Synthesis of Alkylidene-Bridged Cp/Phosphido Group 4 Metal Complexes—Precursors of the "(CpCPR)M–Constrained-Geometry" Catalyst Family

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Phosphide [PHR¹]Li (R¹ = cyclohexyl, phenyl) addition to the fulvenes (C₅H₄)CMe₂ (**1**) and (C₅H₄)CHCMe₃ (**2**) yields the corresponding phosphinoalkyl-substituted cyclopentadienides. Subsequent deprotonation at phosphorus with LDA followed by transmetalation of the resulting [(C₅H₄)CR²R³PR¹]Li₂ dianion equivalents to Cl₂Ti(NMe₂)₂ or Cl₂Zr(NEt₂)₂(THF)₂ yields the corresponding ["CpCPR¹"MX₂] "constrained-geometry" systems (eight examples, **11**-**18**). These systems contain a chiral phosphorus center that is characterized by a low inversion barrier (ΔG^{*}_{inv} ranging from ca. 7.5 to 10.0 kcal mol⁻¹). The structural and some spectroscopic features of the (CpCPR)Ti and Zr complexes were investigated by DFT calculations. Treatment with a large excess of methylalumoxane gave ethene/1-octene copolymerization catalysts. The [(C₅H₄)CMe₂PR¹]ZrX₂ systems gave the most active catalysts in this series.

Introduction

Dimethylsilanediyl-bridged *ansa*-metallocenes have found widespread use as catalyst precursors in homogeneous Ziegler–Natta chemistry.¹ Formal replacement of one Cp (or indenyl) group in this ligand arrangement by an alkylimido moiety (e.g. $[Me_3C-N^-]$) leads to the class of ("CpSiNR")M or "constrained geometry" catalysts, some examples of which have found interesting applications, especially in copolymerization reactions. ^{2–4} Due to the high general interest in this class of olefin polymerization catalysts a number of ligand variations has been described and tested, including systems with additional donor substituents⁵ or longer connecting chains between the Cp and amido functional groups.⁶ Surprisingly, systems where the Cp and amido groups of the constrained-geometry ligands were connected by a C1-based bridging unit instead of the ubiquitous Si1based bridging unit were not explored until recently.⁷ Meanwhile, a number of such alkylidene-bridged Cp/ amido group 4 metal catalyst precursors have been reported.^{8,9} In addition to these "CpCNR" metal complexes some "CpCO" complexes have also been reported, and their catalytic features tested.^{10,11} We have previously described the structures of two examples of related ["CpSiPR"ZrX₂] systems,^{4a,12,13} and we have recently

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Cp/Phosphido Group 4 Metal Complexes

reported the first example of a ("CpCPR")M^{IV}X₂-derived constrained-geometry catalyst system in a preliminary communication.⁸ Before that report, to the best of our knowledge, only a few such ligand systems had been described, e.g. by Jutzi,¹⁴ Hey-Hawkins,¹⁵ and Müller et al.,¹⁶ but not their attachment to the group 4 metals.

It is probably of some interest to study such phosphido analogues of the usual constrained-geometry group 4 metal catalysts to learn what effect the incorporation of a stereogenic phosphorus atom and the increased strain of the ligand framework will have on the catalytic behavior of such catalyst systems. We will, therefore, report here on the synthesis of a small series of such "CpCPR" titanium and zirconium complexes and briefly describe some of their catalytic features.

Synthesis and Spectroscopic Characterization of the ("CpCPR")Ti and -Zr Complexes

Fulvenes have extensively been used as precursors for substituted Cp ligands¹⁷ as well as the ligands of ansa-metallocenes.¹⁸ It is well established that a variety of nucleophiles can add to the electrophilic fulvene C6 carbon atom to form the respective cyclopentadienides.¹⁹ We had used this typical reaction pattern also for the synthesis of specific examples of the "CpCNR" ligand systems. In these cases amide anion equivalents [RNH⁻] were added to a non-CH-acidic fulvene, such as (C₅H₄)-CHCMe₃.8,9

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We have now treated 6-tert-butylfulvene (2) in a similar way with the phosphido nucleophiles Li[PH-(cyclohexyl)] and Li[PH(phenyl)], respectively. In each case, clean addition of the $[R^{1}PH^{-}]$ reagent at the fulvene C6 carbon atom was observed to yield the corresponding substituted cyclopentadienides [(C₅H₄)-CH(CMe₃)PR¹H]Li (4 (92% isolated), 6 (97%)). Each of these functionalized cyclopentadienides contains two persistent chirality centers, one at carbon (C6; see Scheme 1) and the other at phosphorus. Consequently, in each case a mixture of diastereoisomers is obtained (both ca. 3:1). The major isomer of **4** exhibits a pair of ¹H NMR Cp signals at δ 6.10 (2-H/5-H) and δ 6.58 (3-H/4-H). The 6-H resonance occurs at δ 3.00 with a coupling constant to phosphorus of ${}^{2}J_{PH} = 4$ Hz. The ¹H NMR signal of the corresponding P-H moiety is observed at δ 3.23 (¹*J*_{PH} = 204 Hz). The ³¹P NMR resonance occurs at δ –16.4. The minor diastereoisomer of the reagent **4** exhibits its 31 P NMR signal at δ -47.6 $(^{1}J_{\text{PH}} = 183 \text{ Hz})$. In d_{8} -THF solution both isomers show only a single ⁷Li NMR signal at δ –4.9. Complex 6 shows similar NMR features (see the Experimental Section).

The Li-phosphido reagents Li[PHR¹] are much less basic than their Li[NHR] counterparts. We made use of this characteristic feature which allowed us to add the reagents Li[PH(cyclohexyl)] and Li[PH(phenyl)], respectively, to 6,6-dimethylfulvene (1). Although a small fraction of the competing deprotonation reaction took place, the major reaction pathway was addition of the phosphido anion reagents to the electrophilic fulvene carbon center C6 to give the corresponding (phosphi-

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Figure 1. Decoalescence of the ¹H NMR (C₅H₄) signals of **11** (in CDFCl₂/CDF₂Cl/CD₂Cl₂ at 600 MHz; S denotes a residual CDHCl₂ solvent signal).

noalkyl)-functionalized cyclopentadienides [(C₅H₄)CMe₂-PHR¹]Li (**3**, R¹ = cyclohexyl; **5**, R¹ = phenyl), each in ca. 70% yield. Compound **5** exhibits a ³¹P NMR signal at δ -1.1 with a corresponding ¹H NMR P*H* resonance at δ 4.40 (¹*J*_{PH} = 209 Hz). The methyl groups at C6 are diastereotopic, due to the adjacent phosphorus chirality center. They give rise to ¹H NMR features at δ 1.67 (³*J*_{PH} = 7 Hz) and δ 1.61 (³*J*_{PH} = 14 Hz). The C6 carbon atom of **5** shows a ¹³C NMR resonance at δ 28.4 (with ²*J*_{PC} = 20 Hz), and the ⁷Li NMR resonance (in *d*₈-THF/*d*₈toluene 1:10) of **5** is observed at δ -7.5. Compound **3** shows similar NMR features (for details see the Experimental Section).

Treatment of **4** with LDA in THF at 0 °C resulted in deprotonation at phosphorus. The resulting dilithio salt of the "CpCPR" ligand system (**8**) was in this case isolated in ca. 50% yield. The reagent **8** was then reacted with 1 molar equiv of $Cl_2Ti(NMe_2)_2$.^{20a} After removal of lithium chloride the ("CpCPR")TiX₂ complex **12** (see Scheme 1) was isolated as a red-brown oil in 56% yield.

The titanium complex **12** contains a carbon chirality center (C6) that leads to the observation of four ¹H NMR Cp signals at δ 5.71, 5.54, 5.43, and 4.82 (¹³C NMR δ 112.0, 111.0, 110.8, 108.7) and a pair of signals of the diastereotopic $-NMe_2 \sigma$ ligands at titanium (¹H NMR δ 3.11, 2.91; ¹³C NMR δ 48.6, 45.1). The ¹³C NMR resonance of the bridging carbon atom C6 occurs at δ 47.9 with ¹*J*_{PC} = 30 Hz. The ³¹P NMR resonance of complex **12** is strongly temperature dependent. It is almost linearly shifted from δ –25.5 at 353 K to δ –65.5 at 193 K. A discussion and possible explanation will be given in DFT Calculations.

For the preparation of the corresponding ("CpCPPh")-Ti(NMe₂)₂ complex (**14**), the reagent **10** was generated in situ by LDA deprotonation of **6** followed by treatment with the Cl₂Ti(NMe₂)₂ reagent. Complex **14** was isolated in 79% yield as a red-brown oil. It also shows a temperature dependency of the ³¹P NMR shift, although not nearly as pronounced as in **12** (**14**: ³¹P NMR δ –54.4 at 298 K, δ –61.3 at 193 K).

Similarly, deprotonation of **3** or **5** with LDA gave the $Li_2[CpCPR^1]$ reagents **7** ($R^1 =$ cyclohexyl) and **9** ($R^1 =$ phenyl), respectively. Both were treated with Cl_2Ti -

 $(NMe_2)_2$ to yield the corresponding $[CpCPR^1]TiX_2$ complexes **11** (65%) and **13** (56%).

At ambient temperature the NMR spectra are in accord with a symmetry-averaged apparent C_{s} -symmetric structure of these complexes. However, this is due to an equilibration of two enantiomeric structures on the NMR time scale caused by a rapid inversion at the stereogenic phosphorus atom. In a CDFCl₂/CDF₂-Cl/CD₂Cl₂ solvent mixture²¹ lowering the temperature leads to a broadening and decoalescence of the pair of C_5H_4 ¹H NMR signals into two pairs (see Figure 1). At the same time we observe the decoalescence of the single NMe₂ ¹H NMR resonance to a 1:1 pair of signals below 213 K ($\Delta \nu$ = 60 Hz) and also the decoalescence of the signal of the pair of methyl groups at carbon atom C6 ($T_c = 223$, $\Delta v = 150$ Hz). In addition a complex pattern evolves of the ¹H NMR P-cyclohexyl resonances that was not further analyzed. From the Cp, NMe₂, and CMe₂ ¹H NMR coalescences an activation energy of $\Delta G^{\ddagger}(213)$ K) = 10.0 ± 0.5 kcal mol⁻¹ was estimated²² for the phosphorus inversion of complex 11 and the concomitant conformational equilibration of the chiral ligand backbone of the ["CpCP(cyclohexyl)"]Ti(NMe₂)₂ system.

The corresponding ["CpCP(phenyl)"]Ti(NMe₂)₂ system (13) exhibits an analogous chiral structure that is caused by the presence of a stereogenic nonplanar tricoordinate phosphorus center. Consequently at low temperature (<173 K) complex **13** features four separate C_5H_4 ¹H NMR signals, a pair of N(CH₃)₂ resonances, and a pair of C(CH₃)₂ signals (frozen spectrum in CDFCl₂/CDF₂Cl/CD₂Cl₂). Pairwise coalescence is observed upon raising the monitoring temperature. From the temperature-dependent 600 MHz ¹H NMR spectra in the Freon solvent mixture a Gibbs activation energy of $\Delta G^{\ddagger}(213 \text{ K}) = 9.4 \pm 0.5 \text{ kcal mol}^{-1} \text{ was obtained}^{22}$ for the phosphorus inversion process of complex 13. At 298 K only symmetry-averaged NMR spectra of complex 13 are observed (¹H NMR in d_8 -toluene: δ 5.71/5.28 (C₅H₄), δ 3.00 (NMe₂), δ 1.46 (³*J*_{PH} = 11 Hz, CMe₂)), due to this rapid equilibration on the NMR time scale. In addition the ³¹P NMR resonance of 13 shows a marked temperature-dependent chemical shift (δ 3.0 at 298 K, δ –13.0 at 193 K).

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Inversion at phosphorus in phosphanes is usually very slow, which makes trivalent phosphorus in most ligand environments a stable center of chirality.²³ There are, however, a number of cases known where a σ -bonded metal electrophile strongly interacts with the phosphorus lone pair, which may result in a partial double-bond character of the ensuing metal-P interaction.²⁴ A noteworthy example is the bis(phosphido)hafnocene complex **19**, described by Baker et al.,²⁵ which actually exhibits two P atoms in a significantly different bonding situation in the solid state as well as in solution (Scheme 2). The $19 \Rightarrow 19'$ interconversion probably represents a process that is closely related to the dynamic process which is observed here for the complexes **11** and **13**. It is likely that the observed P-inversion process involves a π -bonded P–Ti-type structure. DFT calculations of this process (see below), however, indicate that in our case the π -bonded structure (**20**[‡]) represents a transition state rather than a high-lying intermediate.

The corresponding zirconium complexes were prepared in a similar way. They show analogous features. Treatment of the reagent Li₂[(C₅H₄)CH(CMe₃)P(cyclohexyl)] (8) with Cl₂Zr(NEt₂)₂(THF)₂^{20b} gave the corresponding ["CpCP(cyclohexyl)"Zr(NEt₂)₂] complex 16 as an orange oil in ca. 60% yield. The chiral complex features four separate NMR signals of the C₅H₄ methine units (¹H at δ 6.02, 5.71, 5.56, 5.06; ¹³C at δ 110.3, 108.6, 108.1, 107.8) and a ³¹P NMR signal at δ –69.2 (298 K). The two –NEt₂ groups are different (cis and trans to the CMe₃ substituent at C6). This gives rise to pairs of ¹³C NMR NCH₂ resonances (δ 43.5, 41.4) and NCH₂CH₃ signals (δ 15.9, 15.6). Due to the diastereotopism of the $-NCH_2$ hydrogen atoms in **16**, the corresponding ¹H NMR spectrum is more complicated, giving rise to (in principle) four groups of NCH₂ ¹H NMR signals (found at δ 3.30 (2H), 3.22 (4H), and 3.15 (2H)) and two corresponding NCH₂CH₃ triplets (observed at δ 0.95 and 0.94).

For the preparation of the *P*-phenyl derivative **18** (see Scheme 1) the ligand system $\text{Li}_2[(C_5H_4)CH(CMe_3)P-(phenyl)]$ (**10**) was again generated in situ by treatment of **6** with LDA. The subsequent reaction with $\text{Cl}_2\text{Zr}-(\text{NEt}_2)_2(\text{THF})_2$ gave the ["CpCP(phenyl)"Zr(NEt_2)_2] complex **18** again as an orange oil (59% isolated yield). It shows similar spectroscopic features (see the Experi-





mental Section). The ^{31}P NMR chemical shift of complex 18 (δ –80.7 at 298 K) is almost temperature invariant.

Treatment of the dilithiated reagent Li₂[(C₅H₄)CMe₂P-(phenyl)] (9) with Cl₂Zr(NEt₂)₂(THF)₂ furnished the product 17 (orange oil, 65% isolated). Again, the rapid dynamic conformational equilibration leads to the observation of apparently symmetry-equivalent pairs of groups and substituents for the actual chiral complex 17. At ambient temperature it features ¹³C NMR signals of the NCH₂CH₃ ligands at δ 42.7 (CH₂) and δ 15.8 (CH₃). However, the ¹H NMR spectrum of the N(CH₂- CH_3 ₂ system in 17 is more complicated, due to the diastereotopism of its N–C H_2 nuclei (δ 3.29/3.19), whereas the system only gives rise to a single N(CH₂C- H_3)₂ ¹H NMR methyl resonance at δ 0.92. The ¹³C NMR C6 signal of **17** appears at δ 34.2 (¹ J_{PC} = 22 Hz) with the adjacent C(*C*H₃)₂ resonance at δ 31.4 (²*J*_{PC} = 14 Hz, ¹H NMR δ 1.60 with ³*J*_{PH} = 11 Hz). The Cp–methine hydrogen atoms of complex 17 are observed in d_8 toluene at ambient temperature at δ 5.98 (3-H/4-H) and δ 5.54 (2-H/5-H), respectively. These signals decoalesce at very low temperature (T_{coal} in CDFCl₂/CDF₂Cl/CD₂- Cl_2 at ca. 173 K) to two pairs of C_5H_4 ¹H NMR resonances. From these dynamic ¹H NMR (600 MHz) spectra a Gibbs activation energy of $\Delta G^{\ddagger}(173 \text{ K}) = 7.5$ \pm 0.5 kcal mol⁻¹ was estimated for the conformational equilibration process of complex 17, which includes stereochemical inversion at the phosphorus atom of the ligand system (see Scheme 3). We note that this barrier is markedly lower than that of the corresponding titanium complex 13 (see above).

The complex ["CpCP(cyclohexyl)"Zr(NEt₂)₂] (**15**) was prepared analogously by treatment of **7** with the reagent Cl₂Zr(NEt₂)₂(THF)₂. Complex **15** was isolated in close to 70% yield. Again, it shows dynamic behavior in solution, featuring pairwise decoalescence of its C₅H₄ ¹H NMR signals at very low temperature in CDFCl₂/ CDF₂Cl/CD₂Cl₂ solution. The Gibbs activation energy of this P-inversion process was determined to be ΔG^{\ddagger} -(193 K) = 8.6 \pm 0.5 kcal mol⁻¹.

DFT Calculations

Because X-ray data are unfortunately not available for compounds **11**–**18**, their structures, the inversion barriers, and the ³¹P NMR chemical shifts were investigated by quantum-chemical methods. To test the quantum-chemical methodology, a similar compound, where experimental structural data were available, was considered first. In the zirconium compound **21** (Chart 1), C6 has formally been replaced by a silicon atom and the C₅Me₄ ligand instead of C₅H₄ is present.^{4a,12,13} A detailed comparison between computed and experimental structural data is given in the Supporting Information.

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⁽²⁵⁾ Baker, R. T.; Whitney, J. F.; Wreford, S. S. Organometallics 1983, 2, 1049-1051.



Table 1. Computed (DFT-BP/TZVP) Inversion Barriers, M–P Bond Lengths, and Phosphorus Pyramidalization Angles for Compounds 11a, 13a, 15a, and 17a (See Text) and the Corresponding Transition States for Their Inversion at Phosphorus^a

compd	\mathbb{R}^1	М	$\Delta G^{\circ}_{\rm rel}$ (kcal/mol)	$\Delta G^{\ddagger}_{inv}{}^{b}$ (kcal/mol)	d(P-M) (pm)	(C-P-M)-R ¹ (deg)
11a	Me	Ti	0		257.8	70.2
11a(TS)			7.8	10.0	241.2	4.9
13a	Ph	Ti	0		255.7	57.0
13a(TS)			5.9	9.4	242.6	3.8
15a	Me	Zr	0		270.9	72.2
15a(TS)			6.7	8.6	254.8	4.5
17a	Ph	Zr	0		267.6	56.9
17a(TS)			5.2	7.5	256.5	3.4

 a See Figure 2 for a depiction of the calculated structures. b Experimental values (±0.5 kcal/mol).

Density functional theory (DFT) with a gradientcorrected BP86 functional and AO basis set of valence triple- ζ quality was employed as outlined in more detail in the Experimental Section. The agreement between experiment and theory in the case of **21** was generally good. The bond distances were systematically overestimated by 4-5 pm, and angles deviated only by about 1-2° from experiment. The systematic overestimation of the bond distances between second- and third-row atoms by almost all current density functionals is wellknown but is not expected to influence our general conclusions. To simplify matters, the experimentally investigated compounds 11, 13, 15, and 17 have been slightly modified in the computational procedure; i.e., the substituents on the nitrogen atoms are always methyl and the cyclohexyl moiety in 11 and 15 has also been replaced by a methyl group (11a-17a). The results for these systems are summarized in Table 1. The structures of 11a and 17a and their corresponding transition states (TS) of inversion at phosphorus are shown graphically in Figure 2. For both sets of molecules (11a and 13a with Ti and 15a and 17a with Zr) the effect of the substituent at the phosphorus atom is clearly evident. Replacing Me by Ph leads to shorter M-P bond distances (about 2 pm) and smaller pyramidalization angles (by 13-16°) due to conjugative interactions of the lone-pair orbital with the phenyl ring. The effect is slightly more pronounced for the Zr compounds 15 and 17 than for their Ti analogues. As expected, these structural features furthermore correlate with the barrier heights for inversion at the phosphorus atom. The computed free enthalpies of activation are, in general, in good agreement with those from experiment (about 1-2 kcal too low). The effect of the metal (smaller barrier for the Zr compounds relative to those with Ti) and the substituent effect (about 1 kcal/mol smaller barrier for $R^1 = Ph$) are computed almost quantitatively. The only notable difference between theory and experi-



Figure 2. DFT-BP/TZVP calculated ground-state structures of **11a** and **17a** and their corresponding transition states (TS) of the rapid inversion process at phosphorus.

ment is observed for **13a**, where the barrier deviates by 3.5 kcal/mol. The most striking feature of all TS structures is the shortened M–P bond length. It amounts to about 16 pm for the two compounds with $R^1 = Me$ and 13 pm (Ti) and 11 pm (Zr), respectively, for the two phenyl-substituted systems. This indicates the better ability of the phosphorus lone-pair orbital to interact with the metal fragment in the transition states and explains the small barrier for the inversion process.

These findings, furthermore, allow us to gain a qualitative understanding of the observed temperature dependence of the ³¹P NMR chemical shifts. The ³¹P NMR shielding constants strongly depend on the lengths (and consequently the strengths) of the M-P bond. For example, for 13a we have calculated a change of about 156 ppm when going from the minimum structure to the TS. Because of the asymmetry of the doubleminimum potential energy curve for the inversion process, thermally populated higher vibrational levels have more probability closer to the TS region (i.e. at shorter M-P distances), which thus would strongly affect the observed NMR chemical shift. A quantitative description of this process would require a combined quantum-mechanical/Boltzmann averaging of the computed shielding constants along complex hypersurfaces, which is currently out of reach computationally.

Olefin Polymerization Reactions

The "CpCPR" titanium and zirconium complexes **11**–**18** were used as group 4 metal components for the generation of homogeneous constrained-geometry Ziegler–Natta catalysts. In each case the respective metal diamide complex was activated by treatment with a large excess of methylalumoxane in toluene solution (Al: Zr ratios ranging from ca. 825 to ca. 1450).

All catalyst systems polymerize ethene at 60 °C to give linear polyethylene, but in most cases the catalyst activities were rather low (see Table 2). Noteworthy exceptions are the zirconium catalysts derived from the isopropylidene-bridged Cp/phosphido ligands (**15** and

 Table 2. Ethene Polymerization Reactions with the "CpCPR"Ti/ZrX2 Complexes^a

compd	М	CR ¹ R ² b	PR ^c	amt of cat. $(mg)^f$	Al/M	amt of PE (g)	mp (°C)	act ^g
11	Ti	CMe ₂	Cye	15	825	1.8	129	21
13	Ti	CMe_2	Pĥ	14	840	4.4	130	56
12	Ti	\mathbf{CHR}^d	Cy	11	1200	1.0	128	18
14	Ti	\mathbf{CHR}^d	Pȟ	13	1000	0.6	129	9
15	Zr	CMe_2	Cy	10	1450	8.5	130	193
17	Zr	CMe ₂	Pȟ	20	825	6.9	130	78
16	Zr	\mathbf{CHR}^d	Cy	11	1400	0.3	126	6
18	Zr	CHR^d	Рĥ	17	950	0.4	129	6

^{*a*} For each complex a representative example out of a series of similar experiments is listed. Reactions were carried out in toluene solution, for 1 h at 60 °C, under 2 bar of ethene. ^{*b*} Bridging alkylidene unit. ^{*c*} Hydrocarbyl group at phosphorus. ^{*d*} R = CMe₃. ^{*e*} Cy = cyclohexyl. ^{*f*} Group 4 metal component. ^{*g*} Activity in units of g of PE/((mmol of cat.)(bar of ethene) h).

Table 3. Ethene/1-Octene Copolymerization with the (CpCPR)MX₂ Complexes at 90 °C^a

				amt of					$M_{\rm w}/$
compd	Μ	CR^1R^2	PR	cat. (mg)	Al/M	act^{c}	$\mathbf{a}:\mathbf{b}^d$	$M_{ m w}$	Mn
11	Ti	CMe ₂	Су	13	960	15	6:1	12000	2.6
13	Ti	CMe_2	Ph	15	825	25	5:1	е	
12	Ti	CHR^b	Cy	13	960	18	6:1		
14	Ti	CHR^b	Pĥ	12	1000	5	7:1	14000	1.9
15	Zr	CMe_2	Cy	10	1650	860	6:1	9000 ^f	1.9 ^f
17	Zr	CMe_2	Pĥ	10	1500	400	6:1	8000	1.9
16	Zr	CHR^b	Cy	11	1400	40	6:1	5000	1.9
18	Zr	CHR^b	Pȟ	11	1500	12	6:1	13000	2.1

^{*a*} In toluene solution, for 1 h reaction time, under 2 bar of ethene. Representative examples out of larger series of similar experiments are listed. ^{*b*} R = CMe₃. ^{*c*} Activity in units of (g of copolymer)/((mmol of cat.)(bar of ethene) h). ^{*d*} Ethene/1-octene ratio in the copolymer. ^{*e*} Not determined. ^{*f*} Values from a copolymer obtained at 1 bar of ethene pressure.

17), which show slightly higher ethene polymerization activities under the applied reaction conditions.

More importantly, the **11–18**/MAO systems provide active catalysts for the random copolymerization of ethene with the α -olefin 1-octene. Typical reaction conditions and polymerization results are listed in Table 3. In all cases a reasonable incorporation of the long-chain 1-alkene component was achieved under the selected reaction conditions (90 °C in toluene solution at 2 bar ethene pressure). The characteristic ¹³C NMR spectrum²⁶ of a typical copolymer example, namely the ethene/1-octene copolymer obtained at the most active catalyst system (**15**/MAO, entry 5 in Table 3), is depicted and described in Figure 3.

In the "normal" "CpSiNR"M series the titanium complexes usually seem to give the best catalyst performances.²⁷ In this "CpCPR"M series of complexes the situation seems to be rather different. The catalyst activities depend strongly on the metal and apparently also on the specific substitution pattern of the ligand backbone. All four titanium catalyst systems give rather low activities in ethene/1-octene copolymerization (see Table 3). Generally, their direct zirconium counterparts all seem to be more active catalysts. This is drastically illustrated with the Zr systems [Cp(CMe₂)PCy]ZrX₂ (**15**) and [Cp(CMe₂)PPh]ZrX₂ (**17**), which both give in general

quite acceptable polymerization activities upon MAO activation. The most active system in this series, **15**/MAO, was found to be more than 50 times more active than its titanium analogue **11**/MAO (see Table 3), and the related zirconium system **17**/MAO is still a >15 times more active copolymerization catalyst, as compared to its titanium relative **13**/MAO.

However, not all the "CpCPR"Zr systems give very active catalysts for ethene/1-octene copolymerization. This activity depends critically on the structure and substitution pattern of the respective ligand backbone. This is illustrated by the last two entries in Table 3: the (CpCPR)Zr systems **16** and **18** upon MAO activation give only low-activity polymerization catalysts.

We conclude that the alkylidene-bridged (CpCPR)MX₂ catalyst precursors-relatives of the ubiquitous (CpSiN-R)MX₂ system—are readily available by means of a fulvene route. The systems can be activated by treatment with MAO to give active olefin polymerization and copolymerization catalysts. The titanium complexes seem to be markedly less active than the zirconium systems, and the catalyst activities generally seem to depend critically on the substitution pattern of the backbone, which will leave some room for further catalyst developments in this area. The Me₂C-bridged zirconium complexes (15, 17) give rather active copolymerization catalysts. The molecular weights of the obtained products are rather low (see Table 3), whereas typical 1-octene incorporation ratios were achieved. The study shows that the exchange of groups and atoms at the backbones of the constrained-geometry complex systems has a profound influence on the actual catalyst performance and characteristics, which may open up routes to interesting new catalyst systems and product targets.

Experimental Section

All reactions were carried out under argon using Schlenktype glassware or in a glovebox. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled prior to use. NMR spectra were measured using a Bruker AC 200 P or Varian Unity Plus 600 NMR spectrometer. Most assignments were based on a series of 2D NMR experiments.²⁸ Melting points were determined by differential scanning calorimetry (2010 DSC, Du Pont/STA Instruments). GPC was performed using a Agilant 1100 chromatograph with UV/vis absorbance detector and RI detector. Pentafulvenes **1** and **2**,²⁹ LiPHR (R = Cy, Ph),³⁰ and the reagents Cl₂Zr(NEt₂)₂(THF)₂,^{20b} and Cl₂Ti(NMe₂)₂^{20a} were prepared according to literature procedures. Some of the products were obtained as viscous oils, which were difficult to get analytically pure.

Preparation of Lithium [1-Methyl-1-(cyclohexylphosphido)ethyl]cyclopentadienide (3). Lithium cyclohexylphosphide (920 mg, 7.5 mmol) was suspended in 70 mL of pentane and reacted with 850 mg (8.0 mmol) of 6,6-dimethylfulvene (1) at -78 °C. Over 12 h a white solid precipitated. The solid product was collected by filtration, washed twice with 10 mL of pentane, and dried in vacuo to give 1.21 g (71%) of **3.** ¹H NMR (200.1 MHz, THF-*d*₈): δ 5.62, 5.56 (each m, each 2H, Cp H), 3.00 (dd, ¹*J*_{PH} = 194 Hz, ³*J*_{HH} = 2.1 Hz, 1H, P–H), 1.47 (d, ³*J*_{PH} = 11.2 Hz, 6H, CH₃), 1.73–0.81 (m, 11H, Cy H).

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Figure 3. ¹³C{¹H} NMR spectrum (C_6D_6 , 300 K) of the ethene/1-octene ca. 6:1 copolymer obtained with the **15**/MAO catalyst at 90 °C in toluene (1 bar of ethene pressure).

³¹P NMR (80.1 MHz, THF- d_8): δ 7.42 (dm, ¹ $J_{PH} = 194$ Hz, P–H). ⁷Li NMR (232.8 MHz, THF- d_8 , 298 K): δ –4.9.

Preparation of Lithium [1-(Cyclohexylphosphido)-2,2dimethylpropyl]cyclopentadienide (4). Lithium cyclohexylphosphide (920 mg, 7.5 mmol) was suspended in 70 mL of pentane and reacted with 1.07 g (8.0 mmol) of 6-tert-butylfulvene (2) at -78 °C. Over 12 h a white solid precipitated. The solid was collected by filtration, washed twice with 10 mL of pentane, and dried in vacuo to give 1.58 g (6.9 mmol, 92%) of 4 as a 3:1 mixture of two diastereomers. ¹H NMR (200.1 MHz, THF- d_8 /benzene- d_6 (1:4)): diastereomer A (major), δ 6.58, 6.10 (each m, each 2H, Cp H), 3.23 (ddd, ${}^{1}J_{PH} = 204$ Hz, ${}^{3}J_{HH} =$ ${}^{3}J_{\rm HH} = 6$ Hz, ${}^{3}J_{\rm HH} = 4$ Hz, 1H, P–H), 3.00 (dd, ${}^{2}J_{\rm PH} = 4$ Hz, ${}^{3}J_{\rm HH} = 6$ Hz, 1H, 6-H), 1.27 (s, 9H, C(CH₃)₃), 1.8–1.17 (11H, Cy H); diastereomer B, δ 6.58, 6.10 (each m, each 2H, Cp H), 3.55 (ddd, ${}^{1}J_{PH} = 183$ Hz, ${}^{3}J_{HH} = 6$ Hz, ${}^{3}J_{HH} = 4$ Hz, 1H, P–H), 3.39 (t, ${}^{2}J_{PH} = 6$ Hz, ${}^{3}J_{HH} = 6$ Hz, 1H, 6-H), 1.24 (s, 9H, C(CH₃)₃), 1.8-1.17 (11H, Cy-H). ³¹P NMR (81.0 MHz, THF*d*₈): diastereomer A, δ –16.4 (¹*J*_{PH} = 204 Hz); diastereomer B, δ -47.6 (¹J_{PH} = 183 Hz). ⁷Li NMR (232.8 MHz, THF- d_8 , 298 K): δ -4.9.

Preparation of Lithium [1-Methyl-1-(phenylphosphido)ethyl]cyclopentadienide (5). Lithium phenylphosphide (870 mg, 7.5 mmol) was suspended in 70 mL of pentane and reacted with 850 mg (8.0 mmol) of 6,6-dimethylfulvene (1) at -78 °C. Over 12 h a white solid precipitated. The precipitate was collected by filtration, washed twice with 10 mL of pentane, and dried in vacuo to give 1.21 g (71%) of 5. ¹H NMR (200.1 MHz, THF-*d*₈/benzene-*d*₆ (1:4)): δ 7.24 (m, 2H, Ph H), 7.12 (m, 3H, Ph H), 6.06 (m, 4H, Cp H), 4.40 (d, ¹*J*_{PH} = 209 Hz, 1H, P–H), 1.67 (d, ³*J*_{PH} = 7 Hz, 3H, CH₃), 1.61 (d, ³*J*_{PH} = 14 Hz, 3H, CH₃). ³¹P NMR (200.1 MHz, THF-*d*₈/benzene-*d*₆ (1:10)): δ -1.1 (d, ¹*J*_{PH} = 209 Hz). ⁷Li NMR (232.8 MHz, THF*d*₈/toluene-*d*₈ (1:10), 289–193 K): δ -7.5.

Preparation of Lithium [1-(Phenylphosphido)-2,2dimethylpropyl]cyclopentadienide (6). Lithium phenylphosphide (920 mg, 7.5 mmol) was suspended in 70 mL of pentane and reacted with 1.07 g (8.0 mmol) of 6-*tert*-butylfulvene (**2**) at -78 °C. Over 12 h a white solid precipitated. The solid was collected by filtration, washed twice with 10 mL of pentane, and dried in vacuo to give 1.85 g (97%) of **6** as a mixture of two diastereoisomers (1:3). ¹H NMR (200.1 MHz, benzene-*d*₆/ THF-*d*₈ (4:1)): diastereomer A, δ 7.80, 7.60, 7.05 (each m, 5H, Ph H), 6.09 u. 6.05 (each m, each 2H, Cp H), 4.26 (dd, ¹*J*_{PH} = 220 Hz, ³*J*_{HH} = 5 Hz, 1H, P–H), 3.51 (d, ³*J*_{HH} = 5 Hz, 1H, 6-H), 1.25 (s, 9H, C(CH₃)₃); diastereomer B, δ 7.80, 7.60, 7.05 (each m, 5H, Ph-H), 6.09 and 6.05 (each m, each 2H, Cp H), 4.99 (dd, ${}^{1}J_{PH} = 220$ Hz, ${}^{3}J_{HH} = 5$ Hz, 1H, P–H), 3.45 (d, ${}^{3}J_{HH} = 5$ Hz, 1H, 6-H), 1.19 (s, 9H, C(CH₃)₃). 31 P NMR (81.0 MHz, benzene-*d*₆/THF-*d*₈ (4:1)): diastereomer A, δ –30.5 (d, ${}^{1}J_{PH} = 220$ Hz); diastereomer B, δ –58.2 (d, ${}^{1}J_{PH} = 189$ Hz). 7 Li NMR (232.8 MHz, THF-*d*₈/toluene-*d*₈ (1:10), 289–193 K): δ –7.7.

Deprotonation of 3: Formation of 7. A sample of 228 mg (1.0 mmol) of **3** was dissolved in 5 mL of THF and treated with 107 mg (1.0 mmol) of LDA in 3 mL of THF at 0 °C for 1 h. The solvent was removed, and subsequent recrystallization by diffusion of pentane into a concentrated THF solution gave 187 mg (80%) of **7** as pale yellow crystals. ¹H NMR (200.1 MHz, THF-*d*₈): δ 5.62, 5.56 (each m, each 2H, Cp H), 1.47 (d, ³*J*_{PH} = 11.2 Hz, 6H, 7-H), 1.73–0.81 (m, 11H, Cy H). ³¹P NMR (81.0 MHz, THF-*d*₈): δ 33.3 (s).

Reaction of 4 with LDA: Formation of 8. A sample of 270 mg (1.0 mmol) of **4** was dissolved in 5 mL of THF and treated with 107 mg (1.0 mmol) of LDA in 3 mL of THF at 0 °C for 1 h. The solvent was then removed, and subsequent recrystallization by diffusion of pentane into a concentrated THF solution yielded 135 mg (50%) of **8** as pale yellow crystals. ¹H NMR (200.1 MHz, THF- d_8 /benzene- d_6 (4:1)): δ 5.92, 5.83 (each m, each 2H, Cp H), 1.47 (9H, C(CH₃)₃), 2.42–1.02 (bm, 11H, Cy H). ³¹P NMR (81.0 MHz, THF- d_8 /benzene- d_6): δ –24.3 (s).

Treatment of 5 with LDA: Formation of 9. A sample of 228 mg (1.0 mmol) of **5** was dissolved in 5 mL of THF and treated with 107 mg (1.0 mmol) of LDA in 3 mL of THF at 0 °C for 1 h. The solvent was removed, and subsequent recrystallization by diffusion of pentane in a concentrated THF solution gave 126 mg (54%) of **9** as pale yellow crystals. ¹H NMR (200.1 MHz, THF-*d*₈): δ 7.24 (m, 2H, Ph H), 7.12 (m, 3H, Ph H), 6.06 (m, 4H, Cp H), 1.67 (d, ³*J*_{PH} = 7 Hz, 3H, 7-H), 1.61 (d, ³*J*_{PH} = 14 Hz, 3H, 7-H'). ³¹P{¹H} NMR (81.0 MHz, THF-*d*₈/benzene-*d*₆ (1:4)): δ 28.7 (s).

Preparation of 11. A solution of 117 mg (0.50 mmol) of 7 in 7 mL of THF was added dropwise to 97 mg (0.47 mmol) of Cl₂Ti(NMe₂)₂ in 3 mL of THF at 0 °C. Over 2 h the reaction mixture was stirred at 0 °C. The solvent was removed in vacuo, and the oily residue was treated with 10 mL of pentane. After removal of LiCl by filtration and evaporation of the solvent, 106 mg (65%) of **11** was obtained as a red-brown oil. ¹H NMR (599.8 MHz, toluene- d_8 , 298 K): δ 5.69 (m, 2H, 3-H, 4-H), 5.18 (m, 2H, 2-H, 5-H), 2.99 (s, 12H, NCH₃), 1.92 (m, 2H, 2'-H), 1.76 (m, 2H, 3'-H), 1.60 (m, 1H, 4'-H), 1.53 (d, ³*J*_{PH} = 10 Hz, 6H, C(CH₃)₂), 1.40 (m, 2H, 2'-H'), 1.26 (m, 2H, 3'-H'), 1.22 (m, 1H, 4'-H'), 1.21 (m, 1H, 1'-H). ¹³C{¹H} NMR (150.8 MHz, toluene- d_8 , 298 K): δ 120.0 (C-1), 110.9 (C-3, C-4), 107.2 (C-2, C-5), 46.6 (d, ${}^{3}J_{PC} = 5.2$ Hz, NCH₃), 36.7 (d, ${}^{1}J_{PC} = 38.3$ Hz, C-1'), 34.9 (d, ${}^{2}J_{PC} = 15.1$ Hz, C-2'), 30.5 (C-6), 28.8 (d, ${}^{2}J_{PC} = 14.6$ Hz, C(CH₃)₂), 27.7 (d, ${}^{3}J_{PC} = 9.3$ Hz, C-3'), 27.0 (C-4'). ${}^{31}P{}^{1}H{}$ NMR (202.6 MHz, toluene- d_{8}): δ 14.2 (298 K). Anal. Calcd for C₁₈H₃₃N₂PTi (356.3): C, 60.67; H, 9.33; N, 7.86. Found: C, 61.58; H, 9.15; N, 8.13.

Synthesis of the Titanium Complex 12. A solution of 120 mg (0.50 mmol) of 8 in 7 mL of THF was added dropwise to 98 mg (0.48 mmol) of Cl₂Ti(NMe₂)₂ in 3 mL of THF at 0 °C. Over 2 h the reaction mixture was stirred at 0 °C. The solvent was removed in vacuo, and the oily residue was treated with 10 mL of pentane. After filtration of LiCl and evaporation of the solvent, 108 mg (56%) of 12 was obtained as a red-brown oil. ¹H NMR (599.8 MHz, toluene-d₈, 298 K): δ 5.71, 5.54 (each m, each 1H, 3-H and 4-H), 5.43 (m, 1H, 2-H), 4.82 (m, 1H, 5-H), 3.11, 2.91 (each s, each 6H, NCH₃), 3.08 (s, 2H, 6-H and 1'-H), 1.82 and 1.27 (bm, each 2H, 2'-H), 1.75, 1.18 (bm, each 2H, 3'-H), 1.62 (bm, 2H, 4'-H), 1.22 (s, 9H, $C(CH_3)_3$). ¹³C{¹H} NMR (150.8 MHz, toluene-d₈, 298 K): δ 114.3 (C-1), 112.0 $({}^{1}J_{CH} = 173 \text{ Hz}, \text{ C-5})$, 111.0 and 110.8 $({}^{1}J_{CH} = 175 \text{ Hz}, 174 \text{ Hz},$ C-3 and C-4), 108.7 (d, ${}^{1}J_{CH} = 175$ Hz, ${}^{3}J_{CP} = 4$ Hz, C-2), 48.6 (d, ${}^{1}J_{CH} = 131$ Hz, NC_{α}H₃), 47.9 (d, ${}^{1}J_{CH} = 129$ Hz, ${}^{1}J_{CP} = 30$ Hz, C-6), 45.1 (s, ${}^{1}J_{CH} = 133$ Hz, NC_{β}H₃), 44.8 (${}^{1}J_{CH} = 132$ Hz, C-1'), 34.6 (d, ${}^{1}J_{CP} = 9$ Hz, CMe₃), 29.1 (d, ${}^{1}J_{CH} = 124$ Hz, ${}^{3}J_{CP}$ = 6 Hz, C(CH₃)₃), 28.3 (d, ${}^{1}J_{CH}$ = 125 Hz, ${}^{3}J_{CP}$ = 11 Hz, C-3'), 27.2 (C-4'). ³¹P{¹H} NMR (202.6 MHz, toluene- d_8): δ -25.5 (353 K), -28.7 (333 K), -32.7 (313 K), -36.3 (298 K), -41.0 (b, 273 K), -46.9 (253 K), -53.0 (233 K), -59.3 (213 K), -65.5 (193 K), -68.5 (183 K). Anal. Calcd for C₂₀H₃₇N₂PTi (384.4): C, 62.49; H, 9.70. Found: C, 62.27; H, 9.66.

Preparation of the Titanium Complex 13. A solution of 114 mg (0.50 mmol) of 9 in 7 mL of THF was added dropwise to 98 mg (0.48 mmol) of Cl₂Ti(NMe₂)₂ in 3 mL of THF at 0 °C. Over 2 h the reaction mixture was stirred at 0 °C. The solvent was removed in vacuo, and the oily residue was treated with 10 mL of pentane. After filtration of LiCl and evaporation of the solvent 108 mg (56%) of 13 was obtained as a red-brown oil. ¹H NMR (599.8 MHz, toluene-d₈, 298 K): δ 7.31 (m, 2H, 3'-H), 7.04 (m, 2H, 2'-H), 6.96 (m, 1H, 4'-H), 5.71 (m, 2H, 3-H and 4-H), 5.28 (m, 2H, 2-H and 5-H), 3.00 (s, 12H, NCH₃), 1.46 (d, ${}^{3}J_{PH} = 11$ Hz, 6H, C(CH₃)₂). ${}^{13}C{}^{1}H{}$ NMR (599.8 MHz, toluene- d_8 , 298 K): δ 143.0 (d, ${}^1J_{\rm PC} = 51$ Hz, C-1'), 136.1 (d, ${}^{1}J_{CH} = 155$ Hz, ${}^{3}J_{PC} = 15$ Hz, C-3'), 126.7 (d, ${}^{1}J_{CH} = 155$ Hz, ${}^{2}J_{\text{PC}} = 4.5$ Hz, C-2'), 126.2 (${}^{1}J_{\text{CH}} = 160$ Hz, C-4'), 123.1 (C-1), 111.3 (${}^{1}J_{CH} = 175$ Hz, C-3 and C-4), 107.7 (d, ${}^{1}J_{CH} = 172$ Hz, ${}^{3}J_{PC} = 3$ Hz, C-2 and C-5), 46.7 (d, ${}^{1}J_{CH} = 134$ Hz, ${}^{3}J_{PC} = 5$ Hz, NCH₃), 32.2 (d, ${}^{1}J_{PC}$ = 36 Hz, C-6), 29.7 (d, ${}^{1}J_{CH}$ = 124 Hz, ${}^{2}J_{PC}$ = 15 Hz, CH₃). ${}^{31}P{}^{1}H$ NMR (202.6 MHz, toluene-*d*₈): δ 3.0 ($\nu_{1/2}$ = 5 Hz, 298 K), -0.7 ($\nu_{1/2}$ = 17 Hz, 273 K), -6.9 ($\nu_{1/2}$ = 30 Hz, 233 K), -10.0 ($\nu_{1/2}$ = 27 Hz, 213 K), -13.0 ($\nu_{1/2}$ = 45 Hz, 193 K). Anal. Calcd for C18H27N2PTi (350.3): C, 61.72; H, 7.77. Found: C, 62.17; H, 7.55.

Synthesis of the Titanium Complex 14. A sample of 125 mg (0.50 mmol) of 6 in 5 mL of THF was treated with 53 mg (0.50 mmol) of LDA in 3 mL of THF at 0 °C, and the mixture was stirred for 1 h. The solution of the in situ generated dilithium salt 10 was then added dropwise to a solution of 98 mg (0.48 mmol) of Cl₂Ti(NMe₂)₂ in 3 mL of THF at 0 °C. Over 2 h the reaction mixture was stirred at 0 °C. The solvent was removed in vacuo, and the oily residue was treated with 10 mL of pentane. After filtration of LiCl and evaporation of the solvent 152 mg (79%) of 14 was obtained as a brown oil. ¹H NMR (599.8 MHz, toluene-d₈, 253 K): δ 7.28, 7.03 (each m, each 2H, 2'-H and 3'-H), 6.93 (m, 1H, 4'-H), 5.69 (m, 1H, Cp H), 5.21 (m, 1H, Cp H), 5.38 (m, 1H, Cp H), 5.10 (m, 1H, Cp-H), 3.47 (d, ${}^{2}J_{PH} = 3$ Hz, 1H, 6-H), 2.96, 2.63 (each s, each 6H, NCH₃), 1.26 (s, 9H, C(CH₃)₃). ¹³C{¹H} NMR (100.1 MHz, benzene- d_{θ} , 298 K): δ 131.5 (C-2'), 127.5 (C-3'), 125.0 (C-4'), 112.9, 112.5, 112.0 (each Cp C), 49.0 (C-6), 46.0 (NCH₃), 29.0 (C(CH₃)₃). ³¹P{¹H} NMR (202.6 MHz, toluene- d_8): δ -54.4 (298 K), -55.2 (288 K), -57.5 (253 K), -60.0 (213 K), -61.3 (193

K). Anal. Calcd for $C_{20}H_{31}N_2PTi$ (378.4): C, 63.49; H, 8.26; N, 7.40. Found: C, 62.45; H, 8.52; N, 6.38.

Preparation of the Zirconium Complex 15. A solution of 117 mg (0.50 mmol) of 7 in 7 mL of THF was added dropwise to 214 mg (0.47 mmol) of Cl₂Zr(NEt₂)₂(THF)₂ in 3 mL of THF at 0 °C. Over 2 h the reaction mixture was stirred at 0 °C. The solvent was removed in vacuo, and the oily residue was treated with 10 mL of pentane. After removal of LiCl and evaporation of the solvent 148 mg (69%) of 15 was obtained as an orange oil. ¹H NMR (599.8 MHz, toluene- d_8 , 298 K): δ 5.92 (m, 2H, 3-H and 4-H), 5.47 (m, 2H, 2-H and 5-H), 3.26, 3.15 (each m, each 4H, NCH₂), 1.99 (m, 2H, 2'-H), 1.76 (m, 2H, 3'-H), 1.62 (d, ${}^{3}J_{PH} = 10$ Hz, 6H, C(CH₃)₂), 1.60 (m, 1H, 1'-H), 1.58 (m, 1H, 4'-H), 1.47 (m, 2H, 2'-H'), 1.26 (m, 2H, 3'-H'), 1.23 (m, 1H, 4'-H'), 0.93 (t, ${}^{3}J_{HH} = 6.0$ Hz, 6H, NCH₂CH₃). ¹³C{¹H} NMR (150.8 MHz, toluene-*d*₈, 298 K): δ 124.0 (C-1), 108.1 (C-3 and C-4), 106.4 (d, ${}^{3}J_{PC} = 4$ Hz, C-2 and C-5), 42.5 (d, ${}^{3}J_{PC} < 2$ Hz, NCH₂), 36.0 (d, ${}^{2}J_{PC} = 16$ Hz, C-2'), 35.6 (d, ${}^{1}J_{PC} = 38$ Hz, C-1'), 33.2 (C-6), 30.9 (d, ${}^{2}J_{PC} = 13$ Hz, C(*C*H₃)₂), 27.6 (d, ${}^{3}J_{PC} = 11$ Hz, C-3'), 26.9 (C-4'). ${}^{31}P{}^{1}H{}$ NMR (81.0 MHz, toluene- d_8): δ -11.5 (298 K). Anal. Calcd for C₂₂H₄₁N₂-PZr (455.8): C, 57.98; H, 9.07; N, 6.15. Found: C, 58.27; H, 8.61; N. 4.91.

Synthesis of the Zirconium Complex 16. A solution of 120 mg (0.50 mmol) of 8 in 7 mL of THF was added dropwise to 214 mg (0.47 mmol) of Cl₂Zr(NEt₂)₂(THF)₂ in 3 mL of THF at 0 °C. Over 2 h the reaction mixture was stirred at 0 °C. The solvent was removed in vacuo, and the oily residue was treated with 10 mL of pentane. After filtration of LiCl and evaporation of the solvent 143 mg (59%) of 16 was obtained as a deep orange oil. ¹H NMR (599.8 MHz, toluene-*d*₈, 298 K): δ 6.02, 5.56 (each m, each 1H, 3-H and 4-H), 5.71, 5.06 (each m, each 1H, 5-H and 2-H), 3.31 (s, 1H, 6-H), 3.30 (ABX₃, m, 2H, N_αCH₂CH₃), 3.22 (ABX₃, 4H, N_βCH₂CH₃), 3.15 (ABX₃, 2H, N_αCH₂CH₃), 1.22 (s, 9H, C(CH₃)₃), 0.95 (t, 6H, N_αCH₂CH₃), 0.94 (t, 6H, $N_{\beta}CH_2CH_3$) 1.8–0.9 (br, Cy H, 11H). ¹³C{¹H} NMR (150.8 MHz, toluene-d₈, 298 K): δ 117.5 (C-1), 110.3 and 108.6 (C-2 and C-5), 108.1 and 107.8 (C-3 and C-4), 57.2 (C-6), 43.5 $(N_{\beta}CH_{2}CH_{3})$, 41.4 $(N_{\alpha}CH_{2}CH_{3})$, 28.7 $(C(CH_{3})_{3})$, 15.9 $(N_{\beta}-1)^{-1}$ CH_2CH_3), 15.6 (N_aCH₂CH₃). Cy carbon signals were not resolved. ³¹P{¹H} NMR (81.0 MHz, toluene- d_8): δ –69.2. Anal. Calcd for C24H45N2PZr (483.8): C, 59.58; H, 9.37; N, 5.79. Found: C, 58.35; H, 9.90; N, 5.50.

Preparation of the Zirconium Complex 17. A solution of 114 mg (0.50 mmol) of 9 in 7 mL of THF was added dropwise to 208 mg (0.48 mmol) of Cl₂Zr(NEt₂)₂(THF)₂ in 3 mL of THF at 0 °C. Over 2 h the reaction mixture was stirred at 0 °C. The solvent was removed in vacuo, and the oily residue was treated with 10 mL of pentane. After filtration of LiCl and evaporation of the solvent 146 mg (65%) of 17 was obtained as an orange oil. ¹H NMR (599.8 MHz, toluene- d_8 , 298 K): δ 7.56 (m, 2H, 2'-H), 7.06 (m, 2H, 3'-H), 6.96 (m, 1H, 4'-H), 5.98 (m, 2H, 3-H and 4-H), 5.54 (m, 2H, 2-H and 5-H), 3.29, 3.19 (ABX₃, each m, each 4H, NC H_2 CH₃), 1.60 (d, ${}^{3}J_{PH} = 11$ Hz, 6H, C(CH₃)₂), 0.92 (t, ${}^{3}J_{HH} = 6.9$ Hz, 12H, NCH₂CH₃). ${}^{13}C_{-1}$ {¹H} NMR (150.8 MHz, toluene- d_8 , 298 K): δ 142.5 (d, ¹ J_{PC} = 45 Hz, C-1'), 136.3 (d, ${}^{1}J_{CH} = 158$ Hz, ${}^{2}J_{PC} = 14$ Hz, C-2'), 129.2 $({}^{1}J_{CH} = 157$ Hz, C-4'), 127.6 (d, ${}^{1}J_{CH} = 162$ Hz, ${}^{3}J_{PC} = 5$ Hz, C-3'), 125.8 (C-1), 108.6 (${}^{1}J_{CH} = 173$ Hz, C-3 and C-4), 106.7 (d, ${}^{1}J_{CH} = 171$ Hz, ${}^{3}J_{PC} = 4$ Hz, C-2 and C-5), 42.7 (${}^{1}J_{CH} = 131$ Hz, NCH₂CH₃), 34.2 (d, ${}^{1}J_{PC} = 22$ Hz, C-6), 31.4 (d, ${}^{1}J_{CH} =$ 124 Hz, ${}^{2}J_{PC} = 14$ Hz, $C(CH_{3})_{2}$, 15.8 (${}^{1}J_{CH} = 127$ Hz, NCH₂*C*H₃). ³¹P{¹H} NMR (81.0 MHz, toluene-*d*₈): δ –22.5 (298 K). Anal. Calcd for C₂₂H₃₅N₂PZr (449.7): C, 58.75; H, 7.84; N, 6.23. Found: C, 57.10; H, 7.71; N, 5.81.

Preparation of the Zirconium Complex 18. A sample of 125 mg (0.50 mmol) of **6** in 5 mL of THF was treated with 53 mg (0.50 mmol) of LDA in 3 mL of THF at 0 °C, and the mixture was stirred for 1 h. The solution of **10** was then added dropwise to 214 mg (0.47 mmol) of $Cl_2Zr(NEt_2)_2(THF)_2$ in 3 mL of THF at 0 °C. Over 2 h the reaction mixture was stirred

at 0 °C. The solvent was removed in vacuo, and the oily residue was treated with 10 mL of pentane. After filtration of LiCl and evaporation of the solvent 174 mg (59%) of 18 was obtained as a deep orange oil. ¹H NMR (599.8 MHz, toluened₈, 298 K): δ 7.36, 7.18 (each m, each 2H, 2'-H and 3'-H), 6.82 (m, 1H, 4'-H), 5.90 (m, 1H, Cp H), 5.81 (m, 1H, Cp H), 5.79 (m, 1H, Cp H), 5.27 (m, 1H, Cp-H), 3.62 (d, ${}^{2}J_{PH} = 4$ Hz, 1H, 6-H), 3.19 (ABX₃, m, 4H, N_αCH₂CH₃), 2.94 (ABX₃, 4H, N_βCH₂-CH₃), 1.27 (s, 9H, C(CH₃)₃), 0.98 (t, ${}^{3}J_{CH} = 7$ Hz, 6H, $N_{\alpha}CH_{2}CH_{3}$), 0.56 (t, ${}^{3}J_{CH} = 7$ Hz, 6H, $N_{\beta}CH_{2}CH_{3}$). ${}^{13}C\{{}^{1}H\}$ NMR (100.1 MHz, benzene-d_θ, 298 K): δ 130.0 (C-2'), 127.0 (C-3'), 116.0 (C-1), 110.5, 110.0, 108.5, 107.0 (each Cp C), 47.0 (C-6), 42.0 (N_{β}*C*H₂CH₃), 34.9 (*C*Me₃), 34.0 (N_{α}*C*H₂CH₃), 28.0 $(C(CH_3)_3)$, 16.0 $(N_{\beta}CH_2CH_3)$, 15.5 $(N_{\alpha}CH_2CH_3)$. C-4' was not observed. ³¹P{¹H} NMR (202.6 MHz, toluene- d_8): δ -80.7 (298) K), -81.2 (253 K), -80.7 (213 K), -80.3 (193 K). Anal. Calcd for C₂₄H₃₉N₂PZr (477.8): C, 60.33; H, 8.23; N, 5.86. Found: C, 58.07; H, 8.90; N, 5.67.

Technical Details of the Quantum-Chemical Calculations. The calculations have been performed with the TUR-BOMOLE suite of programs.³¹ All structures have been fully optimized without any symmetry restrictions at the density functional (DFT) level, employing the BP86 functional,³² a large Gaussian AO basis of valence-triple- ζ quality with one set (two for P) of polarization functions (TZVP: C, N [5s3p1d], H [3s1p], P [5s5p2d], Ti [6s4p3d]),33,34 and the resolution-ofthe-identity (RI) approximation to represent the Coulomb operator. 34,35 For zirconium a [5s3p3d] basis set and an effective core potential with 28 core electrons³⁶ has been used. Further calculations of the Cartesian second derivatives were

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(34) All basis sets are available from the TURBOMOLE homepage, http://www.turbomole.com, via FTP Server Button (in the subdirecto-ries basen (AO basis sets) and jbasen (RI basis sets)).

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carried out, yielding only real vibrational frequencies for the minima and exactly one imaginary normal mode (in the range 80-120i cm⁻¹) for the transition states. The calculations of the NMR chemical shifts have been performed also at the DFT-BP86/TZVP level using the GIAO method.

Polymerization Reactions. (a) Ethene Polymerization. A glass autoclave was charged with 200 mL of toluene and 20 mL of a 10% solution of MAO in toluene and then thermostated for 1 h; the solution was then saturated with ethene (at 1 or 2 bar) for 45 min. The catalyst was dissolved in toluene and directly injected in the autoclave. The polymerization reaction was stopped by quenching with 20 mL of aqueous HCl/ methanol (1:1 v/v). The resulting polymer was collected by filtration, washed subsequently with HCl and water, and dried at 80 °C in vacuo overnight. Melting points of the polyethylene samples were measured by DSC.

(b) Ethene-1-Octene Copolymerization. A glass autoclave was charged with 30 mL of toluene, 50 mL of 1-octene, and 20 mL of a 10% solution of MAO in toluene and then thermostated for 1 h and the solution saturated with ethene (at 1 or 2 bar) for 45 min. The catalyst was dissolved in toluene and directly injected into the autoclave. The polymerization reaction was stopped by quenching with 20 mL of aqueous HCl/ methanol (1:1 v/v). The reaction mixture was filtered and washed with water, the solvent was removed in vacuo, and the copolymer was dried at 80 °C in vacuo overnight.

(c) Polymer Characterizations. ¹³C NMR spectra of the copolymer samples (100 mg) were obtained in benzene- d_6 (0.5 mL) at 25 °C (oils) or tetrachloroethane-d₂ (0.5 mL) at 80 °C (solids). The ethene to 1-octene ratio was determined by integration of ¹³C NMR signals (see Figure 3) using the equations

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

ethene/1-octene = $[(3\alpha - 1)/2] + 2$ (2)

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Supporting Information Available: Text and a table giving details of the DFT calculation of **21** and ¹³C NMR data of the compounds 3–9. This material is available free of charge via the Internet at http://pubs.acs.org.

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