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

Peter Jutzi*, Thomas Redeker, Beate Neumann, and Hans-Georg Stammler

Fakultät für Chemie der Universität Bielefeld,
Universitätsstraße 25, D-33615 Bielefeld, Germany
Telefax: (internat.) +49(0)521/1066146

Received June 26, 1996

Key Words: Substituted metallocene complexes / *N*-Functionalized cyclopentadienyl ligands / Ethylene polymerization / Dehydrocupling of phenylsilane

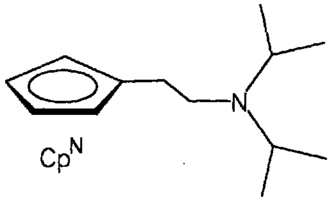
Mixed bent sandwich titanium(IV) complexes containing the donor-substituted [2-(diisopropylamino)ethyl]cyclopentadienyl ($C_5H_4CH_2CH_2N\textit{i}Pr_2 \equiv Cp^N$) ligand are described. The highly moisture-sensitive metallocene dichloride ($C_5H_4CH_2CH_2NN\textit{i}Pr_2$)($C_5H_4SiMe_3$)$TiCl_2$ (**1**) was synthesized by reaction of Cp^NLi with Cp^STiCl_3 ($Cp^S \equiv C_5H_4SiMe_3$). Complex **1** reacts with one equivalent of HCl with protonation of the amino group to give the air- and water-stable metallocene dichloride-hydrochloride $[(C_5H_4CH_2CH_2N(H)\textit{i}Pr_2)(C_5H_4SiMe_3)TiCl_2]^+Cl^-$ (**2**). The structure of **2** was determined by a single-crystal X-ray diffraction study. Compounds **1** and **2** are precursors for ethylene polymerization catalysts. The reaction of **2** with one equivalent of $Na^+B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$ afforded the borate $[(C_5H_4CH_2CH_2N(H)\textit{i}Pr_2)(C_5H_4SiMe_3)TiCl_2]^+B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$ (**3**). The dimethyl compound ($C_5H_4CH_2CH_2N\textit{i}Pr_2$)($C_5H_4SiMe_3$)$TiMe_2$ (**4**) was obtained by reaction of **1** with two equivalents of methyllithium. The diphenoxy complex ($C_5H_4CH_2CH_2N\textit{i}Pr_2$)($C_5H_4SiMe_3$)$Ti(OPh)_2$ (**5**) was prepared analogously with a stoichiometric amount of lithium phenoxide. Compounds **4** and **5** show remarkable activity in the catalytic dehydrocoupling of phenylsilane.

Introduction

The chemistry of donor-functionalized cyclopentadienyl systems is a rapidly growing area for various reasons[1–13]. Under appropriate conditions, the donor atom can coordinate reversibly to the metal center in addition to the cyclopentadienyl system and temporarily block a vacant coordination site. Furthermore, enhanced water solubility may be achieved by quaternization of the amino group in the side chain[3c,d,5].

Very recently, we introduced the [2-(diisopropylamino)ethyl]cyclopentadienyl ligand ($Cp^N \equiv C_5H_4CH_2CH_2N\textit{i}Pr_2$, Figure 1) into the chemistry of titanium and zirconium by synthesizing the bent sandwich complexes $Cp^N_2MR_2$ and $Cp^N_2MCl_2 \times 2$ HCl (M = Ti, Zr)[1a].

Figure 1. The [2-(diisopropylamino)ethyl]cyclopentadienyl ligand



Some of the chemical and physical properties of these compounds are changed dramatically from those of the nonfunctionalized species. The metallocene dichlorides and also the hydrochlorides are excellent precatalysts in the polymerization of ethylene. The alkyl and alkoxy derivatives catalyze the dehydrogenative coupling of phenylsilane to oligosilanes.

In an extension of our studies, we now report on the synthesis of mixed bent sandwich titanium complexes of the type $Cp^NCp^STiR_2$ ($Cp^S = C_5H_4SiMe_3$) with only one diisopropylaminoethyl-substituted cyclopentadienyl ligand (Cp^N). Special emphasis is placed on the catalytic activity of such compounds as precursors in homogeneous Ziegler-Natta ethylene polymerization[14] and in the dehydrocoupling of phenylsilane[15].

Results

I. Syntheses

Treatment of a solution of Cp^STiCl_3 in toluene with a suspension of one equivalent of Cp^NLi in ether leads to the formation of the desired metallocene dichloride ($C_5H_4CH_2CH_2N\textit{i}Pr_2$)($C_5H_4SiMe_3$)$TiCl_2$ (**1**), which can be isolated as an amorphous, orange-red solid in 53% yield (Scheme 1).

Complex **1** shows excellent solubility in polar solvents such as THF and only moderate solubility in nonpolar solvents such as benzene. An amorphous solid of **1** precipitates immediately from a concentrated benzene solution. This solid can only scarcely be redissolved. It is a coordination polymer and not a decomposition product[16]. However, in dilute solution a complete characterization of **1** is possible. ^{1}H-NMR spectroscopy indicates the presence of monomeric species (vide infra). In contrast to the non-donor-

Scheme 1. Synthesis of the *N*-functionalized titanocene dichloride **1**, *N*-protonated titanocene dichloride-hydrochloride **2** and *N*-functionalized titanocenedichloride-borate **3**

$$(C_5H_4CH_2CH_2N\textit{i}Pr_2)Li \xrightarrow[\text{toluene/Et}_2\text{O}]{(C_5H_4SiMe_3)TiCl_3} \underset{\mathbf{1}}{(C_5H_4CH_2CH_2N\textit{i}Pr_2)(C_5H_4SiMe_3)TiCl_2}$$

$$\mathbf{1} \xrightarrow[CH_3OH]{HCl} \underset{\mathbf{2}}{[(C_5H_4CH_2CH_2N(H)\textit{i}Pr_2)(C_5H_4SiMe_3)TiCl_2]^+\ Cl^-}$$

$$\mathbf{2} \xrightarrow[R' = 3,5\text{-}(CF_3)_2C_6H_3]{1\ NaBR'_4,\ Et_2O} \underset{\mathbf{3}}{[(C_5H_4CH_2CH_2N(H)\textit{i}Pr_2)(C_5H_4SiMe_3)TiCl_2]^+\ BR'^-_4}$$

functionalized metallocene dichlorides Cp_2TiCl_2[17] and $CpCp^STiCl_2$[18], **1** is extremely moisture-sensitive. Reaction takes place in protic solvents such as methanol or water, and *N*-protonated species of unknown composition are formed.

The complex Cp^NCp^STiCl (**1**) reacts with one equivalent of hydrogen chloride dissolved in methanol with protonation of the amino group to give the titanocene dichloride-hydrochloride $[(C_5H_4CH_2CH_2N(H)\textit{i}Pr_2)(C_5H_4SiMe_3)TiCl_2]^+\ Cl^-$ (**2**) as a red, amorphous solid in high yield (Scheme 1). Crystallization of the hydrochloride **2** from a CH_2Cl_2/toluene solution affords deep red crystals, which are hygroscopic. It is remarkable that, in contrast to the metallocene dichloride **1**, the hydrochloride **2** is stable against air and moisture. Compound **2** is very soluble in polar solvents such as methanol, dimethyl sulfoxide, acetonitrile, and even in water, where it is stable for several hours of exposure; it is insoluble in nonpolar solvents.

Compound **2** reacts with one equivalent of $Na^+B[3,5\text{-}CF_3)_2C_6H_3]_4^-$ in diethyl ether to give in high yield the borate $[(C_5H_4CH_2CH_2N(H)\textit{i}Pr_2)(C_5H_4SiMe_3)TiCl_2]^+B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$ (**3**) (Scheme 1). Compound **3** is an amorphous, hygroscopic, red solid, which is very soluble in polar solvents such as diethyl ether, chloroform and dimethyl sulfoxide and remarkably soluble in benzene. The stability of **3** against air and moisture is comparable to that of the hydrochloride **2**.

The dimethyl titanium compound $(C_5H_4CH_2CH_2N\textit{i}Pr_2)(C_5H_4SiMe_3)TiMe_2$ (**4**) is obtained in nearly quantitative yield by the reaction of **1** with two equivalents of methyllithium in diethyl ether (Scheme 2)[19].

Scheme 2. Synthesis of the *N*-functionalized dimethyltitanocene **4** from **1** and *N*-functionalized dimethyltitanocene **4** from **2**

$$\mathbf{1} \xrightarrow[Et_2O]{2\ MeLi} \underset{\mathbf{4}}{(C_5H_4CH_2CH_2N\textit{i}Pr_2)(C_5H_4SiMe_3)TiMe_2}$$

$$\mathbf{2} \overset{3\ MeLi,\ Et_2O}{\underset{3\ HCl,\ CH_3OH}{\rightleftarrows}} \underset{\mathbf{4}}{(C_5H_4CH_2CH_2N\textit{i}Pr_2)(C_5H_4SiMe_3)TiMe_2}$$

Complex **4** is a moisture-sensitive, yellow oil with a characteristic odor; it shows a good solubility in polar and nonpolar aprotic solvents such as THF or hexane. The thermal stability of **4** is remarkable. In contrast to the temperature- and light-sensitive complex Cp_2TiMe_2[20], for which an autocatalytic, "catastrophic" decomposition is reported, no decomposition was observed after several days under inert gas at room temperature. The dimethyl compound **4** is also formed by the reaction of **2** with three equivalents of methyllithium in diethyl ether (Scheme 2). The first equivalent of methyllithium deprotonates the *N*-function to generate the metallocene dichloride **1**, which reacts with the further two equivalents of methyllithium to form the dimethyl compound **4**.

Treatment of the dimethyl complex **4** with three equivalents of HCl dissolved in methanol affords the metallocene dichloride-hydrochloride **2** in quantitative yield[21] (Scheme 2). After the evolution of two equivalents of methane and the intermediate formation of the metallocene dichloride **1**, the protonation of the *N*-function in the side chain of the Cp^N ligand leads to the formation of the metallocene dichloride-hydrochloride **2**. No decomposition products were observed.

Treatment of a toluene solution of **1** with two equivalents of lithium phenoxide affords the diphenoxy derivative $(C_5H_4CH_2CH_2N\textit{i}Pr_2)(C_5H_4SiMe_3)Ti(OPh)_2$ (**5**) in excellent yield (Scheme 3).

Scheme 3. Synthesis of the *N*-functionalized titanocenediphenoxide **5**

$$\mathbf{1} \xrightarrow[\text{toluene/benzene}]{2\ PhOLi} \underset{\mathbf{5}}{(C_5H_4CH_2CH_2N\textit{i}Pr_2)(C_5H_4SiMe_3)Ti(OPh)_2}$$

Compound **5** can be isolated as an orange oil which is very soluble in aromatic organic solvents. In contrast to the parent complex $Cp_2Ti(OPh)_2$[22], **5** could not be crystallized.

Compounds **1**–**5** were characterized by ^1H-, ^{13}C-NMR and MS data and by elemental analysis.

II. NMR Spectra

The NMR spectra of **1**–**5** are in agreement with metallocene-type structures with two different pentahapto-bonded monosubstituted cyclopentadienyl ligands, as shown in Figure 2.

In the ^1H-NMR spectra of **1**–**5** (see Table 1), a pair of two pseudotriplets (AA'BB' pattern) is observed for the hydrogen atoms of each cyclopentadienyl ring. The methylene proton signals of the side chain of the Cp^N ligand appear as two multiplets, the signals of the isopropyl group are observed as a multiplet and a doublet. In the spectra of hydrochloride **2** and borate **3**, the methyl signals of the isopropyl groups appear as two doublets. The methyl proton signals of the trimethylsilyl group of the Cp^S ligand appear as a singlet.

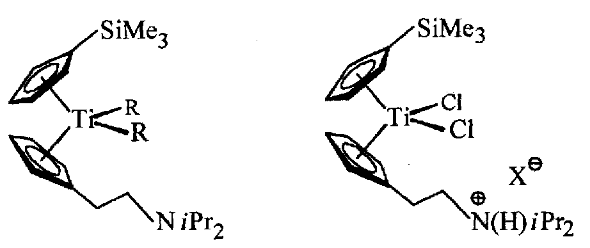
Noncoordination of the diisopropylaminoethyl function in solution can be assumed for the complexes $Cp^NCp^STiR_2$

Table 1. ^{1}H-NMR data of the new complexes **1**–**5**

	C_5H_4[a]	$CpCH_2$	CH_2N	$C\mathit{H}CH_3$	$CHC\mathit{H}_3$	$SiCH_3$[b]
1[c]	5.75, 6.13 (^3J = 2.6 Hz)	2.61	2.93	2.93	0.89	0.30
	5.98, 6.46 (^3J = 2.3 Hz)	(m, 2 H)	(m, 2 H)	(m, 2 H)	(d, 12 H, ^3J = 5.5 Hz)	
2[d]	6.23, 6.42 (^3J = 2.6 Hz)	3.50	3.50	3.64	1.41, 1.49	0.21
	6.61, 6.85 (^3J = 2.3 Hz)	(m, 2 H)	(m, 2 H)[e]	(m, 2 H)	(2 d, 12 H, ^3J = 6.6 Hz)	
3[d]	5.99, 6.47 (^3J = 2.7 Hz)	3.36	3.45	3.82	1.28, 1.35	0.05
	6.63, 6.87 (^3J = 2.3 Hz)	(m, 4 H)	(m, 4 H)[f]	(m, 4 H)	(2 d, 12 H, ^3J = 6.7/ 6.8Hz)	
4[c]	5.38, 5.84 (^3J = 2.6 Hz)	2.69	2.77	2.99	0.99	0.10
	5.98, 6.05 (^3J = 2.4 Hz)	(m, 2 H)	(m, 2 H)	(m, 2 H)	(d, 12 H, ^3J = 6.5 Hz)	
5[c]	5.83, 5.99 (^3J = 2.6 Hz)	2.45	2.53	2.84	0.85	0.21
	5.92, 6.41 (^3J = 2.5 Hz)	(m, 4 H)	(m, 4 H)	(m, 4 H)	(d, 12 H, ^3J = 6.6 Hz)	

[a] 2 t, 4H. – [b] s, 9H. – [c] Measured in C_6D_6. – [d] Measured in $CDCl_3$. – [e] The proton resonance for the NH group in the solvent $CDCl_3$ appears as a broad singlet at δ = 11.2. – [f] The proton resonance for the N–H group in the solvent $CDCl_3$ appears as a broad singlet at δ = 7.28.

Figure 2. Mixed bent sandwich titanium complexes of the type $Cp^NCp^STiR_2$ and $Cp^NCp^STiCl_2$ × HX



$Cp^NCp^STiR_2$ (**1,4,5**)

R = Cl, Me, PhO

$Cp^NCp^STiCl_2$ x HX (**2,3**)

X = Cl, B[3,5-$(CF_3)_2C_6H_3]_4$

(R = Cl **1**, Me **4**, OPh **5**). The signal due to the methyl protons of the diisopropyl group is observed at ca. δ = 0.90. The two multiplets for the methylene protons appear in the range δ = 2.4–2.9. The ring-proton signals are observed in the range δ = 5.4–6.5. These values are nearly identical with those of the diisopropylaminoethyl-substituted cyclopentadiene $C_5H_5CH_2CH_2N\mathit{i}Pr_2$[1a].

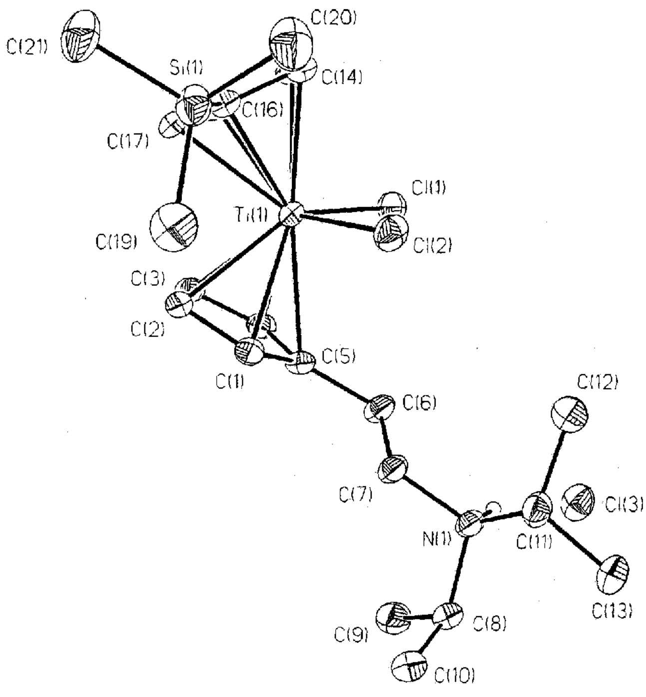
In contrast, the protonated amino function in $Cp^NCp^STiCl_2$ × HCl (**2**) and $Cp^NCp^STiCl_2$ × HB[3,5-$(CF_3)_2C_6H_3]_4$ (**3**) causes a significant change of the ^{1}H-NMR shifts. All signals of the Cp^N ligand in **2** and **3** show a remarkable downfield shift compared to all other complexes (see Table 1). Now the signal of the methyl groups of the isopropyl group is observed in the range δ = 1.11–1.49. The two multiplets for the methylene protons appear in the range δ = 3.3–3.6. The ring-proton signals are observed in the range δ = 6.0–6.9.

The signals of the TiMe groups in $Cp^NCp^STiMe_2$ (**4**) appear as expected as a singlet at δ = 0.12. This chemical shift value is very similar to that of the complexes $Cp^N_2TiMe_2$[1a] and Cp_2TiMe_2[20]. The signals of the hydrogen atoms of the phenoxy groups in $Cp^NCp^STiOPh_2$ (**5**) show only small shift differences compared to those of the compounds $Cp^N_2TiOPh_2$[1a] and Cp_2TiOPh_2[22]. The ^{13}C-NMR data of all compounds show features consistent with the proposed structures (see Experimental).

III. X-ray Crystal Structure Analysis of 2

Suitable crystals of **2** were obtained by crystallization from CH_2Cl_2/toluene. A single-crystal X-ray diffraction study established the expected bent-metallocene type structure. The molecular structure and selected bond lengths and angles are shown in Figure 3.

Figure 3. Crystal structure of **2**; the thermal ellipsoids are drawn at the 50% probability level; the hydrogen atoms attached to the carbon atoms and the toluene molecule in the unit cell are omitted for clarity; selected bond lengths [A] and angles [°]: Ti(1)–Cl(1) 2.3856(14), Ti(1)–Cl(2) 2.3595(14), Ti(1)–Cp^N(centroid) 2.062, Ti(1)–Cp^S(centroid) 2.062, C(5)–C(6) 1.505(4), C(7)–N(1) 1.508(3), N(1)–C(8) 1.527(3), N(1)–H 0.883; Cp^N(centroid)–Ti–Cp^S(centroid) 131.0, Cl(2)–Ti–Cl(1) 94.25



Compound **2** forms monomeric units with a protonated *N*-function in the side chain. The refined *N*–H distance is 0.88(3) Å. The two chlorine atoms together with the centroids of the cyclopentadienyl rings form a considerably distorted tetrahedral coordination geometry around the titanium center with angles ranging from 94.25(5)° (Cl–Ti–Cl') to 131.0° [(Cp)centroid–Ti–(Cp')centroid, see Table 2]. The nearly planar cyclopentadienyl rings are in a staggered conformation. The diisopropylaminoethyl group is arranged at the open side of the sandwich. The trimethylsilyl substituent is arranged in a lateral position. This orientation minimizes the steric interaction of the trimethylsilyl group with the chlorine atoms and with the other cyclopentadienyl ring. As displayed in Table 2 all other average bond parameters for $Cp^NCp^STiCl_2 \times HCl$ (**2**) are within the range established for the complexes $Cp_2^NTiCl_2$[1a] and Cp_2TiCl_2[23].

Table 2. Molecular parameters for $Cp^NCp^STiCl_2 \times HCl$ (**2**), $Cp_2^NTiCl_2$[1a] and Cp_2TiCl_2[23]

Compound	Ti–Cl [Å]	Cl–Ti–Cl [°]	Cp–Ti [Å]	Cp–Ti–Cp [°]
$Cp^NCp^STiCl_2 \times HCl$ (**2**)	2.3595(14) 2.3856(14)	94.25(5)	2.062	131.0
$Cp^N{}_2TiCl_2$[1a]	2.3682(11)	94.40(5)	2.062	132.6
Cp_2TiCl_2[23]	2.364(2)	94.53(6)	2.059	130.97

This demonstrates that the different substitution pattern of the Cp rings in $Cp^NCp^STiCl_2 \times HCl$ (**2**) and $Cp_2^NTiCl_2$[1a] does not significantly affect the basic molecular structure.

IV. Ethylene Polymerization and Phenylsilane Dehydrocoupling

The titanocene dichloride $Cp^NCp^STiCl_2$ **1** and the hydrochloride $Cp^NCp^STiCl_2 \times HCl$ **2** are catalyst precursors for the polymerization of ethylene. In the reaction of the complexes **1** and **2** with 500 equiv. of methylalumoxane (MAO) in toluene the solution turns immediately yellow, which corresponds to the color of the dimethyl compound $Cp^NCp^STiMe_2$ (**4**) in this solvent. This is in agreement with the assumption that MAO acts first as a methylating agent to form the dimethyl compound as intermediate. The further equivalents of MAO abstract one methyl group by forming cationic species, which are the active catalyst system. In the case of the metallocene dichloride-hydrochloride **2**, one equivalent is needed as a deprotonating agent to form the metallocene dichloride **1** as intermediate. The further reaction affording the active catalytic species is analogus to that described above. The reaction mixture was stirred at ambient temperature and ethylene (atmospheric pressure) was bubbled through the solution. An HCl/MeOH mixture was added to terminate the polymerization reaction. The efficiency 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 activities of the catalytic precursors **1** and **2** are comparable to those of the metallocene derivatives $Cp_2^STiCl_2$[14d], $Cp_2^NTiCl_2$[1a] and $Cp_2^NTiCl_2 \times 2\ HCl$[1a].

High catalytic activity in the dehydrocoupling of phenylsilane was observed for the complexes $Cp^NCp^STiMe_2$ (**4**) and $Cp^NCp^STi(OPh)_2$ (**5**). Reaction of these complexes with phenylsilane at room temperature under inert gas over a period of several days leads to the production of oligophenylsilane in excellent yields (75%). The polymer products were recovered by filtration of the reaction solution through a Florisil column, followed by vacuum evaporation of the solvent. The oligophenylsilanes thus obtained are extremely viscous oils.

The oligophenylsilanes synthesized by **4** and **5** exhibit analytical data similar to those described in the literature[1a,15,24]. The ^{1}H-NMR spectra show broad, unresolved signals in the range $\delta = 4.5$ to 5.7, and the ^{29}Si-NMR spectra signals are in the range $\delta = -51$ to -68. The characteristic ν_{SiH} and δ_{SiH} bands are observed at 2090–2120 cm^{-1} and 912–918 cm^{-1}, respectively. The mass spectra show fragments of linear and cyclic oligomers up to the parent ion of the heptamer[25]. The amounts of linear, cyclic and branched oligomers have not yet been determined. A detailed analysis of the oligomers will be the subject of further investigations.

Discussion

Some of the chemical and physical properties of mixed bent sandwich complexes of the type $Cp^NCp^STiR_2$ are changed dramatically compared to those of the nonfunctionalized species.

$Cp^NCp^STiCl_2$ (**1**) is extremely moisture-sensitive. This is due to the base function of the amino group which supports the hydrolysis process by trapping the liberated hydrogen chloride. Furthermore, the solubility of **1** in nonpolar solvents is decreased dramatically in comparison with that of the parent titanocene derivative Cp_2TiCl_2.

In sharp contrast to the dichloride **1**, the hydrochloride **2** shows excellent solubility and stability in polar protic solvents such as methanol and water. Hydrolysis of the M–Cl bonds was not observed, even after exposure for several hours. This phenomenon can be explained by a kind of "intramolecular buffer function" of the protonated amino group[26]. These exceptional properties are of special interest with regard to the organometallic chemistry in water[27].

The additional functionality in **1** and **2** obviously does not reduce their catalytic activity. First attempts to use these compounds in the polymerization of ethylene have been successful (see IV. Polymerization Reactions). The activities of the catalytic precursors $Cp^NCp^STiCl_2$ (**1**) and $Cp^NCp^STiCl_2 \times HCl$ (**2**) are comparable to those of the metallocene derivatives $Cp_2^STiCl_2$[14d], $Cp_2^NTiCl_2$[1a] and $Cp_2^NTiCl_2 \times 2\ HCl$[1a]. Because of their easy handling due to their exceptional stability, the hydrochloride **2** is particularly suitable for application in this kind of catalysis. Mechanistic studies are in progress concerning coordination of the *N*-function during various steps of the catalytic process to stabilize the intermediate cationic species.

Similarly, the additional functionality in **4** and **5** obviously does not reduce the catalytic activity in the dehydrocoupling of phenylsilane (see IV. Dehydrocoupling

Reactions). These compounds catalyze the dehydrogenative coupling of phenylsilane, furnishing oligosilanes in excellent yields. The analytical data obtained are very similar to those for the oligophenylsilanes synthesized with the complexes Cp_2TiR_2[15] and $Cp_2^NTiR_2$[1a] as catalysts. Mechanistic studies concerning the influence of the additional amino function in this kind of catalysis will also be the subject of further investigations.

The financial support of the *Fonds der Chemischen Industrie* (fellowship for T.R.) is gratefully acknowledged. The authors thank the *BASF AG* for the polyethylene analysis and for the gift of ethylene. We further thank the *Witco GmbH* for valuable gifts of MAO.

Experimental

General: All experiments were carried out under dried, oxygen-free argon 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 and 500.1 MHz) and $^{13}C\{^1H\}$(75.5 and 125.8 MHz) NMR spectra: Bruker AM 300 and a Bruker Avance DRX 500 spectrometer. Chemical shifts for ^1H and $^{13}C\{^1H\}$ spectra were recorded in ppm downfield from TMS and referenced with internal deuteriochloroform, deuteriobenzene, deuteriomethanol, deuterium oxide and deuteriodimethyl sulfoxide. – Mass spectra: VG AutoSpec instrument. Only characteristic fragments and isotopes of the highest abundance are listed. – Melting points: Büchi 510 melting point apparatus, sealed capillaries, uncorrected values. – Elemental analyses were carried out by Analytisches Labor der Fakultät für Chemie, Bielefeld.

Materials: $(C_5H_4SiMe_3)TiCl_3$[28] and $NaB[3,5\text{-}(CF_3)_2C_6H_3]_4)$[29] were prepared as described in the literature.

$(C_5H_4CH_2CH_2NiPr_2)(C_5H_4SiMe_3)TiCl_2$ (**1**): To a solution of 1.00 g (3.43 mmol) of $(C_5H_4SiMe_3)TiCl_3$ in 40 ml of toluene cooled to −30 °C, a suspension of 3.43 mmol of Cp^NLi in 20 ml of diethyl ether [prepared by addition of 2.14 ml (3.43 mmol) of *n*-butyllithium (1.6 M in *n*-hexane) to a solution of 0.66 g (3.43 mmol) of Cp^NH in diethyl ether] was added dropwise with stirring. The color of the solution changed immediately from yellow to deep red. The reaction mixture was allowed to warm to room temperature within 1 h and stirred for an additional 5 h. The solution was filtered and the solvent was removed in vacuo. The residue was washed with 2 × 20 ml of cold pentane (−30 °C), leaving **1** as an orange-red solid. – M.p.: 170 °C (dec.). – Yield 0.82 g (53%). – ^1H NMR (C_6D_6): $\delta = 0.30$ (s, 9H, $SiCH_3$), 0.89 (d, $J = 5.5$ Hz, 12H, $\mathrm{CHC}H_3$), 2.61 (m, 2H, $\mathrm{CpC}H_2$), 2.93 (m, 4H, NCH_2, $\mathrm{C}H\mathrm{CH}_3$), 5.74, 5.97, 6.12, 6.46 (4 m, 8H, Cp*H*). – ^{13}C NMR (C_6D_6): $\delta = 0.10$ ($SiCH_3$), 20.9 ($\mathrm{CH}C\mathrm{H}_3$), 32.8 ($\mathrm{Cp}C\mathrm{H}_2$), 45.5 (CH_2N), 47.9 ($C\mathrm{HCH}_3$), 113.8, 119.2, 124.5, 128.5, 130.1 (Cp*C*). – ^{29}Si NMR (C_6D_6): $\delta = -6.80$ ($SiCH_3$). – MS [CI; *m/z* (%)]: 448 (0.5) [M + 1H$^+$], 413 (1) [M − Cl$^+$], 377 (5) [M − 2 Cl$^+$], 178 (3) [$Cp^N - CH_3^+$], 114 (100) [$(iC_3H_7)_2NCH_2^+$]. – $C_{21}H_{35}Cl_2NTiSi$ (448.38): calcd. C 56.25, H 7.86, N 3.12; found C 56.34, H 7.48, N 2.41.

$[(C_5H_4CH_2CH_2N(H)iPr_2)(C_5H_4SiMe_3)TiCl_2]^+ Cl^-$ (**2**): Compound **1** (350 mg, 0.73 mmol) was dissolved in 10 ml of MeOH (saturated with HCl gas) and then stirred for ca. 30 min. The solution was concentrated in vacuo. The residue was washed with 2 × 20 ml diethyl ether, leaving **2** as a red, amorphous, hygroscopic solid. Yield: 300 mg (85%). The product was crystallized from a CH_2Cl_2/toluene mixture as red crystals. – M.p.: 163 °C (dec.). – ^1H NMR (CD_3OD): $\delta = 0.25$ (s, 9H, $SiCH_3$), 1.40, 1.41 (2 d, $J = 6.6$ Hz, 12H, $\mathrm{CHC}H_3$), 3.30 (m, 2H, $\mathrm{CpC}H_2$), 3.60 (m, 2H, NCH_2), 3.77 (m, 2H, $\mathrm{C}H\mathrm{CH}_3$), 6.36 (t, $J = 2.7$ Hz, 2H, Cp*H*), 6.71 (t, $J = 2.5$ Hz, 2H, Cp*H*), 6.76 (t, $J = 2.5$ Hz, 2H,Cp*H*), 6.93 (t, $J = 2.5$ Hz, 2H, Cp*H*). – ^1H NMR ($CDCl_3$): $\delta = 0.21$ (s, 9H, $SiCH_3$), 1.41, 1.49 (2 d, $J = 6.6$ Hz, 12H, $\mathrm{CHC}H_3$), 3.50 (m, 4H, $\mathrm{CpC}H_2$, NCH_2), 3.64 (m, 2H, $\mathrm{C}H\mathrm{CH}_3$), 6.23 (t, $J = 2.6$ Hz, 2H, Cp*H*), 6.42 (t, $J = 2.6$ Hz, 2H, Cp*H*), 6.61 (t, $J = 2.3$ Hz, 2H, Cp*H*), 6.85 (t, $J = 2.6$ Hz, 2H, Cp*H*), 11.2 (br. m, 1H, NH). – ^1H NMR: (D_2O): $\delta = 0.00$ (s, 9H, $SiCH_3$), 1.11, 1.12 [2 d (t), $J = 6.0$, 5.5 Hz, 12H, $\mathrm{CHC}H_3$], 2.67 (m, 2H, $\mathrm{CpC}H_2$), 3.05 (m, 2H, NCH_2), 3.51 (m, 2H, $\mathrm{C}H\mathrm{CH}_3$), 6.24 (m, 2H, Cp*H*), 6.42 (m, 4H, Cp*H*), 6.92 (m, 2H, Cp*H*). – ^{13}C NMR (CD_3OD): $\delta = 0.0$ ($SiCH_3$), 17.4, 19.0 ($\mathrm{CH}C\mathrm{H}_3$), 29.2 ($\mathrm{Cp}C\mathrm{H}_2$), 47.6 (CH_2N), 56.7 ($C\mathrm{HCH}_3$), 114.7, 122.4, 126.5, 130.1, 131.9, 134.7 (Cp*C*). – ^{29}Si NMR (CD_3OD): $\delta = -6.09$ ($SiCH_3$). – $C_{21}H_{36}Cl_3NTiSi$ (484.84): calcd. C 52.02, H 7.48, N 2.88; found C 51.11, H 7.78, N 3.16.

$[(C_5H_4CH_2CH_2N(H)iPr_2)(C_5H_4SiMe_3)TiCl_2]^+ B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$ (**3**): A solution of 780 mg (0.88 mmol) of $Na^+B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$ in 10 ml of diethyl ether was added dropwise with stirring at room temperature to a suspension of 430 mg (0.89 mmol) of **2** in 30 ml of diethyl ether. The reaction mixture was stirred for 5 h. The solution was filtered and the residue was washed with 10 ml of diethyl ether. The combined ethereal phases were concentrated in vacuo, leaving **3** as a red solid. – M.p.: 103–105 °C (dec.). – Yield 1.11 g (96%). – ^1H NMR ($CDCl_3$): $\delta = 0.24$ (s, 9H, $SiCH_3$), 1.28, 1.35 (2 d, $J = 6.7$, 6.8 Hz, 12H, $\mathrm{CHC}H_3$), 3.36 (m, 2H, $\mathrm{CpC}H_2$), 3.45 (m, 2H, NCH_2), 3.82 (m, 2H, $\mathrm{C}H\mathrm{CH}_3$), 5.99 (t, $J = 2.7$ Hz, 2H, Cp*H*), 6.47 (t, $J = 2.7$ Hz, 2H, Cp*H*), 6.63 (t, $J = 2.3$ Hz, 2H, Cp*H*), 6.87 (t, $J = 2.3$ Hz, 2H, Cp*H*), 7.28 (s, br., 1H, NH), 7.51 (s, br., 4H, *para*-phenyl *H*), 7.67 (s, br., 8H, *ortho*-phenyl *H*). – ^1H NMR ([D_6]DMSO): $\delta = 0.20$ (s, 9H, $SiCH_3$), 1.27, 1.28 [2 d (t), $J = 5.9$, 5.7 Hz, 12H, $\mathrm{CH\text{-}C}H_3$], 3.11 (m, 2H, $\mathrm{CpC}H_2$), 3.35 (m, 2H, NCH_2), 3.63 (m, 2H, $\mathrm{C}H\mathrm{CH}_3$), 6.40 (m, 2H, Cp*H*), 6.83 (m, 4H, Cp*H*), 6.97 (m, 2H, Cp*H*), 7.00 (s, br., 8H, *ortho*-phenyl H), 7.67 (s, br., 4H, *para*-phenyl H), 8.79 (s, br., 1H, NH). – ^{13}C NMR ($CDCl_3$): $\delta = -0.40$ ($SiCH_3$), 18.1 ($\mathrm{CH}C\mathrm{H}_3$), 24.2 ($\mathrm{Cp}C\mathrm{H}_2$), 44.0 (CH_2N), 55.0 ($C\mathrm{HCH}_3$), 111.8, 121.9, 126.3, 129.8, 130.4, 135.5 (Cp*C*), 117.9 (*p*-*C*), 129.1 (q, $J_{C\text{-}F} = 26.0$ Hz, *m*-C), 124.5 (q, $J_{C\text{-}F} = 273$ Hz, CF_3), 135.2 (*o*-C), 161.6 (q, $J_{C\text{-}F} = 50$ Hz, *i*-C). – ^{29}Si NMR ($CDCl_3$): $\delta = -3.80$ ($SiCH_3$). – $C_{53}H_{48}NBCl_2F_{24}SiTi$ (1312.614): calcd. C 48.49, H 3.68, N 1.06; found C 47.64, H 4.10, N 1.10.

$(C_5H_4CH_2CH_2NiPr_2)(C_5H_4SiMe_3)TiMe_2$ (**4**)

(a) From $(C_5H_4CH_2CH_2NiPr_2)(C_5H_4SiMe_3)TiCl_2$ (**1**): MeLi (1.55 M in diethyl ether; 1.30 ml, 2.00 mmol) was added dropwise with stirring at −90 °C to a suspension of 450 mg (1.00 mmol) of **1** in 40 ml of diethyl ether. The reaction mixture was allowed to warm slowly to −20 °C. After the solvent of the yellow solution had been removed in vacuo, the residue was extracted with 40 ml of hexane. The extract was filtered and the solvent was removed in vacuo, leaving **4** as a yellow oil. Yield 392 mg (96%).

(b) From $[(C_5H_4CH_2CH_2N(H)iPr_2)(C_5H_4SiMe_3)TiCl]^+ Cl^-$ (**2**): Analogous procedure with three equivalents of MeLi as described above for **1**. Yield 94%. ^1H NMR (C_6D_6): $\delta = 0.10$ (s, 9H, $SiCH_3$), 0.12 (s, 6H, $TiCH_3$), 0.99 (d, $J = 6.5$ Hz, 12H, $\mathrm{CHC}H_3$), 2.69 (m, 2H, $\mathrm{CpC}H_2$), 2.77 (m, 2H, NCH_2), 2.99 (m, 2H, $\mathrm{C}H\mathrm{CH}_3$), 5.38 (t, $J = 2.6$ Hz, 2H, Cp*H*), 5.84 (t, $J = 2.6$ Hz, 2H, Cp*H*), 5.98 (t, $J = 2.4$ Hz, 2H, Cp*H*), 6.05 (t, $J = 2.4$ Hz, 2H, Cp*H*). – ^{13}C NMR (C_6D_6): $\delta = 0.1$ ($SiCH_3$), 21.1 ($\mathrm{CH}C\mathrm{H}_3$), 33.8 ($\mathrm{Cp}C\mathrm{H}_2$), 45.7 ($TiCH_3$), 47.4 (CH_2N), 48.7 ($C\mathrm{HCH}_3$), 110.4, 115.5, 117.1, 120.1, 129.4 (Cp*C*). – ^{29}Si NMR (C_6D_6): $\delta = -7.3$ ($SiCH_3$).

– MS [CI; *m/z* (%)]: 392 (3) $[M - CH_3^+]$, 377 (64) $[M^+ - 2\,CH_3]$, 114 (100) $[(iC_3H_7)_2NCH_2^+]$. $C_{23}H_{41}NSiTi$ (407.55): calcd. C 67.78, H 10.13, N 3.43; found C 67.46, H 10.30, N 3.46.

$(C_5H_4CH_2CH_2NiPr_2)(C_5H_4SiMe_3)Ti(OPh)_2$ (**5**): PhOLi (4.24 mmol) in 20 ml of benzene [prepared by addition of 2.85 ml (4.24 mmol) of *n*-butyllithium (1.49 M in *n*-hexane) to a solution of 0.39 g (4.24 mmol) of phenol in benzene] was added dropwise with stirring to a suspension of 0.95 g (2.12 mmol) of **1** in 30 ml of toluene cooled to −30°C. The reaction mixture was allowed to warm to room temperature within 4 h and then stirred for 14 h. The solution was filtered and the solvent was removed in vacuo, leaving **5** as an orange-colored oil. Yield 1.01 g (85%). – ^1H NMR (C_6D_6): δ = 0.21 (s, 9H, $SiCH_3$), 0.85 (d, J = 6.6 Hz, 12H, $CHCH_3$), 2.45 (m, 2H, $CpCH_2$), 2.53 (m, 2H, NCH_2), 2.84 (m, 2H, $CHCH_3$), 5.83 (t, J = 2.6 Hz, 2H, Cp*H*), 5.92 (t, J = 2.5 Hz, 2H, Cp*H*), 5.99 (t, J = 2.6 Hz, 2H, Cp*H*), 6.41 (t, J = 2.5 Hz, 2H, Cp*H*), 6.86 (m, 6H, *ortho-* and *para*-PhH), 7.11 (t, J = 7.4 Hz, 4H, *meta*-PhH). – ^{13}C NMR (C_6D_6): δ = −0.30 ($SiCH_3$), 21.0 ($CHCH_3$), 32.4 ($CpCH_2$), 45.7 (CH_2N), 48.4 ($CHCH_3$), 113.1, 119.2, 123.3, 129.6, 130.5, 137.8 (Cp*C*), 115.6 (*ortho*-PhC), 118.6 (*para*-PhC), 129.4 (*meta*-PhC), 170.7 (Ph*C*). – ^{29}Si NMR (C_6D_6): δ = −7.24 ($SiCH_3$). – MS [CI; *m/z* (%)]: 564 (1) $[M + 1H^+]$, 471 (1) $[M - PhO^+]$, 378 (1) $[M - 2\,PhO^+]$, 114 (52) $[(iC_3H_7)_2NCH_2^+]$, 95 (27) $[C_6H_7O^+]$, 73 (8) $[SiMe_3^+]$. $C_{33}H_{45}NO_2TiSi$ (563.69): calcd. C 70.31, H 8.04, N 2.48; found C 69.69, H 8.38, N 2.15.

Polymerization Studies: Ethylene (BASF AG) was used without further purification. Methylalumoxane (MAO) was obtained from Witco, (Bergkamen, Germany) as a 10 wt.-% toluene solution (4.9% wt.-% aluminium, 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 ethylene.

Ethylene Polymerization Studies

(a) With $(C_5H_4CH_2CH_2NiPR_2)(C_5H_4SiMe_3)TiCl_2$ (**1**): MAO (10.9 ml, 18.1 mmol) was added under ethylene to 16.2 mg (36.1 μmol) of **1** in 10 ml of toluene. After 2 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. Yield 0.90 g; productivity: 12 kg **PE** $([M][C_2H_4]h)^{-1}$; M_w: 15237; M_N: 5185; M_W/M_N: 2.9[30], [η] (dl/g) 0.38.

(b) With $[(C_5H_4CH_2CH_2N(H)iPr_2)(C_5H_4SiMe_3)TiCl_2]^+\ Cl^-$ (**2**): MAO (25 ml, 42 mmol) was added under ethylene to 38.0 mg (84.7 μmol) of **2** in 20 ml of toluene. After 3.13 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. Yield 3.6 g; productivity: 14 kg **PE** $([M][C_2H_4]h)^{-1}$; M_w: 24163; M_N: 7601; M_W/M_N: 3.2[30], [η] (dl/g) 0.34.

Phenylsilane Polymerization Studies:

(a) With $(C_5H_4CH_2CH_2NiPr_2)(C_5H_4SiMe_3)TiMe_2$ (**4**): Phenylsilane (2.38 g, 21.7 mmol) was added under argon to 126 mg (0.31 mmol) of **4** in 5 ml of toluene. Evolution of gas commenced. After 3 d at room temperature the solution was filtered through a column of Florisil. The polymer was recovered by elution with 40 ml of toluene followed by vacuum evaporation of the eluent. The product was obtained as a colorless, extremely viscous liquid. Yield 1.66 g (70%). – ^1H NMR (C_6D_6): 4.49–5.70 (m, (PhSi*H*), 6.80–7.95 (m, Ph*H*). – ^{29}Si NMR (C_6D_6): −51.4–(−62.3). MS [EI; *m/z* (%)]: 105 (100) $[PhSi^+]$, 106 (33) $[PhSiH^+]$, 107 (30) $[PhSiH_2^+]$, 133 (4) $[PhSi_2^+]$, 183 (2) $[Ph_2SiH^+]$, 210 (13) $[Ph_2Si_2^+]$, 240 (5) $[Ph_2Si_3H^+]$, 259 (39) $[Ph_3Si^+]$, 266 (6) $[Ph_2Si_4^+]$, 287 (7) $[Ph_3Si_2^+]$, 315 (4) $[Ph_3Si_3^+]$, 343 (8) $[Ph_3Si_4^+]$, 372 (4) $[Ph_3Si_5H^+]$, 421 (6) $[Ph_4Si_4H^+]$, 450 (7) $[Ph_4Si_5H_2^+]$, 636 (4) $[Ph_6Si_6H_6^+]$, 741 (1) $[Ph_7Si_7H_6^+]$. – IR (KBr): $\tilde{\nu}_{Si\text{-}H}$ = 2087.3, 912 cm^{-1}.

(b) With $(C_5H_4CH_2CH_2NiPr_2)(C_5H_4SiMe_3)Ti(OPh)_2$ (**5**): Phenylsilane (848 mg, 8.07 mmol) was added under argon to 65.0 mg (115 μmol) of **5** in 10 ml of toluene. Evolution of gas commenced. After 3 d at room temperature the solution was applied to a column of Florisil. The polymer was recovered by elution with 20 ml of toluene followed by vacuum evaporation of the eluent. The product was obtained as a colorless, extremely viscous liquid. Yield 490 mg (75%). – ^1H NMR (C_6D_6): 4.49–5.20 (m, (PhSi*H*), 6.90–7.80 (m, Ph*H*). – ^{29}Si NMR (C_6D_6): −59–(−68). – MS [EI, *m/z* (%)]: 105 (100) $[PhSi^+]$, 106 (52) $[PhSiH^+]$, 107 (34) $[PhSiH_2^+]$, 133 (6) $[PhSi_2^+]$, 183 (97) $[Ph_2SiH^+]$, 210 (25) $[Ph_2Si_2^+]$, 240 (15) $[Ph_2Si_3H^+]$, 259 (82) $[Ph_3Si^+]$, 266 (5) $[Ph_2Si_4^+]$, 287 (22) $[Ph_3Si_2^+]$, 316 (15) $[Ph_3Si_3H^+]$, 343 (6) $[Ph_3Si_4^+]$, 376 (5) $[Ph_3Si_5H_5^+]$, 421 (6) $[Ph_4Si_4H^+]$, 453 (12) $[Ph_4Si_5H_5^+]$, 636 (1) $[Ph_6Si_6H_6^+]$. – IR: $\tilde{\nu}_{Si\text{-}H}$ = 2122, 918 cm^{-1}.

Crystal-Structure Determination[31] *of* **2**·toluene: Empirical formula: $C_{28}H_{44}Cl_3NSiTi$; molecular mass: 576.98; crystal size: 1.00 × 0.40 × 0.10 mm; crystal color: red; crystal system: triclinic; space group: $P\bar{1}$; a = 7.603(4) Å, b = 13.053(5) Å, c = 16.60(1) Å; α = 109.91(3)°; β = 94.84(4)°; γ = 98.03(4)°; V = 1517.9(13) $Å^3$; Z = 2; $d_{calcd.}$ = 1.262 g/cm^3; μ = 0.603 mm^{-1}; radiation: Mo-K_α (λ = 0.71073 Å), $F(000)$ = 612; diffractometer: Siemens $P2_1$; scan type: ω; temperature: 173 K; $2\Theta_{max}$ = 55°; absorption correction: none; reflections collected 7492 ($+h$, $\pm k$, $\pm l$); independent reflections: 6968 (R_{int} = 0.0342); all non-hydrogen atoms were refined anisotropically, H(1) refined isotropically, hydrogen atoms of methyl groups refined with idealized geometry with $U_{(eq)} = 1.5\ U_{(eq)}$ of the corresponding C atom, other hydrogen atoms refined at calculated positions using a riding model with $U_{(eq)\,=\,1.2}U_{(eq)}$; parameters refined: 319; structure solution: direct methods; R_F = 0.0464 for 4762 reflections with $I > 2\sigma I$; wR_F^2 = 1183 for all data (6965 reflections); $w = [1/\sigma^2(F_o^2) + (0.0572\ P)^2]$ where $P = (F_o^2 + 2\ F_c^2)/3$; largest difference peak and hole: 0.4 and −0.4 $e/Å^3$; programs: Siemens SHELXTL plus/SHELXL-93.

---

[1] [1a] P. Jutzi, T. Redeker, B. Neumann, H.-G. Stammler, *Organometallics* **1996** in press. – [1b] P. Jutzi, J. Dahlhaus, M. Bangel, *J. Organomet. Chem.* **1993**, *460*, C13. – [1c] P. Jutzi, M. O. Kristen, J. Dahlhaus, B. Neumann, H.-G. Stammler, *Organometallics* **1993**, *12*, 2980. – [1d] P. Jutzi, J. Dahlhaus, M.-O. Kristen, *J. Organomet. Chem.* **1993**, *450*, C1.

[2] [2a] J. Dahlhaus, P. Jutzi, M. Bangel, *J. Organomet. Chem.* **1993**, *474*, 55. – see also reviews[2b] P. Jutzi, J. Dahlhaus, *J. Coord. Chem. Rev.* **1994**, *137*, 179. – [2c] P. Jutzi, U. Siemeling, *J. Organomet. Chem.* **1995**, *500*, 175 and references cited therein.

[3] [3a] J. Jutzi, M. Bangel, *J. Organomet. Chem.* **1994**, *480*, C18. – [3b] P. Jutzi, M. O. Kristen, B. Neumann, H.-G. Stammler, *Organometallics* **1994**, *13*, 3854. – [3c] P. Jutzi, J. Kleimeier, *J. Organomet. Chem.* **1995**, *486*, 287. – [3d] P. Jutzi, T. Redeker, B. Neumann, H.-G. Stammler, *J. Organomet. Chem.* **1995**, *498*, 127. – [3e] P. Jutzi, J. Kleimcier, T. Redeker, B. Neumann, H.-G. Stammler, *J. Organomet. Chem.* **1995**, 498.

[4] [4a] M. D. Fryzuk, S. S. H. Mao, M. J. Zarvorotko, L. R. Mac Gillivray, *J. Am. Chem. Soc.* **1993**, *115*, 5336. – [4b] J. C. Flores, J. W. C. Chien, M. D. Rausch, *Organometallics* **1994**, *13*, 4140. – [4c] W. A. Herrmann, M. J. A. Morawietz, T. Priermeier, K. Mashima, *J. Organomet. Chem.* **1995**, 291. – [4d] M. D. Fryzuk, S. S. H. Mao, P. B. Duval, S. J. Rettig, *Polyhedron* **1995**, *14*, 11. – [4e] Y. Mu, W. E. Piers, L. R. Mac Gillivray, M. J. Zarvorotko, *Polyhedron* **1995**, *14*, 1. – [4f] S. Barry, A. Kucht, H. Kucht, M. D. Rausch, *J. Organomet. Chem.* **1995**, *489*, 195. – [4g] K.-H. Thiele, Ch. Schließburg, B. Neumüller, *Z. anorg. allg. Chem.* **1995**, *621*, 1106. – [4h] K. A. Butakoff, D. A. Lemenovskii, P.

Mountford, L. G. Kuz'mina, A. V. Churakov, *Polyhedron* **1995**, *15*, 489. – [4i] M. Enders, R. Rudolph, H. Pritzkow, *Chem. Ber.* **1996**, *129*, 459.

[5] A. Avey, T. J. R. Weakley, D. R. Tyler, *J. Am. Chem. Soc.* **1993**, *115*, 7706.

[6] T.-F. Wang, Y.-S. Wen, *J. Organomet. Chem.* **1992**, *439*, 155.

[7] W. A. Herrmann, R. Anwander, F. C. Munck, W. Scherer, *Chem. Ber.* **1993**, *126*, 331.

[8] [8a] T.-F. Wang, T.-Y. Lee, Y.-S. Wen, L.-K. Lin, *J. Organomet. Chem.* **1991**, *403*, 353. – [8b] T.-F. Wang, T.-Y. Lee, J.-W. Chou, C.-W. Ong, *J. Organomet. Chem.* **1992**, *423*, 31.

[9] [9a] J. Okuda, *Chem. Ber.* **1990**, *123*, 1649. – [9b] J. Okuda, K. E. du Plooy, W. Massa, H.-C. Kang, U. Rose, *Chem. Ber.* **1996**, *129*, 275.

[10] U. Böhme, K.-H. Thiele, *J. Organomet. Chem.* **1994**, *472*, 39.

[11] P. J. Shapiro, E. Bunel, W. P. Schäfer, J. E. Bercaw, *Organometallics* **1990**, *9*, 867.

[12] [12a] J. C. Leblanc, C. Moïse, A. Maisonnat, R. Poilblanc, C. Charrier, F. Mathey, *J. Organomet. Chem.* **1982**, *231*, C43. – [12b] D. M. Bensley Jr., E. A. Mintz, *J. Organomet. Chem.* **1988**, *353*, 93. – [12c] T. J. Clark, T. A. Nile, D. McPhail, A. McPhail, *Polyhedron* **1989**, *8*, 1804. – [12d] J. Szymoniak, J. Besançon, A. Dormond, C. Moïse, *J. Org. Chem.* **1990**, *55*, 1429. – [12e] M. Ogasa, D. T. Mallin, D. W. Macomber, M. D. Rausch, R. D. Rogers, A. N. Rollins, *J. Organomet. Chem.* **1991**, *405*, 41. – [12f] R. Fandos, A. Meetsma, J. H. Teuben, *Organometallics* **1991**, *10*, 59. – [12g] G. Erker, R. Aul, *Chem. Ber.* **1991**, *124*, 1301. – [12h] D. A. Laske, R. Duchateau, J. H. Teuben, *J. Organomet. Chem.* **1993**, *462*, 149. – [12i] R. T. Kettenbach, W. Bonrath, H. Butenschön, *Chem. Ber.* **1993**, *126*, 1657. – [12j] T. Cuenca, J. C. Flores, P. J. Rayo, *J. Organomet. Chem.* **1993**, *462*, 191. – [12k] H. G. Alt, J. S. Han, U. Thewalt, *J. Organomet. Chem.* **1993**, *456*, 89. – [12l] J. Okuda, *Comments Inorg. Chem.* **1994**, *16*, 185. – [12m] A. H. Cowley, C. S. King, A. Decken, *Organometallics* **1995**, *14*, 20. – [12n] J. Okuda, K. E. du Plooy, P. J. Foscano, *J. Organomet. Chem.* **1995**, *495*, 195. – [12o] J. Christoffers, R. G. Bergman, *Angew. Chem.* **1995**, *107*, 2423. – [12p] R. E. v. H. Spence, W. E. Piers, *Organometallics* **1995**, *14*, 4617. – [12q] J. Foerstner, R. Kettenbach, R. Goddard, H. Butenschön, *Chem. Ber.* **1996**, *129*, 319.

[13] [13a] C. Charrier, F. Mathey, *J. Organomet. Chem.* **1979**, *170*, C41. – [13b] Q. Huang, Y. Qian, *Synthesis* **1987**, 910. – [13c] J. Okuda, K. H. Zimmermann, *J. Organomet. Chem.* **1988**, *344*, C1. – [13d] J. Okuda, K. H. Zimmermann, *Chem. Ber.* **1989**, *122*, 1645. – [13e] H. Lehmkuhl, J. Näser, G. Mehler, T. Keil, F. Danowski, R. Benn, R. Mynott, G. Schroth, B. Gabor, C. Krüger, P. Betz, *Chem. Ber.* **1991**, *124*, 441. – [13f] J. Okuda, K. H. Zimmermann, *Chem. Ber.* **1992**, *125*, 637. – [13g] U. Siemeling, *J. Chem. Soc., Chem. Commun.* **1992**, 1335. – [13h] Y. N. C. Chan, G. S. W. Craig, R. R. Schrock, R. E. Cohen, *Chem. Mater.* **1992**, *4*, 885. – [13i] U. Siemeling, *J. Organomet. Chem.* **1992**, *429*, C14. – [13j] M. Lin, K. A. Fallis, G. A. Anderson, N. P. Rath, M. Y. Chiang, *J. Am. Chem. Soc.* **1992**, *114*, 4687. – [13k] U. Siemeling, B. Neumann, H.-G. Stammler, *Chem. Ber.* **1993**, *126*, 1311. – [13l] U. Siemeling, G. Hüffmann, *J. Organomet. Chem.* **1994**, *475*, 229. – [13m] U. Siemeling, U. Vorfeld, B. Neumann, H.-G. Stammler, *Chem. Ber.* **1995**, *128*, 481. – [13n] U. Siemeling, *Chem. Ber.* **1995**, *128*, 1135.

[14] See reviews and references cited therein[14a] H. Sinn, W. Kaminsky, *Adv. Org. Chem.* **1980**, *18*, 99. – [14b] M. Bochmann, *Nachr. Chem. Tech. Lab.* **1993**, *41*, 1220. – [14c] J. Okuda, *Nachr. Chem. Tech. Lab.* **1993**, *41*, 8. – [14d] P. C. Möhring, N. J. Coville, *J. Organomet. Chem.* **1994**, *479*, 1. – [14e] H.-H. Brintzinger, D. Fischer, R. Mühlhaupt, B. Rieger, R. Waymouth, *Angew. Chem.* **1995**, *107*, 1255. – [14f] M. Bochmann, *J. Chem. Soc. Dalton Trans.* **1996**, 255.

[15] [15a] C. Aitken, J. F. Harrod, E. Samuel, *J. Organomet. Chem.* **1985**, *279*, C11. – [15b] C. Aitken, J. F. Harrod, E. Samuel, *Can. J. Chem.* **1986**, *64*, 1677. – [15c] R. West, *J. Organomet. Chem.* **1986**, *300*, 327. – [15d] C. Aitken, J. F. Harrod, U. S. Gill, *Can. J. Chem.* **1987**, *65*, 1804. – [15e] C. Aitken, J.-P. Barry, F. Gauvin, J. F. Harrod, A. Malek, D. Rousseau, *Organometallics* **1989**, *8*, 1732. – [15f] T. D. Tilley, *Comments Inorg. Chem.* **1990**, *10*, 37. – [15g] Y. Mu, C. Aitken, B. Cote, J. F. Harrod, E. Samuel, *Can. J. Chem.* **1991**, *69*, 264. – [15h] J. P. Banovetz, K. M. Stein, R. M. Waymouth, *Organometallics* **1991**, *10*, 3430. – [15i] E. Hengge, M. Weinberger, *J. Organomet. Chem.* **1992**, *433*, 21. – [15j] T. D. Tilley, *Acc. Chem. Res.* **1993**, *26*, 22. – [15k] E. Hengge, M. Weinberger, *J. Organomet. Chem.* **1993**, *443*, 167. – [15l] T. Imori, R. H. Heyn, T. D. Tilley, A. L. Rheingold, *J. Organomet. Chem.* **1995**, *493*, 83. – [15m] S. Bourg, R. J. P. Corriu, M. Enders, J. J. E. Moreau, *Organometallics* **1995**, *14*, 564.

[16] This could be proved by the reaction of the solid with hydrochloric acid dissolved in methanol. The polymer structure was destroyed and the protonation of the *N*-function results in the formation of the monomeric metallocene dichloride hydrochloride **2** in nearly quantitative yield.

[17] G. Wilkinson, J. M. Birmingham, *J. Am. Chem. Soc.* **1954**, *76*, 4281.

[18] K. C. Ott, E. J. deBoer, R. H. Grubbs, *Organometallics* **1984**, *3*, 223.

[19] The diphenyl complex $Cp^{N}Cp^{S}TiPh_2$ can be obtained analogously by the reaction of **1** with two equivalents of phenyllithium in diethyl ether. The ^{1}H- and ^{13}C-NMR spectra show the presence of biphenyl (8%), which could not be removed.

[20] [20a] K. Clauss, H. Bestian, *Liebigs Ann. Chem.* **1962**, *654*, 8. – [20b] U. Thewalt, T. Wöhrle, *J. Organomet. Chem.* **1994**, *464*, C17. – [20c] F. N. Tebbe, G. W. Parshall, G. S. Reddy, *J. Am. Chem. Soc.* **1978**, *100*, 3611.

[21] This reaction is not described in the experimental section.

[22] K. Andrä, *J. Organomet. Chem.* **1968**, *11*, 567.

[23] A. Clearfield, D. K. Warner, C. H. Saladarriaga-Molina, R. Ropal, I. Bernal, *Can. J. Chem.* **1975**, *53*, 1622.

[24] R. N. Kniseley, V. A. Fassel, E. E. Conrad, *Spectrochim. Acta* **1959**, 651.

[25] With the spectrometer used, only fragments $m/z < 1000$ could be detected.

[26] The nucleophilic attack of the hydroxide anion is probably the first step in the decomposition process of the dichloride **1**. In the case of the hydrochloride **2** the protonated amino group can function as an intramolecular buffer.

[27] W. A. Herrmann, C. W. Kohlpainter, *Angew. Chem.* **1993**, *105*, 1588.

[28] P. Jutzi, M. Kuhn, *J. Organomet. Chem.* **1979**, *173*, 221.

[29] M. Brookhart, B. Grant, A. F. Volpe Jr., *Organometallics* **1992**, *11*, 3920.

[30] Molecular weights and molecular weight destributions were determined by the BASF AG (Ludwigshafen).

[31] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405754, the names of the authors, and the journal citation.

[96128]