Structural Features of Me_2Si-Bridged Cp/Phosphido Group 4 Metal Complexes, “CpSiP” Constrained-Geometry Ziegler−Natta Catalyst Precursors

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Double deprotonation of $[(C_5Me_4H){-}SiMe_2{-}PH(\text{cyclohexyl})]$ (**4**) was achieved by treatment with *n*-butyllithium in THF/pentane to afford the dianionic ligand $[(C_5Me_4)\text{-}SiMe_2{-}P(\text{cyclohexyl})]^{2-}$ as its dilithio salt (**5**). The reagent **5** was transmetalated by subsequent treatment with $[Cl_2Ti(NMe_2)_2]$ (**6a**) to yield the dimethylsilanediyl-bridged Cp*/phosphido titanium complex $[(C_5Me_4){-}SiMe_2{-}PCy]Ti(NMe_2)_2$ (**7a**; 67% isolated yield). The analogous reaction of **5** with $[Cl_2Zr(NEt_2)_2(THF)_2]$ (**6b**) gave $[(C_5Me_4){-}SiMe_2{-}PCy]Zr(NEt_2)_2$ (**7b**; isolated in 59% yield). Single crystals of the complexes **7a**,**b** were obtained from pentane. The X-ray crystal structure analyses revealed distorted “constrained geometry” group 4 metal complex structures due to the presence of a chiral, nonplanar coordination geometry at the phosphorus atom. Complexes **7a**,**b** both give active homogeneous Ziegler−Natta catalysts for ethene/1-octene copolymerization upon activation with excess methylalumoxane.

Introduction

The Me_2Si-bridged Cp*/amido titanium (and zirconium) complexes of the type **A** (in Chart 1) have become the precursors of an important class of homogeneous Ziegler−Natta catalysts.[1,2] In contrast to many bis-Cp and bis(indenyl) Group 4 derived systems, they have been especially useful in the formation of ethene/1-alkene copolymers when activated with, for example, methylalumoxane.[3] Most of these “constrained geometry” catalysts are actually derived from the parent compound **A**, where a substituted Cp-type ligand is connected to some alkyl- or arylamido group by means of a bridging R^1R^2Si unit.[4] Other bridging units have only seldom been used; we have contributed examples that contain a vinylidene bridge ($H_2C{=}C$)[5,6] and recently reported catalysts where the Cp and amido moieties were connected by means of methylene (H_2C) or alkylidene (R^1R^2C) linkers.[7] These “CpCN” metal catalysts produce ethene/1-octene copolymers with similarly high 1-alkene incorporations as compared to the original “CpSiN” group 4 metal complex derived systems.

Other element combinations are rare. Royo and Cuenca have described “CpSiO” systems,[8] and we have recently published related “CpCO”M^{IV}-derived catalysts.[9] Both organometallic catalyst precursor types are dimeric (see Chart 1). We have also described the first examples of C_1-bridged constrained-geometry “CpCP” catalysts.[7] These titanium or zirconium complexes contain an alkylidene-linked Cp/phosphido ligand combination. Some examples of this series showed an excellent ethene/1-alkene copolymerization catalyst behavior with regard to both very high catalyst activities *and* high α-olefin incorporation. Surprisingly little has been known about the related “CpSiP” group 4 metal catalyst systems. An arylphosphido example has been reported in the patent literature.[10] Hey-Hawkins et al. had described the corresponding “CpSiP”Li_2 dianion equivalent but reported an unexpected reaction pathway that proceeded with dephosphorylation upon its treat-

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† X-ray crystal structure analyses.

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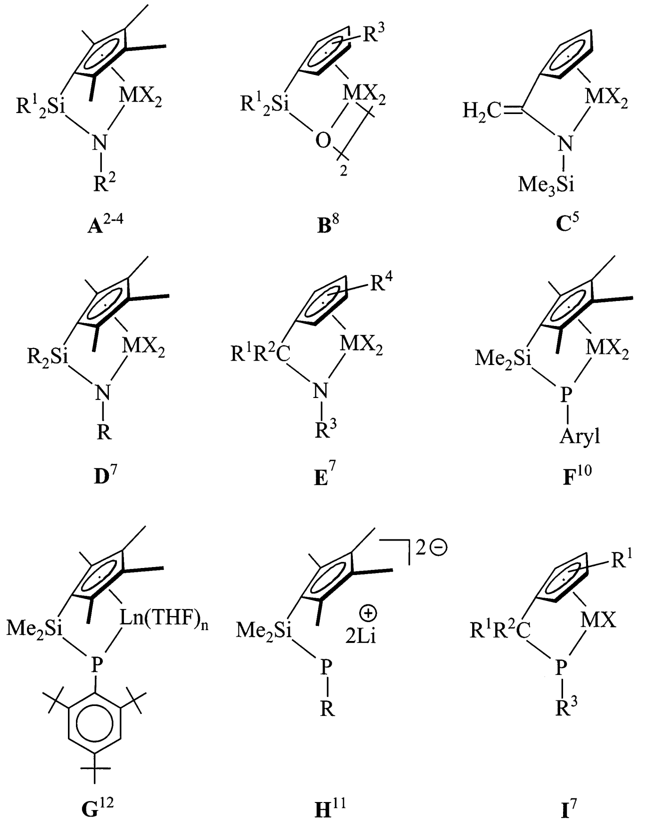
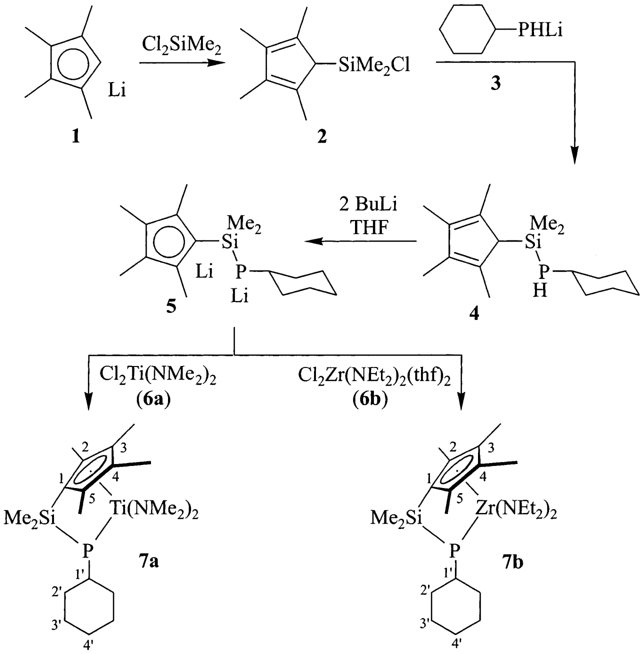
Chart 1



M = Group 4 Metal, X = halide or dialkylamide

ment with $ZrCl_4$.[11] Hou et al. recently reported the attachment of such ligands to lanthanoid metals and described the first X-ray crystal structure analysis, to our knowledge, of such a "CpSiP"Ln constrained-geometry complex.[12] We have now prepared a pair of $[(Me_4C_5)-SiMe_2-P(cyclohexyl)]TiX_2$ and $-ZrX_2$ complexes. These are, to the best of our knowledge, the first examples of such "CpSiP"$M^{IV}X_2$ systems that were characterized by X-ray diffraction. The structural features, which are quite different from those of the related conventional "CpSiN"$M^{IV}X_2$ complexes, and some chemical characteristics of these complexes are described in this paper.[13,14]

Scheme 1



Results and Discussion

The synthesis of the "CpSiP" ligand system followed the pathways originally outlined by Bercaw and Shapiro[1] and later modified by Stevens et al.[10] and by Hey-Hawkins et al.[11] for the introduction of the phosphido group. Tetramethylcyclopentadiene was deprotonated by treatment with *n*-butyllithium in hexane, followed by treatment with dimethyldichlorosilane. The silylated CpH system was then reacted with the (cyclohexyl)PHLi reagent in THF/pentane. Nucleophilic substitution at silicon was achieved selectively, and the neutral ligand system **4** was isolated in >80% yield (Scheme 1). Double deprotonation was achieved by treatment of **4** with *n*-butyllithium in THF/pentane to give the dilithio derivative of the "CpSiP" ligand system (**5**), again in >80% yield. The dianionic ligand system features a single ^{31}P NMR resonance in [D$_8$]THF at δ −137.9 (the neutral precursor **4** shows a ^{31}P NMR doublet in [D$_6$]-benzene at δ −129.2 ($^1J_{PH}$ = 192 Hz)).

The reaction of the dilithio CpSiP reagent **5** with $TiCl_4$ or $ZrCl_4$ turned out to give complicated product mixtures that probably contained some of the compounds already described by Hey-Hawkins et al.[11] In contrast, the reactions of **5** with the corresponding group 4 metal dichlorobis(dialkylamido) reagents were very clean and gave the corresponding CpSiP group 4 metal complexes in good yield.

The reaction of the (CpSiP)Li$_2$ reagent **5** with $Cl_2Ti(NMe_2)_2$ (**6a**)[15] was carried out in THF at −78 °C. After workup at room temperature the corresponding (CpSiP)-$Ti(NMe_2)_2$ complex (**7a**) was obtained in close to 70% yield. The corresponding (CpSiP)Zr complex was prepared analogously by treatment of the doubly deprotonated ligand system (**5**) with $Cl_2Zr(NEt_2)_2(THF)_2$ (**6b**)[16] in tetrahydrofuran. The (CpSiP)$Zr(NEt_2)_2$ complex **7b**

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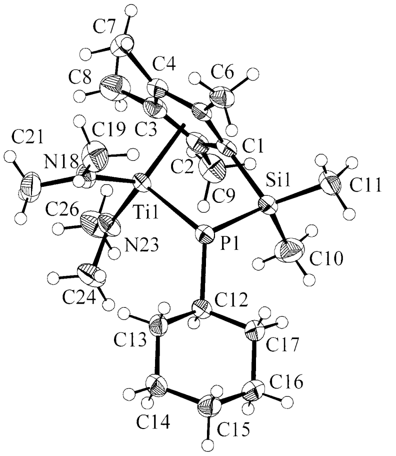

Figure 1. Side view of the molecular structure of the titanium complex **7a** (the independent molecule **7a-B** is depicted). Selected bond lengths (Å) and angles (deg): Ti1−N18 = 1.924(2), Ti1−N23 = 1.904(2), Ti1−P1 = 2.504(1), P1−Si1 = 2.213(1), P1−C12 = 1.877(3), Si1−C1 = 1.879(3); N18−Ti1−N23 = 101.7(1), N18−Ti1−P1 = 98.1(1), N23−Ti1−P1 = 112.8(1), Ti1−P1−Si1 = 87.4(1), Ti1−P1−C12 = 121.0(1), Si1−P1−C12 = 112.7(1), P1−Si1−C1 = 91.8(1).

was obtained in close to 60% yield. Single crystals of **7a**,**b** were obtained from concentrated pentane solutions of these group 4 metal amide complexes at room temperature. This allowed us to characterize each of the complexes (**7a**,**b**) by an X-ray crystal structure analysis.

The X-ray crystal structure analysis of the titanium complex **7a** (Figure 1) shows the presence of a constrained-geometry framework that is substantially distorted and thus different from the typical appearance of the usual Cp/amido examples of this general class of compounds.[5,7] In the crystal two independent (enantiomorphic) molecular entities of **7a** were found. They are chemically equivalent but show variations in a few details. Therefore, the characteristic structural properties of molecule **7a-A** will be given with the corresponding **7a-B** values in brackets.

In **7a** the tetramethylcyclopentadienyl ring is rather uniformly η^5 coordinated to the transition-metal center. The respective Ti−C(Cp) bond lengths range from 2.359(3) to 2.455(3) Å [**7a-B**: 2.378(3)−2.436(3) Å]. The remaining ligands at titanium complement its pseudotetrahedral coordination geometry. The nitrogen atoms of the two dimethylamido ligands are each trigonal-planar coordinated (sum of bonding angles at N18 356.9° [360.0°] and at N23 359.4° [360.0°]).

The Ti−N23 bond length amounts to 1.904(3) Å [1.904(2) Å], and the Ti−N18 bond is in the same range at 1.917(3) Å [1.924(2) Å]. The σ-ligand angle N18−Ti−N23 was found at 103.2(2)° [101.7(1)°]. The adjacent titanium to phosphorus bond is much longer at 2.544(1) Å [2.504(1) Å].[17] It is the coordination geometry at phosphorus that makes the complexes **7** so different from the previously reported constrained-geometry systems. As expected, the bonds at P1 are not coplanar but the coordination geometry at the phosphorus atom in **7a** is strongly distorted toward tetrahedral. The sum of the bonding angles at P1 in the molecule **7a-B** amounts to 321.1°. In the independent molecule **7a-A** this value is also far away from 360° but also substantially different from the **7a-B** value at 310.1°. This indicates a rather shallow energy profile for a distortion of the bond angles at phosphorus in complex **7a** with regard to inversion via planar tricoordinate P.[18]

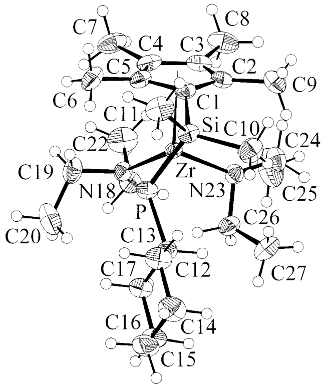

Figure 2. Backside projection of the molecular structure of complex **7b**, showing the significantly distorted ligand framework. Selected bond lengths (Å) and angles (deg): Zr−N18 = 2.059(2), Zr−N23 = 2.027(2), Zr−P = 2.648(1), P−Si = 2.223(1), P−C12 = 1.873(2), Si−C1 = 1.884(2); N18−Zr−N23 = 101.2(1), N18−Zr−P = 104.9(1), N23−Zr−P = 117.7(1), Zr−P−Si = 86.9(1), Zr−P−C12 = 122.7(1), Si−P−C12 = 111.6(1), P−Si−C1 = 94.2(1). For additional data see the text.

The individual bond angles at phosphorus are determined by the constrained ligand framework and they are, therefore, quite different from one another. The C12−P1−Si1 angle is found in the typical tetrahedral range at 106.1(1)° [112.7(1)°], whereas the C12−P1−Ti angle is slightly larger at 117.9(1)° [121.0(1)°] and the endocyclic Si1−P1−Ti angle is at an expected low value of 86.1(1)° [87.4(1)°]. The corresponding bond lengths are 1.880(3) Å [1.877(3) Å] (P1−C12) and 2.220(1) Å [2.213(1) Å] (P1−Si1).

The strongly bent geometry at phosphorus significantly influences the remaining bond angles at titanium. The dimethylamido group oriented syn to the phosphorus lone pair shows a smaller N18−Ti−P1 bond angle at titanium (96.7(1)° [98.1(1)°]) than the dimethylamido group that is located on the side of the cyclohexyl substituent (N23−Ti−P1 = 108.1(1)° [112.8(1)°]).

The steric constraints of the ligand framework also influence the observed bonding features at the bridging Me_2Si moiety. The C1−Si1 bond length is in the normal range (1.880(3) Å [1.879(3) Å]), but the endocyclic C1−Si1−P1 angle at silicon is greatly reduced (93.1(1)° [91.8(1)°]). However, the C1−Si1 vector is only marginally tilted toward the center of the molecule (sum of bonding angles at C1 356.0° [355.7°]).

The zirconium complex **7b** shows a similar structure (Figure 2). The individual bond lengths of the ligand atoms to the heavier central metal atom are, of course, longer than in **7a**, but the overall characteristics are related. The zirconium atom is pseudotetrahedrally coordinated to a η^5-Me_4C_5-[Si] ligand (with Zr−C(Cp) bonds ranging from 2.509(2) to 2.561(2) Å), the amido

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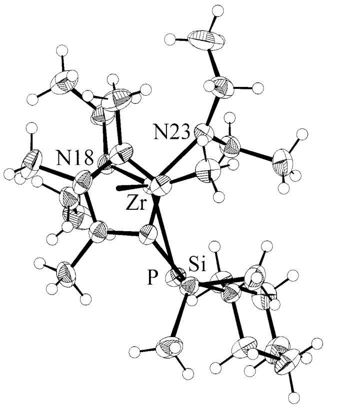


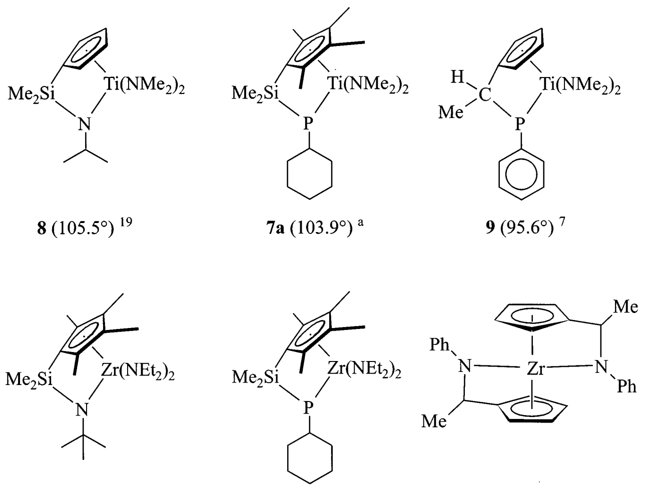
Figure 3. Top projection of complex **7b**.

nitrogen centers N18 (Zr−N18 = 2.059(2) Å) and N23 (Zr−N23 = 2.027(2) Å), and the phosphido moiety (Zr−P = 2.648(1) Å). In nonbridged Cp$_2$Zr(X)−PHAr or Cp$_2$Zr(X)−PR$_2$ systems the Zr−P bond lengths are typically found in a range between ca. 2.51 and 2.73 Å. From representative reference compounds it must be assumed that the lower values indicate significant metal−phosphorus π-interaction. The value observed here for complex **7b**, Zr−P = 2.648(1) Å, is rather long (as compared with e.g. Cp$_2$Zr(Cl)−P(SiMe$_3$)$_2$ at 2.547(6) Å or Cp$_2$Zr(Cl)−PH(aryl) at 2.543(3) Å).[20] The N18−Zr−N23 angle in **7b** amounts to 101.2(1)°. Again the N−Zr−P angles are quite different (N18−Zr−P = 104.9(1)°, N23−Zr−P = 117.7(1)°). This difference again probably originates from the strongly pyramidalized coordination geometry at phosphorus (sum of bonding angles 321.2°; Zr−P−Si = 86.9(1)°, C12−P−Zr = 122.7(1)°, C12−P−Si = 111.6(1)°). The Si−P bond length in **7b** is found at 2.223(1) Å, and the endohedral angle at silicon (C1−Si−P) amounts to 94.2(1)° (sum of bonding angles at C1 356.1°).

Figures 2 and 3 provide two views that illustrate the significantly distorted frameworks of these constrained-geometry catalyst precursors. The characteristic distortion originates from the introduction of the phosphorus chirality center. In contrast, the Me$_2$Si- and R^{1}R^{2}C-bridged Cp/amido group 4 metal complexes contain a nonchiral planar-tricoordinate nitrogen center as part of their bridged, formally dianionic ligand system.

The alleged characteristic feature of the "constrained geometry" systems is their rather open space in front of the (Cp′−SiMe$_2$−NR/PR)M unit at the active catalyst stage.[4] Therefore, it had been suggested to use the Cp(centroid)−metal−NR(PR) framework angle as a quantitative measure for this potentially characteristic feature. The smaller this framework angle, the more pronounced the typical "constrained geometry" features should be, according to this rather narrow, specific definition. We are not so sure whether this large and important family of Ziegler−Natta catalysts should (and can) be classified by such a singular structural feature, but a comparison of the Cp(centroid)−M−NR(PR) angle among a series of examples may provide one useful parameter for a relative structural characterization.

Chart 2. Comparison of Cp(centroid)−Metal−Nitrogen/Phosphorus Framework Angles That Characterize the Increasing Backbone Strain in a Series of Constrained-Geometry Systems[a]



8 (105.5°) [19] **7a** (103.9°) [a] **9** (95.6°) [7]

10 (100.2°) [19] **7b** (98.2°) [a] **11** (90.1°) [7]

[a] The footnote *a* denotes this work.

In the (Cp*−SiMe$_2$−NR)TiX$_2$-type complexes, which are the precursors of the most active ethene/1-alkene copolymerization catalysts of the "constrained geometry" type, Cp(centroid)−Ti−N angles of ca. 105° are observed (see Chart 2). The (Cp−CHR^1−NR)Ti(NR$_2$)$_2$ systems recently reported by us contain considerably more constrained ligand frameworks, exhibiting Cp(centroid)−Ti−N angles that are smaller by ca. 10°. Nevertheless, the catalysts derived from **9** seem to be of lower activity than the typical (Cp*−SiMe$_2$−NR)Ti systems, although their 1-octene incorporation ratio in the copolymer is in the same range. The (Cp*−SiMe$_2$−PR)Ti(NR$_2$)$_2$ system described here (**7a**) is almost in the same Cp(centroid)−Ti−P framework angle range with the conventional (Cp−SiMe$_2$−NR)Ti systems; e.g., **7a** deviates only by less than 2° from the corresponding value observed in **8** (see Chart 2).

A similar trend is observed in the zirconium series. The phosphorus-containing system **7b** exhibits a Cp(centroid)−Zr−P framework angle of 98.2° that deviates only marginally from the Cp(centroid)−Zr−N angle (100.2°) of the corresponding silylene-bridged Cp/amido zirconium complex **10** (see Chart 2).

The ^{1}H NMR spectrum of the zirconium complex **7b** shows only one set of signals of the N(Et$_2$)$_2$ groups, two signals of the C$_5$(CH$_3$)$_4$ moiety (δ 2.18, 1.89), and a single Si(CH$_3$)$_2$ resonance at δ 0.67 at room temperature in d_8-toluene solvent in addition to the complex cyclohexyl resonances. This "symmetric" appearance is, however, not due to a different structure of **7b** in solution. It originates from a dynamic NMR behavior caused by a rapid enantiomerization process of the chiral phosphorus center. This inversion process could be slowed and eventually frozen out on the ^{1}H NMR time scale at very

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Table 1. Details of the Ethene Polymerization and Ethene/1-Octene Copolymerization Reactions Carried out with the Homogeneous 7a(Ti)/MAO and 7b(Zr)/MAO Ziegler−Natta Catalyst Systems

(a) Ethene Polymerization, in Toluene at 60 °C, 1 h Reaction Time

cat.	amt of cat., mg	Al/M	amt of PE, g	mp, °C	act[a]
7a(Ti)	15	1100	2.4	127	40
	15	1100	2.1	125	35
7b(Zr)	16	1100	4.0	126	66
	14	1650	1.4	125	35

(b) Ethene/1-Octene Copolymerization, in 50% Toluene/50% 1-Octene at 90 °C, 1 h Reaction Time

cat.	amt of cat., mg	Al/M	press. of C_2H_4, bar	amt of copolym, g	ethene/ octene[b]	act[a]
7a(Ti)	13.2	1070	1	0.4	7:1	13
	12.9	1100	2	0.9	6:1	16
7b(Zr)	15.9	1100	1	0.4	9:1	14
	13.2	1320	2	0.5	6:1	9

[a] Catalyst activity in g of polymer/((mmol of cat.)(bar of ethene) h). [b] Ethene/1-octene ratio in the obtained copolymer.

low temperatures in a $CDClF_2/CDCl_2F$ Freon solvent mixture.[21] In the low-temperature ^1H NMR spectrum in this specific solvent one eventually observes at 143 K the expected two differentiated pairs of η^5-$C_5(CH_3)_4$ resonances ($\Delta\nu = 75$ and 87 Hz) as well as a 1:1 intensity pair of $Si(CH_3)_2$ ^1H NMR signals. From the decoalescence behavior of the $Si(CH_3)_2$ ^1H NMR signals ($T_c = 160$ K in the Freon solvent mixture) the Gibbs activation energy of the intramolecular inversion process at the adjacent phosphorus atom was estimated[22] at $\Delta G^{+}_{\mathrm{invP}}(160\ \mathrm{K}) = 7.5 \pm 0.5$ kcal mol^{-1}.

The complexes **7a** (Ti) and **7b** (Zr) were both activated by treatment with methylalumoxane[23] (Al:transition metal ratios ca. 1070−1650) in toluene solution to give active homogeneous Ziegler−Natta catalysts. We carried out a few ethene polymerizations at 2 bar of ethylene pressure. Polyethylene was obtained in each case with a moderate activity (see Table 1). The **7a**/MAO and **7b**/MAO catalysts were active in ethene/1-octene copolymerization. Generally, good incorporation ratios of the 1-alkene were observed in the reactions carried out at 1 or 2 bar of ethylene pressure in 50% 1-octene solutions in toluene at 90 °C, but the catalyst activities were much lower than previously observed with the very active [Cp*−SiMe$_2$N(*tert*-butyl)]TiX$_2$ or [Cp−CMe$_2$−P(cyclohexyl)]TiX$_2$/MAO catalyst systems.[4,5,7] The ethene/1-octene ratio in the obtained copolymer samples was determined by ^{13}C NMR spectroscopy.[24] Figure 4 shows a typical example. The copolymer obtained with the **7a**/MAO catalyst at 1 bar of ethene pressure has a molecular weight of $M_w \approx 50\,000$ (GPC relative to polystyrene at 145 °C in 1,2,4-trichlorobenzene) with $M_w/M_n = 2.1$. $M_w \approx 30\,000$ ($M_w/M_n = 1.6$) was found for the ethene/1-octene copolymer obtained with the **7b**/MAO catalyst under the same conditions.

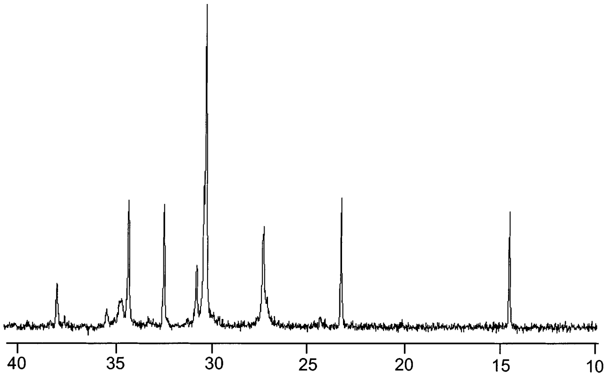

Figure 4. ^{13}C NMR spectrum of the ethene/1-octene copolymer obtained with the **7a**(Ti)/MAO catalyst at 90 °C (2 bar of ethene pressure) in toluene/50% 1-octene solution (Al/Ti ratio 1100).

Experimental Section

Reactions with organometallic reagents were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. Polymerization and copolymerization reactions were carried out as previously described by us for related (CpCN)MX$_2$/MAO catalysts.[7] The [Cp*−SiMe$_2$−P(cyclohexyl)]Li$_2$ ligand system (**5**) was prepared analogously, as recently described by Hey-Hawkins et al.[11]

Bis(dimethylamido)[((cyclohexylphosphido-*κP*)dimethylsilyl)-*η*^{5}-tetramethylcyclopentadienyl]titanium (7a). A suspension of 153 mg (0.50 mmol) of the dilithiated ligand system **5** in 5 mL of THF was cooled to −78 °C. A solution of 98 mg (0.47 mmol) of $Cl_2Ti(NMe_2)_2$ (**6a**) in 2 mL of THF was added dropwise to the suspension. The mixture was then warmed to room temperature with stirring. After 4 h of stirring at ambient temperature the solvent was removed in vacuo and the brown residue taken up in pentane. Precipitated lithium chloride was removed by filtration. Removal of the solvent from the clear pentane solution gave complex **7a** as a brown oil. Yield of **7a**: 144 mg (67%, relative to the amount of the starting material **5**). Single crystals for the X-ray crystal structure analysis were obtained from a concentrated pentane solution at room temperature: mp 127 °C, 254 °C dec. Anal. Calcd for $C_{21}H_{41}N_2PSiTi$ (428.5): C, 58.86; H, 9.64; N, 6.54. Found: C, 58.73; H, 9.53; N, 6.41. ^1H NMR (toluene-d_8, 599.8 MHz, 298 K): δ 3.05 (s, 12H, NCH$_3$), 2.15 (1H), 1.95 (2H), 1.76 (2H), 1.58 (2H), 1.47 (2H), 1.28 (2H), 1.22 (2H) (each broad, Cy), 2.08 (d, $\sum(^4J_{PH} + {}^5J_{PH}) = 0.7$ Hz, 6H, 2,5-CH$_3$), 1.71 (s, 6H, 3,4-CH$_3$), 0.65 (d, $^3J_{PH} = 2.5$ Hz, 6H, SiMe$_2$). $^{13}C\{^1H\}$ NMR (toluene-d_8, 150.8 MHz, 298 K): δ 127.8 (C-2,5), 125.3 (C-3,4), 104.9 (C-1), 46.8 (d, $^3J_{PC} = 6.1$ Hz, NCH$_3$), 37.5 (d, $^nJ_{PC} = 10.0$ Hz, Cy), 34.8 (d, $^1J_{PC} = 23.4$ Hz, C-1′), 27.8 (d, $^nJ_{PC} = 10.2$ Hz, Cy), 26.8 (s, Cy), 15.4 (d, $\sum(^3J_{PC} + {}^4J_{PC}) = 8.9$ Hz, 2,5-CH$_3$), 10.9 (3,4-CH$_3$), 5.1 (d, $^2J_{PC} = 10.8$ Hz, Si(*C*H$_3$)$_2$). GHSQC (toluene-d_8, 150.8/599.8 MHz, 298 K): $\delta(^{13}C)/\delta(^1H)$ 46.8/3.05 (N*C*H$_3$/NC*H*$_3$), 37.5/1.95, 1.47; 27.8/1.76, 1.28; 26.8/1.58, 1.22 (Cy/Cy), 34.8 /2.15 (*C*-1′/1′-*H*), 15.4/2.08 (2,5-*C*H$_3$/2,5-C*H*$_3$), 10.9/1.71 (3,4-*C*H$_3$/3,4-C*H*$_3$), 5.1/0.65 (C-6 /6-H). GHMBC (toluene-d_8, 150.8/599.8 MHz, 298 K): $\delta(^{13}C)/\delta(^1H)$ 127.8/2.08, 1.71 (C-2,5/2,5-C*H*$_3$, 3,4-C*H*$_3$), 125.3/2.08, 1.71 (C-3,4/2,5-C*H*$_3$, 3,4-C*H*$_3$), 104.9/2.08, 0.65 (C-1/2,5-C*H*$_3$, 6-H). $^{31}P\{^1H\}$ NMR (toluene-d_8, 242.5 MHz): $\delta^{31}P$ ($\nu_{1/2}$, T) 16.1 (20 Hz, 298 K), 11.4 (28 Hz, 273 K), 3.1 (51 Hz, 233 K), −1.6 (48 Hz, 213 K), −7.2

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(70 Hz, 193 K). ^{29}Si{INEPTRD} (toluene-d_8, 39.8 MHz): δ −8.2 (d, $^1J_{PSi} = 33.1$ Hz).

X-ray Crystal Structure Analysis of 7a: formula $C_{21}H_{41}N_2PSiTi$, $M = 428.52$, red crystal, 0.35 × 0.30 × 0.15 mm, $a = 8.835(1)$ Å, $b = 9.865(1)$ Å, $c = 31.069(1)$ Å, $\alpha = 89.50(1)°$, $\beta = 88.60(1)°$, $\gamma = 63.88(1)°$, $V = 2430.6(4)$ Å^3, $\rho_{calcd} = 1.171$ g cm^{-3}, $\mu = 4.75$ cm^{-1}, empirical absorption correction via SORTAV ($0.851 \leq T \leq 0.932$), $Z = 4$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.710\,73$ Å, $T = 198$ K, ω and φ scans, 15 211 reflections collected ($\pm h, \pm k, \pm l$), ($\sin\theta)/\lambda = 0.66$ Å^{-1}, 11 200 independent ($R_{int} = 0.028$) and 7946 observed reflections ($I \geq 2\sigma(I)$), 489 refined parameters, R1 = 0.057, wR2 = 0.156, maximum (minimum) residual electron density 1.12 (−0.61) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Bis(diethylamido)[((cyclohexylphosphido-κP)dimethylsilyl)-η^5-tetramethylcyclopentadienyl]zirconium (7b). Analogously to the method described above, 153 mg (0.50 mmol) of **5** in 5 mL of THF was reacted with 214 mg (0.47 mmol) of $Cl_2Zr(NEt_2)_2(THF)_2$ (**6b**) in 2 mL of THF. Workup as described above gave 156 mg (59%) of **7b** as an orange oil (single crystals from pentane): mp 121 °C, 249 °C dec). Anal. Calcd for $C_{25}H_{49}N_2PSiZr$ (528.0): C, 56.87; H, 9.35; N, 5.31. Found: C, 56.33; H, 9.14; N, 5.07. ^{1}H NMR (toluene-d_8, 599.8 MHz, 298 K): δ 3.33, 3.18 (ABX$_3$, each 4H, NCH_2CH$_3$), 2.18 (d, $\sum(^4J_{PH} + {}^5J_{PH}) = 0.6$ Hz, 6H, 2,5-CH$_3$), 2.00 (m, 1H, 1′-H), 1.92, 1.50 (each m, each 2H, 2′-H), 1.89 (s, 6H, 3,4-CH$_3$), 1.75, 1.25 (each m, each 2H, 3′-H), 1.55, 1.20 (each m, each 1H, 4′-H), 0.94 (t, $^3J_{HH} = 6.9$ Hz, 12H, NCH$_2$CH_3), 0.67 (d, $^3J_{PH} = 2.6$ Hz, SiMe$_2$). GCOSY (toluene-d_8, 599.8 MHz, 298 K): δ(^{1}H)/δ(^{1}H) = 3.33/3.18, 0.94 (NCH_2/NCH_2CH$_3$, NCH$_2$CH_3), 1.92/1.50 (2′-CH_2/2′-CH_2), 1.75/ 1.25 (3′-CH_2/3′-CH_2), 1.55/1.20 (4′-CH_2/4′-CH_2). ^{13}C{^{1}H} NMR (toluene-d_8, 150.8 MHz, 298 K): δ 128.2 (d, $\sum(^2J_{PC} + {}^3J_{PC}) = 1.5$ Hz, C-2,5), 123.3 (C-3,4), 104.7 (d, $\sum(^2J_{PC} + {}^2J_{PC}) = 13.0$ Hz, C-1), 40.8 (d, $^1J_{CH} = 130$ Hz, $^3J_{PC} = 1.9$ Hz, NCH$_2$CH$_3$), 38.2 (d, $^2J_{PC} = 11.7$ Hz, C-2′), 32.2 (d, $^1J_{PC} = 18.1$ Hz, C-1′), 28.0 (d, $^3J_{PC} = 10.9$ Hz, C-3′), 26.7 (d, $^4J_{PC} = 0.6$ Hz, C-4′), 15.5 ($^1J_{CH} = 126$ Hz, NCH$_2$$CH_3$), 15.2 (d, $^1J_{CH} = 127$ Hz, $\sum(^3J_{PC} + {}^4J_{CP}) = 9.7$ Hz, 2,5-CH$_3$), 11.2 ($^1J_{CH} = 129$ Hz, 3,4-CH$_3$), 5.58 (d, $^1J_{CH} = 120$ Hz, $^2J_{PC} = 10.8$ Hz, Si(CH$_3$)$_2$). GHSQC (toluene-d_8, 150.8/599.8 MHz, 298 K): δ(^{13}C)/δ(^{1}H) 40.8/3.33, 3.18 (NCH$_2$/NCH_2), 38.2/1.92, 1.50 (C-2′/2′-CH_2), 32.2/2.00 (C-1′/1′-CH), 28.0/1.75, 1.25 (C-3′/3′-CH_2), 26.7/1.55, 1.20 (C-4′/4′-CH_2), 15.5/0.94 (NCH$_2$$CH_3$/NCH$_2CH_3$), 15.2/2.18 (2,5-$CH_3$/2,5-C$H_3$), 11.2/1.89 (3,4-$CH_3$/3,4-C$H_3$), 5.58/0.67 (C-6/6-H). GHMBC (toluene-d_8, 150.8/599.8 MHz, 298 K): δ(^{13}C)/δ(^{1}H) δ 128.2/2.18, 1.89 (C-2,5/2,5-CH_3, 3,4-CH_3), 123.3/2.18, 1.89 (C-3,4/2,5-CH_3, 3,4-CH_3), 104.7/2.18, 0.67 (C-1/2,5-CH_3, 6-H), 40.8/3.33, 3.18, 0.94 (NCH$_2$/NCH_2CH_3), 15.5/3.33, 3.18 (NCH$_2$$CH_3$/NC$H_2$). ^{31}P{^{1}H} NMR (toluene-d_8, 242.5 MHz): δ^{31}P ($\nu_{1/2}$, T) −75.5 (40 Hz, 298 K), −79.5 (183 Hz, 253 K), −81.3 (40 Hz, 233 K), −83.1 (28 Hz, 213 K). ^{29}Si{INEPTRD} (toluene-d_8, 202.6 MHz): δ −10.6 (d, $^1J_{PSi} = 30.6$ Hz).

X-ray Crystal Structure Analysis of 7b: formula $C_{25}H_{49}N_2PSiZr$, $M = 527.94$, yellow crystal, 0.35 × 0.25 × 0.10 mm, $a = 9.371(1)$ Å, $b = 9.983(1)$ Å, $c = 16.397(1)$ Å, $\alpha = 73.10(1)°$, $\beta = 84.84(1)°$, $\gamma = 83.74(1)°$, $V = 1456.2(2)$ Å^3, $\rho_{calcd} = 1.204$ g cm^{-3}, $\mu = 4.87$ cm^{-1}, empirical absorption correction via SORTAV ($0.848 \leq T \leq 0.953$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.710\,73$ Å, $T = 198$ K, ω and φ scans, 13 774 reflections collected ($\pm h, \pm k, \pm l$), ($\sin\theta)/\lambda = 0.66$ Å^{-1}, 6849 independent ($R_{int} = 0.036$) and 5713 observed reflections ($I \geq 2\sigma(I)$), 281 refined parameters, R1 = 0.034, wR2 = 0.075, maximum (minimum) residual electron density 0.34 (−0.38) e Å^{-3}, hydrogens calculated and refined as riding atoms. Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a Nonius FR591 rotating anode generator. Programs used: data collection, COLLECT (Nonius BV, 1998); data reduction, Denzo-SMN;[25] absorption correction, SORTAV;[26] structure solution, SHELXS-97;,[27] structure refinement, SHELXL-97;[28] graphics, DIAMOND[29] and SCHAKAL.[30]

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Supporting Information Available: Tables giving details of the X-ray crystal structure analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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