

[Bis(amido)cyclodiphosph(III)azane]dichlorozirconium Complexes for Ethene Polymerization

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A series of new zirconium dichloride complexes bearing bulky *cis*-bis(amido)cyclodiphosph(III)azane ligands, [(RN)₂(*t*BuNP)₂]ZrCl₂ [R = phenyl (**7**), diphenylmethyl (**8**), 2,6-diethylphenyl (**9**), 2,5-di-*tert*-butylphenyl (**10**), and 2,6-diisopropylphenyl (**11**)] were prepared in high yields by a two-step synthetic route. The structure of *cis*-[(Ph₂CHN)(*t*BuNP)₂]Zr(NMe₂)₂ (**8a**), determined by X-ray analysis, shows that the zirconium atom has a distorted trigonal-bipyramidal configuration consisting of four equidistant metal–amido nitrogen bonds and an additional coordination between the metal and a nitrogen atom from the cyclodi-

phosph(III)azane ring. After methylaluminoxane activation, these complexes exhibit moderate to high activities in ethene polymerization and produce high molar mass polyethene (*M_w* up to 1100 kg/mol). Polymerization experiments reveal that the behavior of bis(amido)cyclodiphosph(III)azane-based Zr^{IV} catalysts depends on the nature and steric bulkiness of the amido substituents, reaction temperature, MAO/zirconium ratio, as well as monomer pressure.

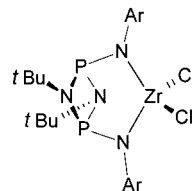
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Introduction

Group 4 metal complexes bearing bi- or tridentate^[1–7] diamido ligands have attracted considerable attention as a new generation of early transition metal based polymerization catalysts.^[8,9] After methylaluminoxane (MAO) activation, highly electrophilic 10-electron cationic species, [(R₂N)₂ZrR]⁺, which serve as active catalytic sites, form.^[8] This type of nonmetallocene complex has the advantage that the electronic character, geometry and steric hindrance of the catalytic center can be easily controlled through rational ligand design. To date, an impressive number of transition metal complexes have been synthesized^[8,9] and applied for α -olefin polymerization,^[10–13] in particular ethene polymerization.^[14–17]

Recently, novel bis(amido) complexes of Group 4 metals based on the cyclodiphosph(III)azane framework were reported.^[18–21] Due to the fact that these complexes possess a tetrahedral coordination of the metal center and the chloride ions are in a *cis* position, they can be considered as potential catalyst precursors for olefin polymerization. As an augmentation to our previous studies on nonmetallo-

cene polymerization catalysts,^[22–25] we have developed a straightforward synthesis towards new [bis(amido)cyclodiphosph(III)azane]Ti^{IV} complexes bearing sterically hindered aryl substituents and investigated them as ethene polymerization catalysts.^[26] After MAO activation, these Ti complexes were able to polymerize ethene with moderate activity and produce polymers with high molar mass and narrow molar mass distribution (MMD). Here we describe an efficient synthetic route to the new [bis(amido)cyclodiphosph(III)azane]Zr complexes and report on the results of an investigation of their catalytic behavior in ethene polymerization as well as on the properties of the produced polymers.



Results and Discussion

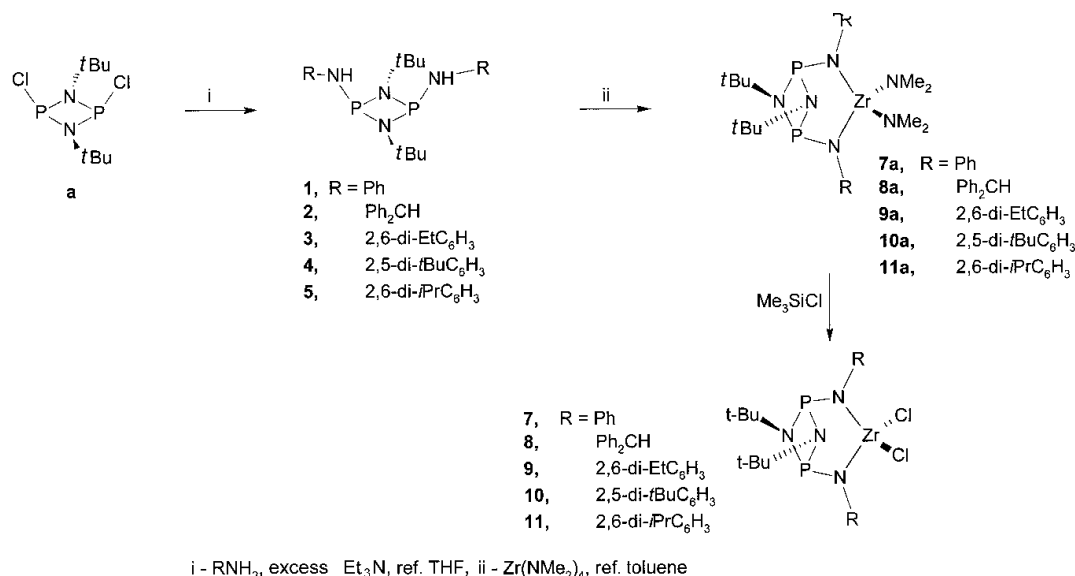
Synthesis of Ligand Precursors

A series of cyclodiphosph(III)azanes, **1–5**, were prepared in high yields by reaction of the appropriate anilines with dichlorocyclodiphosph(III)azane **a** in the presence of excess Et₃N, as was reported earlier (Scheme 1).^[26] The X-ray

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Scheme 1

analysis (solid state) and NMR spectroscopic data have shown that these compounds favor a *cis* conformation – the most desirable arrangement for coordination chemistry applications. The solid-state structure of *cis*-[(Ph₂CHNH)-(*t*BuNP)]₂ (**2**, Figure 1, Tables 1 and 2) also supports the previously observed *cis* orientation of the bulky amino substituents. However, this structure differs sharply from previously reported structures for *cis*-bis(amino)cyclodiphosph(III)azanes; according to X-ray crystallographic analysis, the NH groups in all other known cyclodiphosph(III)azanes^[27,28] adopt the *endo* orientation relative to the P–N ring, while in **2** these substituents have the *exo,endo* orientation (Figure 1). Such an unusual structural feature has been reported earlier for *cis*-[(*t*BuNH)-(*t*BuNPS)]₂ with P^V only.^[29] Furthermore, the distortion of the P–N ring is diminished as indicated by the P–N bond lengths and the planarity of the ring. It can be assumed that the reduced ring distortion is mainly a consequence of the unique *exo,endo* orientation.

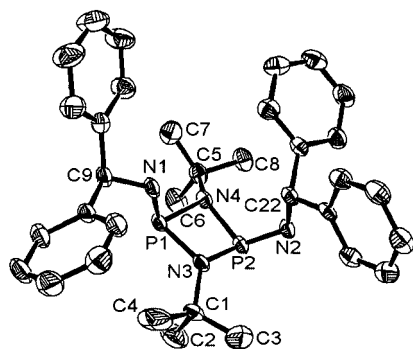


Figure 1. ORTEP plot of **2** with thermal ellipsoids drawn at 50% probability level; all hydrogen atoms are omitted for clarity

Table 1. Crystallographic data for **2** and **8a**

	2	8a
Empirical formula	C ₃₄ H ₄₂ N ₄ P ₂	C ₃₈ H ₅₂ N ₆ P ₂ Zr
Formula mass	568.66	746.02
Space group	P $\bar{1}$	P2 ₁ /n
<i>a</i> [Å]	10.449(1)	10.715(2)
<i>b</i> [Å]	12.419(1)	20.287(4)
<i>c</i> [Å]	13.493(1)	18.055(4)
α [°]	75.39(1)	
β [°]	73.57(1)	96.31(3)
γ [°]	74.65(1)	
<i>V</i> [Å ³]	1589.5(2)	3900.9(14)
<i>d</i> _{calcd.} [g cm ⁻³]	1.188	1.270
<i>Z</i>	2	4
μ [cm ⁻¹]	14.52	3.98
λ [Å]	1.54179	0.71073
<i>T</i> [K]	193(2)	173(2)
<i>R</i> ^[a]	0.053	0.0927
<i>R</i> _w ^[b]	0.1549	0.2060

^[a] $R = \Sigma(F_o - F_c)/\Sigma F_o$ for observed reflections [$I > 2\sigma(I)$]. ^[b] $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ for all data.

Synthesis of Complexes

The most common synthetic route to the transition metal complexes that have an anionic ligand is a transmetalation reaction. According to this general strategy, *cis*-[(PhNH)(*t*BuNP)]₂ (**1**) and *cis*-[(2,6-di-*i*PrC₆H₃NH)₂(*t*-BuNP)] (**5**) ligands were first deprotonated with BuLi, and the obtained Li salts were then treated with ZrCl₄ in toluene at –78 °C. The resulting reaction mixtures were analyzed by ³¹P NMR spectroscopy. When ligand **1** was used, only one product ($\delta_P = 145$ ppm, see Supporting Information) was observed. The same transformation with ligand **5** leads to a complex mixture of unidentified products. According to data published previously, the signal at $\delta = 145$ ppm is assigned to the Zr^{IV} complex that has two cyclodiphosph(III)azane ligands attached to the metal center.^[20] In

Table 2. Selected structural parameters for compounds **2** and **8a**

Compound 2			
Distances [Å]		Angles [°]	
P1–N4	1.727(2)	N3–P1–N4	81.20(10)
P2–N3	1.722(2)	P1–N3–P2	97.52(11)
P2–N4	1.728(2)	P1–N4–P2	97.41(11)
P1–P2	2.5957(9)	C1–N3–P1	126.59(16)
P2–N2	1.677(2)	C5–N4–P1	123.57(16)
N3–C1	1.468(3)	N2–P2–N4	107.96(10)
N4–C5	1.486(3)	N2–P2–N3	105.13(10)
N1–C9	1.468(3)	C9–N1–P1	122.51(17)
		C22–N2–P2	126.99(16)

Compound 8a			
Distances [Å]		Angles [°]	
P1–N3	1.773(7)	N61–Zr1–N51	100.0(3)
P1–N4	1.746(7)	N61–Zr1–N2	117.9(3)
P2–N2	1.702(7)	N51–Zr1–N1	106.7(2)
N3–C1	1.515(10)	N2–Zr1–N1	108.5(2)
N1–C9	1.467(9)	N61–Zr1–N3	104.8(3)
Zr1–N1	2.141(6)	N51–Zr1–N3	153.8(3)
Zr1–N2	2.113(7)	P2–N3–Zr1	92.0(3)
Zr1–N3	2.439(7)	N3–P2–P4	81.1(3)
Zr1–N51	2.046(7)	P1–N3–P2	97.9(4)
		C9–N1–P1	118.5(5)

fact, the salt metathesis route was unselective in the preparation of corresponding titanium(IV) bis(amido)complexes also, and alternative synthetic routes were therefore looked for.^[26] As in the case of Ti^{IV}, the direct metalation of the ligand precursors by amine elimination^[17] appeared to be the most efficient method. According to ¹H and ³¹P NMR spectroscopic data, the reaction of Zr(NMe₂)₄ with **1–5** leads selectively to the bis(amido)complexes [(RN)-(tBuNP)]₂Zr(NMe₂)₂ (**7a–11a**) (Scheme 1).

However, it is well known that bis(amido) early transition metal complexes are less active catalyst precursors in polymerization of α -olefins than the corresponding dichloro derivatives. Treatment of bis(amido)[*cis*-bis(amido)cyclodiphosph(III)azane]zirconium complexes **7a–11a** with excess chlorotrimethylsilane in toluene selectively gave the desired dichlorozirconium derivatives **7–11** in high yields (Scheme 1). These complexes have been characterized by NMR spectroscopy, elemental analysis, and mass spectroscopic methods. According to the ¹H NMR spectra, the *cis*-[(RN)₂(tBuNP)₂]ZrCl₂ complexes show C₂ symmetry in solution and reveal the equivalence of all aromatic substituents.

X-ray structures of [*cis*-bis(amido)cyclodiphosph(III)azane]zirconium complexes are rather rare, and only one structure involving [bis(amido)cyclodiphosph(III)azane]-ZrX₂-type complexes, namely *cis*-[(tBuN)₂(tBuNP)₂]ZrX₂ (X = Cl, **6**),^[18,20] has been reported. The crystals of *cis*-[(Ph₂CHN)₂(tBuNP)₂]Zr(NMe₂)₂ (**8a**) suitable for X-ray analysis were successfully grown from a saturated Et₂O solution at –20 °C. In the structure of **8a** the four amido N–Zr bonds and an additional coordination of the cyclodiphosph(III)azane ring nitrogen to the zirconium atom define a rather distorted trigonal-bipyramidal configuration of the metal center. The amido nitrogen atoms are located in the

corners of a zirconium-centered tetrahedron (Figure 2). In general, all amido–zirconium bonds are equidistant (average 2.110 Å), while the Zr–N coordination bond is significantly longer (2.448 Å) (Tables 1 and 2). The N–M–N angles range from 100° to 123.19°. The geometry of the ligand moiety **2** is changed due to the coordination to the zirconium atom, and the P–N(amido) bonds adopt an *endo,endo* orientation relative to the cyclodiphosph(III)-azane ring. Overall, the Zr–N coordination is similar to those reported for *cis*-[(tBuN)₂(tBuNP)₂]ZrCl₂ and *cis*-[(PhN)₂(tBuNP)₂]Zr.^[20]

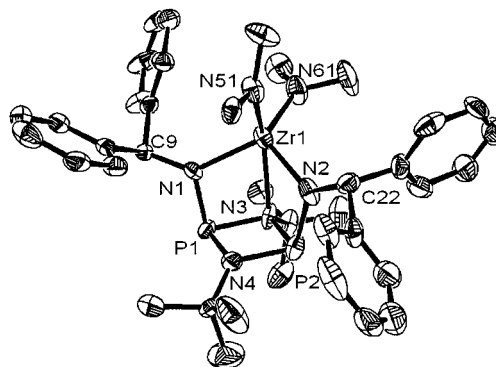


Figure 2. ORTEP plot of **8a** with thermal ellipsoids drawn at 50% probability level; all hydrogen atoms are omitted for clarity

Ethene Polymerization

Despite a certain interest in *cis*-bis(amido)cyclodiphosph(III)azane-based zirconium complexes, few preliminary reports concerning their polymerization properties have been published.^[18–20] In order to evaluate the influence of the structure of the catalyst precursors on polymerization properties, we carried out a detailed ethene polymerization investigation. In general, MAO-activated zirconium complexes **6–11** reveal moderate to high catalytic activity and, according to obtained data, the size of the substituents at the amido nitrogen atoms has a significant effect on the catalytic behavior (Table 3).

Under the chosen polymerization conditions (50 °C and 3.8 bars), **6**/MAO bearing *tert*-butyl groups shows the highest average activity in the series of catalysts (Entry 1, Table 3). When ethene polymerization is conducted under the same conditions, there are two distinct differences in the behavior of catalyst **6**/MAO from that of its Ti^{IV} analog; the catalytic activity is significantly higher for **6**/MAO as it remains high during the whole polymerization reaction, while *cis*-[(tBuN)₂(tBuNP)₂]TiCl₂/MAO gives a remarkably high initial activity that decreases drastically after a few minutes. In addition, **6**/MAO produces polyethene with narrow polydispersity, whereas the corresponding Ti^{IV} catalyst is prone to produce polyethylene with bimodal MMD.^[26] These facts indicate the higher stability of the [bis(amido)cyclodiphosph(III)azane]Zr catalytic species.

Replacement of the *tert*-butyl groups with diphenylmethyl (**8**) leads to dramatic changes in the catalyst

Table 3. Ethene polymerization data for complexes 6–11

Entry ^[a]	Catalyst	Concentration [μmol]	Reaction temp. [°C]	Time [min]	Yield [g]	Activity ^[b]	M_w [g/mol]	M_w/M_n	T_m [°C]
1	6	1.5	50	30	5.8	24058	228 000	2.17	134
2	7	10	50	30	1.63	1031	1 132 000	3.32	134
3	8	10	50	30	1.53	973	1 042 000	22.18	131
4	9	10	50	30	1.89	1181	1 039 000	3.41	138
5	10	10	50	30	2.93	2534	306 000	4.10	133
6	11	10	50	30	4.05	7000	672 000	2.84	136

^[a] MAO (Al/M = 1000), 200 mL of toluene, 3.8 bar of ethylene. ^[b] kg PE/(mol_{cat} × [C₂H₄] × h).

behavior. The activity decreases substantially and the produced polyethene has a high M_w (1040 kg/mol) and bimodal MMD (see Supporting Information). The series of catalysts **7**/MAO, **9**/MAO, **10**/MAO, and **11**/MAO bearing phenyl, 2,6-diethylphenyl, 2,5-di-*tert*-butylphenyl, and 2,6-diisopropylphenyl groups, respectively, reveal a clear enhancement of activity with increased steric bulk on the arylamido substituents. The activity as well as the properties of the polymer material are strongly connected to the ligand design. The molar mass of polyethene varies between 230 and 1130 kg/mol and polymers with diverse MMDs and different modalities are obtained.

Reaction temperature as well as monomer concentration are the key factors, which define the activity of catalysts and also the properties of the polymers produced. Ethene was polymerized at 30, 50, 60, and 70 °C to evaluate the influence of polymerization temperature on the catalytic activity and polymer properties (Figure 3). The steric bulkiness of the amido substituents is crucial for the catalyst behavior, in particular, the polymerization activity, as well as

the stability of these Zr catalysts. The *tert*-butyl substituents in **6**/MAO seem to create a highly propitious environment for the catalytically active center, and already at 30 °C a very high activity is observed. However, the activity decreases to one third when the temperature increases from 30 to 70 °C, whereas the molar mass of polyethene and the MMD are slightly enhanced (Figure 4). Polymerization activities of the other catalysts are much lower but not as sensitive to the temperature changes and show their highest values at temperatures between 50 and 60 °C. At higher temperatures deactivation of the catalytically active species occurs. Quite unexpectedly, the produced polyethene possesses maximum molar mass values at 50 °C. The decrease in M_w at higher temperatures is often explained by a change in relative rates of chain propagation and β-H elimination.^[30] This seems to be a plausible explanation here as well. The lower M_w values at 30 °C remain unexplained but could be caused by another competing chain termination route, e.g. chain transfer to aluminum.

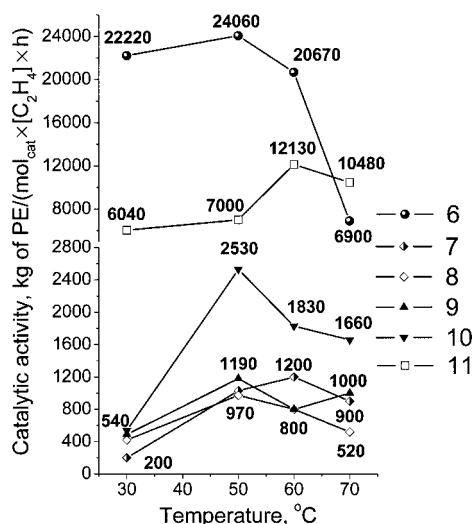


Figure 3. Catalytic activity as a function of polymerization temperature for [(*t*BuN)(*t*BuNP)]₂ZrCl₂ (**6**), [(PhN)(*t*BuNP)]₂ZrCl₂ (**7**), [(Ph₂CHN)(*t*BuNP)]₂ZrCl₂ (**8**), [(2,6-Et₂C₆H₃N)(*t*BuNP)]₂ZrCl₂ (**9**), [(2,5-*t*Bu₂C₆H₃N)(*t*BuNP)]₂ZrCl₂ (**10**), and [(2,6-*i*Pr₂C₆H₃N)(*t*BuNP)]₂ZrCl₂ (**11**) as catalyst precursors; the numeric values of the observed average activities are also given for the corresponding graph points; activity is expressed as kg of PE × (mol_{cat} × [C₂H₄])⁻¹; experimental conditions used: MAO (Al/M = 1000), 3.8 bar of ethylene

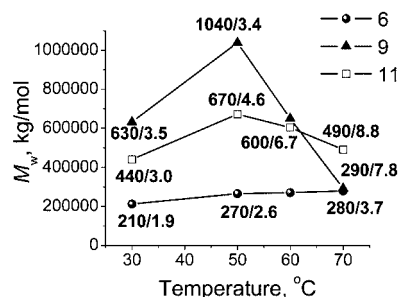


Figure 4. Molar mass of polyethene as a function of polymerization temperature with selected catalyst precursors [(*t*BuN)(*t*BuNP)]₂ZrCl₂ (**6**), [(2,6-Et₂C₆H₃N)(*t*BuNP)]₂ZrCl₂ (**9**), and [(2,6-*i*Pr₂C₆H₃N)(*t*BuNP)]₂ZrCl₂ (**11**); the numeric values of M_w (in kg/mol) as well as polydispersities are given

All cyclodiphosph(III)azane catalysts were tested with ethene concentrations ranging from 0.15 to 0.8 mol/L (2–8 bar at 50 °C). The highest average productivity (calculated from the yield of polymer) is 22 800 kg of PE/mol_{cat} × h for **6**/MAO at 8 bar. The maximum catalytic activity for **6**–**10**/MAO is reached at low ethene concentrations (Fig-

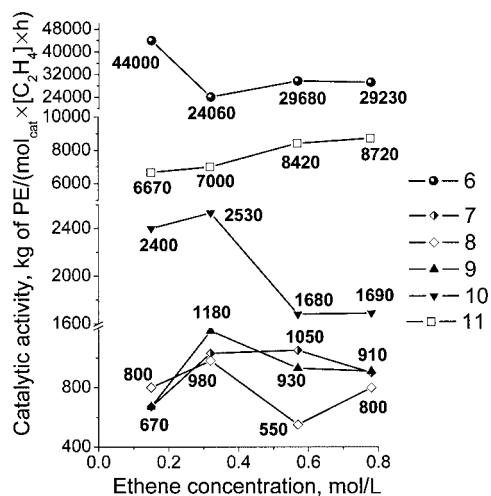


Figure 5. Catalytic activity of complexes as a function of ethene concentration for $[(t\text{BuN})(t\text{BuNP})_2\text{ZrCl}_2]$ (**6**), $[(\text{PhN})(t\text{BuNP})_2\text{ZrCl}_2]$ (**7**), $[(\text{Ph}_2\text{CHN})(t\text{BuNP})_2\text{ZrCl}_2]$ (**8**), $[(2,6\text{-Et}_2\text{C}_6\text{H}_3\text{N})(t\text{BuNP})_2\text{ZrCl}_2]$ (**9**), $[(2,5\text{-}i\text{Bu}_2\text{C}_6\text{H}_3\text{N})(t\text{BuNP})_2\text{ZrCl}_2]$ (**10**), and $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})(t\text{BuNP})_2\text{ZrCl}_2]$ (**11**) as catalyst precursors; the numeric values of the observed average activities are also given for the corresponding graph points; activity is expressed as $\text{kg of PE} \times (\text{mol}_{\text{cat}} \times [\text{C}_2\text{H}_4] \times \text{h})^{-1}$; experimental conditions used: MAO ($\text{Al}/\text{M} = 1000$), polymerization temperature 50°C

ure 5). It has been suggested that at higher monomer concentrations, due to enhanced polymer formation, the active complex becomes quickly embedded in the swollen-gel-like polymer matrix, which leads to the diffusion-controlled reaction conditions.^[31]

Despite the increased monomer pressure enhancing the productivity of catalysts (yield of polymer), the molar mass of polymers produced by **6**/MAO and **11**/MAO are slightly reduced (Figure 6). This fact indicates the presence of β -H transfer to the monomer as a major chain-termination mechanism. However, in the case of **10**/MAO, where aniline is unsymmetrically substituted with *tert*-butyl substituents, the dominating chain termination reaction changes from β -H transfer to the monomer to β -H transfer to the metal center as the molar mass of polyethylene appreciably increases from 310 kg/mol at 3.8 bar of ethene to 1480 kg/mol at 8 bar.^[32]

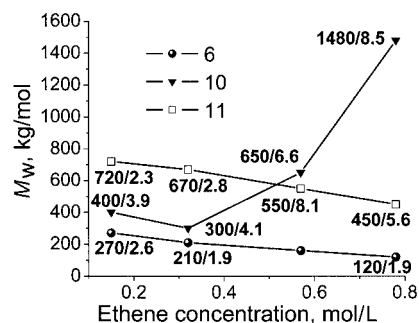


Figure 6. Molar mass of polyethylene as a function of ethene concentration with selected catalyst precursors $[(t\text{BuN})(t\text{BuNP})_2\text{ZrCl}_2]$ (**6**), $[(2,5\text{-}i\text{Bu}_2\text{C}_6\text{H}_3\text{N})(t\text{BuNP})_2\text{ZrCl}_2]$ (**10**), and $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})(t\text{BuNP})_2\text{ZrCl}_2]$ (**11**); the numeric values of M_w (in kg/mol) as well as polydispersities are given

Depending on the ligand structure, the catalysts have different responses to variations in MAO concentration e.g. the polymerization activity of **6**/MAO significantly decreases when the Al/Zr ratio increases (Figure 7). Even though **6**/MAO possesses a high polymerization activity, it is vulnerable to higher temperatures and MAO concentrations. Hence, we assume that the *tert*-butyl groups of **6**/MAO are not bulky enough to protect the catalytic center from deactivation. It has been proposed that the coordination of Lewis acidic MAO to the electron-pair-donating P^{III} atoms in the cyclodiphosph(III)azane ring can initiate the destruction of the catalyst during the polymerization process.^[19]

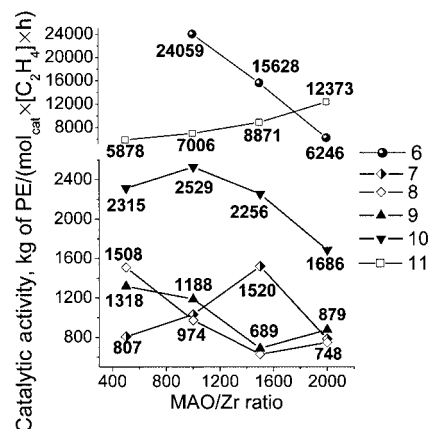


Figure 7. Catalytic activity of complexes as a function of MAO/Zr ratio for $[(t\text{BuN})(t\text{BuNP})_2\text{ZrCl}_2]$ (**6**), $[(\text{PhN})(t\text{BuNP})_2\text{ZrCl}_2]$ (**7**), $[(\text{Ph}_2\text{CHN})(t\text{BuNP})_2\text{ZrCl}_2]$ (**8**), $[(2,6\text{-Et}_2\text{C}_6\text{H}_3\text{N})(t\text{BuNP})_2\text{ZrCl}_2]$ (**9**), $[(2,5\text{-}i\text{Bu}_2\text{C}_6\text{H}_3\text{N})(t\text{BuNP})_2\text{ZrCl}_2]$ (**10**), and $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})(t\text{BuNP})_2\text{ZrCl}_2]$ (**11**) as catalyst precursors; the numeric values of the observed average activities are also given for the corresponding graph points; activity is expressed as $\text{kg of PE} \times (\text{mol}_{\text{cat}} \times [\text{C}_2\text{H}_4] \times \text{h})^{-1}$; experimental conditions used: 3.8 bar of ethylene, polymerization temperature 50°C

According to the polymerization results, diphenylmethyl substituents are not able to provide a suitable surrounding for the highly active metal center and, in addition, **8**/MAO is sensitive to increased MAO concentrations. Increasing the size of substituents at the aniline moiety improves the shielding at the cationic metal center, and the activity of **10**/MAO, with 2,5-di-*tert*-butylphenyl groups, is enhanced up to an MAO/Zr ratio of 1000. In fact, the sterically most demanding 2,6-diisopropylphenyl groups in **11**/MAO efficiently protect the catalytically active site, and it is the only catalyst that gradually enhances the polymerization activity with increasing MAO/Zr ratio. While the bulky ligand protects the catalytic species from destructive side reactions, it also congests the actual polymerization site and the observed activity for **11**/MAO is thus lower than for **6**/MAO.

Published solid-state structures (Figure 2^[18–20,26]) of [bis-(amido)cyclodiphosph(III)azane]Zr and -Ti complexes show that the environment of the P atoms remains rather open regardless of the changes in the bulkiness of the amino substituents. It appears in this study that the observed correlation between the stability of the catalytically active species

and the size of amido substituents could be better explained if destructive MAO interaction with metal–ligand bonding was the major decomposition pathway for the catalysts.

Conclusion

New [bis(amido)cyclodiphosph(III)azane]zirconium complexes [(RN)(*t*BuNP)₂ZrCl₂ (7–11) [R = Ph (7), Ph₂CH (8), 2,6-Et₂C₆H₃ (9), 2,5-*t*Bu₂C₆H₃ (10), 2,6-*i*Pr₂C₆H₃ (11)] were synthesized by reaction of the corresponding ligand precursors with Zr(NMe₂)₄. The amido complexes were successfully transformed into the dichloro derivatives [(RN)(*t*BuNP)₂ZrCl₂ (7–11) with excess Me₃SiCl. MAO-activated 7–11 display moderate to high activities in ethene polymerization. The catalyst behavior is dependent on the bulk of the ligand substituents. The nature and size of the amido substituents play a great role in defining the catalytic activity of the investigated Zr complexes as well as the polymer properties. From the series of catalysts studied here, only 11/MAO revealed increased activity in the range 500–2000 for the MAO/Zr ratio as well as in the polymerization temperature range 30–60 °C.

Experimental Section

General Remarks: All manipulations were performed under argon in a glovebox or using standard Schlenk techniques. Hydrocarbon and ether solvents were refluxed in the presence of sodium and benzophenone, distilled, and stored under an inert gas in the presence of sodium flakes. Dichloromethane was refluxed in the presence of CaH₂ powder and distilled before use. Mass spectra were measured with a JEOL SX102 spectrometer and the ¹H and ¹³C NMR spectra were recorded with a Varian Gemini 200 MHz spectrometer. The ¹H and ¹³C NMR spectra are referenced relative to CHCl₃ (δ = 7.24 ppm and 77.0 ppm, respectively) and C₆D₅H (δ = 7.15 ppm and 128.0 ppm, respectively). ³¹P NMR spectra were collected with a Bruker AMX 400 spectrometer and phosphorus signals were referenced relative to an external 85% H₃PO₄ solution. Elemental analyses were performed by Analytische Laboratorien Prof. Dr. H. Malissa, G. Reuter GmbH, Lindlar, Germany. High-temperature gel permeation chromatography of polyethylene samples (GPC) was performed in 1,2,4-trichlorobenzene at 145 °C using a Waters HPLC 150C. *tert*-Butylamine and phosphorus trichloride were purchased from Merck and purified by distillation under argon (*t*BuNH₂ from sodium hydroxide). Arylamines and diphenylmethanamine were received from Aldrich and distilled in vacuo from sodium hydroxide before use. Chlorotrimethylsilane was purchased from Fluka and used as received. Zr(NMe₂)₄ was purchased from Aldrich and used as a toluene solution. Methylaluminoxane (MAO, 30 wt.% solution in toluene) was received from Borealis Polymers Oy.

Ligand Synthesis: *cis*-[Cl(*t*BuNP)]₂ (**a**) was prepared according to modified literature procedures.^[29] The cyclodiphosph(III)azane ligands *cis*-[(PhNH)(*t*BuNP)]₂ (**1**), *cis*-[(Ph₂CHNH)(*t*BuNP)]₂ (**2**), *cis*-[(2,6-di-EtC₆H₃NH)₂(*t*BuNP)]₂ (**3**), *cis*-[(2,5-di-*t*BuC₆H₃NH)₂(*t*BuNP)]₂ (**4**), and *cis*-[(2,6-di-*i*PrC₆H₃NH)₂(*t*BuNP)]₂ (**5**) were prepared as described previously.^[26] [(*t*BuN)₂(*t*BuNP)₂]ZrCl₂ (**6**) was prepared according to the literature.^[18]

[(PhN)₂(*t*BuNP)₂]ZrCl₂ (7): A solution of Zr(NMe₂)₄ (1.56 g, 5.86 mmol) in toluene (20 mL) was added with a syringe to a toluene solution of *cis*-[(PhNH)₂(*t*BuNP)]₂ (2.28 g, 5.86 mmol, 30 mL) at 0 °C. The reaction mixture was then refluxed for 16 h, and the obtained bis(dimethylamido)zirconium complex [(PhN)(*t*BuNP)]₂Zr(NMe₂)₂ (**7a**) was characterized by NMR spectroscopy. ¹H NMR (200 MHz, C₆D₆, 29 °C): δ_H = 1.19 (s, 18 H, *t*Bu), 2.93 (s, 12 H, NMe₂), 6.81 (t, *J* = 6.6 Hz, 2 H, *o*-H), 7.26 (m, 8 H, Ph) ppm. ¹³C{¹H} NMR (50.3 MHz, C₆D₆, 29 °C): δ_C = 29.7 [t, *J*_{PC} = 6.87 Hz, C(CH₃)₃], 40.94 (Me₂NZr), 53.2 [t, *J*_{PC} = 12.5 Hz, C(CH₃)₃], 119.36 (Ph), 129.7 (Ph), 150.0 (Ph) ppm. ³¹P{¹H} NMR (162 MHz, C₆D₆, 21 °C): δ_P = 124 ppm. The bis(amido) complex [(PhN)(*t*BuNP)]₂Zr(NMe₂)₂ was converted into the corresponding dichloro derivative **7** by reaction with excess Me₃SiCl (1.3 g, 1.5 mL, 11.7 mmol) at 0 °C. The obtained reaction mixture was stirred at room temperature overnight. The volatiles were removed in vacuo, and the residue was extracted with a mixture of hexane and CH₂Cl₂ (1:1). After filtration and evaporation of the solvents, the product was dried in vacuo to give a pale-yellow powder containing 1 equiv. of Me₂NH per Zr (2.03 g; 60%) C₂₀H₂₈Cl₂N₄P₂Zr·Me₂NH (593.6): calcd. C 44.51, H 5.94, N 11.80; found C 44.79, H 6.19, N 11.44. ¹H NMR (200 MHz, C₆D₆, 29 °C): δ_H = 1.32 (s, 18 H, *t*Bu), 1.80 (br. s, Me₂NH), 6.82 (t, *J* = 7.7 Hz, 2 H, *p*-H), 7.09 (t, *J* = 7.7 Hz, 4 H, *m*-H), 7.50 (d, *J* = 7.7 Hz, 4 H, *o*-H) ppm. ¹³C{¹H} NMR (50.3 MHz, C₆D₆, 29 °C): δ_C = 28.65 [t, *J*_{PC} = 7.4 Hz, C(CH₃)₃], 32.2 (Me₂NH), 54.25 [t, *J*_{PC} = 9.15 Hz, C(CH₃)₃], 124.0, 129.5, 150.2 ppm. ³¹P{¹H} NMR (162 MHz, C₆D₆, 21 °C): δ_P = 145.03 (s) ppm. MS(EI): *m/z* (%) = 548 (10) [M⁺], 503 (6) [M⁺ – Cl], 388 (10) [ligand].

[(Ph₂CHN)₂(*t*BuNP)₂]ZrCl₂ (8): A toluene solution of Zr(NMe₂)₄ (0.52 g, 1.97 mmol, 20 mL) was added with a syringe to a solution of *cis*-[(Ph₂CHNH)₂(*t*BuNP)]₂ (1.12 g, 1.97 mmol) in toluene (10 mL) at 0 °C. The reaction mixture was then refluxed for 16 h, and the bis(dimethylamido)zirconium complex [(Ph₂CHN)₂(*t*BuNP)]₂Zr(NMe₂)₂ (**8a**) was isolated according to a procedure described earlier. ¹H NMR (200 MHz, C₆D₆, 29 °C): δ_H = 1.30 (s, 18 H, *t*Bu), 2.70 (12 H, NMe₂), 5.57 (dd, 2 H, Ph₂CH), 7.09 (m, 20 H, Ph-H) ppm. Crystals suitable for X-ray analysis were obtained by slow crystallization from saturated Et₂O solution at –20 °C. The bis(amido) complex [(Ph₂CHN)₂(*t*BuNP)]₂Zr(NMe₂)₂ (**8a**) was converted into the corresponding dichloro derivative **8** by reaction with excess Me₃SiCl (2.31 g, 2.0 mL, 21.28 mmol) at 0 °C. The obtained reaction mixture was stirred at room temperature overnight. The volatiles were removed in vacuo, and the residue was extracted with a mixture of hexane and CH₂Cl₂ (1:1). The crude product was washed with cold pentane and dried under vacuum (yield 0.95 g). The remaining pentane solution was kept in a freezer at –20 °C for 3 d, and a second crop of product (0.27 g) was isolated as a white powder by removing the pentane with a syringe. Total yield 1.22 g, 85%. C₃₄H₄₀Cl₂N₄P₂Zr (728.8): calcd. C 56.03, H 5.53, N 7.69; found C 55.85, H 6.30, N 7.50. ¹H NMR (200 MHz, C₆D₆, 29 °C): δ_H = 1.21 (s, 18 H, *t*Bu), 6.08 (t, 2 H, Ph₂CH), 7.14–7.28 (m, 16 H, Ph), 7.68 (d, *J* = 7.0 Hz, 4 H, *p*-H) ppm. ¹³C{¹H} NMR (50.3 MHz, C₆D₆, 29 °C): δ_C = 30.88 [t, *J*_{PC} = 7.25 Hz, C(CH₃)₃], 51.88 [t, *J*_{PC} = 11 Hz, C(CH₃)₃], 98.4 (Ph₂CH), 126.85 (Ph), 128.6 (Ph), 150.8 (Ph) ppm. ³¹P{¹H} NMR (162 MHz, C₆D₆, 21 °C): δ_P = 102.0 (s) ppm. MS(EI): *m/z* (%) = 691 (5) [M⁺ – Cl], 566 (60) [ligand].

[(2,6-Et₂C₆H₃N)₂(*t*BuNP)₂]ZrCl₂ (9): A toluene solution of *cis*-[(2,6-Et₂C₆H₃NH)₂(*t*BuNP)]₂ (1.5 g, 3.0 mmol, 20 mL) and Zr(NMe₂)₄ (0.8 g, 2.99 mmol) in toluene (10 mL) was treated as in the case of **8**. The bis(dimethylamido)zirconium complex [(2,6-

$\text{Et}_2\text{C}_6\text{H}_3\text{N}_2(\text{tBuNP})_2\text{Zr}(\text{NMe}_2)_2$ (**9a**) was isolated according to a previously described procedure. ^1H NMR (200 MHz, C_6D_6 , 29°C): $\delta_{\text{H}} = 1.33$ (s, 18 H, *t*Bu), 1.40 (t, 12 H, CH_3CH_2), 3.03 and 3.19 (2 s, 12 H, NMe_2), 3.08 (q, 8 H, CH_3CH_2), 7.16 (m, 6 H, Ar) ppm. Me_3SiCl (4.8 mL, 4.15 g, 38.2 mmol) was added with a syringe to a stirred solution of $[(2,6\text{-Et}_2\text{C}_6\text{H}_3\text{N}_2)(\text{tBuNP})_2]\text{Zr}(\text{NMe}_2)_2$. The reaction mixture was stirred at room temperature overnight. The solvent was removed under vacuum. An orange residue was first extracted with hexane (30 mL) and then twice with a mixture of hexane (20 mL) and CH_2Cl_2 (7 mL). After solvent evaporation, the obtained dichloro complex was dried under vacuum to give the yellow-orange oil (1.6 g, 80.8%). $\text{C}_{28}\text{H}_{44}\text{Cl}_2\text{N}_4\text{P}_2\text{Zr}$ (660.8): calcd. C 50.90, H 6.71, N 8.48; found C 50.47, H 7.06, N 8.64. ^1H NMR (200 MHz, C_6D_6 , 29°C): $\delta_{\text{H}} = 1.41$ (s, 18 H, *t*Bu), 1.49 (t, 12 H, CH_3CH_2), 3.16 (q, $J = 7.69$ Hz, 8 H, CH_3CH_2), 7.20–7.33 (m, 6 H, Ar) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, C_6D_6 , 29°C): $\delta_{\text{C}} = 14.92$ (t, $J_{\text{PC}} = 1.53$ Hz, CH_3CH_2), 26.4 (d, $J = 9.9$ Hz, CH_3CH_2), 31.23 [t, $J_{\text{PC}} = 6.48$ Hz, $\text{C}(\text{CH}_3)_3$], 51.53 [t, $J_{\text{PC}} = 14.5$ Hz, $\text{C}(\text{CH}_3)_3$], 123.3 (Ar), 127.1 (Ar), 135.75 (Ar), 138.13 (t, $J = 1.9$ Hz, Ar) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 21°C): $\delta_{\text{P}} = 115.6$ (s) ppm. MS(EI): m/z (%) = 661 (1) [M^+], 626 (3) [$\text{M}^+ - \text{Cl}$], 500 (80) [ligand].

[(2,5-*t*Bu₂C₆H₃N)₂(*t*BuNP)₂] ZrCl_2 (10**):** A toluene solution of *cis*-[(2,5-*t*Bu₂C₆H₃NH)₂(*t*BuNP)₂] (2.29 g, 3.74 mmol, 30 mL) was treated with $\text{Zr}(\text{NMe}_2)_4$ (1.0 g, 3.74 mmol) in toluene (10 mL) as in the case of **8**. The obtained bis(dimethylamido)zirconium complex [(2,5-*t*Bu₂C₆H₃N)₂(*t*BuNP)₂] $\text{Zr}(\text{NMe}_2)_2$ (**10a**) was characterized by NMR spectroscopy. ^1H NMR (200 MHz, C_6D_6 , 29°C): $\delta_{\text{H}} = 1.44$ (s, 36 H, *t*BuAr), 1.57 (s, 18 H, *t*Bu), 3.03–3.28 (12 H, NMe_2), 7.0 (dd, $J_1 = 6.2$, $J_2 = 2.2$ Hz, 2 H, 4-HPh), 7.35 (2 H, 3-HPh), 8.25 (dd, $J_1 = 3.1$, $J_2 = 2.2$ Hz, 2 H, 2-HPh) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, C_6D_6 , 29°C): $\delta_{\text{C}} = 31.0$ [5-(CH_3)₃CAr], 31.34 [t, $J_{\text{PC}} = 6.48$ Hz, (CH_3)₃C], 31.54 [2-(CH_3)₃CAr], 33.11 [5-(CH_3)₃CAr], 33.3 [2-(CH_3)₃CAr], 43.8 (NMe_2), 51.7 [t, $J_{\text{PC}} = 13.7$ Hz, (CH_3)₃C], 113.85 (Ar), 114.5 (Ar), 117.17 (Ar), 127.0 (Ar), 141.9 (Ar), 150.0 (t, $J = 1.15$ Hz, Ar) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 21°C): $\delta_{\text{P}} = 99.8$ (s) ppm. Me_3SiCl (5.1 mL, 4.34 g, 40 mmol) was added with a syringe to a toluene solution of [(2,5-*t*Bu₂C₆H₃N)₂(*t*BuNP)₂] $\text{Zr}(\text{NMe}_2)_2$. The reaction mixture was stirred at room temperature overnight. All volatiles were removed under vacuum. The residue was extracted three times with a mixture of hexane (30 mL) and CH_2Cl_2 (20 mL). The extracts were combined and the solvent was removed in vacuo. The product, a yellow powder, was dried under vacuum. Yield 2.4 g, 83%. $\text{C}_{36}\text{H}_{60}\text{Cl}_2\text{N}_4\text{P}_2\text{Zr}$ (773.0): calcd. C 55.94, H 7.82, N 7.25; found C 55.16, H 8.52, N 7.96. ^1H NMR (200 MHz, C_6D_6 , 29°C): $\delta_{\text{H}} = 1.44$ (s, 36 H, *t*BuAr), 1.57 (s, 18 H, *t*Bu), 7.0 (dd, 2 H, $J_1 = 6.22$, $J_2 = 2.2$ Hz, 4-HPh), 7.36 (2 H, 3-HPh), 8.25 (2 H, $J_1 = 3.3$, $J_2 = 2.2$ Hz, 2-HPh) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, C_6D_6 , 29°C): $\delta_{\text{C}} = 31.0$ [5-(CH_3)₃CAr], 31.34 [t, $J_{\text{PC}} = 6.6$ Hz, (CH_3)₃C], 31.54 [2-(CH_3)₃CAr], 33.1 [5-(CH_3)₃CAr], 33.7 [2-(CH_3)₃CAr], 51.7 [t, $J_{\text{PC}} = 13.73$ Hz, (CH_3)₃C], 113.8 (Ar), 114.5 (Ar), 117.15 (Ar), 136.95 (Ar), 140.7 (Ar), 150.0 (t, $J = 1.53$ Hz, Ar) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 21°C): $\delta_{\text{P}} = 99.8$ (s) ppm. MS(EI): m/z (%) = 772 (40) [M^+], 735 (20) [$\text{M}^+ - \text{Cl}$], 612 (90) [ligand].

[(2,6-*i*Pr₂C₆H₃N)₂(*t*BuNP)₂] ZrCl_2 (11**):** A toluene solution of *cis*-[(2,6-*i*Pr₂C₆H₃NH)₂(*t*BuNP)₂] (1.91 g, 3.44 mmol, 20 mL) was treated with $\text{Zr}(\text{NMe}_2)_4$ (0.92 g, 3.44 mmol) in toluene (10 mL) as in the case of **8**. The bis(dimethylamido)zirconium complex [(2,6-*i*Pr₂C₆H₃N)₂(*t*BuNP)₂] $\text{Zr}(\text{NMe}_2)_2$ (**11a**) obtained was characterized by NMR spectroscopy. ^1H NMR (200 MHz, C_6D_6 , 29°C): $\delta_{\text{H}} = 1.32$ (s, 18 H, *t*Bu), 1.37 [d, 24 H, (CH_3)₂CH], 3.08–3.16 (m,

12 H, NMe_2), 3.92 [m, 4 H, (CH_3)₂CH], 7.0–7.3 (6 H, Ar) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 21°C): $\delta_{\text{P}} = 115.45$ (s) ppm. Me_3SiCl (4.5 mL, 3.8 g, 35 mmol) was added with a syringe to a toluene solution of [(2,6-*i*Pr₂C₆H₃N)₂(*t*BuNP)₂] $\text{Zr}(\text{NMe}_2)_2$ at 0°C . The reaction mixture obtained was stirred at room temperature overnight. The product (yellow oil) was isolated as in the case of **9**. Yield 2.28 g, 92.3%. $\text{C}_{32}\text{H}_{52}\text{Cl}_2\text{N}_4\text{P}_2\text{Zr}$ (716.9): calcd. C 53.61, H 7.31, N 7.82; found C 53.50, H 7.17, N 7.80. ^1H NMR (200 MHz, C_6D_6 , 29°C): $\delta_{\text{H}} = 1.37$ (s, 18 H, *t*Bu), 1.42 [d, 24 H, (CH_3)₂CH], 3.97 [m, $J = 6.96$ Hz, 4 H, (CH_3)₂CH], 7.12–7.28 (6 H, Ar) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, C_6D_6 , 29°C): $\delta_{\text{C}} = 24.17$ [t, $J = 1$ Hz, (CH_3)₂CH], 31.37 [t, $J_{\text{PC}} = 6.7$ Hz, (CH_3)₃C], 32.2 [d, $J = 0.8$ Hz, (CH_3)₂CH], 51.8 [t, $J_{\text{PC}} = 14.6$ Hz, (CH_3)₃C], 123.3 (Ar), 124.0 (Ar), 128.3 (Ar), 141 (Ar) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 21°C): $\delta_{\text{P}} = 115.47$ (s) ppm. MS(EI): m/z (%) = 716 (3) [M^+], 681 (2) [$\text{M}^+ - \text{Cl}$], 556 (20) [ligand].

Polymerization Experiments: A 1-L Büchi glass autoclave (or a steel autoclave at a pressure of 8 bar) was charged with dry toluene (200 mL), cocatalyst (MAO), and thermostatted to the required temperature. The autoclave was saturated with ethylene, and a desired amount of precatalyst solution was then injected. The monomer pressure (± 50 mbar), temperature ($\pm 0.5^\circ\text{C}$), and monomer consumption were controlled by real-time monitoring. Polymerization was quenched with 10% HCl solution in methanol, and the polymer precipitated quantitatively by pouring the solution into methanol (400 mL), acidified with a small amount of aqueous hydrochloric acid. The polymer materials obtained were washed several times with methanol and water, and dried at 60°C . The polymerization activities were calculated as $\text{kg of PE} \times (\text{mol}_{\text{cat}} \times [\text{C}_2\text{H}_4] \times \text{h})^{-1}$ from experimental data to adjust the changes in the ethene concentration in toluene. The values of $[\text{C}_2\text{H}_4]$ for different ethene pressures and polymerization temperatures were taken from ref.^[33]

X-ray Crystallographic Study: The crystal data of *cis*-[(Ph₂CHNH)₂(*t*BuNP)₂] (**2**) were collected with an Enraf–Nonius CAD-4 single-crystal diffractometer at 193(2) K using $\text{Cu-K}\alpha$ radiation (graphite monochromator), $\lambda = 1.54179 \text{ \AA}$ (scan type $\omega/2\theta$). Intensities were corrected for Lorentz and polarization effects and for absorption, XCAD4.^[34–36] The crystal data of [(Ph₂CHN)₂(*t*BuNP)₂] $\text{Zr}(\text{NMe}_2)_2$ (**8a**) were collected with a Nonius KappaCCD area-detector diffractometer at 173(2) K using $\text{Mo-K}\alpha$ radiation (graphite monochromator), $\lambda = 0.71073 \text{ \AA}$. Data reduction: COLLECT.^[37] Absorption correction: SADABS.^[38] Solution and refinement: SHELX-97,^[39] direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined in calculated positions. The displacement factors of the H atoms were $1.2 \times (1.5 \times)$ that of the host atom. Graphics: SHELXTL/PC.^[40] CCDC-231525 and -231526 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/contents/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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