Metallacyclodisiladiazanes of Titanium and Zirconium; Synthesis, Structure and Polymerization Studies

Felix Jäger, Herbert W. Roesky*, Hendrik Dorn, Syed Shah, Mathias Noltemeyer, and Hans-Georg Schmidt

Institut für Anorganische Chemie der Universität Göttingen,
Tammannstraße 4, D-37077 Göttingen, Germany

Received October 10, 1996

Keywords: Disilylamides / Group 4 complexes / Polymerization / Metallacycles / Titanium / Zirconium

A series of metallacyclodisiladiazanes has been prepared. Lithiated $(SiMe_2NH\mathit{t}Bu)_2$ (**1**) reacts with $TiCl_4 \cdot 2$ THF to give $(SiMe_2N\mathit{t}Bu)_2TiCl_2$ (**4**). Methylation or fluorination of **4** leads to $(SiMe_2N\mathit{t}Bu)_2TiMe_2$ (**8**) and $(SiMe_2N\mathit{t}Bu)_2TiF_2$ (**9**), respectively. The reaction of $ZrCl_4 \cdot 2$ THF with lithiated **1** or $[SiMe_2NH(4\text{-}FC_6H_4)]_2$ (**2**) yields $(SiMe_2N\mathit{t}Bu)_2ZrCl_2$ (**5**) and $[SiMe_2N(4\text{-}FC_6H_4)]_2ZrCl_2 \cdot$ THF (**7**), respectively. The lithiated ligand $[SiMe_2NH(2,6\text{-}\mathit{i}Pr_2C_6H_3)]_2$ (**3**) reacts with noncoordinated $ZrCl_4$ to give $[SiMe_2N(2,6\text{-}\mathit{i}Pr_2C_6H_3)]_2ZrCl_2$ (**6**). X-ray structural analysis of **9** showed it to be a fluorine-bridged dimer in the solid state. Compounds **4**, **6**, **8** and **9** were found to be catalysts for the polymerization of ethylene.

At present, the industrial synthesis of polyethylene and polypropylene is carried out using catalysts of the Ziegler-Natta type. However, contemporary research in the area of polymerization catalysts is mainly concerned with the utilization of chiral metallocenes. Most of these catalytically active metallocenes have the same basic structure, consisting of two η^5-bonded cyclopentadienyl rings and two halide or alkyl ligands around a group-4 metal atom.

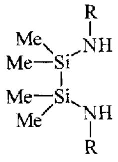
ansa-Metallocenes[1] and metallocenes with a silylamido-substituted cyclopentadienyl ligand[2] were created to optimize the stereospecific properties of the catalytic systems. These metallocenes, together with methylalumoxane (MAO) as cocatalyst, are able to catalyse the synthesis of isotactic polypropylene[3–5].

In 1991, the Exxon Chemical company patented catalysts for the production of isotactic polypropylene based on bis(amido) transition metal compounds of group 4[6]. In this group of compounds the cyclopentadienyl ring is replaced by a second silylamido group. An example is the complex bis[bis(trimethylsilyl)amido]zirconium dichloride which was first synthesized by Andersen[7]. Unlike the familiar propylene polymerization catalysts, this complex has freely rotating amino groups. Since it is desirable for olefin polymerization catalysts to have a rigid ligand system, our aim was to bridge the two silylamido groups of the Andersen-type compound.

Results

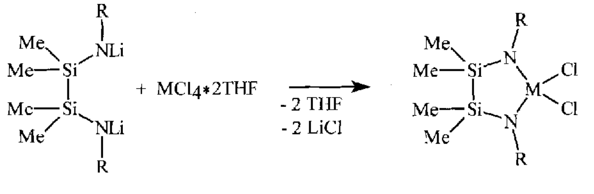
The ligand we employed for the preparation of the more rigid systems was first prepared by Wannagat et al.[8] (Figure 1).

Figure 1. The chelating ligand 1,2-dialkylaminotetramethyldisilane; **1**: R = *t*Bu; **2**: R = $4\text{-}FC_6H_4$; **3**: R = $2,6\text{-}\mathit{i}Pr_2C_6H_3$



To date, only complexes of boron, tin and lead have been prepared using derivatives of this disilylamide[9–11]. In these investigations the compound 1,2-bis(*tert*-butylamino)tetramethyldisilane **1** has proven to be the best reagent, due to its thermal stability which is probably a consequence of the sterically demanding *t*Bu groups. **1** was prepared by the smoothly-proceeding reaction of $\mathit{t}BuNH_2$ with 1,2-dichlorotetramethyldisilane. The novel ligand, 1,2-bis(4-fluorophenylamino)tetramethyldisilane **2**, was prepared analogously using 4-fluoroaniline with triethylamine as a base. 1,2-Bis(2,6-diisopropylphenylamino)tetramethyldisilane **3** could not be prepared by the same route. Instead, the lithium salt of 2,6-diisopropylaniline[12] was generated and then allowed to react with 1,2-dichlorotetramethyldisilane. With these ligands we prepared a series of bridged bis(silylamido) complexes of the group 4 metals (Scheme 1).

Scheme 1. Syntheses of **4**, **5**, **6** and **7**; **4**: M = Ti, R = *t*Bu; **5**: M = Zr, R = *t*Bu; **6**: M = Zr, R = $2,6\text{-}\mathit{i}Pr_2C_6H_3$; **7**: M = Zr, R = $4\text{-}FC_6H_4$



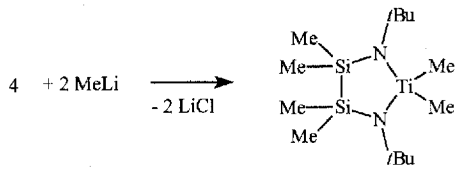
These complexes were prepared by salt-elimination reactions using the metal tetrachloride THF-adducts and the lithiated silylamides, with the exception of complex **6**, which was prepared using noncoordinated $ZrCl_4$. Complex **7** crystallized with one coordinating molecule of THF. Titanium complex **4** was obtained as a yellow microcrystalline material in low yield from *n*-hexane. It was found to be moisture-sensitive and decomposed in air leading to black products.

Only in the case (R = *t*Bu) was a well-defined titanium chloride product obtained. With ligand **2** (with the smaller aryl group R = $4-FC_6H_4$) the spirocyclic compound was formed as well. This is in agreement with the investigations of Bürger et al.[13–15], who prepared a series of spirotitanacyclopentanes with *N*-methylated silylamides. After the reaction of lithiated ligand **2** with $TiCl_4 \cdot 2$ THF, separation of the monosubstituted complex from the disubstituted complex was not possible.

The zirconium compounds **5**, **6** and **7** are less moisture-sensitive and were obtained as white solids by crystallization from toluene. The coordinating THF could be stripped-off from **5** by vacuum sublimation, but this was not possible for complex **7**.

From titanium chloride complex **4** we were able to prepare the methyl derivative **8** and the fluorinated complex **9**. Complex **8** was obtained by treating **4** with two molar equivalents of methyllithium (Scheme 2). It was found to be very soluble in organic solvents and crystallized as white needles from *n*-pentane at −90 °C.

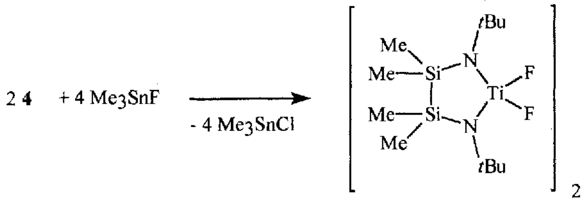
Scheme 2. Synthesis of **8**



8

The fluorinated complex **9** was prepared by using Me_3SnF as fluorinating agent (Scheme 3). This new fluorination method was developed by Roesky et al.[16].

Scheme 3. Synthesis of **9**

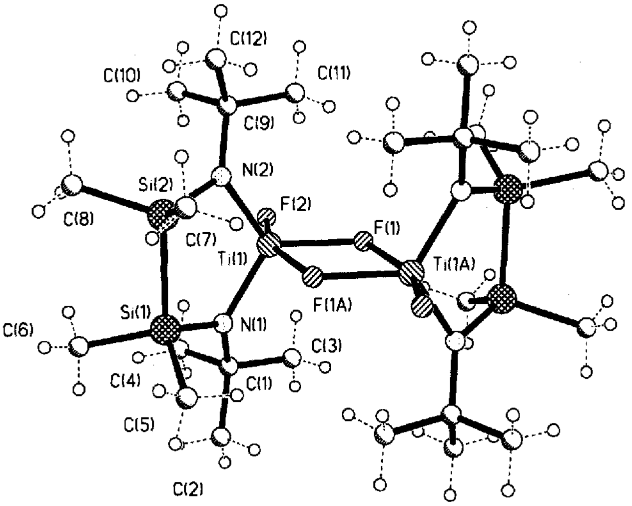


9

Attempts to apply these reactions to the analogous zirconium complexes according to Schemes 2 and 3 were unsuccessful. The compounds showed poor reactivity compared to their titanium counterparts.

From complexes **5** and **9** we were able to obtain single crystals suitable for X-ray structural analysis (Figure 2). Complex **5** crystallized with one coordinating molecule of THF. However, we were unable to perform a satisfactory refinement of its structure because THF is very disordered in the crystal.

Figure 2. Molecular structure of $[(SiMe_2NtBu)_2TiF_2]_2$ (**9**)



Complex **9** has a dimeric structure in the solid state. Both metal atoms are bridged by two fluorine atoms, thereby forming a distorted four-membered Ti_2F_2 ring. The Ti(1)−F(2) bond distance is 1.817 Å, which, as expected, is shorter than the bridging Ti(1)−F(1) bond (1.967 Å). These values are in agreement with those found for $[Cp^*TiF_3]_2$[17]. This compound is comparable to **9** having a similar dimeric structure bridged by two fluorine atoms. In this case the bridging Ti−F distance is 2.011 Å and the average value of the Ti−F distances of the terminal fluorines is 1.829 Å. In Table 1, selected bond lengths [Å] and angles [°] of **6** are given.

Table 1. Selected bond lengths and angles for $[(SiMe_2NtBu)_2TiF_2]_2$ (**9**)

Distances [Å]	Angles (°)
Ti(1)-F(2) 1.817(12)	N(1)-Ti(1)-N(2) 113.8(7)
Ti(1)-N(1) 1.880(12)	Si(1)-N(1)-Ti(1) 106.1(9)
Ti(1)-F(1) 1.967(11)	N(1)-Si(1)-Si(2) 103.1(6)
Si(1)-Si(2) 2.380(10)	Si(2)-N(2)-Ti(1) 106.3(9)
	N(2)-Si(2)-Si(1) 102.3(6)
	F(1)-Ti(1)-F(1)#1 70.4(5)
	Ti(1)-F(1)-Ti(1)#1 109.6(5)

On the basis of ^{19}F NMR evidence, **9**, like Cp^*TiF_3, exists as a monomer in solution. The spectrum shows only one sharp singlet at $\delta = 120.49$ ($\delta = 109.50$ for Cp^*TiF_3) which suggests that in solution only terminal fluorines are present.

Polymerization studies using the new compounds showed activity in the polymerization of ethylene. Compounds **4**, **8** and **9** catalysed the polymerization process at room temperature in the presence of approximately 800 molar equivalents of MAO. Complex **8** exhibited the highest activity of 10^5 g PE/(mol Ti · h · atm). The dichloride **4** showed only half the activity of **8** in catalytic polymerization, while the reaction with compound **9** led only to minor yields of polyethylene. Interestingly, the titanium compounds were more effective than the zirconium compounds, of which only complex **6** showed any catalytic activity. The results of all the polymerization experiments are collated in Table 2.

Table 2. Results of the polymerization using compounds **4**, **6**, **8** and **9**

Compound	4	6	8	9
yield PE [g]	0.40	0.02	1.50	0.10
activity [g PE/ (mol M•h•atm)]	45300	2290	101000	6900

Polymerization experiments with propylene resulted only in low yields of an oily liquid and further analysis was not undertaken.

Discussion

We have prepared a series of metallacyclodisiladiazanes of group 4 and have demonstrated their catalytic activity in polymerizing ethylene, but found them to be less effective than the established metallocene-type complexes, which have activities up to $3 \cdot 10^8$ g PE/(mol M · h · atm)[18]. To our surprise, we found a lower activity for the zirconium compounds than for the titanium compounds. This is in contrast to the behaviour of the known group-4 catalysts[19], in which the zirconium metallocenes normally have a higher activity than their titanium analogues.

The titanium compounds we prepared show the expected characteristics in their catalytic behaviour. Methylated compound **8** is a better catalyst than the halogenated derivatives. This is consistent with other homogeneous catalysts which are activated by methylalumoxane[20].

The low activity of fluorine compound **9** is difficult to judge because few group-4 fluorine complexes with which comparisons can be made are known. However, we are currently performing polymerization experiments with a series of new fluorine compounds so as to classify their properties. The first results show higher polymerization activities for the fluorine compounds, with smaller ratios of MAO, in comparison with the corresponding chlorine compounds[21].

At this point it is not possible to make a clear statement regarding the catalytic potential of this group of metallacyclodisiladiazanes. Obviously, the Cp derivatives have proven to be most suitable as homogeneous polymerization catalysts. They combine electronic and steric effects to give an ideal complex for polymerization catalysis[22].

Nevertheless, we believe that there is sufficient scope for optimizing the bridged and nonbridged bis(silylamido) complexes reported herein for possible applications. Although these compounds have been known for a long time, the Exxon patent shows the industrial interest in this class of compounds.

The high activity of the silylamido complexes is probably due to the electron-withdrawing effect of the silicon atom. The Lewis acidity of the central metal will be increased by the silicon atom pulling electron density through the nitrogen-metal bond. Therefore, it is this property of the silicon atom which can be considered as the driving force in ethylene polymerizations with these complexes. Besides this effect of lowering the electron density at the central metal, Bürger et al. found that the silicon atom has a stabilizing effect on the whole molecule[23]. In addition to their work on titanacyclopentanes[15–17], they also prepared a series of titanasilylamido cyclobutanes, e.g. $SiMe_2(N\textit{t}Bu)_2TiCl_2$. The authors varied the nitrogen bonded alkyl group, but only in the case of a trimethylsilyl group did they obtain a stable titanium complex which remained intact on sublimation.

We plan to investigate this "silicon effect" in the metallacyclodisiladiazanes. We anticipate that replacement of alkyl groups by trialkylsilyl groups will lead to greater stability as well as to enhanced polymerization activities.

We thank the *Deutsche Forschungsgemeinschaft* and the *Bundesministerium für Bildung und Forschung* for financial support of this work.

Experimental Section

All manipulations were performed under an inert atmosphere of dry nitrogen using Schlenk techniques or in a nitrogen glove box. Solvents were dried over sodium/potassium alloy and distilled prior to use. – NMR spectra were obtained with a Bruker AM 250 and were recorded in $[D_6]$benzene or in $CDCl_3$ with tetramethylsilane or $CFCl_3$ as external standard. EI mass spectra were measured on Finnigan MAT 8230 or Varian MAT CH 5 instruments. Infrared spectra were acquired on a Bio-Rad FTS-7. Elemental analyses were obtained from the Mikroanalytisches Labor Beller, Göttingen, Germany, or in our institute[24]. – 1,2-Dichlorotetramethyldisilane[25], 1,2-bis(*tert*-butylamino)tetramethyldisilane **1**[9], the lithium salt of 2,6-diisopropylaniline[12] and Me_3SnF[16] were synthesized according to literature methods.

Preparation of $[SiMe_2NH(4\text{-}FC_6H_4)]_2$ (**2**): 4-Fluoroaniline (23.74 g, 213.6 mmol) and triethylamine (21.60 g, 213.6 mmol) were dissolved in diethyl ether (1000 ml). Then, a solution of 1,2-dichlorotetramethyldisilane (20.00 g, 106.8 mmol) in diethyl ether (100 ml) was slowly added at room temperature. Immediately, a white precipitate was formed which was filtered off after 48 h of stirring. The diethyl ether was subsequently removed from the filtrate and the remaining yellow oil was distilled. At 135 °C (10^{-3} Torr) a slightly yellow liquid was collected which solidified after two days. Yield 20.59 g (61.2 mmol, 57%). – M.p. 42 °C. – ^1H NMR (250 MHz, $CDCl_3$): δ = 6.82–6.76 (m, 4H, Ph H), 6.58–6.44 (m, 4H, Ph H), 3.24 (s, 2H, NH), 0.28 [s, 12H, $Si(CH_3)_2$]. – $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 116.8 (s, NC), 116.7 (s, NC*C*), 115.7 (s, FC*C*), 114.9 (FC), –0.1 (s, SiC). – ^{19}F NMR (235 MHz, $CDCl_3$): δ = –128.14 (s, CF). – MS (70 eV); *m/z* (%): 336 (26) $[M^+]$, 168 (100) $[M^+/2]$. – $C_{16}H_{22}F_2N_2Si_2$ (336.5): calcd. C 57.11, H 6.59, F 11.29, N 8.32; found C 54.2, H 6.7, F 11.0, N 8.0.

Preparation of $[SiMe_2NH(2,6\text{-}iPr_2C_6H_3)]_2$ (**3**): 1,2-Dichlorotetramethyldisilane (5.40 g, 28.8 mmol) was added to lithiated 2,6-diisopropylaniline (10.57 g, 57.7 mmol) in diethyl ether (100 ml) at –40 °C. The mixture was warmed to room temperature and the diethyl ether was subsequently removed in vacuo. Then, *n*-hexane (100 ml) was added and the suspension was filtered. The solvent was removed once more and the residue was distilled. B.p. 149 °C (10^{-3} Torr). Yield 8.53 g (18.2 mmol, 66%). – ^1H NMR (250 MHz, $CDCl_3$): δ = 7.11–6.93 (m, 6H, Ph H), 3.24–3.43 [m, 4H, $C\textit{H}(CH_3)_2$], 2.39 (s, 2H, NH), 1.19 [d, *J* = 6.91 Hz, 24H, $CH(C\textit{H}_3)_2$], 0.11 [s, 12H, $Si(CH_3)_2$]. – ^{29}Si NMR (50 MHz, $CDCl_3$): δ = –7.7 [s, $\textit{Si}(CH_3)_2$]. – MS (70 eV); *m/z* (%): 468 (3)

[M$^+$], 162 (100). – $C_{28}H_{48}N_2Si_2$ (468.9): calcd. C 71.73, H 10.32, N 5.98, Si 11.98; found C 71.4, H 10.5, N 6.29, Si 11.4.

Preparation of $(SiMe_2NtBu)_2TiCl_2$ (**4**): 1,2-Bis(*tert*-butylamino)-tetramethyldisilane (7.00 g, 26.9 mmol) was lithiated in THF (300 ml) with a 2.5 M *n*BuLi solution (22.3 ml, 55.9 mmol) at room temperature. When gas evolution ceased this mixture was added dropwise to a solution of $TiCl_4 \cdot 2$ THF (8.99 g, 26.9 mmol) in THF (300 ml) at −92°C. The mixture was then warmed to room temperature and the solvent was removed in vacuo. The black, solid residue was dissolved in toluene (500 ml) and filtered. The toluene was removed and the precipitate was redissolved in *n*-hexane (200 ml). Subsequently, the solution was filtered again and the filtrate was reduced to a volume of 40 ml. Cooling at −32°C overnight afforded 1.90 g (5.0 mmol, 19%) of a yellow solid. – M.p. 180°C. – ^{1}H NMR (250 MHz, C_6D_6): δ = 1.45 (s, 18H, *t*Bu), 0.22 [s, 12H, $Si(CH_3)_2$]. – IR (Nujol, KBr): ν = 1467 cm^{-1} (s), 1363 (m), 975 (m), 800 (m), 503 (m), 414 (m). – MS (70 eV); *m/z* (%): 376 (5) [M$^+$], 319 (100) [M$^+$ – *t*Bu]. – $C_{12}H_{30}N_2Cl_2Si_2Ti$ (377.4): calcd. C 38.19, H 8.01, Cl 18.79, N 7.42; found C 37.7, H 8.1, Cl 17.2, N 7.5.

Preparation of $(SiMe_2NtBu)_2ZrCl_2$ (**5**): 1,2-Bis(*tert*-butylamino)-tetramethyldisilane (4.0 g, 15.4 mmol) was lithiated as in the preparation of **4**. This mixture was added dropwise to a solution of $ZrCl_4 \cdot 2$ THF (5.8 g, 15.4 mmol) in THF (60 ml) at −92°C. Subsequently, the mixture was warmed to room temperature and the solvent was removed in vacuo. The residue was then taken up in toluene (200 ml) and filtered through a layer of Celite. The toluene was removed again and the residue was washed using *n*-pentane (100 ml). Sublimation of the residue at 140°C (10^{-3} Torr) afforded 4.2 g of white crystals (10.0 mmol, 65%). – M.p. 233°C. – ^{1}H NMR (250 MHz, C_6D_6): δ = 1.42 (s, 18H, *t*Bu), 0.29 [s, 12H, $Si(CH_3)_2$]. – IR (Nujol, KBr): ν = 1466 cm^{-1} (s), 1186 (s), 1033 (w), 967 (s), 816 (s), 507 (w), 376 (w). – MS (70 eV); *m/z* (%): 420 (20) [M$^+$], 73 (100). – $C_{12}H_{30}Cl_2N_2Si_2Zr$ (420.7): calcd. C 34.26, H 7.19, Cl 16.86, N 6.66; found C 33.6, H 7.1, Cl 16.4, N 6.2.

Preparation of $[SiMe_2N(2,6\text{-}iPr_2C_6H_3)]_2ZrCl_2$ (**6**): **3** (5.89 g, 12.56 mmol) was lithiated in diethyl ether (50 ml) as in the preparation of **4**. This mixture was added dropwise to a solution of $ZrCl_4$ (2.85 g, 12.23 mmol) in diethyl ether (50 ml) at 0°C and stirred for 12 h to complete the reaction. Subsequently, the solvent was removed in vacuo and the residue was dissolved in toluene. The precipitated LiCl was filtered off and the filtrate was reduced in volume, whereupon white needles started to crystallize. After filtration and drying in vacuo, 5.59 g (8.92 mmol, 71%) of **8** was obtained. – M.p. 278°C (decomposition). – ^{1}H NMR (250 MHz, C_6D_6): δ = 7.19–7.03 (m, 6H, Ph H), 3.59 [sept, *J* = 6.80 Hz, 4H, $CH(CH_3)_2$], 1.36 [d, *J* = 6.75 Hz, 12H, $CH(CH_3)_2$], 1.26 [d, *J* = 6.82 Hz, 12H, $CH(CH_3)_2$], 0.23 [s, 12H, $Si(CH_3)_2$]. – IR (Nujol, KBr): ν = 1250 cm^{-1} (s), 1180 (s), 1107 (w), 904 (w), 775 (s), 579 (w), 353 (m). – MS (70 eV); *m/z* (%): 628 (100) [M$^+$], 585 (82) [M$^+$ – *i*Pr]. – $C_{28}H_{46}Cl_2N_2Si_2Zr$ (629.0): calcd. C 53.47, H 7.37, N 4.45, Si 8.93; found C 49.7, H 7.1, N 4.4, Si 8.0.

Preparation of $[SiMe_2N(4\text{-}FC_6H_4)]_2ZrCl_2 \cdot THF$ (**7**): **2** (3.0 g, 8.92 mmol) was lithiated in toluene (150 ml) with a 2.5 M solution of *n*BuLi (7.1 ml, 17.75 mmol) at room temperature. To this solution, $ZrCl_4 \cdot 2$ THF (3.4 g, 8.92 mmol) was added and the mixture was heated for 8 h. After cooling to room temperature, the LiCl was filtered off and the filtrate was reduced to a volume of 30 ml. Cooling overnight afforded 2.0 g (3.52 mmol, 39%) of white crystals. – M.p. 181°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.15–6.80 (m, 8H, Ph H), 3.80 (m, 4H, THF), 1.46 (m, 4H, THF), 0.25 [s, 12H, $Si(CH_3)_2$]. – ^{19}F NMR (235 MHz, $CDCl_3$): δ = −122.31 (s, PhF). – MS (70 eV); *m/z* (%): 497 (18) [M$^+$ – THF], 73 (100). – $C_{20}H_{28}Cl_2F_2N_2OSi_2Zr$ (568.8): calcd. C 42.24, H 4.96, Cl 12.47, N 4.93; found C 40.9, H 5.0, Cl 12.0, N 4.3.

Preparation of $(SiMe_2NtBu)_2TiMe_2$ (**8**): To a solution of **4** (1.00 g, 2.7 mmol) in diethyl ether (60 ml) was added a 1.6 M MeLi solution (3.3 ml, 5.3 mmol) at 0°C. The solution was warmed to room temperature and all volatiles were removed in vacuo. Subsequently, the residue was extracted with two 40 ml portions of *n*-hexane and the combined extracts were reduced to a volume of 10 ml. The yellow solution was cooled at −90°C overnight, whereupon light-green needles crystallized. Yield 0.34 g (10.1 mmol, 37%). – M.p. 100°C. – ^{1}H NMR (250 MHz, C_6D_6): δ = 1.60 (s, 18H, *t*Bu), 0.91 [s, 6H, $Ti(CH_3)_2$], 0.26 [s, 12H, $Si(CH_3)_2$]. – IR (Nujol, KBr): ν = 1360 cm^{-1} (m), 1186 (m), 997 (s), 815 (s), 520 (w). – MS (70 eV); *m/z* (%): 336 (8) [M$^+$], 130 (100). – $C_{14}H_{36}N_2Si_2Ti$ (336.5): calcd. C 49.97, H 10.78, N 8.32; found C 47.5, H 10.3, N 7.2.

Preparation of $(SiMe_2NtBu)_2TiF_2$ (**9**): **4** (0.25 g, 0.66 mmol) was stirred togehter with Me_3SnF (0.24 g, 1.32 mmol) in toluene (50 ml) at room temperature. After 24 h, all volatiles were removed in vacuo and the residue was washed with cold *n*-hexane (10 ml) leaving 0.17 g (0.55 mmol, 75%) of a bright-yellow powder. – M.p. 130°C. – ^{1}H NMR (250 MHz, C_6D_6): δ = 1.31 (s, 18H, *t*Bu), 0.24 [s, 12H, $Si(CH_3)_2$]. – ^{19}F NMR (235 MHz, C_6D_6): δ = 120.49 (s, TiF_2). – IR (Nujol, KBr): ν = 1467 cm^{-1} s, 1363 m, 1179 w, 975 m, 800 m, 503 m, 414 m. – MS (70 eV); *m/z* (%): 344 (8) [M$^+$], 312 (100) [M$^+$ – 2 CH_3]. – $C_{16}H_{30}F_2N_2Si_2Ti$ (344.5): calcd. C 41.84, H 8.78, F 11.03, N 8.13; found C 38.8, H 8.3, F 11.4, N 7.1.

General Procedure for Polymerization Reactions: A Schlenk flask (250 ml) was charged with toluene (140 ml) and saturated with bubbling ethylene (propylene) at a pressure of 1 atmosphere. At the same time, a 30% solution of MAO in toluene (5 ml, 27.20 mmol) was added via a syringe to a solution of 0.03 mmol of the compound in toluene (10 ml). After 10 min of prereaction, the catalyst was injected into the flask while the olefin was still bubbling through the solution. After 30 min, ethanol (10 ml), and subsequently hydrochloric acid (10 ml), were injected into the reactor to terminate the reaction. The polymer produced was filtered off, washed with water and ethanol and dried in vacuo for 12 h. – M.p. of polyethylene (all samples): 130°C. – $(C_2H_4)_n$ calcd. C 85.63, H 14.37; found C 84.5, H 14.4.

Table 3. Crystallographic data for **9**

formula	$C_{24}H_{60}F_4N_4Si_4Ti_2$
mol. mass	688.9
crystal size [mm]	0.80 × 0.80 × 0.50
cryst. system	triclinic
space group	*P*1bar
lattice constants	
a [Å]	11.030(2)
b [Å]	11.930(2)
c [Å]	15.559(3)
α [°]	79.71(1)
β [°]	73.42(1)
γ [°]	74.70(1)
Z	2
T [K]	153(2)
μ [mm^{-1}]	0.591
θ range [°]	3.56–22.54
largest diff. [e Å^{-3}] peak/hole	0.358/–0.310
no. of rflns. (measd.)	7843
no. of rflns. (indep.)	4866
R (int)	0.0141
*R*1 [*I* > 2σ(*I*)]	0.0257
*wR*2 (all data)	0.0718

X-ray Structure Determination of **5** *and* **9**: Crystal data for the structure of **9** are given in Table 3. All data were collected at low temperature using an oil-coated shock-cooled crystal[26] on a Stoe-Siemens AED instrument with Mo-K_α (λ = 0.71073 Å) radiation. The structure was solved by direct methods using SHELXS-90[27] and refined with all data on F^2 with a weighting scheme of $\omega^{-3} = \sigma^2(F_o^2) + (g1P)^2 + g2P$ with $P = (F_o^2 + 2\ F_c^2)/3$ using SHELXS-93[28]. In **9**, the positions of the hydrogen atoms were geometrically idealized and refined using a riding model. Selected bond lengths and angles of **6** are given in Table 1[29].

---

[1] F. R. W. P. Wild, L. Zsolnai, G. Huttner, H. H. Brintzinger, *J. Organomet. Chem.* **1982**, *232*, 233–247.

[2] J. Okuda, *Chem. Ber.* **1990**, *123*, 1649–1651.

[3] J. A. Ewen, *J. Am. Chem. Soc.* **1984**, *106*, 6355–6364.

[4] W. Kaminsky, K. Külper, H. H. Brintzinger, F. R. W. P. Wild, *Angew. Chem.* **1985**, *97*, 507–508; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 507–508.

[5] J. A. M. Canich (Exxon Chemical), US Pat. 5 026 798, **1990**.

[6] J. A. M. Canich, H. W. Turner (Exxon Chemical), PCT/US91/09676, **1991**.

[7] R. A. Andersen, *Inorg. Chem.* **1979**, *18*, 2928–2932.

[8] U. Wannagat, H. Autzen, M. Schlingmann, *Z. Anorg. Allg. Chem.* **1976**, *419*, 41–47.

[9] U. Wannagat, G. Eisele, M. Schlingmann, *Z. Anorg. Allg. Chem.* **1977**, *429*, 83–87.

[10] K. Horchler, C. Stader, B. Wrackmeyer, *Inorg. Chim. Acta* **1986**, *117*, L39–L40.

[11] B. Wrackmeyer, C. Stader, K. Horchler, H. Zhou, D. Schlosser, *Inorg. Chim. Acta* **1990**, *176*, 205–214.

[12] D. K. Kennepohl, S. Brooker, G. M. Sheldrick, H. W. Roesky, *Chem. Ber.* **1991**, *124*, 2223–2225.

[13] H. Bürger, K. Wiegel, U. Thewalt, D. Schomburg, *J. Organomet. Chem.* **1975**, *87*, 301–309.

[14] H. Bürger, K. Wiegel, *J. Organomet. Chem.* **1977**, *124*, 279–292.

[15] H. Bürger, K. Wiegel, *Z. Anorg. Allg. Chem.* **1976**, *419*, 157–162.

[16] A. Herzog, F.-Q. Liu, H. W. Roesky, A. Demsar, K. Keller, M. Noltemeyer, F. Pauer, *Organometallics* **1994**, *13*, 1251–1256.

[17] M. Sotoodeh, I. Leichtweis, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, *Chem. Ber.* **1993**, *126*, 913–919.

[18] J. C. W. Chien, B. Xu, *Makromol. Chem., Rapid Commun.* **1993**, *14*, 109–114.

[19] P. C. Möhring, N. J. Coville, *J. Organomet. Chem.* **1994**, *479*, 1–29.

[20] M. Bochmann, *Nachr. Chem. Lab. Tech.* **1993**, *41*, 1220–1228.

[21] H. Dorn, S. Shah, H. W. Roesky, unpublished results.

[22] J. Okuda, *Nachr. Chem. Lab. Tech.* **1993**, *41*, 8–14.

[23] H. Bürger, D. Beiersdorf, *Z. Anorg. Allg. Chem.* **1979**, *459*, 111–118.

[24] The C values found for most of the compounds are systematically lower than the calculated ones. This is caused by silicon carbide formation during the oxidation process.

[25] H. Sakurai, K. Tominaga, T. Watanabe, M. Kumada, *Tetrahedron Lett.* **1966**, *45*, 5493–5497.

[26] T. Kottke, D. Stalke, *Appl. Crystallogr.* **1993**, *26*, 615.

[27] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[28] G. M. Sheldrick, SHELXL-93, program for crystal structure refinement, University of Göttingen, Germany **1993**.

[29] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int.code +(1223) 336-033, e-mail: teched@chemcrys.cam.ac.uk), by quoting the deposition number CCDC-100117.

[96212]