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Synthesis of a $[(\pi\text{-Cyano-nacnac})\text{Cp}]$ zirconium Complex and Its Remote Activation for Ethylene Polymerization

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The NC-nacnacH ligand (**2**) was prepared by the deprotonation of the unsymmetrically N5-phenyl, N1-2,6-diisopropylphenyl substituted bis(imino) acetylacetonate nacnacH system (**1**) with *n*-butyllithium followed by cyanation with tosyl cyanide. Subsequent deprotonation (KH) gave the [NC-nacnac]K salt (**3**), which was transmetalated by reacting it with $\text{CpZrCl}_3(\text{dme})$, to yield the complex (NC-nacnac)- CpZrCl_2 (**5**). Addition of one molar equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ gave $[(\text{C}_6\text{F}_5)_3\text{B-NC-nacnac}]\text{CpZrCl}_2$ (**6**). The compounds **2**, **5**, and **6** were characterized by X-ray diffraction. Activation of **5** with MAO gave an active homogeneous Ziegler–Natta catalyst for ethylene polymerization. The (NC-nacnac) CpZrCl_2 /MAO system is ca. 7 times more active than the CN-free reference system (nacnac) CpZrCl_2 (**4**)/MAO. The $\text{B}(\text{C}_6\text{F}_5)_3$ -containing system **6**/MAO has an activity similar to **5**/MAO but allows for much lower MAO concentration before the catalytic activity ceases.

Introduction

After the development of the very successful metallocene catalysts, several efficient catalyst systems, based on early and late transition metals,¹ supported mainly by multi-dentate NO, NN, and NNN ligands have been investigated.² One of the main reasons is the facile access to a large variety of bi-, tri-, and even tetradentate ligands, which can coordinate and effectively stabilize transition metals, providing access to complexes that in the presence of cocatalysts generate very active catalytic species for olefin polymerization.^{2,3} As metallocene systems are highly dependent on the use of

expensive cocatalysts such as MAO,⁴ there has been increased interest in developing systems that require less, or ideally no, cocatalyst in order to make the processes more profitable. Remarkable examples in late transition metal systems include the DuPont Versipol system,⁵ which has shown that the proper design and synthesis of organometallic complexes can lead to enhancements in catalytic activity, even with reduced cocatalyst concentrations. In addition, it has been possible to develop compounds that do not require cocatalysts (single component).⁶ These catalysts are often better suited for the preparation of specialty oligomers and polymers incorporating polar functionalities. Some ligand frameworks (e.g., the salicylimine derivatives) have been utilized in the preparation of catalyst systems based on zirconium and provide extremely high activity for ethylene polymerization.⁷ The catalysts can also produce novel polypropylene structures.⁸

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Interesting new “concepts” have been applied to catalytic systems to improve and better control the reactivity, reduce the cocatalyst concentration, and have a better control over polymer properties. This concept involves the synthesis of ligands with an additional functionality, for example Lewis bases such as CO and CN groups, in the ligand backbone.⁹ This functionality allows for the complexation of a Lewis acid and the generation of a zwitterionic species, which alters the electronic properties of the metal center. The strong Lewis acid tris(pentafluorophenyl)borane, B(C₆F₅)₃, is particularly capable of strongly coordinating and polarizing these kinds of functionalities in late transition metal complexes.¹⁰

To our knowledge the activation or additional activation through an exocyclic functionality has not been reported for early transition metal olefin polymerization complexes. However, the complexation of Lewis acids to metallocenes has been demonstrated for a number of systems, including constrained geometry complexes and coordination complexes.¹¹ In some cases, the Lewis acid is chemically attached to the ligand and interacts directly with the alkyl group bound to the metal center.¹² Other structures are derived from the well-known

constrained geometry complexes that combine aromatic rings and mono- or bidentate ligands to a transition metal.¹³

Particularly interesting cases are the early transition metal complexes (Ti, Zr, and Cr) derived from the combination of a β -diketiminate ligand containing a Cp ring, which has been used as an initiator of olefin polymerization and moderator for the polymerization of vinyl acetate, respectively.¹⁴

Herein, we report on the synthesis, characterization, and reactivity of a catalytic zirconium system that was designed to produce a cationic active site and also to benefit from removal of electron density from the metal center by the action of a Lewis acid on the ligand framework. We decided to use a specially functionalized bis(imino) acetylacetonate ligand (NC-nacnac), which is a derivative of an interesting class of ligands that has found increasing use in coordination chemistry of late transition metals including some unusual coordination chemistry of coinage metals.¹⁵

Results and Discussion

The reaction sequence begins with deprotonation of the previously described nacnac ligand (**1**)¹⁶ with *n*-butyllithium followed by the reaction of the resulting anion with the reagent tosyl cyanide (Ts-CN). This selectively introduced the cyano functional group at the C3 position of the ligand framework to give NC-nacnacH (**2**), isolated in 55% yield, Scheme 1.

The ligand system **2** was characterized by C, H, N elemental analysis, spectroscopically, and by X-ray diffraction. It features ¹³C NMR resonances of a typical conjugated enamino heterocarbonyl system (see Table 1). The ¹³C NMR signal of the cyano carbon atom was found at δ 121.2 ppm. The 2,6-diisopropylphenyl substituent at N1 features the ¹H/¹³C NMR signal of pairwise diastereotopic isopropyl CH₃ groups [isopropyl CH: δ 2.87 ppm (¹H), 28.9 ppm (¹³C)]. The IR ν (CN) band of compound **2** is found at 2192 cm⁻¹.

The X-ray crystal structure analysis shows a U-shaped C₃N₂ core with alternating bond lengths. The N1–H vector is oriented toward the inner side into the direction of N5, with which it probably forms a hydrogen bridge. Both the aryl substituents at N1 and N5 are substantially rotated out of the central plane toward a perpendicular orientation (see Table 2 and Figure 1). The C≡N bond is short and the C3–C7–N8 fragment is nearly linear.

Deprotonation of **2** was achieved by treatment with potassium hydride in THF at room temperature (12 h). The reaction proceeded cleanly with evolution of dihydrogen to give the salt [NC-nacnac]K (**3**) in 90% yield as a dark yellow solid (see Table 1 for characteristic spectroscopic features).

Treatment of **3** with one molar equivalent of CpZrCl₃·(dme) (THF, rt, 12 h) gave the (NC-nacnac)CpZrCl₂ complex **5**. It was isolated as an orange solid in 84% yield.

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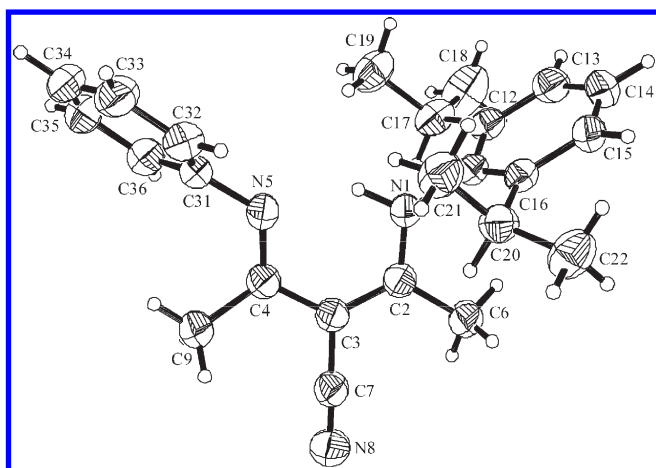
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Table 1. Selected Spectroscopic Parameters of the NC-nacnac Systems **2**, **3**, **5**, and **6**

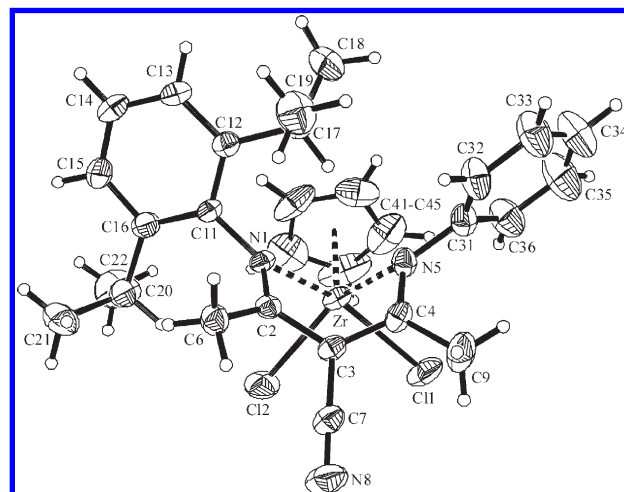
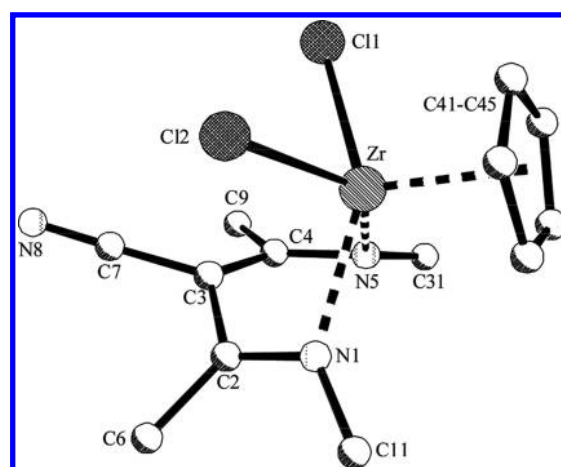
	2 ^a	3 ^a	5 ^b	6 ^a
δ ¹³ C NMR				
C=N ^{ph}	166.2	164.3	168.3	170.8
C ^{CN}	82.1	76.4	73.0	64.7
C=N ^{Ar}	166.9	171.6	171.3	171.4
C \equiv N	121.2	136.1	119.9	n.o
δ ¹ H NMR				
Cp			6.34	5.95
H C ^{iPr}			3.33, 2.76	3.22, 2.54
Me ^{Ph} , Me ^{Ar}	2.87	3.15	2.27, 2.31	1.86, 1.79
Me ^{iPr}	2.00, 1.92	2.36, 1.95	1.33, 1.21, 1.19, 0.92	1.18, 1.14, 0.90, 0.57
IR [cm ⁻¹]				
$\tilde{\nu}$ (CN)	2192	2134	2210	2278

^a NMR spectra in C₆D₆ solution. ^b NMR spectra in CD₂Cl₂ solution.**Table 2.** Selected Structural Parameters of the NC-nacnac Systems **2**, **5**, and **6**^a

	2	5	6
Zr–N1		2.305(3)	2.313(3)
Zr–C3		2.658(3)	2.583(3)
Zr–N5		2.227(3)	2.261(3)
Zr–C2		2.863(3)	2.849(3)
Zr–C4		2.703(3)	2.716(3)
Zr–C11		2.4695(9)	2.4701(10)
Zr–C12		2.4546(10)	2.4395(10)
C2–N1	1.330(2)	1.301(4)	1.296(4)
C2–C3	1.400(2)	1.463(4)	1.479(4)
C3–C4	1.450(2)	1.425(5)	1.448(4)
C4–N5	1.300(2)	1.324(4)	1.310(4)
C3–C7	1.429(2)	1.437(4)	1.409(4)
C7–N8	1.151(2)	1.140(4)	1.135(4)
N1–C2–C3	120.0(2)	116.8(3)	115.5(3)
C2–C3–C4	124.8(2)	122.4(3)	121.6(3)
C3–C4–N5	118.9(2)	118.1(3)	115.5(3)
C3–C7–N8	179.2(2)	179.0(4)	174.6(4)
C2–N1–C11–C12	101.8(2)	97.9(4)	90.4(4)
C4–N5–C31–C32	113.9(2)	−68.2(5)	108.2(4)

^a Bond lengths in Å, angles and dihedral angles in deg.**Figure 1.** View of the molecular structure of the NC-nacnac ligand system **2**.

It features a ¹H NMR Cp singlet of 5H intensity at δ 6.34 (¹³C: δ 118.8) and a pair of C2/C4–CH₃ resonances of the unsymmetrically substituted NC-nacnac core at δ 2.31/2.27

**Figure 2.** Molecular structure of complex **5**.**Figure 3.** Side view of the slightly boat-shaped central core of complex **5**.

(¹³C: δ 23.6/21.7). The isopropyl groups of the dipp substituent at N1 are different, giving rise to a pair of CHMe₂ methine proton NMR resonances and a total of four corresponding ¹H NMR CH₃ doublets. For further details see Table 1 and the Supporting Information.

Complex **5** was characterized by X-ray diffraction. It features a η^5 -Cp ligand at zirconium with Zr–C(Cp) bond lengths in a range between 2.471(4) and 2.487(4) Å. The NC-nacnac ligand is bound in a U-shaped form. While it appears that the Zr atom has interactions with all five members of the ligating ring, making it metallocene-like, the Zr–C/N bond lengths are systematically alternating, producing the strongest interaction of the N1/C3/N5 atoms with the Zr center. The Zr–N1 and Zr–N5 bond lengths are short (see Table 2 and Figure 2). The Zr–C3 bond length of 2.658(3) Å indicates a strong metal carbon interaction, whereas the adjacent Zr–C2/Zr–C4 bond lengths are markedly longer (see Table 2), and consequently, these interactions must be considered weaker. This pattern of metal–C/N bond lengths results in a typical deviation of the NC-nacnac ligand from planarity into the direction of a boat-shaped arrangement (see Figure 3). Overall the core of complex **5** remotely resembles a bent metallocene structure (see Figures 2 and 3) with the open N1/N5 side pointing toward the narrow backside of the wedge-like structure.

Scheme 1

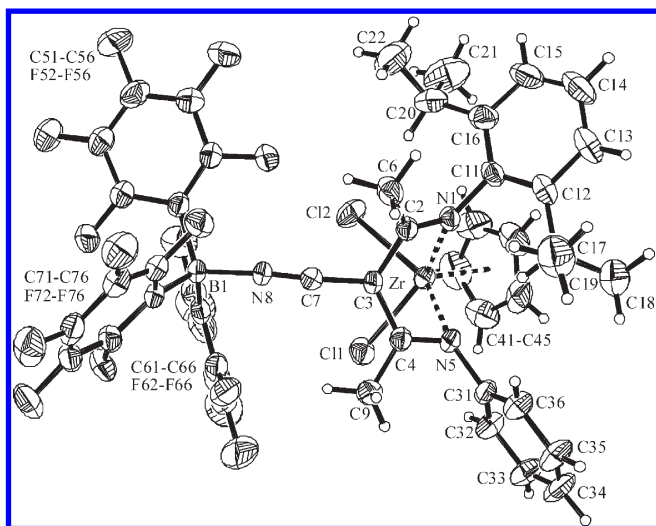
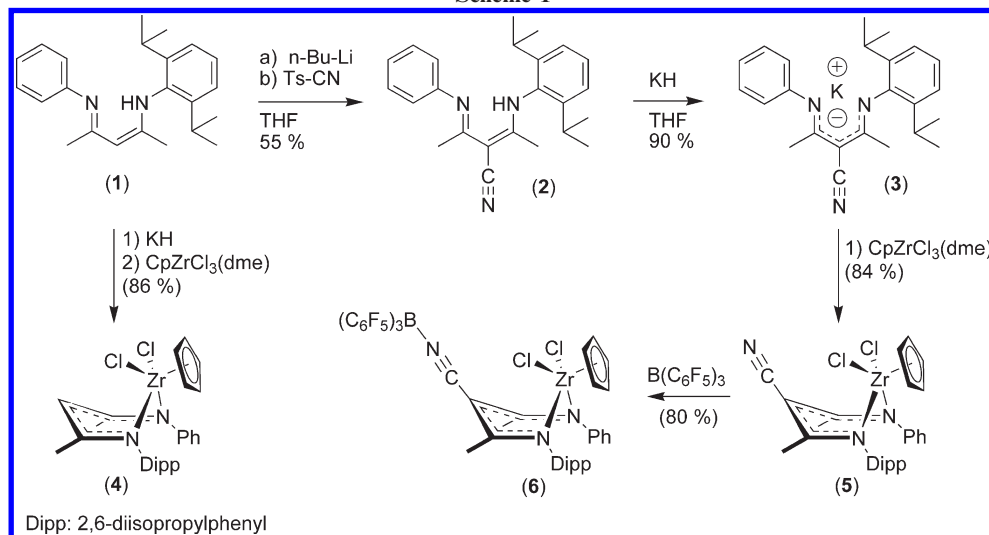


Figure 4. Molecular structure of the $\text{B}(\text{C}_6\text{F}_5)_3(\text{NC-nacnac})\text{CpZr-Cl}_2$ adduct **6**.

The C3–C7–N8 (C–C≡N) vector is oriented toward the open front side of the (lig)CpZrCl₂ geometry. In the projection it is unsymmetrically located between the Zr–C11/Zr–Cl2 vectors, but closer to Cl2.

For comparison for the polymerization experiments (see below) we have also prepared the related CN-free system (nacnac)CpZrCl₂ (**4**). This was obtained by deprotonation of the nacnacH derivative (**1**) with potassium hydride followed by the reaction of the resulting ligand salt with CpZrCl₃(dme) (see Scheme 1). The complex (nacnac)CpZrCl₂ (**4**) was isolated as a pale yellow solid in 80% yield (see the Experimental Section and the Supporting Information for its characterization).

The strong boron Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ added cleanly to the nitrile functionality of complex (NC-nacnac)CpZrCl₂ (**5**) to yield the new complex **6**. We purified it by crystallization from pentane/toluene and isolated it as a light yellow solid in 80% yield. The IR $\tilde{\nu}(\text{CN})$ band is shifted very characteristically upon Lewis acid adduct formation from 2210 cm^{-1} in **5** to 2278 cm^{-1} in **6**. The shifting of the C≡N stretching band by 68 cm^{-1} to higher wavenumbers indicates a strengthening of the C≡N triple bond, which is typically caused by

Table 3. Selected Ethylene Polymerization Reactions^a

entry	catalyst	Al/Zr ^b	T ^c	yield ^d	A ^e	M _n ^f	M _w ^f	PDI	T _m ^g
1	5	1000	45	0.28	244	163	338	2.1	135
2	5	1000	60	0.38	334	128	264	2.1	137
3	5	1000	75	0.96	845	65	138	2.1	137
4	5	1000	90	1.13	993	22	64	2.7	134
5	5	500	75	0.72	635	60	113	1.9	135
6	5	250	75	0.48	424	55	109	2.0	136
7	6	500	75	0.75	654	64	155	2.4	139
8	6	250	75	0.72	630	65	141	2.2	139
9	6	125	75	0.10	88	35	60	1.7	136
10	6	50	75	0.01	10				
11	5*	500	75	0.95	830	49	86	1.8	137
12	6*	500	75	1.17	1029	71	141	2.0	136
13	4	500	75	0.10	90	38	85	2.2	136

^a Polymerizations were carried out in 100 mL autoclave reactors with 6.8 μmol of Zr in 30 mL of toluene and 50 psi of ethylene pressure. The cocatalyst was MAO (MAO was added with an addition funnel when indicated with an asterisk (*)). Duration of reaction was 10 min. ^b Al/Zr ratio used. ^c Temperature of reaction (in °C). ^d Polymer obtained (in g). ^e Activity in kg polymer/(mol Zr h). ^f $\times 10^3$ g/mol. ^g In °C.

decreasing electrostatic electron repulsion by adding a Lewis acid to the nitrile lone pair.¹⁷ The strengthening of the C≡N bond upon $\text{B}(\text{C}_6\text{F}_5)_3$ addition even shows up in the X-ray crystal structure analysis of **6** (see Figure 4). In the adduct **6** we find a C≡N bond length (C7–N8) of 1.135(4) Å, which is not significantly different from that found in the direct precursor **5** (C7–N8: 1.140(4) Å).

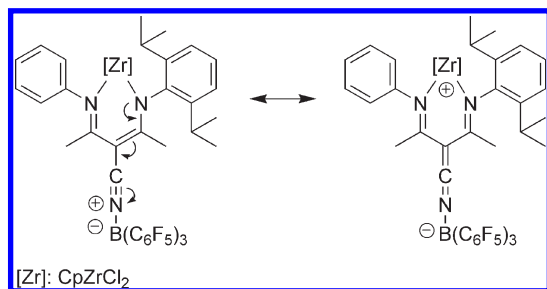
$\text{B}(\text{C}_6\text{F}_5)_3$ coordinates in a linear fashion to the NC-nacnac ligand in **6** (C7–N8–B1: 167.4(4)°, N8–B1: 1.586(4) Å). The C7–N8–B1(C_6F_5)₃ unit is oriented toward the open side of the pseudometallocene wedge in **6**. In the projection the C3–C7 vector almost bisects the Cl1–Zr–Cl2 angle (see Figure 4).

Ethylene Polymerization

A series of ethylene polymerizations were carried out using compounds **4–6** under various reaction conditions, with MAO as the coactivator (Table 3). In all cases, one observes

(17) (a) Jacobsen, H.; Berke, H.; Döring, S.; Kehr, G.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1999**, *18*, 1724–1735. See also: (b) Jacobsen, H.; Berke, H.; Brackemeyer, T.; Eisenblätter, T.; Erker, G.; Fröhlich, R.; Meyer, O.; Bergander, K. *Helv. Chim. Acta* **1998**, *81*, 1692–1709. (c) Brackemeyer, T.; Erker, G.; Fröhlich, R. *Organometallics* **1997**, *16*, 531–536.

Scheme 2



the formation of high molecular weight PE. Entries 1–4 show the behavior of **5** over a range of temperatures. There is a substantial increase in activity when the temperature is increased from 45 °C (244 kg/mol h) to 90 °C (993 kg/mol h), consistent with an increase in the rate of propagation. The result in entry 4 also demonstrates that the system is stable at high temperatures, and despite the increased polydispersity of the product, its GPC trace remains monomodal (see the Supporting Information). As was expected, the molecular weights of the resulting polymers decrease from 338 to 62 kg/mol upon increasing the temperature in this range. Entries 3, 5, and 6 show the results obtained at different Al/Zr ratios with **5**/MAO. Comparison of these entries shows that the ethylene consumption decreases by nearly 200 units when the Al/Zr ratio is reduced from 1000 to 500 to 250. There is also a slight decrease in the molecular weight of the products.

It is informative at this point to compare the ethylene polymerization activities obtained with **4** and **5**. Complex **4** in the presence of MAO has an activity of ca. 90 kg PE (mol Zr)^{−1} h^{−1} (at 75 °C and 500 Al/Zr ratio), while the system **5** under the same conditions shows an activity of 635 kg PE (mol Zr)^{−1} h^{−1}, 7 times higher. Clearly, complex **5** is a precursor to a significantly more active catalytic species, most likely as a result of the interaction between the Lewis acid and the exocyclic CN functionality. This interaction generates a reduction in the electron density at the zirconium center by inductive effects, as shown in Scheme 2. This causes the metal center to become more electrophilic, resulting in increased activities.

To verify these phenomena, we decided to use the isolated B(C₆F₅)₃ adduct (**6**), obtained by treating the precatalyst **5** with one equivalent of B(C₆F₅)₃ in toluene. Entry 7 demonstrates that when **6** is activated with MAO, the resulting activity and molecular weight are similar to those obtained with **5** under the same conditions (entry 5). In terms of the polymer properties, the **6**/MAO system produces more linear polyethylene with slightly higher melting points and slightly higher polydispersities. When the ratio of Al/Zr was gradually lowered, the activity remained constant until an Al/Zr ratio of 250. The adduct was also studied at lower Al/Zr ratios of 125 and 50 (entries 8 and 9, respectively); however a substantial decrease in the activity was observed, most likely because the coactivator concentrations were below the minimal content of MAO necessary to alkylate and generate the catalytic species. However the performance of these systems is remarkable, even at such low equivalents of MAO.

To minimize the probability of deactivation of the catalytic species in the reaction medium, the polymerizations were initiated by introducing MAO to a stirring solution of precatalysts (**5** or **6**) in the presence of ethylene via a pressure addition funnel. Under such conditions, the complexes exhibited an increase in catalytic activity of 19% (entries 11 and 12). Higher

activity is observed with the adduct (**6**) because the activator is required to generate only the catalytic species, since the CN functionality is already bound by the B(C₆F₅)₃.

Thermal analysis of the polymer products was performed using differential scanning calorimetry (DSC). Samples were scanned from 25 to 200 at 10 °C/min. One sharp thermal transition around 136 (±3) °C was observed for the PE obtained from the three systems under study. Variation in the reaction conditions did not change the linearity of the products.

Conclusion

In short, we have reported the synthesis and full characterization of a new type of active early transition metal catalyst precursor that can be used to polymerize olefins to high molecular weight in the presence of low concentrations of coactivators. Comparison with the reactivity observed with the Cp-diimine complex **4** illustrates that the presence of the carbonitrile functionality in **5** leads to a substantial increase in activity for ethylene polymerization under otherwise analogous reaction conditions.

On the basis of the considerations above, we propose that the increase in reactivity of **5** versus **4** is a result of the attachment of a Lewis acid to the exocyclic nitrogen site on the propagating cationic species. This has been probed indirectly by isolating the B(C₆F₅)₃-**5** adduct (**6**), which results in a similar activity in the presence of ethylene to that of **5**. Furthermore, the use of the adduct makes it possible to reduce the MAO concentration to 250 Al/Zr ratio without any detriment to the activity, as observed with **5**. The general concept was previously illustrated by late transition metals.^{10h,i,j–l,m} A straightforward explanation, Scheme 2, is a reduction of the electron density at the zirconium center by inductive effects, making the metal center more electrophilic. Additionally, the CN base functionality has another advantage; due to the sp hybridization, it is geometrically located in an opposite direction to the metal center, making it more probable that the Lewis acid interacts and thus has an electronic influence on the metal center, which is reflected in the improved performance of the catalytic system. The addition of MAO in the presence of ethylene shows an improvement in the catalytic activity for **5** and **6**; however the improvement was higher in the case of the B(C₆F₅) adduct **6**, supporting the notion that adduct formation plays an important role in these systems. Further optimization of reaction conditions, types of activators, alkylation reagents, and variations in α-cyano-β-diimine frameworks will enable improvements in polymerization control. Our current efforts are aimed at delineating the behavior of these systems in α-olefin and cyclic monomer copolymerizations, alkylation of the metal center, and heterogenization of this type of exocyclic-functionalized complexes.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques. All reagents were used as received from Aldrich unless otherwise specified. Ethylene was purchased from Matheson Tri-Gas (research grade, 99.99% pure). Toluene, THF, ether, and pentane were distilled from benzophenone ketyl. All polymerization reactions were carried out in a Parr autoclave reactor as described below. Toluene for polymerization was distilled from sodium benzophenone. The following instruments were used for the physical characterization of the compounds. NMR: Varian Inova 500 (¹H: 500 MHz, ¹³C: 126 MHz, ¹⁹F: 470 MHz,

^{11}B : 160 MHz), Bruker Unity Plus 600 (^1H : 600 MHz, ^{13}C : 151 MHz, ^{19}F : 564 MHz, ^{11}B : 64 MHz) and Bruker Advance 400. Most NMR assignments were supported by additional 2D experiments. IR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets, and in solution using C_6D_6 as solvent. X-ray crystal structure analyses: Data sets were collected with Nonius KappaCCD diffractometers, in the case of Mo-radiation equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, 276, 307–326), absorption correction SORTAV (R. H. Blessing, *Acta Crystallogr.* **1995**, A51, 33–37; R. H. Blessing, *J. Appl. Crystallogr.* **1997**, 30, 421–426) and Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr.* **2003**, A59, 228–234), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, A46, 467–473), structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr.* **2008**, A64, 112–122), graphics XP (BrukerAXS, 2000). Graphics show thermal ellipsoids at the 50% probability level. R values are given for the observed reflections; wR_2 values for all.

Preparation of Compound 2. $n\text{-BuLi}$ (3.4 mL, 1.6 M, 5.5 mmol) was added dropwise to a stirred solution of 2-(2,6-diisopropylphenyl)aminopent-2-ene-4-(phenyl)imine (**1**)¹⁶ in THF (40 mL) (1.4 g, 4.2 mmol) at -78°C . The reaction was allowed to warm to room temperature over 2 h to afford the lithium salt. The resulting yellow suspension was then cooled to -78°C , and $p\text{-toluenesulfonyl cyanide}$ (0.9 g, 5.0 mmol) in THF (10 mL) was added. The reaction mixture was again allowed to warm to room temperature over 24 h. From this mixture, all volatiles were removed under vacuum, and the residue was dissolved in CH_2Cl_2 (50 mL). This was washed with brine ($2 \times 100\text{ mL}$), dried over Na_2SO_4 , and filtered. The solvent was subsequently removed under vacuum to yield a light brown oil. Precipitation from methanol provided a light yellow solid of 3-cyano-2-(2,6-diisopropylphenyl)aminopent-2-ene-4-(phenyl)imine (**2**) in 55% yield. Single crystals suitable for X-ray diffraction studies were obtained by evaporation of an acetone solution of compound **2** at room temperature ($\text{C}_{24}\text{H}_{29}\text{N}_3$ ($M = 359.59\text{ g/mol}$): C 80.16, H 8.13, N 11.69; found: C 79.85, H 8.74, N 11.02). IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ 2192 ($\nu(\text{C}\equiv\text{N})$, s). ^1H NMR (500 MHz, C_6D_6 , 298 K): δ 14.56 (s, 1H, NH), 7.09 (m, 1H, $p\text{-Ar}$), 7.02 (m, 2H, $m\text{-Ar}$), 7.01 (m, 2H, $m\text{-Ph}$), 6.86 (m, 1H, $p\text{-Ph}$), 6.69 (m, 2H, $o\text{-Ph}$), 2.87 (hept, $J = 6.9\text{ Hz}$, 2H, HC^{IPr}), 2.00 (s, 3H, $^{\text{N}=\text{C}}\text{Me}^{\text{Ph}}$), 1.92 (s, 3H, $^{\text{N}=\text{C}}\text{Me}^{\text{Ar}}$), 1.05 (d, $J = 6.9\text{ Hz}$, 6H, Me^{IPr}), 0.99 (d, $J = 6.9\text{ Hz}$, 6H, Me^{IPr}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): δ 166.9 ($\text{C}=\text{N}^{\text{Ar}}$), 166.2 ($\text{C}=\text{N}^{\text{Ph}}$), 144.8 ($i\text{-Ph}$), 142.4 ($o\text{-Ar}$), 138.3 ($i\text{-Ar}$), 129.3 ($m\text{-Ph}$), 127.0 ($p\text{-Ar}$), 124.9 ($p\text{-Ph}$), 123.8 ($m\text{-Ar}$), 123.0 ($o\text{-Ph}$), 121.2 ($\text{C}\equiv\text{N}$), 82.1 (C^{CN}), 28.9 (HC^{IPr}), 24.3 (Me^{IPr}), 22.5 (Me^{IPr}), 19.4 ($^{\text{N}=\text{C}}\text{Me}^{\text{Ph}}$), 19.3 ($^{\text{N}=\text{C}}\text{Me}^{\text{Ar}}$) ppm.

X-ray crystal structure analysis of **2**: formula $\text{C}_{24}\text{H}_{29}\text{N}_3$, $M = 359.50$, colorless crystal $0.45 \times 0.25 \times 0.05\text{ mm}$, $a = 10.3543(4)\text{ \AA}$, $b = 21.0372(9)\text{ \AA}$, $c = 10.4706(5)\text{ \AA}$, $\beta = 112.054(2)^\circ$, $V = 2113.88(16)\text{ \AA}^3$, $\rho_{\text{calc}} = 1.130\text{ g cm}^{-3}$, $\mu = 0.510\text{ mm}^{-1}$, empirical absorption correction ($0.803 \leq T \leq 0.975$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 1.54178\text{ \AA}$, $T = 223(2)\text{ K}$, ω and ϕ scans, 14 753 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.60\text{ \AA}^{-1}$, 3717 independent ($R_{\text{int}} = 0.051$) and 2996 observed reflections [$I \geq 2\sigma(I)$], 254 refined parameters, $R = 0.051$, $wR_2 = 0.140$, max. (min.) residual electron density 0.23 (-0.17) e \AA^{-3} , hydrogen atoms calculated and refined as riding atoms.

Preparation of the Potassium Salt 3. Compound **2** (0.28 g, 0.8 mmol) and KH (63 mg, 1.6 mmol) were stirred in THF for 12 h. The reaction showed rapid gas evolution. The slightly cloudy mixture was filtered through Celite, and excess THF was removed under vacuum. A dark yellow powder corresponding to compound **3** was isolated in 90% yield ($\text{C}_{24}\text{H}_{28}\text{N}_3\text{K} \cdot \text{C}_4\text{H}_8\text{O}$ ($M = 469.71\text{ g/mol}$): C 71.60, H 7.72, N 8.94; found: C 72.15, H 7.37, N 9.13). IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ 2134 ($\nu(\text{C}\equiv\text{N})$, s). ^1H NMR (500 MHz, C_6D_6 , 343 K): δ 7.19 (m, 2H, $m\text{-Ar}$), 7.15 (m, 2H,

$m\text{-Ph}$), 7.08 (m, 1H, $p\text{-Ar}$), 6.84 (m, 1H, $p\text{-Ph}$), 6.49 (m, 2H, $o\text{-Ph}$), 3.15 (hept, $^3J = 6.9\text{ Hz}$, 2H, HC^{IPr}), 2.36 (s, 3H, $^{\text{N}=\text{C}}\text{Me}^{\text{Ph}}$), 1.95 (s, 3H, $^{\text{N}=\text{C}}\text{Me}^{\text{Ar}}$), 1.27 (d, $^3J = 6.9\text{ Hz}$, 6H, Me^{IPr}), 1.21 (d, $^3J = 6.9\text{ Hz}$, 6H, Me^{IPr}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 343 K): δ 171.6 ($\text{C}=\text{N}^{\text{Ph}}$), 164.3 ($\text{C}=\text{N}^{\text{Ar}}$), 153.2 ($i\text{-Ph}$), 148.4 ($i\text{-Ar}$), 138.5 ($o\text{-Ar}$), 136.1 ($\text{C}\equiv\text{N}$), 129.8 ($m\text{-Ph}$), 123.6 ($m\text{-Ar}$), 122.9 ($p\text{-Ar}$), 122.3 ($o\text{-Ph}$), 122.1 ($p\text{-Ph}$), 76.4 (C^{CN}), 28.6 (HC^{IPr}), 24.1 (Me^{IPr}), 23.5 (Me^{IPr}), 21.5 ($^{\text{N}=\text{C}}\text{Me}^{\text{Ar}}$), 20.8 ($^{\text{N}=\text{C}}\text{Me}^{\text{Ph}}$) ppm.

Preparation of Complex 4. 2-(2,6-Diisopropylphenyl)aminopent-2-ene-4-(phenyl)imine (**1**) (90 mg, 0.27 mmol) and KH (22 mg, 0.54 mmol) were stirred in THF for 12 h. The reaction showed rapid gas evolution. The slightly cloudy mixture was filtered through Celite and added dropwise to $\text{CpZrCl}_3(\text{dme})$ (95 mg, 0.27 mmol) in THF. The reaction mixture was stirred for 6 h. The resulting yellow solution was filtered over Celite. The solvent volume was reduced, and pentane and ether were added separately to wash the solid. A light yellow powder corresponding to compound **4** was isolated in 86% yield ($\text{C}_{28}\text{H}_{34}\text{Cl}_2\text{N}_2\text{Zr}$ ($M = 560.71\text{ g/mol}$): C 59.97, H 6.11, N 4.99; found: C 59.32, H 5.89, N 5.21). ^1H NMR (500 MHz, CD_2Cl_2 , 298 K): δ 7.46 (m, 2H, $m\text{-Ph}$), 7.32 (m, 2H, $m\text{-p-Ar}$), 7.31 (m, 1H, $p\text{-Ph}$), 7.23 (br, 2H, $o\text{-Ph}$), 7.21 (m, 1H, $m'\text{-Ar}$), 6.30 (s, 5H, Cp), 5.70 (s, 1H, CH), 3.60 (hept, $^3J = 6.7\text{ Hz}$, 1H, $\text{HC}^{\text{IPr}(o)}$), 2.70 (hept, $^3J = 6.7\text{ Hz}$, 1H, $\text{HC}^{\text{IPr}(o')}$), 2.07 (s, 3H, $^{\text{N}=\text{C}}\text{Me}^{\text{Ar}}$), 2.02 (s, 3H, $^{\text{N}=\text{C}}\text{Me}^{\text{Ph}}$), 1.36 (d, $^3J = 6.7\text{ Hz}$, 3H, $\text{Me}^{\text{IPr}(o)}$), 1.20 (d, $^3J = 6.7\text{ Hz}$, 3H, $\text{Me}^{\text{IPr}(o')}$), 1.18 (d, $^3J = 6.7\text{ Hz}$, 3H, $\text{Me}^{\text{IPr}(o')}$), 0.92 (d, $^3J = 6.7\text{ Hz}$, 3H, $\text{Me}^{\text{IPr}(o')}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 298 K): δ 168.4 ($\text{C}=\text{N}^{\text{Ar}}$), 161.8 ($\text{C}=\text{N}^{\text{Ph}}$), 150.0 ($i\text{-Ph}$), 144.6 ($i\text{-Ar}$), 143.6 ($o\text{-Ar}$), 141.5 ($o'\text{-Ar}$), 129.4 ($m\text{-Ph}$), 127.8 ($p\text{-Ar}$), 126.5 ($p\text{-Ph}$), 125.9 ($m\text{-Ar}$), 124.6 (br, $o\text{-Ph}$), 124.3 ($m'\text{-Ar}$), 117.6 (Cp), 90.8 (CH), 27.79 ($\text{HC}^{\text{IPr}(o)}$), 27.76 ($\text{HC}^{\text{IPr}(o')}$), 25.7 ($\text{Me}^{\text{IPr}(o)}$), 25.0 ($\text{Me}^{\text{IPr}(o')}$), 24.6 ($\text{Me}^{\text{IPr}(o')}$), 24.1 ($^{\text{N}=\text{C}}\text{Me}^{\text{Ar}}$), 23.2 ($\text{Me}^{\text{IPr}(o')}$), 23.1 ($^{\text{N}=\text{C}}\text{Me}^{\text{Ph}}$) ppm.

Preparation of Complex 5. The potassium salt **3** (89 mg, 0.25 mmol) in THF (2 mL) was added to $\text{CpZrCl}_3(\text{dme})$ ¹⁸ (100 mg, 0.25 mmol) in THF. The reaction mixture was stirred for 12 h. The resulting orange solution was filtered over Celite. The solvent volume was reduced, and pentane and ether were added separately to wash the solid. A light brown powder was isolated in 84% yield. Single crystals for X-ray crystal structure analysis were grown by evaporation of C_6D_6 solution of compound **5** at room temperature ($\text{C}_{29}\text{H}_{33}\text{Cl}_2\text{N}_3\text{Zr} \times \text{C}_4\text{H}_8\text{O}$ ($M = 657.83\text{ g/mol}$): C 60.25, H 6.28, N 6.39; found: C 59.92, H 6.41, N 5.97). IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ 2210 ($\nu(\text{C}\equiv\text{N})$, s). ^1H NMR (500 MHz, CD_2Cl_2 , 298 K): δ 7.52 (m, 2H, $m\text{-Ph}$), 7.38 (m, 1H, $p\text{-Ph}$), 7.37 (m, 2H, $m\text{-p-Ar}$), 7.26 (m, 1H, $m'\text{-Ar}$), 7.20 (br, 2H, $o\text{-Ph}$), 6.34 (s, 5H, Cp), 3.33 (hept, $^3J = 6.6\text{ Hz}$, 1H, $\text{HC}^{\text{IPr}(o)}$), 2.76 (hept, $^3J = 6.7\text{ Hz}$, 1H, $\text{HC}^{\text{IPr}(o')}$), 2.31 (s, 3H, $^{\text{N}=\text{C}}\text{Me}^{\text{Ar}}$), 2.27 (s, 3H, $^{\text{N}=\text{C}}\text{Me}^{\text{Ph}}$), 1.33 (d, $^3J = 6.6\text{ Hz}$, 3H, $\text{Me}^{\text{IPr}(o)}$), 1.21 (d, $^3J = 6.7\text{ Hz}$, 3H, $\text{Me}^{\text{IPr}(o')}$), 1.19 (d, $^3J = 6.6\text{ Hz}$, 3H, $\text{Me}^{\text{IPr}(o')}$), 0.92 (br d, $^3J = 6.7\text{ Hz}$, 3H, $\text{Me}^{\text{IPr}(o')}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 298 K): δ 171.3 ($\text{C}=\text{N}^{\text{Ar}}$), 168.3 ($\text{C}=\text{N}^{\text{Ph}}$), 148.5 ($i\text{-Ph}$), 143.14 ($i\text{-Ar}$), 143.07 ($o\text{-Ar}$), 140.7 ($o'\text{-Ar}$), 129.8 ($m\text{-Ph}$), 128.6 ($p\text{-Ar}$), 127.4 ($p\text{-Ph}$), 126.4 ($m\text{-Ar}$), 124.5 ($m'\text{-Ar}$), 124.0 (br, $o\text{-Ph}$), 119.9 (br, $\text{C}\equiv\text{N}$), 118.8 (Cp), 73.0 (br, C^{CN}), 28.1 ($\text{HC}^{\text{IPr}(o')}$), 27.9 ($\text{HC}^{\text{IPr}(o)}$), 25.9 ($\text{Me}^{\text{IPr}(o)}$), 25.2 ($\text{Me}^{\text{IPr}(o')}$), 24.4 ($\text{Me}^{\text{IPr}(o')}$), 23.6 ($^{\text{N}=\text{C}}\text{Me}^{\text{Ar}}$), 22.7 ($\text{Me}^{\text{IPr}(o')}$), 21.7 ($^{\text{N}=\text{C}}\text{Me}^{\text{Ph}}$) ppm.

X-ray crystal structure analysis of **5**: formula $\text{C}_{29}\text{H}_{33}\text{Cl}_2\text{N}_3\text{Zr} \cdot \text{C}_4\text{H}_8\text{O}$, $M = 657.81$, colorless crystal $0.35 \times 0.15 \times 0.05\text{ mm}$, $a = 10.2577(1)\text{ \AA}$, $b = 13.2092(2)\text{ \AA}$, $c = 13.6742(3)\text{ \AA}$, $\alpha = 72.173(1)^\circ$, $\beta = 87.628(1)^\circ$, $\gamma = 68.432(2)^\circ$, $V = 1635.03(5)\text{ \AA}^3$, $\rho_{\text{calc}} = 1.336\text{ g cm}^{-3}$, $\mu = 0.529\text{ mm}^{-1}$, empirical absorption

(18) (a) Lund, E. C.; Livinghouse, T. *Organometallics* **1990**, 9, 2426–2427. See also: (b) Erker, G.; Sarter, C.; Albrecht, M.; Dehnicke, S.; Krüger, C.; Raabe, E.; Schlund, R.; Benn, R.; Ruffiska, A.; Mynott, R. *J. Organomet. Chem.* **1990**, 382, 89–102. (c) Erker, G.; Sarter, C.; Werner, S.; Krueger, C. *J. Organomet. Chem.* **1989**, 377, C55–C58. (d) Erker, G.; Berg, K.; Treschanke, L.; Engel, K. *Inorg. Chem.* **1982**, 21, 1277–1278.

correction ($0.837 \leq T \leq 0.974$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and ϕ scans, 15 500 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.66$ Å⁻¹, 7414 independent ($R_{\text{int}} = 0.063$) and 5757 observed reflections [$I \geq 2\sigma(I)$], 413 refined parameters, $R = 0.052$, $wR_2 = 0.133$, max. (min.) residual electron density 0.70 (−0.81) e Å⁻³, solvent molecule refined with split positions, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 6. One equivalent of tris(pentafluorophenyl)borane (114 mg in 1 mL of toluene, 0.22 mmol) was added to a toluene solution of **5** (130 mg, 0.22 mmol). The reaction mixture was stirred for 12 h and filtered through Celite, and the volatiles were removed under vacuum. Compound **6** was isolated as a light yellow solid in 80% yield. Single crystals for X-ray crystallography were grown by evaporation of a C₆H₆ solution of compound **6** at room temperature (C₄₇H₃₃BCl₂·F₁₅N₃Zr·C₆H₆ ($M = 1175.80$ g/mol): C 54.14, H 3.34, N 3.57; found C 55.03, H 3.80, N 3.33). IR (KBr): $\tilde{\nu}$ /cm⁻¹ ($\nu(\text{C}\equiv\text{N})$, s). ¹H NMR (600 MHz, C₆D₆, 298 K): δ 7.03 (m, 2H, *m*-Ph), 7.00 (m, 2H, *m*-,*p*-Ar), 6.94 (m, 1H, *p*-Ph), 6.90 (br, 2H, *o*-Ph), 6.85 (m, 1H, *m'*-Ar), 5.95 (s, 5H, Cp), 3.22 (hept, ³*J* = 6.9 Hz, 1H, HC^{iPr(o)}), 2.54 (hept, ³*J* = 6.9 Hz, 1H, HC^{iPr(o')}), 1.86 (s, 3H, N^{=C}Me^{Ph}), 1.79 (s, 3H, N^{=C}Me^{Ar}), 1.18 (d, ³*J* = 6.9 Hz, 3H, Me^{iPr(o)}), 1.14 (d, 3H, ³*J* = 6.9 Hz, Me^{iPr(o')}), 0.90 (d, ³*J* = 6.9 Hz, 3H, Me^{iPr(o')}) 0.57 (d, ³*J* = 6.9 Hz, 3H, Me^{iPr(o')}) ppm. ¹³C{¹H} NMR (151 MHz, C₆D₆, 298 K): δ 171.4 (C=N^{Ar}), 170.8 (C=N^{Ph}), 148.4 (dm, ¹*J*_{FC} ≈ 247 Hz), 140.7 (dm, ¹*J*_{FC} ≈ 253 Hz), 137.6 (dm, ¹*J*_{FC} ≈ 247 Hz) (C₆F₅), 147.3 (*i*-Ph), 142.8 (*o*-Ar), 141.9 (*i*-Ar), 139.5 (*o'*-Ar), 129.7 (*m*-Ph), 128.9 (*p*-Ar), 127.5 (*p*-Ph), 126.6 (*m*-Ar), 124.0 (*m'*-Ar), 123.1 (br, *o*-Ph), 118.9 (Cp), 64.7 (C^N), 27.9 (HC^{iPr(o')}), 27.7 (HC^{iPr(o)}), 26.1 (Me^{iPr(o)}), 25.2 (Me^{iPr(o')}), 23.5 (Me^{iPr(o')}), 23.1 (N^{=C}Me^{Ar}), 22.1 (Me^{iPr(o')}), 21.4 (N^{=C}Me^{Ph}), n.o. (C≡N, *i*-C₆F₅) ppm. ¹⁹F NMR (564 MHz, C₆D₆, 298 K): δ −133.8 (m, 2F, *o*-C₆F₅), −156.1 (t, ³*J*_{FF} = 20.5 Hz, 1F, *p*-C₆F₅), −163.3 (m, 2F, *m*-C₆F₅) ppm. ¹¹B{¹H} NMR (192 MHz, C₆D₆, 298 K): n.o.

X-ray crystal structure analysis of **6**: formula C₄₇H₃₃BCl₂·F₁₅N₃Zr·C₆H₆, $M = 1175.80$, colorless crystal $0.25 \times 0.15 \times 0.12$ mm, $a = 11.5478(1)$ Å, $b = 13.8426(2)$ Å, $c = 18.8875(3)$ Å, $\alpha = 101.636(1)^\circ$, $\beta = 105.908(1)^\circ$, $\gamma = 106.604(1)^\circ$, $V = 2650.95(6)$ Å³, $\rho_{\text{calc}} = 1.473$ g cm⁻³, $\mu = 0.400$ mm⁻¹, empirical absorption correction ($0.907 \leq T \leq 0.954$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and ϕ scans, 20 995 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] =$

0.66 Å⁻¹, 12 255 independent ($R_{\text{int}} = 0.045$) and 10 634 observed reflections [$I \geq 2\sigma(I)$], 670 refined parameters, $R = 0.064$, $wR_2 = 0.176$, max. (min.) residual electron density 1.58 (−0.81) e Å⁻³, solvent molecule refined with restraints, hydrogen atoms calculated and refined as riding atoms.

Homopolymerization of Ethylene. Polymerizations were carried out in a Parr autoclave reactor (100 mL), loaded inside a glovebox with an appropriate amount (6.8 μmol) of the precatalyst (**4**, **5**, or **6**) and the corresponding MAO with toluene, such that the final volume of the toluene solution was 30 mL. The reactor was sealed inside the glovebox (where indicated, MAO was put into the addition funnel). The reactor was attached to an ethylene line, and the gas was fed continuously into the reactor to a pressure of 50 psi. The pressurized reaction mixture was stirred at temperatures ranging from 45 to 90 °C. After 10 min, the ethylene was vented and acetone was added to quench the polymerization. The precipitated polymer was collected by filtration and dried overnight. The obtained polymers were characterized by gel permeation chromatography (GPC). GPC analysis was performed on a Polymer Laboratories high-temperature GPC system (model PL 220) equipped with a refractive index detector. Samples were run at 150 °C in spectroscopic grade 1,2,4-trichlorobenzene (TCB), stabilized with BHT (0.5 g BHT/4 L solvent). Molecular weights were calculated by using a universal calibration from narrow polystyrene standards in the molecular weight range of 580 to 7.5 million g/mol. Mark–Houwink parameters of $a = 0.7$ and $k = 47.7$ were utilized to correct for polyethylene. Polymer melting points were measured on a TA Instruments differential scanning calorimeter (model DSC 290 module, TA Instruments) at a rate of 10 °C/min for two cycles in the temperature range 25–200 °C.

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Supporting Information Available: Text and figures giving further experimental and spectroscopic details and CIF files (**2**, **5**, and **6**) giving crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.