl_2$ (2), $(C_5H_5)_2TiCl_2$,[31b] and $(C_5H_4Me)_2TiCl_2$[31a]

compound	Ti−Cl (Å)	Cl−Ti−Cl (deg)	Cp−Ti (Å)	Cp−Ti−Cp (deg)
$(C_5H_4CH_2CH_2N^iPr_2)_2TiCl_2$ (**2**)	2.3682(11)	94.40(5)	2.062	132.6
$(C_5H_5)_2TiCl_2$	2.364(2)	94.53(6)	2.059	130.97
$(C_5H_4Me)_2TiCl_2$	2.362(2)	93.15(8)	2.067	130.2

The polyphenylsilanes synthesized by **6**−**8** and **10** exhibit analytical data similar to those described above. The ^1H NMR spectra show broad, unresolved signals in the range of 4.5−5.5 ppm and the ^{29}Si NMR spectra in the range of −55 to −65 ppm. The characteristic ν_{SiH} and δ_{SiH} bands are observed at 2090−2110 cm^{-1} and at 910−920 cm^{-1}, respectively. The mass spectra show fragments of linear and cyclic polymers up to the parent ion of the octamer.[34] The amount of linear, cyclic, and branched oligomers has not yet been determined. A detailed analysis of the polymers will be subject of further investigations.

V. Effect of the (Diisopropylamino)ethyl Function. Metallocene dichlorides Cp_2MCl_2 (M = Ti, Zr) are electronically unsaturated (16-VE species) and act as weak Lewis acids.[35] Therefore, they should react with Lewis bases like tertiary amines to form adducts of the type $Cp_2MCl_2 \leftarrow NR_3$. Such reactions are rarely discussed in the literature and are controversial.[36] In our experiments with Cp_2MCl_2 (M = Ti, Zr) and the tertiary amines $EtNMe_2$ and EtN^iPr_2, respectively, no adducts could be isolated. Furthermore, ^1H NMR spectroscopic investigations gave no evidence for an interaction between the metallocene dichlorides and the amines in solution.

A Lewis acid−Lewis base interaction between a metal center and the N atom of the amino group in the functionalized $Cp^{=}$ and $Cp^{\wedge}$ ligands ($Cp^{=} = C_5H_4CH_2CH_2NMe_2$; $Cp^{\wedge} = C_5Me_4CH_2CH_2NMe_2$) could be proved for many complexes of s-, p-, d-, and f-block elements.[1−8] Due to the potential chelate effect of the N-functionalized side chains, the metallocene dichlorides of the type $Cp^{=}{}_2MCl_2$, which had been synthesized by our group only recently,[7] and the metallocene dichlorides of the type $Cp^N{}_2MCl_2$ (this work) might show an intramolecular coordination. But until now, such an intramolecular interaction has not been observed for this kind of metallocene-type complex.

However, an intermolecular coordination of the N-functionalized side chains is observed in $Cp^{=}{}_2MCl_2$ as well as in $Cp^N{}_2MCl_2$. Amorphous solids precipitate from concentrated benzene solutions. These solids are coordination polymers and not decomposition products.[22,37] The coordination polymer of $Cp^{=}{}_2MCl_2$ precipitates immediately. In contrast, the precipitation process of the compounds $Cp^N{}_2MCl_2$ takes several days. The smaller tendency for an intermolecular coordination of $Cp^N{}_2MCl_2$ can be attributed to steric effects of the bulkier (diisopropylamino)ethyl-functionalized side chain. Due to the lower polymerization tendency a complete characterization of $Cp^N{}_2MCl_2$ in dilute solution is possible. ^1H NMR spectroscopy indicates the presence of monomeric species. Furthermore, it is possible to grow crystals of monomeric **2** from a dilute toluene solution (see section III, X-ray Crystal Structure Analysis of **2**). There is no evidence of an interaction of the N-functions with the metal centers for the monomers either in solution or in the solid state.

In contrast to the parent complexes Cp_2MCl_2, the N-functionalized derivatives $Cp^N{}_2MCl_2$ are extremely air- and moisture-sensitive. This is due to the effect of the amino group which supports the hydrolysis process by trapping the evolving hydrogen chloride. A comparable phenomenon is described by Rausch et al.[10b] for the half-sandwich species $Cp^{=}TiCl_3$.

In the hydrochlorides $Cp^N{}_2MCl_2 \cdot 2HCl$ (**4**, **5**), the amino groups in their protonated forms dramatically change the solubility as well as the stability toward air and moisture. In contrast to $Cp^N{}_2MCl_2$, the hydrochlorides **4** and **5** show an excellent solubility and stability in polar solvents such as chloroform and acetonitrile. Furthermore, solvolysis of the M−Cl bonds in protic solvents such as methanol is not observed. Complex **4** is stable even in water for several hours. This phenomenon can be explained by a kind of “intramolecular buffer function” of the protonated amino groups.[38]

The first attempts to use the metallocene dichlorides $Cp^N{}_2MCl_2$ and also the protonated species $Cp^N{}_2MCl_2 \cdot 2HCl$ in the polymerization of ethylene have been successful (see section IV, Polymerization Reactions). Because of their high stability to air and moisture, the hydrochlorides $Cp^N{}_2MCl_2 \cdot 2HCl$ **(4)** and **(5)** are preferred candidates as precursors in Ziegler−Natta catalysis. Mechanistic studies concerning coordination of the N-functions during various steps of the catalytic process to stabilize the intermediate cationic species are in progress.

Similary, the additional side chains obviously do not reduce the catalytic activity of the alkyl and phenoxy derivatives $Cp^N{}_2MR_2$ (**6**−**8**, **10**; R = Me, Bz, PhO) in the dehydrocoupling of phenylsilane (see section IV, Dehydrocoupling Reactions). The yields of produced polymers and the degrees of polymerization are comparable to those of the analogous parent complexes Cp_2MR_2.[21] Mechanistic studies concerning the influence of the additional amino functions in this kind of catalysis will be also the subject of further investigations.

VI. Conclusion. It has been demonstrated that it is possible to synthezise metallocene-type compounds of titanium and zirconium containing two (diisopropylamino)ethyl-substituted cyclopentadienyl ligands (Cp^N).

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(33) (a) Kniseley, R. N.; Fassel, V. A.; Conrad, E. E. *Spectrochim. Acta* **1959**, 651. (b) Höfler, F.; Bauer, G.; Hengge, E. *Spectrochim. Acta* **1976**, *32a*, 1435.

(34) On the spectrometer used, only fragments with *m/z* <1000 could be detected.

(35) (a) Karsch, H. H.; Deubelly, B.; Hofmann, J.; Pieper, U.; Müller, G. *J. Am. Chem. Soc.* **1988**, *110*, 3654. (b) Hey-Hawkins, E.; Lindenberg, F. *Chem. Ber.* **1992**, *125*, 1815. (c) Lindenberg, F.; Hey-Hawkins, E. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1531. See also references cited therein.

(36) (a) Anagnostopoulos, A. K. *Chem. Chron. Epistem. Ekdosis* **1969**, *34*, 140. (b) Baye, L. J. *Synth. Inorg. Met.-Org. Chem.* **1972**, *2*, 47.

(37) This could be proved by the reaction of the solid with methanolic HCl. The polymer structure is destroyed, and the protonation of the N-functions results in the formation of the monomer metallocene dichlorides dihydrochlorides $Cp^{=}{}_2MCl_2 \cdot 2HCl$ in nearly quantitative yields.

(38) The nucleophilic attack of the hydroxide anion is probably the first step in the decomposition process of the dichlorides **2** and **3**. In case of the hydrochlorides **4** and **5**, the protonated amino group can function as an intramolecular buffer.

(1) In dilute solution, the metallocene dichlorides **2** and **3** exist as monomers without an intramolecular coordination of the amino groups; in concentrated solution, the formation of polymers by an intermolecular coordination is a rather slow process. The crystal structure of the coordination polymer has been unknown until now. The structure of the monomer species could be determined for **2** by an X-ray crystal structure analysis. There is no evidence for an interaction of the N-functions with the metal center.

(2) The solubility of the complexes $Cp^N{}_2MCl_2$ (**2**, **3**) in nonpolar solvents is raised dramatically in comparison to that of the parent metallocene derivatives Cp_2MCl_2.

(3) The hydrochlorides $Cp^N{}_2MCl_2\cdot 2HCl$ (**4**, **5**) show an exceptional stability to air and moisture. Furthermore, their high solubilty in protic solvents is of special interest with regard to organometallic chemistry in water.[39]

(4) The metallocene dichlorides **2** and **3** and also the hydrochlorides **4** and **5** are precatalysts in the polymerization of ethylene. Because of their easy handling due to their exceptional stability, the hydrochlorides **4** and **5** are particulary suitable for employment in this kind of catalysis.

(5) The alkyl and alkoxy derivatives $Cp^N{}_2MR_2$ (**6**−**8**) catalyze the dehydrogenative coupling of phenylsilane to oligosilanes in excellent yields.

Experimental Section

General Comments. All experiments were carried out under an atmosphere of dried, oxygen-free argon by using standard Schlenk techniques. When ethylene was used as a reagent, the gas provided a protective atmosphere. Solvents were dried by using standard procedures and distilled prior to use. All other reagents were used as purchased. ^1H (300.1 MHz) and $^{13}C\{^1H\}$ (75.5 MHz) NMR spectra were obtained using a Bruker AM 300 spectrometer. Chemical shifts for ^1H and $^{13}C\{^1H\}$ spectra were recorded in ppm downfield from TMS and referenced with internal deuteriochloroform, deuteriobenzene, deuterioacetonitrile, or deuteriomethanol. The mass spectra were determined by using a VG AutoSpec instrument. Only characteristic fragments and isotopes of the highest abundance are listed. Melting points were determined in sealed capillaries with a Büchi 510 melting point determination apparatus and are uncorrected. Elemental analyses were carried out by Analytisches Labor der Fakultät für Chemie, Bielefeld, Germany.

Materials. Titanium tetrachloride was distilled prior to use. Zirconium tetrachloride was used as purchased. $Zr(NMe_2)_4$ was prepared as described in the literature.[40]

$C_5H_5CH_2CH_2N^iPr_2 \equiv Cp^NH$ (1). Over 1 h, to a solution of 17.62 g (200 mmol) of CpNa in 100 mL of THF cooled to 0 °C (prepared by addition of 13.2 g (200 mmol) of CpH to a suspension of 4.60 g (200 mmol) of NaH in THF) was added dropwise with stirring 30.1 g (184 mmol) of 2-chloro-1-(diisopropylamino)ethane. The reaction mixture was warmed to room temperature within 1 h and then refluxed for an additional 2 h. After the solvent was removed in vacuo (20 Torr) the residue was hydrolyzed with 150 mL of water and extracted with 3 × 100 mL of petroleum ether. The combined organic layers were dried with sodium sulfate. Volatile products were removed in vacuo, and the crude product was distilled (76−77 °C/2 Torr) to yield 21.2 g (110 mmol, 60%) of the (diisopropylamino)ethyl-substituted cyclopentadiene **1** in the form of a colorless liquid as a mixture of two isomer. ^1H NMR ($CDCl_3$): δ 0.99, 1.00 (2d, $^3J = 3.2$ Hz, 2 × 6H, $\mathrm{CHC}H_3$), 2.44−2.50 (m, 2 H, $\mathrm{CpC}H_2$), 2.54−2.61 (m, 2H, $\mathrm{C}H_2\mathrm{N}$), 2.90−2.93 (m, 2H, allyl−Cp *H*), 2.97−3.07 (m, 2H, $\mathrm{C}H\mathrm{CH_3}$), 6.01, 6.16, 6.22, 6.24, 6.40, 6.43 (m, 3H, vinyl−Cp *H*). ^1H NMR (C_6D_6): δ 0.94, 0.96 (2 d, $^3J = 4.5$ Hz, 2 × 6H, $\mathrm{CHC}H_3$), 2.50−2.57 (m, 2 H, $\mathrm{CpC}H_2$), 2.62−2.68 (m, 2H, $\mathrm{C}H_2\mathrm{N}$), 2.77−2.80 (m, 2H, allyl−Cp *H*), 2.87−2.97 (m, 2H, $\mathrm{C}H\mathrm{CH_3}$), 6.00, 6.21, 6.23, 6.32, 6.49, 6.52 (m, 3H, vinyl−Cp *H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 20.6 ($\mathrm{CH}C\mathrm{H_3}$), 32.6, 33.2 ($\mathrm{Cp}C\mathrm{H_2}$), 41.1, 43.5 ($C\mathrm{H_2N}$), 45.2, 45.9 (allyl−Cp *C*), 48.5, 48.7 ($C\mathrm{HCH_3}$), 126.1, 126.4, 130.3, 132.3, 133.2, 134.9 (ring $-C\mathrm{H}=$), 145.6, 148.1 (ring $=C\mathrm{CH_2CH_2}$). MS (EI; *m/z* (relative intensity, %)): 178 ($[M - CH_3]^+$, 5), 114 ($(^iC_3H_7)_2NCH_2{}^+$, 100), 72 ($(CH_2NH(^iC_3H_7)^+$, 42). Anal. Calcd for $C_{13}H_{23}N$ (193.33): C, 80.76; H, 11.99; N, 7.24. Found: C, 80.45; H, 11.92; N, 7.00.

$(\eta^5\text{-}C_5H_4CH_2CH_2N^iPr_2)_2TiCl_2$ (2). To a solution of 1.92 g (10.1 mmol) of $TiCl_4$ dissolved in 80 mL of toluene cooled to −40 °C was added dropwise with stirring a suspension of 20.2 mmol of Cp^NLi in 80 mL of diethyl ether (prepared by addition of 12.6 mL (20.2 mmol) of *n*-butyllithium (1.6 M in *n*-hexane) to a solution of 3.90 g (20.2 mmol) of Cp^NH in diethyl ether). The reaction mixture was warmed to room temperature over 6 h and then stirred for an additional 10 h. The deep red solution was filtered, and the solvent was removed in vacuo. The residue was washed with 3 × 30 mL of cold pentane (−40 °C), leaving 2.5 g (4.97 mmol, 49%) of **2** as a deep red solid. The product can be crystallized from toluene to form red crystals. ^1H NMR (C_6D_6): δ 0.90 (d, $^3J = 6.6$ Hz, 24H, $\mathrm{CHC}H_3$), 2.60 (m, 4H, $\mathrm{CpC}H_2$), 2.93 (m, 8H, $\mathrm{NC}H_2$, $\mathrm{C}H\mathrm{CH_3}$), 5.76 (t, $^3J = 2.6$ Hz, 4H, Cp *H*), 6.13 (t, $^3J = 2.7$ Hz, 4H, Cp *H*). ^{13}C NMR (C_6D_6): δ 21.0 ($\mathrm{CH}C\mathrm{H_3}$), 33.1 ($\mathrm{Cp}C\mathrm{H_2}$), 45.6 ($C\mathrm{H_2N}$), 48.2 ($C\mathrm{HCH_3}$), 114.6, 122.9 (ring $-C\mathrm{H}=$), 136.7 (ring $=C\mathrm{CH_2CH_2}$). MS (LSIMS; *m/z* (relative intensity, %)): 503 ($[M + 1H]^+$, 3), 468 ($[M - 2Cl]^+$, 3), 114 ($[(^iC_3H_7)_2NCH_2]^+$, 100), 65 ($[C_5H_5]^+$, 8). Mp: 156 °C dec. Anal. Calcd for $C_{26}H_{44}Cl_4N_2Ti$ (503.43): C, 62.03; H, 8.80; N, 5.56. Found: C, 61.92; H, 8.68; N, 5.43.

$(\eta^5\text{-}C_5H_4CH_2CH_2N^iPr_2)_2ZrCl_2$ (3). To a suspension of 2.35 g (10.10 mmol) of $ZrCl_4$ in 80 mL of toluene cooled to −40 °C was added dropwise with stirring a suspension of 20.20 mmol of Cp^NLi in 80 mL of diethyl ether (prepared by addition of 12.60 mL (20.20 mmol) of *n*-butyllithium (1.6 M in *n*-hexane) to a solution of 3.90 g (20.20 mmol) of Cp^NH in diethyl ether). The reaction mixture was warmed to room temperature over 4 h and then stirred for an additional 24 h. The yellow solution was filtered, and the solvent was removed in vacuo. The residue was washed with 2 × 50 mL of cold (−40 °C) pentane, leaving 3.15 g (5.80 mmol, 57%) of **3** as a pale yellow solid. The product can be crystallized from toluene to form colorless needles. ^1H NMR (C_6D_6): δ 0.90 (d, $^3J = 6.6$ Hz, 24H, $\mathrm{CHC}H_3$), 2.57 (t, $^3J = 6.5$ Hz, 4H, $\mathrm{CpC}H_2$), 2.82 (m, 4H, $\mathrm{NC}H_2$), 2.90 (m, 4H, $\mathrm{C}H\mathrm{CH_3}$), 5.77 (t, $^3J = 2.7$ Hz, 4H, Cp *H*), 6.02 (t, $^3J = 2.7$ Hz, 4H, Cp *H*). ^{13}C NMR (C_6D_6): δ 21.1 ($\mathrm{CH}C\mathrm{H_3}$), 33.0 ($\mathrm{Cp}C\mathrm{H_2}$), 47.0 ($C\mathrm{H_2N}$), 48.6 ($C\mathrm{HCH_3}$), 109.1, 113.2, 113.5, 117.1 (ring $-C\mathrm{H}=$), 130.3 (ring $=C\mathrm{CH_2CH_2}$). MS (LSIMS; *m/z* (relative intensity, %)): 545 ($[M + 1H]^+$, 1), 114 ($[(^iC_3H_7)_2NCH_2]^+$, 100), 65 ($[C_5H_5]^+$, 2). Mp: 120 °C dec. Anal. Calcd for $C_{26}H_{44}N_2Cl_2Zr$ (546.78): C, 57.11; H, 8.11; N, 5.12. Found: C, 56.86; H, 8.73; N, 4.93.

$[(\eta^5\text{-}C_5H_4CH_2CH_2N(H)^iPr_2)_2TiCl_2]^{2+}Cl^-{}_2$ (4). A 550 mg (1.09 mmol) amount of **2** was dissolved in 15 mL of MeOH (saturated with HCl gas) and then stirred for ca. 30 min. The solution was evaporated in vacuo, leaving 628 mg (1.09 mmol, 100%) of **4** as an orange-brown solid. The product can be crystallized from acetonitrile to form deep red crystals. ^1H NMR (CD_3OD): δ 1.39, 1.40 (2d, $^3J = 6.6$ Hz, 24H, $\mathrm{CHC}H_3$), 3.33 (m, 4H, $\mathrm{CpC}H_2$), 3.56 (m, 4H, $\mathrm{NC}H_2$), 3.78 (m, 4H, $\mathrm{C}H\mathrm{CH_3}$), 6.44 (t, $^3J = 2.5$ Hz, 4H, Cp *H*), 6.74 (t, $^3J = 2.7$ Hz, 4H, Cp *H*). ^1H NMR (CD_3CN): δ 1.36, 1.43 (2 d, $^3J = 6.5$ Hz, 24H, $\mathrm{CHC}H_3$), 3.32 (m, 8H, $\mathrm{CpC}H_2$, $\mathrm{NC}H_2$), 3.63 (m, 4H, $\mathrm{C}H\mathrm{CH_3}$), 6.49 (m, 4H, Cp *H*), 6.61 (m, 4H, Cp *H*), 10.90 (broad s, 2H, N*H*). ^{13}C NMR (CD_3OD): δ 17.2, 18.8 ($\mathrm{CH}C\mathrm{H_3}$), 29.2 ($\mathrm{Cp}C\mathrm{H_2}$), 47.3 ($C\mathrm{H_2N}$), 56.5 ($C\mathrm{HCH_3}$), 115.8, 125.1 (ring

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$-C\mathrm{H}{=}$), 132.6 (ring $={C}\mathrm{CH_2CH_2}$). Mp: 177 °C dec. Anal. Calcd for $\mathrm{C_{26}H_{46}Cl_4N_2Ti}$ (576.35): C, 54.18; H, 8.04; N, 4.86. Found: C, 53.89; H, 8.30; N, 4.72.

$[(\eta^5\text{-}\mathrm{C_5H_4CH_2CH_2N(H)^iPr_2})_2\mathrm{ZrCl_2}]^{2+}\mathrm{Cl^-}_2$ (5). A 530 mg (0.97 mmol) amount of **3** was dissolved in 15 mL of MeOH (saturated with HCl gas), and the mixture was then stirred for ca. 30 min. Volatile products were removed in vacuo, leaving 600 mg (0.97 mmol, 100%) of **5** as a colorless solid. An analytically pure compound could be obtained by crystallization from acetonitrile. ^{1}H NMR ($\mathrm{CD_3OD}$): δ 1.39, 1.41 (2 d, $^3J = 6.6$ Hz, 24H, $\mathrm{CHC}H_3$), 3.19 (m, 4H, $\mathrm{CpC}H_2$), 3.46 (m, 4H, $\mathrm{NC}H_2$), 3.78 (m, 4H, $\mathrm{C}H\mathrm{CH_3}$), 6.45 (t, $^3J = 2.7$ Hz, 4H, Cp H), 6.61 (t, $^3J = 2.7$ Hz, 4H, Cp H). ^{1}H NMR ($\mathrm{CD_3CN}$): δ 1.36, 1.43 (2 d, $^3J = 6.5$ Hz, 24H, $\mathrm{CHC}H_3$), 3.24 (m, 8H, $\mathrm{CpC}H_2$, $\mathrm{NC}H_2$), 3.63 (m, 4H, $\mathrm{C}H\mathrm{CH_3}$), 6.47 (m, 4H, Cp H), 6.50 (m, 4H, Cp H), 10.90 (br s, 2H, $\mathrm{N}H$). ^{13}C NMR ($\mathrm{CD_3OD}$): δ 17.3, 18.9 ($\mathrm{CH}C\mathrm{H_3}$), 28.8 ($\mathrm{Cp}C\mathrm{H_2}$), 48.0 ($C\mathrm{H_2N}$), 56.6 ($C\mathrm{HCH_3}$), 113.5, 119.7 (ring $-C\mathrm{H}{=}$), 129.2 (ring $={C}\mathrm{CH_2CH_2}$). Mp: 170 °C dec. Anal. Calcd for $\mathrm{C_{26}H_{46}N_2Cl_4Zr}$ (619.70): C, 50.39; H, 7.48; N, 4.52. Found: C, 50.18; H, 7.35; N, 4.60.

$(\eta^5\text{-}\mathrm{C_5H_4CH_2CH_2N^iPr_2})_2\mathrm{TiMe_2}$ (6). From $(\mathrm{C_5H_4CH_2CH_2N^iPr_2})_2\mathrm{TiCl_2}$ (2). To a suspension of 300 mg (0.60 mmol) of **2** in 20 mL of diethyl ether cooled to −50 °C was added dropwise with stirring 0.75 mL (1.20 mmol) of methyllithium (1.6 M in diethyl ether). The reaction mixture was warmed to room temperature within 6 h and then stirred for an additional 10 h. After the solvent of the dark solution was removed in vacuo, the residue was extracted with 15 mL of toluene. The extract was filtered and the solvent was removed in vacuo, leaving 260 mg (0.56 mmol, 94%) of **6** as a deep yellow oil.

From $[(\mathrm{C_5H_4CH_2CH_2N(H)^iPr_2})_2\mathrm{TiCl_2}]^{2+}\mathrm{Cl^-}_2$ (4). Analogous procedures with 4 equiv of methyllithium were followed, as described above for **2**; yield 87%. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.1 (s, 6H, $\mathrm{TiC}H_3$), 0.98 (d, $^3J = 6.6$ Hz, 24H, $\mathrm{CHC}H_3$), 2.56 (m, 4H, $\mathrm{CpC}H_2$), 2.74 (m, 4H, $\mathrm{NC}H_2$), 2.97 (m, 4H, $\mathrm{C}H\mathrm{CH_3}$), 5.47 (t, $^3J = 2.5$ Hz, 4H, Cp H), 5.80 (t, $^3J = 2.5$ Hz, 4H, Cp H). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 21.1 ($\mathrm{CH}C\mathrm{H_3}$), 33.6 ($\mathrm{Cp}C\mathrm{H_2}$), 44.9 ($\mathrm{Ti}C\mathrm{H_3}$), 47.3 ($C\mathrm{H_2N}$), 48.6 ($C\mathrm{HCH_3}$), 111.0, 114.7 (ring $-C$). MS (LSIMS; *m/z* (relative intensity, %)): 463 ($[\mathrm{M + 1H}]^+$, 4), 432 ($[\mathrm{M - 2CH_3}]^+$, 6), 114 ($[(^i\mathrm{C_3H_7})_2\mathrm{NCH_2}]^+$, 100), 65 ($[\mathrm{C_5H_5}]^+$, 5). Anal. Calcd for $\mathrm{C_{28}H_{50}N_2Ti}$ (462.60): C, 72.69; H, 10.89; N, 6.05. Found: C, 71.82; H, 11.27; N, 5.77.

$(\eta^5\text{-}\mathrm{C_5H_4CH_2CH_2N^iPr_2})_2\mathrm{ZrMe_2}$ (7). From $(\mathrm{C_5H_4CH_2CH_2N^iPr_2})_2\mathrm{ZrCl_2}$ (3). To a suspension of 740 mg (1.35 mmol) of **3** in 30 mL of diethyl ether cooled to −70 °C was added dropwise with stirring 1.69 mL (2.70 mmol) of methyllithium (1.6 M in diethyl ether). The reaction mixture was warmed to room temperature over 6 h and then stirred for an additional 10 h. After the solvent of the yellow solution was removed in vacuo, the residue was extracted with 15 mL of toluene. The extract was filtered and the solvent was removed in vacuo, leaving 640 mg (1.26 mmol, 94%) of **7** as a yellow oil.

From $[(\mathrm{C_5H_4CH_2CH_2N(H)^iPr_2})_2\mathrm{ZrCl_2}]^{2+}\mathrm{Cl^-}_2$ (5). Analogous procedures with 4 equiv of MeLi as were followed, described above for **3**; yield 89%. ^{1}H NMR ($\mathrm{C_6D_6}$): δ −0.06 (s, 6H, $\mathrm{ZrC}H_3$), 0.96 (d, $^3J = 6.5$ Hz, 24H, $\mathrm{CHC}H_3$), 2.63 (m, 8H, $\mathrm{CpC}H_2$, $\mathrm{NC}H_2$), 2.95 (m, 4H, $\mathrm{C}H\mathrm{CH_3}$), 5.56 (t, $^3J = 3.4$ Hz, 4H, Cp H), 5.82 (t, $^3J = 3.4$ Hz, 4H, Cp H). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 21.1 ($\mathrm{CH}C\mathrm{H_3}$), 30.3 ($\mathrm{Zr}C\mathrm{H_3}$), 33.1 ($\mathrm{Cp}C\mathrm{H_2}$), 47.4 ($C\mathrm{H_2N}$), 48.6 ($C\mathrm{HCH_3}$), 107.9, 111.5 (ring $-C\mathrm{H}{=}$), 126.7 (ring $={C}\mathrm{CH_2CH_2}$). MS (CI; *m/z* (relative intensity, %)): 505 ($[\mathrm{M + 1H}]^+$, 4), 193 ($[\mathrm{Cp^N}]^+$, 13), 114 ($[(^i\mathrm{C_3H_7})_2\mathrm{NCH_2}]^+$, 100). Anal. Calcd for $\mathrm{C_{28}H_{50}N_2Zr}$ (505.94): C, 66.47; H, 9.96; N, 5.53. Found: C, 64.87; H, 9.74; N, 5.00.

$(\eta^5\text{-}\mathrm{C_5H_4CH_2CH_2N^iPr_2})_2\mathrm{TiBz_2}$ (8). From $(\mathrm{C_5H_4CH_2CH_2N^iPr_2})_2\mathrm{TiCl_2}$ (2). Over 20 min, to a suspension of 946 mg (1.87 mmol) of **2** in 70 mL of diethyl ether cooled to −60 °C was added dropwise with stirring 4.40 mL (3.65 mmol) of benzylmagnesium bromide (0.83 M in ether) diluted in 45 mL of diethyl ether. The reaction mixture was warmed to room temperature over 6 h and then stirred for an additional 10 h. After the solvent of the red-brown suspension was removed in vacuo, the residue was extracted with 40 mL of toluene. The extract was filtered, and the solvent was removed in vacuo. The red-brown residue was washed with 40 mL of cold (−60 °C) pentane, leaving 470 mg (0.76 mmol, 41%) of **8** as a purple solid. Crystallization from toluene affords purple crystals.

From $[(\mathrm{C_5H_4CH_2CH_2N(H)^iPr_2})_2\mathrm{TiCl_2}]^{2+}\mathrm{Cl^-}_2$ (4). Analogous procedures with 4 equiv of benzylmagnesium bromide were used, as described above for **2**; yield 38%. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.92 (d, $^3J = 6.6$ Hz, 24H, $\mathrm{CHC}H_3$), 2.00 (s, 4H, $\mathrm{TiC}H_2$), 2.14 (m, 4H, $\mathrm{CpC}H_2$), 2.53 (m, 4H, $\mathrm{NC}H_2$), 2.88 (m, 4H, $\mathrm{C}H\mathrm{CH_3}$), 5.72 (t, $^3J = 2.5$ Hz, 4H, Cp H), 5.77 (t, $^3J = 2.5$ Hz, 4H, Cp H), 6.93 (m, 6H, ortho and para Bz H), 7.22 (t, $^3J = 7.6$ Hz, 4H, meta Bz H). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.95 (d, $^3J = 6.5$ Hz, 24H, $\mathrm{CHC}H_3$), 1.81 (s, 4H, $\mathrm{TiC}H_2$), 2.14 (m, 4H, $\mathrm{CpC}H_2$), 2.53 (m, 4H, $\mathrm{NC}H_2$), 2.96 (m, 4H, $\mathrm{C}H\mathrm{CH_3}$), 5.80 (t, $^3J = 2.5$ Hz, 4H, Cp H), 5.85 (t, $^3J = 2.5$ Hz, 4H, Cp H), 6.74 (d, $^3J = 7.1$ Hz, 4H, ortho Bz H), 6.81 (t, $^3J = 7.3$ Hz, 2H, para Bz H), 7.12 (t, $^3J = 7.7$ Hz, 4H, meta Bz H). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 21.1 ($\mathrm{CH}C\mathrm{H_3}$), 33.0 ($\mathrm{Cp}C\mathrm{H_2}$), 47.3 ($C\mathrm{H_2N}$), 48.5 ($C\mathrm{HCH_3}$), 73.3 ($\mathrm{Ti}C\mathrm{H_2}$), 114.9, 117.4 (Cp ring C), 121.8 (para Bz C_4), 126.4 (meta Bz C_3), 128.8 (ortho Bz C_2), 129.3 (Cp ring $={C}\mathrm{CH_2CH_2}$), 154.5 (Bz C_1). MS (CI; *m/z* (relative intensity, %)): 432 ($[\mathrm{M - 2C_7H_7}]^+$, 6), 114 ($[(^i\mathrm{C_3H_7})_2\mathrm{NCH_2}]^+$, 100), 91 ($[\mathrm{C_7H_7}]^+$, 4). Mp: 91 °C dec. Anal. Calcd for $\mathrm{C_{40}H_{58}N_2Ti}$ (614.79): C, 78.14; H, 9.50; N, 4.55. Found: C, 77.36; H, 9.63; N, 4.46.

$(\eta^5\text{-}\mathrm{C_5H_4CH_2CH_2N^iPr_2})_2\mathrm{ZrBz_2}$ (9). From $(\mathrm{C_5H_4CH_2CH_2N^iPr_2})_2\mathrm{ZrCl_2}$ (3). To a suspension of 940 mg (1.72 mmol) of **3** in 70 mL of diethyl ether cooled to −50 °C was added dropwise with stirring 4.14 mL (3.44 mmol) of benzylmagnesium bromide (0.83 M in ether) diluted in 45 mL of diethyl ether over 20 min. The reaction mixture was warmed to room temperature within 6 h and then stirred for an additional 10 h. After the solvent of the yellow suspension was removed in vacuo, the residue was extracted with 40 mL of toluene. The extract was filtered, and the solvent was removed in vacuo. The yellow residue was washed with 40 mL of cold (−60 °C) pentane, leaving 590 mg (0.90 mmol, 52%) of **9** as a bright yellow solid.

From $[(\mathrm{C_5H_4CH_2CH_2N(H)^iPr_2})_2\mathrm{ZrCl_2}]^{2+}\mathrm{Cl^-}_2$ (5). Analogous procedures with 4 equiv of benzylmagnesium bromide were followed, as described above for **3**; yield 57%. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.92 (d, $^3J = 6.6$ Hz, 24H, $\mathrm{CHC}H_3$), 1.95 (s, 4H, $\mathrm{ZrC}H_2$), 2.30 (m, 4H, $\mathrm{CpC}H_2$), 2.49 (m, 4H, $\mathrm{NC}H_2$), 2.88 (m, 4H, $\mathrm{C}H\mathrm{CH_3}$), 5.56 (t, $^3J = 2.7$ Hz, 4H, Cp H), 5.68 (t, $^3J = 2.7$ Hz, 4H, Cp H), 6.92 (t, $^3J = 7.3$ Hz, 2H, para Bz H), 6.98 (d, $^3J = 7.1$ Hz, 4H, ortho Bz H), 7.25 (t, $^3J = 7.5$ Hz, 4H, meta Bz H). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 21.0 ($\mathrm{CH}C\mathrm{H_3}$), 32.5 ($\mathrm{Cp}C\mathrm{H_2}$), 47.6 ($C\mathrm{H_2N}$), 48.4 ($C\mathrm{HCH_3}$), 61.3 ($\mathrm{Zr}C\mathrm{H_2}$), 111.4, 123.9 (Cp ring C), 121.1 (para Bz C_4), 126.1 (ortho and meta Bz C_2 and C_3), 126.8 (Cp ring $={C}\mathrm{CH_2CH_2}$), 152.8 (Bz C_1). MS (CI; *m/z* (relative intensity, %)): 565 ($[\mathrm{M - C_7H_7}]^+$, 17), 194 ($[\mathrm{Cp^NH + H}]^+$, 3), 178 ($[\mathrm{Cp^NH - CH_3}]^+$, 3), 114 ($[(^i\mathrm{C_3H_7})_2\mathrm{NCH_2}]^+$, 34), 91 ($[\mathrm{C_7H_7}]^+$, 7), 72 ($[\mathrm{CH_2NH}(^i\mathrm{C_3H_7})]^+$, 2). Mp: 85 °C dec.

$(\eta^5\text{-}\mathrm{C_5H_4CH_2CH_2N^iPr_2})_2\mathrm{Ti(OPh)_2}$ (10). To a suspension of 1.25 g (2.48 mmol) of **2** in 30 mL of toluene cooled to −20 °C was added dropwise with stirring 497 mg (4.97 mmol) of PhOLi in 20 mL of benzene (prepared by addition of 3.11 mL (4.97 mmol) of *n*-butyllithium (1.6 M in *n*-hexane) to a solution of 468 mg (4.97 mmol) of phenol in benzene). The reaction mixture was warmed to room temperature over 6 h and then stirred for an additional 10 h. The solution was filtered, and the solvent was removed in vacuo. The yellow residue was washed with 40 mL of pentane, leaving 1.38 g (2.23 mmol, 89%) of **10** as a yellow solid. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.88 (d, $^3J = 6.6$ Hz, 24H, $\mathrm{CHC}H_3$), 2.52 (m, 4H, $\mathrm{CpC}H_2$), 2.60 (m, 4H, $\mathrm{NC}H_2$), 2.87 (m, 4H, $\mathrm{C}H\mathrm{CH_3}$), 5.80 (t, $^3J = 2.5$ Hz, 4H, Cp H), 5.93 (t, $^3J = 2.5$ Hz, 4H, Cp H), 6.84 (t, $^3J = 7.3$ Hz, 2H, para Ph H), 6.91 (t, $^3J = 7.6$ Hz, 4H, ortho Ph H), 7.23 (t, $^3J = 7.4$ Hz, 4H, meta Ph H). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 21.0 ($\mathrm{CH}C\mathrm{H_3}$), 32.5 ($\mathrm{Cp}C\mathrm{H_2}$), 45.6 ($C\mathrm{H_2N}$), 48.4 ($C\mathrm{HCH_3}$), 113.0, 119.1, 138.3 (Cp

C), 114.4 (ortho Ph *C*), 118.6 (para Ph *C*), 129.4 (meta Ph *C*), 170.9 (Ph *C*). MS (CI; *m/z* (relative intensity, %)): 619 ($[M + 1H]^+$, 1), 525 ($[M - PhO]^+$, 1), 432 ($[M - 2PhO]^+$, 4), 114 ($[({}^iC_3H_7)_2NCH_2]^+$, 48), 95 ($[C_6H_7O]^+$, 32). Mp: 82 °C. Anal. Calcd for $C_{38}H_{54}N_2O_2Ti$ (618.73): C, 73.76; H, 8.79; N, 4.52. Found: C, 73.82; H, 8.78; N, 4.18.

(η^5-$C_5H_4CH_2CH_2N^iPr_2)_2Zr(NMe_2)_2$ (11). A solution of 210 mg (0.79 mmol) of $Zr(NMe_2)_4$ and 303 mg (1.57 mmol) of Cp^NH in 15 mL of toluene was heated to gentle reflux for 5 h. All volatile products were completly removed in vacuo (100 °C/0.01 Torr), leaving 440 mg (0.78 mmol, 99%) of **11** as a bright yellow oil. ^1H NMR (C_6D_6): δ 0.99 (d, $^3J = 6.6$ Hz, 24H, $CHCH_3$), 2.62 (m, 8H, $CpCH_2$, NCH_2), 2.91 (s, 12H, $ZrNCH_3$), 2.96 (m, 4H, $CHCH_3$), 5.88 (t, $^3J = 2.7$ Hz, 4H, Cp *H*), 6.00 (t, $^3J = 2.7$ Hz, 4H, Cp *H*). ^{13}C NMR (C_6D_6): δ 21.1 ($CHCH_3$), 32.9 ($CpCH_2$), 47.5 (CH_2N), 48.8 ($CHCH_3$), 49.4 ($ZrNCH_3$), 108.8, 111.0 (ring $-CH{=}$), 123.8 (ring $=CCH_2$). MS (CI; *m/z* (relative intensity, %)]: 472 ($[M - 2NHMe_2]^+$, 0.5), 194 ($[Cp^NH + H]^+$, 10), 178 ($[Cp^NH - CH_3]^+$, 5), 114 ($[({}^iC_3H_7)_2NCH_2{}^+]$, 65), 46 ($[NHMe_2 + H]^+$, 28). Anal. Calcd for $C_{30}H_{56}N_4Zr$ (564.02): C, 63.88; H, 10.00; N, 9.93. Found: C, 63.69; H, 10.57; N, 8.95.

Polymerization Studies. Ethylene (BASF AG) was used without further purification. Methylaluminoxane was obtained from Witco (Bergkamen, Germany) as a 10 wt % toluene solution (4.9% wt % aluminum, density ~0.9 g/mL, average molar mass of the MAO oligomers 900−1100 g/mol). All polymerization reactions were performed in toluene solution at room temperature. The ethylene polymerization reactions took place under a pressure of 1 atm of ethylene.

Ethylene Polymerization Studies. With ($C_5H_4CH_2CH_2N^iPr_2)_2TiCl_2$ (2). A 22 mg (40.0 μmol) amount of **2** was dissolved in 5 mL of toluene. Under an ethylene atmosphere 12.0 mL (20.0 mmol) of MAO was introduced. After 5 min the clear yellow solution became turbid, and after 4 h the polymerization was quenched by pouring the solution into acidified methanol. The product was filtered off, washed with water and acetone, and dried to constant weight (2.50 g): productivity in g of PE $[M]^{-1}$ $[C_2H_4]^{-1}$ h^{-1}, 0.16×10^5;[41] M_w, 311 537; M_n, 190 12; M_w/M_n, 16.4.[42]

With ($C_5H_4CH_2CH_2N^iPr_2)_2ZrCl_2$ (3). A 20.0 mg (40.0 μmol) amount of **3** was dissolved in 5 mL of toluene. Under an ethylene atmosphere 12 mL (20.0 mmol) of MAO was introduced. After 1 h the clear yellow solution became turbid, and after 4 h the polymerization was quenched by pouring the solution into acidified methanol. The product was filtered off, washed with water and acetone, and dried to constant weight (840 mg): productivity in g of PE $[M]^{-1}$ $[C_2H_4]^{-1}$ h^{-1}, 0.053×10^5;[41] M_w, 230 452; M_n, 11 276; M_w/M_n, 20.4.[42]

Phenylsilane Polymerization Studies. With ($C_5H_4CH_2CH_2N^iPr_2)_2TiMe_2$ (6). 30 mg (0.07 mmol) amount of **6** was dissolved in 5 mL of toluene. Under an argon atmosphere 493 mg (4.54 mmol) phenylsilane was added to this solution. Evolution of gas commenced. After it was stirred for 2 days at room temperature, the solution was added to a column of Florisil. The polymer was recovered by elution with toluene followed by vacuum evaporation of the eluent. The product was obtained as a colorless, extremely viscous liquid (370 mg, 76%). ^1H NMR (C_6D_6): 4.49−5.60 (m, $(PhSi\ H)_x$), 6.90−7.98 (m, Ph *H*). ^{29}Si NMR (C_6D_6): −54 to −64. MS (EI; *m/z* (relative intensity, %)): 105 ($PhSi^+$, 100), 106 ($PhSiH^+$, 52), 107 ($PhSiH_2{}^+$, 30), 133 ($PhSi_2{}^+$, 4), 183 (Ph_2SiH^+, 7), 210 ($Ph_2Si_2{}^+$, 10), 240 ($Ph_2Si_3H^+$, 4), 259 (Ph_3Si^+, 87), 266 ($Ph_2Si_4{}^+$, 9), 287 ($Ph_3Si_2{}^+$, 9), 316 ($Ph_3Si_3H^+$, 6), 343 ($Ph_3Si_4{}^+$, 14), 372 ($Ph_3Si_5H^+$, 11), 421 ($Ph_4Si_4H^+$, 11), 450 ($Ph_4Si_5H_2{}^+$, 18), 526 ($Ph_5Si_5H^+$, 7), 634 ($Ph_6Si_6H_4{}^+$, 5), 636 ($Ph_6Si_6H_6{}^+$, 5), 740 ($Ph_7Si_7H_5{}^+$, 12), 846 ($Ph_8Si_8H_6{}^+$, 1). IR (KBr): ν_{Si-H} 2091.2, 911 cm^{-1}.

With ($C_5H_4CH_2CH_2N^iPr_2)_2ZrMe_2$ (7). A 50 mg (0.10 mmol) amount of **7** was dissolved in 5 mL of toluene. Under an argon atmosphere 760 mg (7.00 mmol) of phenylsilane was added to this solution. Evolution of gas commenced. After the solution was stirred for 2 days at room temperature, it was added to a column of Florisil. The polymer was recovered by elution with toluene followed by vacuum evaporation of the eluent. The product was obtained as a colorless, extremely viscous liquid (600 mg, 79%). ^1H NMR (C_6D_6): 4.49−5.60 (m, $(PhSi\ H)_x$), 6.82−7.95 (m, Ph *H*). ^{29}Si NMR (C_6D_6): −54 to −63. MS (EI; *m/z* (relative intensity, %)): 105 ($PhSi^+$, 100), 106 ($PhSiH^+$, 55), 107 ($PhSiH_2{}^+$, 39), 133 ($PhSi_2{}^+$, 6), 183 (Ph_2SiH^+, 94), 210 ($Ph_2Si_2{}^+$, 17), 240 ($Ph_2Si_3H^+$, 6), 259 (Ph_3Si^+, 81), 266 ($Ph_2Si_4{}^+$, 8), 287 ($Ph_3Si_2{}^+$, 14), 316 ($Ph_3Si_3H^+$, 9), 343 ($Ph_3Si_4{}^+$, 13), 372 ($Ph_3Si_5H^+$, 11), 421 ($Ph_4Si_4H^+$, 12), 450 ($Ph_4Si_5H_2{}^+$, 15), 526 ($Ph_5Si_5H^+$, 8), 634 ($Ph_6Si_6H_4{}^+$, 5), 740 ($Ph_7Si_7H_5{}^+$, 6). IR (KBr): ν_{Si-H} 2090.2, 910 cm^{-1}.

With ($C_5H_4CH_2CH_2N^iPr_2)_2TiBz_2$ (8). A 28 mg (0.05 mmol) amount of **8** was dissolved in 5 mL of toluene. Under an argon atmosphere 496 mg (4.60 mmol) of phenylsilane was added to the solution. A weak evolution of gas commenced. After it was stirred for 3 days at room temperature, the dark solution was added to a column of Florisil. The polymer was recovered by elution with toluene followed by vacuum evaporation of the eluent. The product was obtained as a colorless, extremely viscous liquid (300 mg, 61%). ^1H NMR (C_6D_6): 4.49−5.30 (m, $(PhSi\ H)_x$), 6.88−7.75 (m, Ph *H*). ^{29}Si NMR (C_6D_6): −58.7 to −64.9. MS (EI; *m/z* (relative intensity, %)): 105 ($PhSi^+$, 100), 106 ($PhSiH^+$, 32), 107 ($PhSiH_2{}^+$, 31), 133 ($PhSi_2{}^+$, 14), 183 (Ph_2SiH^+, 91), 210 ($Ph_2Si_2{}^+$, 27), 240 ($Ph_2Si_3H^+$, 31), 259 (Ph_3Si^+, 90), 266 ($Ph_2Si_4{}^+$, 24), 287 ($Ph_3Si_2{}^+$, 29), 316 ($Ph_3Si_3H^+$, 31), 343 ($Ph_3Si_4{}^+$, 30), 372 ($Ph_3Si_5H^+$, 8), 421 ($Ph_4Si_4H^+$, 30), 450 ($Ph_4Si_5H_2{}^+$, 14), 526 ($Ph_5Si_5H^+$, 4), 634 ($Ph_6Si_6H_4{}^+$, 2), 636 ($Ph_6Si_6H_6{}^+$, 4), 742 ($Ph_7Si_7H_7{}^+$, 1). IR (KBr): ν_{Si-H} 2086.9, 917 cm^{-1}.

With ($C_5H_4CH_2CH_2N^iPr_2)_2Ti(PhO)_2$ (10). An 88 mg (0.142 mmol) amount of **10** was dissolved in 10 mL of toluene. Under an argon atmosphere 1.05 g (9.90 mmol) of phenylsilane was added to the solution. A weak evolution of gas commenced. After it was stirred for 3 days at room temperature, the dark solution was added to a column of Florisil. The polymer was recovered by elution with toluene followed by vacuum evaporation of the eluent. The product was obtained as a colorless, extremely viscous liquid (810 mg, 77%). ^1H NMR (C_6D_6): 4.49−5.17 (m, $(PhSi\ H)_x$), 6.90−7.80 (m, Ph *H*). ^{29}Si NMR (C_6D_6): −55.1 to −68.3. MS (EI; *m/z* (relative intensity, %)): 105 ($PhSi^+$, 100), 106 ($PhSiH^+$, 14), 107 ($PhSiH_2{}^+$, 25), 133 ($PhSi_2{}^+$, 7), 183 (Ph_2SiH^+, 81), 210 ($Ph_2Si_2{}^+$, 9), 240 ($Ph_2Si_3H^+$, 8), 259 (Ph_3Si^+, 86), 266 ($Ph_2Si_4{}^+$, 28), 287 ($Ph_3Si_2{}^+$, 10), 316 ($Ph_3Si_3H^+$, 10), 343 ($Ph_3Si_4{}^+$, 33), 372 ($Ph_3Si_5H^+$, 5), 421 ($Ph_4Si_4H^+$, 30), 450 ($Ph_4Si_5H_2{}^+$, 13), 526 ($Ph_5Si_5H^+$, 3), 634 ($Ph_6Si_6H_4{}^+$, 1), 636 ($Ph_6Si_6H_6{}^+$, 1). IR (KBr): ν_{Si-H} 2109, 916 cm^{-1}.

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Supporting Information Available: Tables of crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles for **2** (7 pages). Ordering information is given on any current masthead page.

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(41) In the analogous polymerization reactions, the metallocene dichloride dihydrochlorides $Cp^N{}_2MCl_2 \cdot 2HCl$ (**4**, **5**) show nearly the same productivities as the nonprotonated metallocene dichlorides $Cp^N{}_2MCl_2$ (**2**, **3**).

(42) Molecular weights and molecular weight destributions were determined by BASF AG (Ludwigshafen, Germany).