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Synthesis and Structure of Bifunctional Zirconocene/Borane Complexes and Their Activation for Ethylene Polymerization

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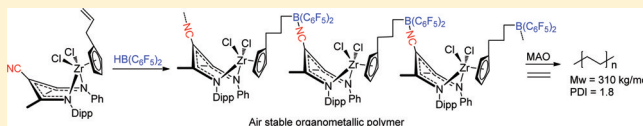
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Supporting Information

ABSTRACT: The potassium salt of **1** was transmetalated by reaction with (Cp-allyl)ZrCl₂(dme), yielding the complex (NC-nacnac)Cp-allylZrCl₂ (**2**). Addition of 1 molar equiv of B(C₆F₅)₃ gave [(C₆F₅)₃B-NC-nacnac]Cp-allylZrCl₂ (**3**), and the subsequent addition of 1 molar equiv of HB(C₆F₅)₂ to **3** gave the hydroborated species [((C₆F₅)₃B-NC-nacnac)Cp-(CH₂)₃-B(C₆F₅)₂]ZrCl₂ (**4**). The hydroboration of **2** with 1 molar equiv of HB(C₆F₅)₂ gave an insoluble product. This product was fully characterized by ¹¹B and ¹³C solid-state NMR and IR, which showed that the hydroboration followed by intermolecular adduct formation (R-B(C₆F₅)₂-NC-NC-R') occurs, resulting in an organometallic polymer (**5**). In addition to the CN-free [nacnac]Cp-allylZrCl₂ (**6**), the hydroborated derivative [(nacnac)Cp-(CH₂)₃-B(C₆F₅)₂] (**7**) was also prepared. Complexes **2**–**7** were activated with methylaluminoxane (MAO) and gave active catalysts for ethylene polymerization. The polymers produced were linear and had high molecular weight, with polydispersities (PDI) of less than 2, indicating that the catalysts are single site. The presence of the allyl group on the Cp ring was found to increase the molecular weight of the materials produced. In addition to discrete complexes, an organometallic polymer (**5**) was formed. This compound is air stable and, while not very soluble, polymerizes ethylene with good activity.



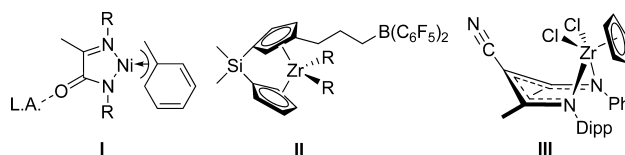
INTRODUCTION

Homogeneous metallocene Ziegler–Natta catalysis¹ and various types of related “post-metallocene” catalysts usually require specific activation by strongly Lewis acidic cocatalysts.² The most commonly applied activating reagents are methylaluminoxanes. They usually serve two purposes, namely nucleophilic methylation at the metal center combined with electrophilic removal of a methyl anion equivalent generating a reactive alkyl metal cation salt or ion pair, respectively, that starts the olefin polymerization chain upon exposure to the olefin monomer. A variety of related reagents were employed alternatively, including B(C₆F₅)₃³ or various very bulky [R₃C⁺][B(C₆F₅)₄[−]] salts.^{4,5}

Some Lewis acidic components can, however, carry out additional functions, except direct activation, when added to a suitable molecular Ziegler–Natta polymerization catalyst precursor.⁶ They can be added to a Lewis base function at the metal complex. This may make the metal center more electrophilic and result in a more active catalyst at the activated stage but at the same time serve as bulky substituents and influence the catalytic process by that property. Complexes I in Chart 1 are typical examples.^{7–9}

Lewis acidic centers can alternatively be covalently attached at the core of the catalyst precursor by a suitable tether.¹⁰ Complex II in Chart 1 is a typical example. The intramolecular Lewis acid may become actively involved in the activation step but again may also serve as a bulky substituent at the catalyst periphery. In this study we have introduced both of these Lewis acid derived functionalities

Chart 1



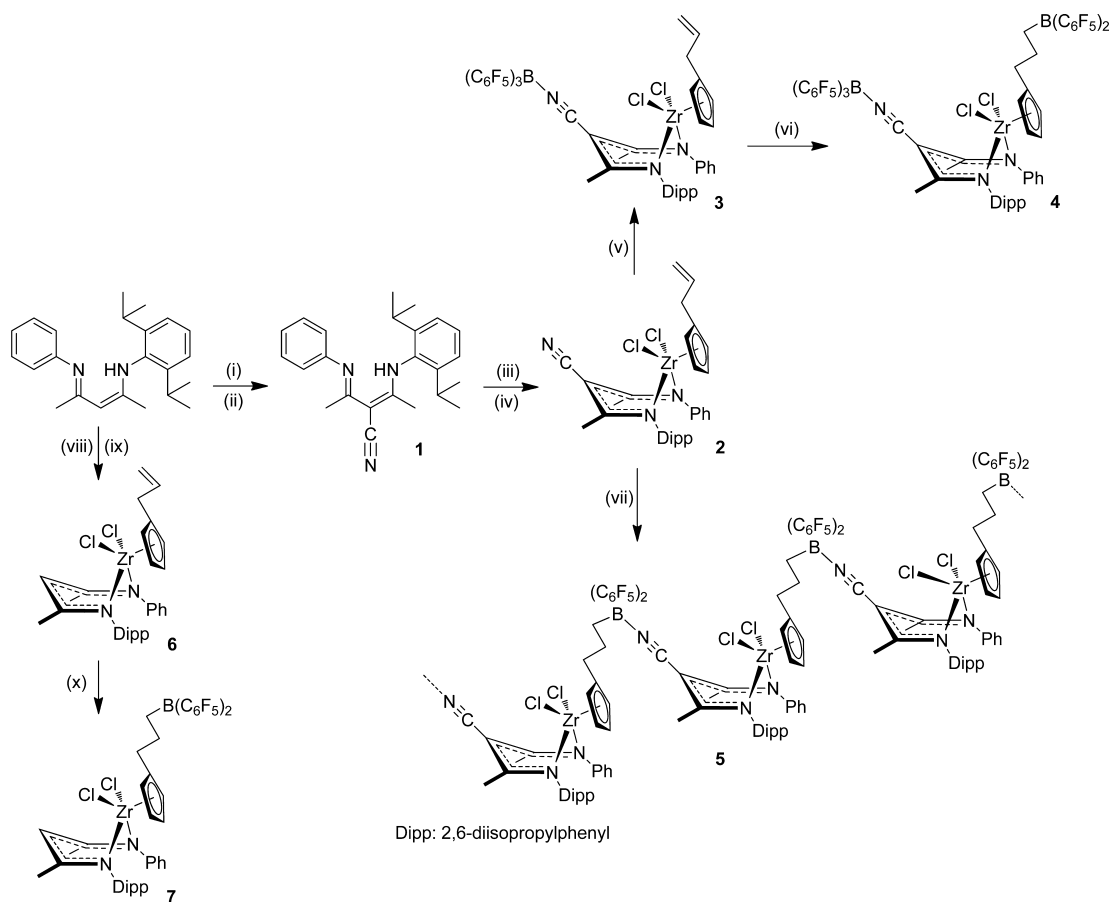
at a simple catalyst precursor. We chose the complex system **4** (see Scheme 1), which is closely related to III.^{12,13} It contains a B(C₆F₅)₃ function coordinated to a cyano substituent at a conjugated position of a nacnac ligand at zirconium combined with a -B(C₆F₅)₂ function tethered to the adjacent Cp ring.^{14,15} We will see how the combination of steric and electronic effects of these different boron-centered functionalities will affect the olefin polymerization process taking place after suitable activation.

RESULTS AND DISCUSSION

The synthesis of [π -(NC-nacnac)- η^5 -allylcyclopentadienyl]-zirconium dichloride types of precursors for reaction with boranes was straightforwardly accomplished using commonly employed transmetalation, hydroboration, and addition reactions, as outlined in Scheme 1. The precursor [η^5 -(2-propenyl)cyclopentadienyl]-zirconium trichloride dimethoxyethane was synthesized using

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Scheme 1.^a

^aLegend: (i) *n*-BuLi, C₄H₈O; (ii) *p*-toluenesulfonyl cyanide, C₄H₈O; (iii) KH, C₄H₈O; (iv) (Cp-allyl)ZrCl₃(dme), CH₂Cl₂, room temperature, 65%; (v) B(C₆F₅)₃, CH₂Cl₂, room temperature, 86%; (vi) HB(C₆F₅)₂, CH₂Cl₂, room temperature, 87%; (vii) HB(C₆F₅)₂, CH₂Cl₂, room temperature, 78%; (viii) KH, C₄H₈O; (ix) (Cp-allyl)ZrCl₃(dme), CH₂Cl₂, room temperature, 85%; (x) HB(C₆F₅)₂, toluene, room temperature, 87%.

Table 1. Selected Spectroscopic Parameters of the NC-nacnac Systems 2–7

	2	3	4	5	6	7
$\delta(^{13}\text{C})$						
C=N ^{Ph}	168.0	171.6	170.8	170.9 ^a	161.7	161.3
C ^{CN}	72.7	63.9	63.9	64.4 ^a		
C=N ^{Ar}	171.1	170.8	171.4	170.9 ^a	168.3	168.0
–CH ₂ –(C6)	35.4	35.4	33.5	33.6 ^a	35.4	33.7
–CH=Cp-allyl(C7)	137.0	136.5			137.7	
=CH ₂ Cp-allyl(C8)	116.4	116.7			115.8	
$\delta(^1\text{H})$						
–CH=Cp-allyl(7H)	6.01	5.97			6.02	
=CH ₂ Cp-allyl(8H)	5.05	5.05/5.03			5.03/5.01	
H ^{CiPr}	3.36	3.21	3.26		3.63	3.90
	2.76	2.78	2.58		2.69	2.72
Me ^{Ph}	2.27	2.20	1.88		2.03	1.76
Me ^{Ar}	2.30	2.22	1.81		2.06	1.56
Me ^{iPr}	1.33	1.31	1.25		1.35	1.44
	1.20	1.23	1.15		1.20	1.18
	1.17	1.21	0.92		1.14	1.01
	0.91	0.96	0.59		0.92	0.72
IR (cm ^{–1})						
$\nu(\text{C}\equiv\text{N})$	2213	2280	2284	2279		

^aFrom solid state NMR.

literature procedures.¹⁶ Subsequently, transmetalation with 1 molar equiv of the previously reported NC-nacnac

potassium salt¹² (CH₂Cl₂, room temperature, 4 h) gave the (NC-nacnac)Cp-allylZrCl₂ complex 2, isolated as a light yellow

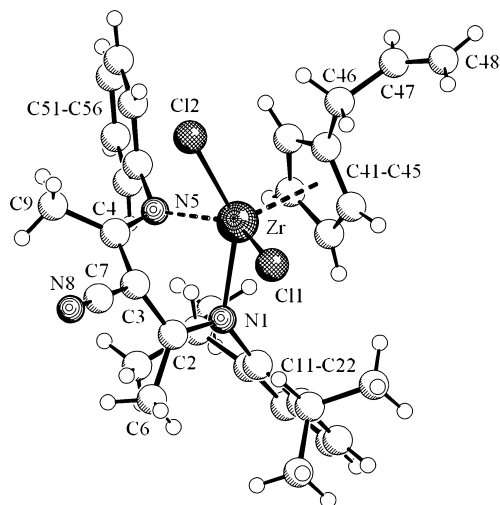


Figure 1. Molecular structure of complex 2.

characteristic HC^{iPr} and Me^{iPr} resonances of the isopropyl group in the ^1H NMR (see Table 1 and the Supporting Information). The $\nu(\text{CN})$ IR band is shifted upon the formation of the Lewis acid adduct from 2213 cm^{-1} in **2** to 2280 cm^{-1} in **3**, as is typically observed in such a situation.^{12,18} The X-ray crystal structure analysis of **3** showed that the $\text{B}(\text{C}_6\text{F}_5)_3$ group is coordinated in a linear fashion to the NC-nacnac ligand, with a $\text{C}(7)\text{--N}(8)\text{--B}(1)$ bond angle of $167.2(3)^\circ$. The $\text{C}(7)\text{--N}(7)\text{--B}(1)(\text{C}_6\text{F}_5)_3$ vector is oriented toward the open side of the pseudo-metallocene wedge in **3** (see Figure 2).

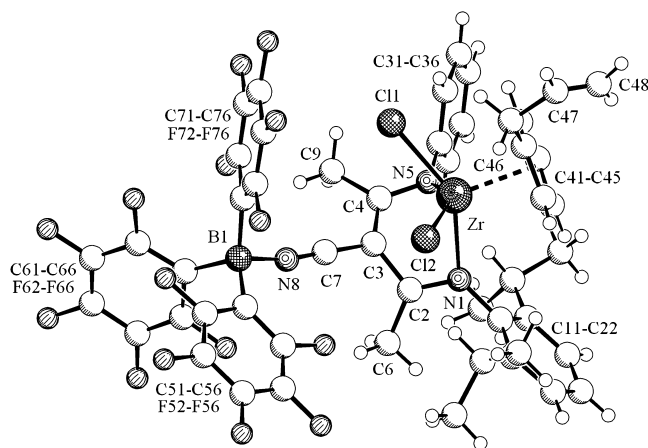


Figure 2. Molecular structure of complex 3.

The allyl moiety on the Cp ring bisects the $\text{Cl}(1)\text{--Zr--Cl}(2)$ angle (see Figure 2) similar to that observed in **2**. The $\text{Zr--C}(3)$ and $\text{Zr--C}(41)$ distances in compound **3** are slightly shorter compared to those in compound **2**, while the $\text{Cl}(1)\text{--Zr--Cl}(2)$ angle is slightly larger. The double bond of the allyl functionality is oriented perpendicular to the Cp plane.

Hydroboration of the olefinic group in the $[(\text{C}_6\text{F}_5)_3\text{B--NC--nacnac}]\text{Cp--allylZrCl}_2$ (**3**) substrate with the $\text{HB}(\text{C}_6\text{F}_5)_2$ reagent^{14d,e} proceeds to completion essentially upon mixing of the reagents, as indicated by the immediate disappearance of characteristic olefinic resonances of the 2-propenyl group in the

^1H NMR ($-\text{CH}=\text{Cp--allyl}$, $=\text{CH}_2\text{Cp--allyl}$ at δ 5.97 and 5.05/5.03 ppm, respectively) and the complete dissolution of the normally only partially soluble borane. As expected, the pair of C_6F_5 groups on the tricoordinate planar boron atom (**B2**) (Figure 3)

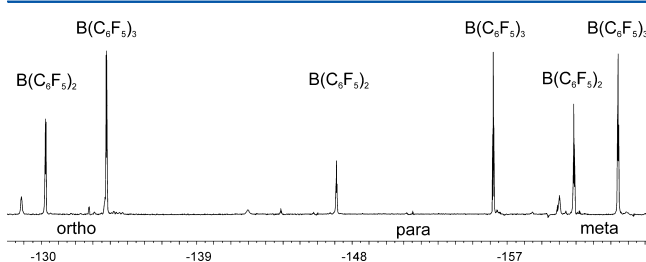


Figure 3. ^{19}F NMR (564 MHz, C_6D_6 , 298 K) spectrum of compound 4.

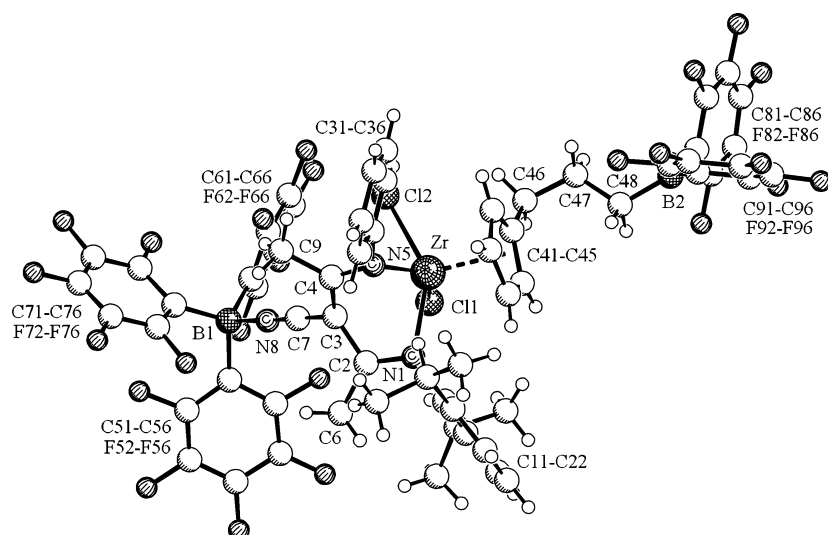
behaves in a symmetry-equivalent fashion in solution, producing a single set of *o*-, *p*- and *m*- ^{19}F NMR resonances at δ -130.3 , -147.1 , and -160.9 ppm, respectively. A single set of C_6F_5 resonances at δ -133.8 (*o*), -156.2 (*p*), and -163.4 ppm (*m*) was observed for the $\text{B}(\text{C}_6\text{F}_5)_3$ group coordinated to the nitrile function (Figure 3).

Compound **4** was isolated by precipitation from a concentrated toluene solution by the addition of pentane and collected as a white solid in ca. 86% yield. Compound **4** is stable at room temperature but is highly susceptible to coordination by 1 equiv of any Lewis base present in the system, and so donor solvents are to be avoided when handling this compound.¹⁹

Single crystals suitable for the X-ray crystal structure determination of **4** were obtained by diffusion of CH_2Cl_2 /pentane into a toluene solution at room temperature. In the solid state, the $(\text{C}_6\text{F}_5)_3\text{B--NC--nacnac}$ fragment in complex **4** follows the same coordination mode and boat-shaped configuration (see Figures 4 and 5) as previously observed in this type of compound,¹² including compounds **2** and **3** (see Figures 1 and 2). However, there are substantial increases in the $\text{Zr--C}(2)/\text{C}(3)/\text{C}(4)$ bond lengths compared to those in compounds **2** and **3**, consistent with a more crowded metal center (see Table 2).

Due to the geometric constraints in this type of system, the attached $-(\text{CH}_2)_3\text{B}(\text{C}_6\text{F}_5)_2$ side chain is oriented away from the metal center with the trimethylene moiety resting in a position which roughly bisects the Cl--Zr--Cl angle in the projection (Figure 5). The $-(\text{CH}_2)_3\text{B}(\text{C}_6\text{F}_5)_2$ chain is fully extended to maximize the distance between the Zr center and the bulky $\text{B}(\text{C}_6\text{F}_5)_2$ group (see Figures 4 and 5). This orientation of the $-(\text{CH}_2)_3\text{B}(\text{C}_6\text{F}_5)_2$ fragment generates a B--Zr--B plane which roughly bisects the bidentate ligand and the Cp ring. This extended conformational arrangement is characterized by the corresponding dihedral angles $\text{C}(42)\text{--C}(41)\text{--C}(46)\text{--C}(47) = -92.8(9)^\circ$, $\text{C}(41)\text{--C}(46)\text{--C}(47)\text{--C}(48) = 50.9(14)^\circ$, and $\text{C}(46)\text{--C}(47)\text{--C}(48)\text{--B}(2) = -175.2(10)^\circ$.

The bifunctional complex **2** was reacted with 1 molar equiv of $[\text{BH}(\text{C}_6\text{F}_5)_2]_n$ in toluene or CH_2Cl_2 at room temperature (see Scheme 1).^{20,14} The reaction took place rapidly and proceeded to completion essentially upon mixing of the reagents. After a few minutes a white solid precipitated, which was collected by filtration and washed with fresh solvent (CH_2Cl_2), to give **5** in a yield of 78%. The IR $\nu(\text{C}\equiv\text{N})$ band of compound **5** is found at 2279 cm^{-1} , which suggests that the boron interaction with the CN functionality is similar to that observed for compounds **3** and **4**. Unfortunately, the product of



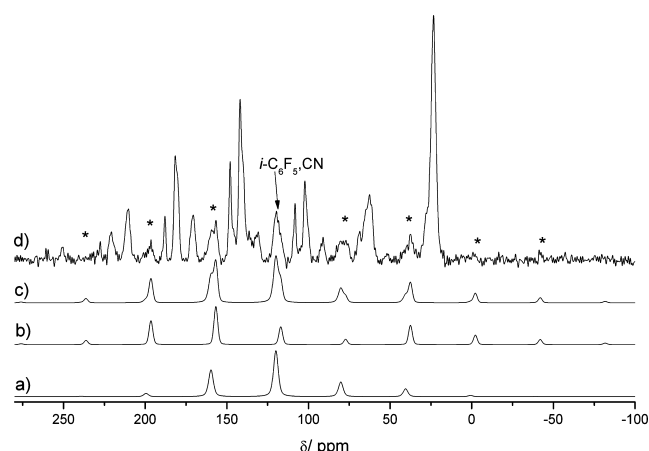


Figure 7. $^{13}\text{C}\{^1\text{H}\}$ slow-spinning DD-CPMAS spectrum (d) of polymer **5** using a spinning speed of 4 kHz. The spectrum was acquired at 9.4 T. Spinning sidebands for the resonance of interest at about 120 ppm are marked with an asterisk. The simulated spinning sideband pattern (c) indicates two contributions given in (a) and (b): the two ipso carbon atoms of the C_6F_5 ligand at 120 ppm (a) and the nitrile carbon at 117 ppm (b). Simulated spectra are based on $|\Delta\sigma| = 135.0$ ppm and $\eta = 0.35$ for (a) and $|\Delta\sigma| = 262.5$ ppm and $\eta = 0.05$ for (b).

components for model compound **3** confirm these assignments (see Table 3 and Figure S6).

Table 3. Experimental CSA Parameters Extracted from the Slow-Spinning DD-CPMAS Spectrum Using the DMFIT²² Software^a

assignt	$\delta(^{13}\text{C})$ (ppm)	$ \Delta\sigma $ (ppm)	η
5 $\text{C}\equiv\text{N}$	117.0 ^a	262.5 ^a	0.05 ^a
5 $i\text{-C}_6\text{F}_5$	120.0 ^a	135.0 ^a	0.35 ^a
3 $\text{C}\equiv\text{N}$	120.8 ^a	270.0 ^a	0.04 ^a
3 $i\text{-C}_6\text{F}_5$	120.0 ^a	181.0 ^a	0.10 ^a
3 $i\text{-C}_6\text{F}_5$	119.0 ^a	159.3 ^a	0.30 ^a
3 $\text{C}\equiv\text{N}$	117.7 ^b	247.4 ^b	0.03 ^b
3 $i\text{-C}_6\text{F}_5$	114.6 ^b /115.1 ^b /116.8 ^b	145.7 ^b /140.2 ^b /146.4 ^b	0.04 ^b /0.14 ^b /0.16 ^b

^aExperimental (a) and theoretical DFT CSA parameters (b). The following convention is used: $\Delta\sigma = \sigma_{33} - 1/2(\sigma_{11} + \sigma_{22})$, $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{\text{iso}})$, and $|\sigma_{33} - \sigma_{\text{iso}}| > |\sigma_{11} - \sigma_{\text{iso}}| > |\sigma_{22} - \sigma_{\text{iso}}|$. The calculated values for the axiality of the CSA values are slightly underestimated, presumably as a consequence of the chosen GGA level.

The proposed peak assignments can be justified further by comparison with the structurally related compound **3**, for which the ^{13}C NMR peak assignment has been successfully achieved by liquid-state NMR, solid-state NMR, and ab initio calculations of magnetic shieldings (see Table S3 and Figure S4, Supporting Information). In addition to small changes in the chemical shifts for some carbon sites (e.g., the central carbon of the conjugated enamino heterocarbonyl system; see Figure 6c) a significant broadening of the ^{13}C peaks is observed in case of polymer **5**, presumably resulting from a lower degree of crystallinity as often observed in polymeric systems.

The ^{11}B MAS NMR spectrum acquired with ^1H TPPM-15 decoupling of polymer **5** (see Figure 8a) shows a single resonance affected by anisotropic second-order quadrupolar perturbations. The simulation of this spectrum yields an isotropic chemical shift of -7.4 ppm, a quadrupolar coupling constant C_Q of 1.9 MHz, and an electric field gradient asymmetry parameter η of 0.58, indicating a four-coordinated boron atom whose environment is

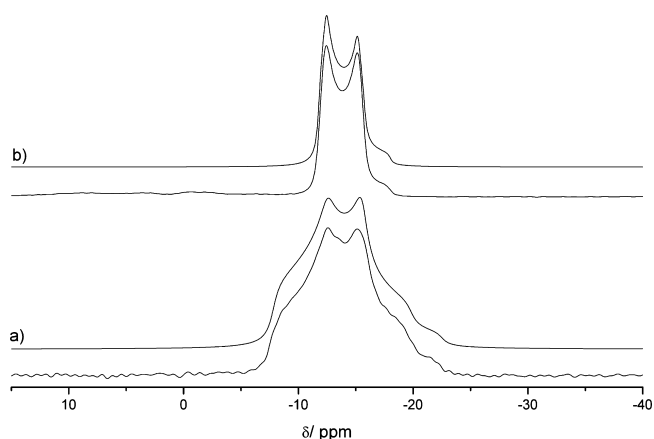


Figure 8. (a) (bottom) Experimental ^{11}B MAS NMR spectrum measured for polymer **5** at 9.4 T with ^1H decoupling (TPPM-15) using a sample spinning frequency of 14 kHz and (top) simulation of the central transition line shape, using $\delta_{\text{cs}} = -7.4$ ppm, $C_Q = 1.9$ MHz, and $\eta = 0.58$. (b) (bottom) Experimental ^{11}B MAS NMR spectrum measured for reference compound **3** at 11.7 T with a sample spinning frequency of 14 kHz and (top) simulation of the central transition line shape, using $\delta_{\text{cs}} = -11.1$ ppm, $C_Q = 1.7$ MHz, and $\eta = 0.16$.

strongly distorted by three different types of ligands. The low-frequency shift of the boron resonance also suggests a partially negatively charged 4-fold-coordinated boron species and consequently argues in favor of the formation of a Lewis acid/base adduct with the nitrile group. Previous work has shown that trigonal alkyl boron compounds obtained by hydroboration of several alkene substrates with $\text{HB}(\text{C}_6\text{F}_5)_2$ resonate typically near 70 ppm^{14,15} and that the isotropic shifts for tricoordinated boron range between 0 and 120 ppm.²³ In comparison, the more symmetric bonding in the four-coordinated reference compound **3** leads to an EFG tensor that is much closer to axially symmetric ($\delta_{\text{cs}} = -11$ ppm, $C_Q = 1.7$ MHz, $\eta = 0.16$) (see Figure 8b). DFT calculations at a GGA level yield C_Q and η values of 1.8 MHz and 0.07, respectively, in reasonable agreement with the experimental data. Nevertheless, also in the case of compound **3** a distortion from axial symmetry is observed due to the Lewis acid/base adduct formation, which highlights the remarkable sensitivity of ^{11}B MAS NMR to small changes in the local environments of the boron nuclei.

In principle, the strongly Lewis acidic borane might have been able to form an adduct with the nitrile group. However, on the basis of the insolubility of the final product, the hydroboration of the pendant $\text{C}=\text{C}$ double bond takes place first, followed by the intermolecular adduct formation with the nitrile group, giving the organometallic polymer **5**, as shown in Scheme 1 and verified by ^{11}B and ^{13}C solid-state NMR spectroscopy.

The related CN-free system (*nacnac*)Cp-allylZrCl₂ (**6**) was prepared for comparison. This complex was obtained by deprotonation of the *nacnac*H ligand precursor with potassium hydride followed by the reaction with Cp-allylZrCl₃(dme) in CH_2Cl_2 at ambient temperature (see Scheme 1). The complex (*nacnac*)Cp-allylZrCl₂ (**6**) was isolated as a pale yellow solid in 85% yield (see the Experimental Section and the Supporting Information for its characterization).

Complex **6** was characterized by X-ray diffraction. It features a typical constrained geometry with independent Cp-propenyl and *nacnac* ligands bound to the Zr center. The $-\text{CH}_2\text{CH}=\text{CH}_2$ unit was found oriented toward the front side of the bent *nacnac*/Cp wedge. The observed conformational arrangement

of the propenyl unit in the crystal is almost coplanar with the Cp ring, with the ZrCl_2 side spatially open (see Figure 9;

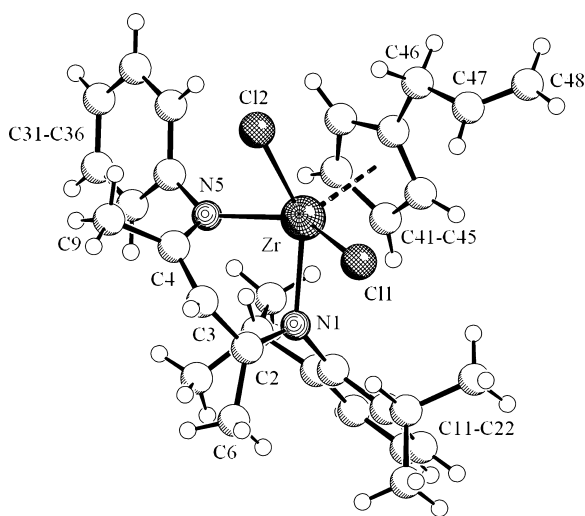


Figure 9. Molecular structure of complex 6.

dihedral angles $\text{C}(42)\text{--}\text{C}(41)\text{--}\text{C}(46)\text{--}\text{C}(47) = 175.6(4)^\circ$ and $\text{C}(41)\text{--}\text{C}(46)\text{--}\text{C}(47)\text{--}\text{C}(48) = 121.4(5)^\circ$.

The nacnac ligand is in a boat conformation, as was observed in compounds 2–4. However, the C(3) (methine unit in Figure 9) is 0.086 Å farther away from the zirconium in comparison with the case for complex 2 ($\text{Zr}\text{--}\text{C}(3) = 2.717(2)$ and $2.631(2)$ Å, respectively).

Hydroboration of 6 proceeded smoothly upon treatment with 1 equiv of $\text{HB}(\text{C}_6\text{F}_5)_2$,¹⁴ yielding compound 7 (Scheme 1). Like the hydroboration of other olefinic substrates including compounds 2 and 3 with $\text{HB}(\text{C}_6\text{F}_5)_2$, the reaction proceeded to completion essentially upon mixing of the reagents, as indicated by the immediate disappearance of characteristic olefinic resonances of the 2-propenyl group in the ^1H NMR, $-\text{CH}=\text{C}_{\text{Cp-allyl}}$ and $=\text{CH}_2^{\text{Cp-allyl}}$ at 6.02 and 5.03/5.01 ppm, respectively (for more details see the Supporting Information). Complex 7 shows a broad ^{11}B NMR resonance at ca. $\delta +74$ ppm, which is characteristic for trigonal alkyl boron compounds obtained by hydroboration of alkene substrates,^{10d,e} and three typical ^{19}F NMR signals corresponding to the pair of symmetry-equivalent C_6F_5 substituents at boron ($\delta -130.1$ (o), -147.8 (p), -161.1 ppm (m)). The $^1\text{H}/^{13}\text{C}$ NMR spectra show the presence of two non-equivalent isopropyl groups of the diisopropylphenyl substituent at N1, giving rise to a pair of CHMe_2 methine ^1H NMR resonances at $\delta 3.90/2.72$ ppm (^{13}C 27.6/27.4 ppm) and a total of four corresponding ^1H NMR CH_3 doublets. For further details see Table 1 and the Supporting Information.

Ethylene Polymerization. A series of ethylene polymerization reactions were carried out using compounds 2–7 under specific reaction conditions, with MAO as the coactivator (Table 4). In all cases, one observes the formation of high-molecular-weight PE with a melting point of ca. 136°C , indicating that the material is linear. Entry 1 shows the behavior of the $(\text{NC-nacnac})\text{CpZrCl}_2/\text{MAO}$ system under these reaction conditions. Comparison with complexes 2–4 under the same conditions (entries 2–4) shows that the addition of the allyl substituent to the cyclopentadienyl ring results in a decrease in activity of ca. 20%. This was not unexpected as the allyl (2) and alkyl- $\text{B}(\text{C}_6\text{F}_5)_2$ moieties increase the steric environment around the zirconium metal center, reducing the rate of polymerization.

Table 4. Selected Ethylene Polymerization Reactions^a

entry	complex no.	activity ^b	M_n^c	M_w^c	PDI	T_m^d
1	ref	1520	99	175	1.8	135
2	2	1109	185	342	1.8	136
3	3	1061	144	295	2.1	135
4	4	1037	157	302	1.9	135
5	5	966	161	306	1.9	135
6	5 ^e	1080	144	282	2.0	135
7	5 ^f	1115	172	310	1.8	135
8	6	630	171	313	1.8	136
9	7	780				135

^aPolymerizations were carried out in a 100 mL autoclave reactor with 6.8 μmol of Zr in 30 mL of toluene and 178 psi of ethylene pressure. The cocatalyst was MAO (the Al/Zr ratio was 500/1). The duration of the reaction was 10 min, and the temperature of the reaction was 75°C . ^bActivity in kg of polymer/((mol of Zr) h). ^c 10^3 g/mol. ^dIn $^\circ\text{C}$. ^eExposed to the air as a solid for 17 h, before addition into the reactor. ^fExposed to the air as a solid for 28 h, before addition into the reactor.

Surprisingly, the molecular weight of the materials increased significantly, which may be an indication that the presence of the allyl or the alkyl- $\text{B}(\text{C}_6\text{F}_5)_2$ functionalities retard termination of the growing polymer chain. Under these conditions all of the complexes show similar polymerization activities and molecular weights of the materials produced (entries 2–4). In addition all of the complexes have a PDI less than 2, which is an indication that the systems are single site. No additional effect was observed in the polymerizations of the presence of the alkyl- $\text{B}(\text{C}_6\text{F}_5)_2$ group on the Cp ring (hydroborated complex 4) (entry 4) that has an activity and molecular weight distribution which is similar to that observed in complexes 2 and 3. The polymerization behavior of complex 5 shows perhaps the most interesting behavior of all the complexes. Using the same conditions as for the other complexes, it gave similar activities and molecular weights. When the complex was exposed to air prior to the polymerization reaction (for 17 or 28 h), there was no change in the polymerization activity or in the molecular weight of the polymer produced, whereas when the other complexes were exposed to air, no polymer was produced. This is most likely due to the polymeric nature of the complex due to the $\text{R}\text{--}\text{B}(\text{C}_6\text{F}_5)_2\text{--}\text{NC--R'}$ intermolecular interactions, which stabilizes the structure and prevents side reactions at boron. In addition, the structure likely limits oxygen access to the Zr metal center, hindering the decomposition process.

Entries 8 and 9, which refer to reactions with complexes 6 and 7, respectively, illustrate the importance of the CN in the ligand backbone. Comparison of entry 8 with entry 2 shows that the presence of the CN increases the polymerization activity significantly (ca. 470 kg of polymer/((mol of Zr) h)). At the same time, entry 9 allows the evaluation of the effect of the $-(\text{CH}_2)_3\text{--}\text{B}(\text{C}_6\text{F}_5)_2$ interaction on the polymerization activity, which resulted in an increase of ca. 150 kg of polymer/((mol of Zr) h) over entry 8. These results indicate that, while the bidentate imine ligand has a dominant effect on the electronic environment of the catalyst system, the Cp allyl ligand has a marked effect on the molecular weight.

CONCLUSION

In this contribution, zirconium complex 2 bearing both a nacnac-CN and a Cp-allyl ligand was synthesized and characterized. As this compound bears two functional groups which are available for reaction with Lewis acids, it was decided

to explore the modification of the compound via the controlled reaction with soluble Lewis acids. Derivatives of **2** selectively bearing a Lewis acid function tethered to the Cp ring or coordinated to the nacnac-CN ligand or both were isolated. In addition an organometallic polymer was obtained upon the selective hydroboration of the allyl functionality in **2**. A detailed analysis of these complexes was undertaken, and single-crystal X-ray crystal structures were obtained for all complexes except **5**, which was characterized by solid-state MAS NMR spectroscopy. The solid-state NMR spectra of **5** show that the organometallic monomers are connected by interaction of the Cp-tethered $B(C_6F_5)_2$ Lewis acid with the cyano functionality in the nacnac-CN ligand backbone. These complexes were activated for ethylene polymerization by MAO. In addition, it was found that the organometallic polymer showed an unusual stability in air and was able to polymerize ethylene even after exposure to air for 28 h. The presence of the two distinct functionalities and the ability to selectively form Lewis acid adducts allowed for the evaluation of the effect of these groups on the polymerization activity and polymer properties. It was found that the Cp group affected the molecular weight of the materials more so than the bis-imine ligand, whereas changes to the bis-imine ligand were found to affect the polymerization activity more than changes to the Cp ligand. Finally, we are particularly intrigued by the air stability of the organometallic polymer **5**, and future work will be conducted using this complex to evaluate how this stability can best be taken advantage of.

EXPERIMENTAL SECTION

General Remarks. 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; ^{13}C , 126 MHz; ^{19}F , 470 MHz; ^{11}B , 160 MHz), Bruker Unity Plus 600 (1H , 600 MHz; ^{13}C , 151 MHz; ^{19}F , 564 MHz; ^{11}B , 192 MHz) and Bruker Avance 400. Most NMR assignments were supported by additional 2D experiments. FT-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,³¹ data reduction Denzo-SMN,³² absorption correction SORTAV³³ and Denzo,³⁴ structure solution SHELXS-97,³⁵ structure refinement SHELXL-97,³⁶ graphics XP³⁷ and SCHAKAL.³⁸ R1 values are given for the observed reflections and wR2 values for all reflections. CCDC 818691–818694 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax, (internat.) +44(1223)336-0333; e-mail, deposit@ccdc.cam.ac.uk).

Compound 2. A solution of the potassium salt of **1** (910 mg, 1.94 mmol) in CH_2Cl_2 (5 mL) was added to trichloro(η^5 -allyl-cyclopentadienyl)zirconium–dme (dme = dimethoxyethane) (760 mg, 1.93 mmol) in CH_2Cl_2 . The reaction mixture was stirred for 4 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 yellow powder corresponding to compound **2** was isolated in 65% yield (815 mg, 1.25 mmol). Single crystals of

compound **2** suitable for X-ray crystal structure analysis were grown by diffusion of pentane into toluene at room temperature. Anal. Calcd for $C_{32}H_{37}Cl_2N_3Zr$ ($M = 625.79$): C, 61.42; H, 5.96; N, 6.71. Found: C, 61.77; H, 6.09; N, 6.58. IR (KBr): $\tilde{\nu}/cm^{-1}$ 2213 ($\nu(C\equiv N)$, s). 1H NMR (600 MHz, CD_2Cl_2 , 298 K): δ/ppm 7.51 (m, 2H, *m*-Ph), 7.37 (m, 1H, *p*-Ph), 7.36 (m, 2H, *p,m*-Ar), 7.24 (m, 1H, *m'*-Ar), 7.19 (br, 2H, *o*-Ph), 6.36 (m, 1H, 2-H), 6.31 (m, 1H, 5-H), 6.01 (m, 1H, 7-H), 5.90 (m, 1H, 4-H), 5.71 (m, 1H, 3-H), 5.05 (m, 2H, 8-H), 3.63 (m, 2H, 6-H), 3.36 (hept, $^3J = 6.8$ Hz, 1H, $HC^{iPr(o)}$), 2.76 (hept, $^3J = 6.7$ Hz, 1H, $HC^{iPr(o')}$), 2.30 (s, 3H, Me^Ar), 2.27 (s, 3H, Me^{Ph}), 1.33 (d, $^3J = 6.8$ Hz, 3H, $Me^{iPr(o)}$), 1.20 (d, $^3J = 6.8$ Hz, 3H, $Me^{iPr(o')}$), 1.17 (d, $^3J = 6.7$ Hz, 3H, $Me^{iPr(o')}$), 0.91 (br d, $^3J = 6.7$ Hz, 3H, $Me^{iPr(o')}$). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2 , 298 K): δ/ppm 171.1 ($C\equiv N^{Ar}$), 168.0 ($C\equiv N^{Ph}$), 148.6 (*i*-Ph), 143.2 (*i*-Ar), 143.1 (*o*-Ar), 140.7 (*o'*-Ar), 137.0 (C7), 135.8 (C1), 129.8 (*m*-Ph), 128.5 (*p*-Ar), 127.2 (*p*-Ph), 126.3 (*m*-Ar), 124.5 (*m'*-Ar), 124.0 (br, *o*-Ph), 119.0 (C2), 118.8 (C5), 118.5 (C3), 116.6 (C4), 116.4 (C8), 72.7 (C^{CN}), 35.4 (C6), 28.1 ($HC^{iPr(o)}$), 27.8 ($HC^{iPr(o')}$), 25.9 ($Me^{iPr(o)}$), 25.1 ($Me^{iPr(o')}$), 24.5 ($Me^{iPr(o')}$), 23.6 (Me^Ar), 22.8 ($Me^{iPr(o)}$), 21.8 (Me^{Ph}), n.o. (CN).

Compound 3. One equivalent of tris(pentafluorophenyl)borane (147 mg in 1 mL of CH_2Cl_2 , 0.29 mmol) was added to a CH_2Cl_2 solution of **2** (180 mg, 0.29 mmol). The reaction mixture was stirred for 4 h and filtered over Celite, and the volatiles were removed under vacuum, washed with 10 mL of toluene/pentane (1/1), and then washed with pentane (5 mL). Compound **3** was isolated as a colorless solid in 86% yield (281 mg, 0.247 mmol). Single crystals suitable for X-ray crystal structure analysis were grown by evaporation of a C_6H_6 solution of compound **3** at room temperature. IR (KBr): $\tilde{\nu}/cm^{-1}$ 2280 ($\nu(C\equiv N)$, s). Anal. Calcd for $C_{50}H_{37}BCl_2F_{15}N_3Zr$ ($M = 1137.77$): C, 52.78; H, 3.28; N, 3.69. Found: C, 52.60; H, 3.76; N, 3.83. 1H NMR (500 MHz, CD_2Cl_2 , 298 K): δ/ppm 7.55 (m, 2H, *m*-Ph), 7.42 (m, 1H, *p*-Ph), 7.40 (m, 2H, *m*-, *p*-Ar), 7.29 (m, 1H, *m'*-Ar), 7.20 (br, 2H, *o*-Ph), 6.36 (m, 1H, 2-H)^t, 6.33 (m, 1H, 5-H)^t, 5.97 (m, 1H, 7-H), 5.93 (m, 1H, 4-H)^t, 5.75 (m, 1H, 3-H)^t, 5.05 (dm, $^3J = 10.1$ Hz, 1H, 8-H), 5.03 (dm, $^3J = 16.8$ Hz, 1H, 8-H), 3.60 (m, 2H, 6-H), 3.21 (hept, $^3J = 6.8$ Hz, 1H, $HC^{iPr(o)}$), 2.78 (hept, $^3J = 6.8$ Hz, 1H, $HC^{iPr(o')}$), 2.22 (s, 3H, Me^Ar)^t, 2.20 (s, 3H, Me^{Ph})^t, 1.31 (d, $^3J = 6.8$ Hz, 3H, $Me^{iPr(o)}$), 1.23 (d, $^3J = 6.8$ Hz, 3H, $Me^{iPr(o')}$), 1.21 (d, $^3J = 6.8$ Hz, 3H, $Me^{iPr(o')}$), 0.96 (d, $^3J = 6.8$ Hz, 3H, $Me^{iPr(o')}$)^t, (tentative assignment). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2 , 298 K): δ/ppm 171.6 ($C\equiv N^{Ph}$)^t, 170.8 ($C\equiv N^{Ar}$)^t, 148.3 (dm, $^1J_{FC} \approx 243$ Hz), 140.5 (dm, $^1J_{FC} \approx 250$ Hz), 137.5 (dm, $^1J_{FC} \approx 248$ Hz) (C_6F_5), 147.4 (*i*-Ph), 142.7 (*o*-Ar), 142.0 (*i*-Ar), 140.1 (*o'*-Ar), 137.1 (C1), 136.5 (C7), 130.2 (*m*-Ph), 129.2 (*p*-Ar), 128.0 (*p*-Ph), 126.7 (*m*-Ar), 124.7 (*m'*-Ar), 123.4 (br, *o*-Ph), 119.8 (C2,5)^t, 119.6 (C3)^t, 117.5 (C4)^t, 116.7 (C8), 116.4 (br, *i*- C_6F_5), 63.9 (C^{CN}), 35.4 (C6), 28.4 ($HC^{iPr(o)}$), 28.0 ($HC^{iPr(o')}$), 26.1 ($Me^{iPr(o)}$), 25.4 ($Me^{iPr(o')}$), 24.1 (Me^{Ph}), 23.8 ($Me^{iPr(o')}$), 22.5 ($Me^{iPr(o)}$), 22.2 (Me^Ar), n.o. ($C\equiv N$) (tentative assignment). ^{19}F NMR (564 MHz, CD_2Cl_2 , 298 K): δ/ppm -134.1 (m, 2F, *o*- C_6F_5), -157.8 (t, $^3J_{FF} = 20.3$ Hz, 1F, *p*- C_6F_5), -164.5 (m, 2F, *m*- C_6F_5), ($\Delta\delta(^{19}F_{m,p}) = 6.8$). $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2 , 298 K): δ/ppm -10.6.

Compound 4. One equivalent of bis(pentafluorophenyl)borane (50 mg in 1 mL of toluene, 0.14 mmol) was added to a toluene suspension of **3** (160 mg, 0.14 mmol). The reaction mixture was stirred for 4 h, and then the volatiles were removed under vacuum, washed with pentane (10 mL), and removed; fresh pentane was added (10 mL), and this mixture was stirred for 12 h. After this time, the solid was decanted, more fresh pentane was added (10 mL), and this mixture was stirred for an additional 12 h. A white solid (182 mg, 0.123 mmol) corresponding to compound **4** was recovered by filtration in 87% yield. Single crystals suitable for X-ray crystal structure analysis were grown by diffusion of CH_2Cl_2 / pentane into a toluene solution at room temperature. IR (KBr): $\tilde{\nu}/cm^{-1}$ 2284 ($\nu(C\equiv N)$, s). Anal. Calcd for $C_{62}H_{38}B_2Cl_2F_{25}N_3Zr$ ($M = 1483.71$): C, 50.19; H, 2.58; N, 2.83. Found: C, 50.58; H, 2.90; N, 3.03. 1H NMR (600 MHz, C_6D_6 , 298 K): δ/ppm 7.07 (m, 1H, *m*-Ph), 7.02 (m, 2H, *m*-, *p*-Ar), 6.96 (m, 3H, *p*-, *o*-Ph), 6.87 (m, 1H, *m'*-Ar), 6.21 (m, 1H, 2-H)^t, 6.14 (m, 1H, 5-H)^t, 5.71 (m, 1H, 4-H)^t, 5.53 (m, 1H,

3-H), 3.26 (hept, $^3J = 6.6$ Hz, 1H, $\text{HC}^{\text{ipr}(\text{o})}$), 2.85 (m, 2H, 6-H), 2.58 (hept, $^3J = 6.8$ Hz, 1H, $\text{HC}^{\text{ipr}(\text{o})}$), 1.88 (s, 3H, Me^{Ph}), 1.81 (s, 3H, Me^{Ar}), 1.76 (m, 2H, 8-H), 1.70 (m, 2H, 7-H), 1.25 (d, $^3J = 6.6$ Hz, 3H, $\text{Me}^{\text{ipr}(\text{o})}$), 1.15 (d, $^3J = 6.6$ Hz, 3H, $\text{Me}^{\text{ipr}(\text{o})}$), 0.92 (d, $^3J = 6.8$ Hz, 3H, $\text{Me}^{\text{ipr}(\text{o})}$), 0.59 (d, $^3J = 6.8$ Hz, 3H, $\text{Me}^{\text{ipr}(\text{o})}$) (tentative assignment). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 298 K): δ /ppm 171.4 ($\text{C}=\text{N}^{\text{Ar}}$), 170.8 ($\text{C}=\text{N}^{\text{Ph}}$), 147.3 (*i*-Ph), 142.7 (*o*-Ar), 141.8 (*i*-Ar), 139.6 (*o*-Ar), 138.2 (C1), 129.7 (*m*-Ph), 129.0 (*p*-Ar), 127.6 (*p*-Ph), 126.6 (*m*-Ar), 124.1 (*m*'-Ar), 123.1 (*o*-Ph), 118.8 (C5), 118.79, 118.78 (C2,3), 116.4 (C4), 63.9 (C^{CN}), 33.5 (C6), 31.6 (br, C8), 27.9 ($\text{HC}^{\text{ipr}(\text{o})}$), 27.8 ($\text{HC}^{\text{ipr}(\text{o})}$), 26.1 ($\text{Me}^{\text{ipr}(\text{o})}$), 25.9 (C7), 25.2 ($\text{Me}^{\text{ipr}(\text{o})}$), 23.5 ($\text{Me}^{\text{ipr}(\text{o})}$), 23.3 (Me^{Ar}), 22.2 ($\text{Me}^{\text{ipr}(\text{o})}$), 21.5 (Me^{Ph}), n.o. (CN) (C_6F_5 not listed). ^{19}F NMR (564 MHz, C_6D_6 , 298 K): δ /ppm -130.3 (m, 4F, *o*-F), -147.1 (t, $^3J_{\text{FF}} = 20.4$ Hz, 2F, *p*-F), -160.9 (m, 4F, *m*-F) ($\text{B}(\text{C}_6\text{F}_5)_2$) ($\Delta\delta(^{19}\text{F}_{\text{m.p.}}) = 13.8$), -133.8 (m, 6F, *o*-F), -156.2 (t, $^3J_{\text{FF}} = 20.7$ Hz, 3F, *p*-F), -163.4 (m, 6F, *m*-F) ($\text{B}(\text{C}_6\text{F}_5)_3$) ($\Delta\delta(^{19}\text{F}_{\text{m.p.}}) = 7.2$).

Compound 5. One equivalent of bis(pentafluorophenyl)borane (83 mg in 1 mL of CH_2Cl_2 , 0.24 mmol) was added to a solution of **2** in CH_2Cl_2 (150 mg, 0.24 mmol). After a few minutes a white solid started to precipitate, and the reaction mixture was stirred for 4 h. A white solid corresponding to compound **5** was recovered by filtration and washed several times with fresh CH_2Cl_2 ; 78% yield (181 mg, 0.186 mmol). Compound **5** was insoluble in noncoordinating solvents. IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ 2279 ($\nu(\text{C}\equiv\text{N})$, s). Anal. Calcd for $\text{C}_{62}\text{H}_{38}\text{B}_2\text{Cl}_2\text{F}_{25}\text{N}_3\text{Zr}$ ($M = 1448.71$): C, 54.39; H, 3.94; N, 4.32. Found: C, 52.07; H, 3.65; N, 4.05.

Compound 6. The potassium salt of 2-(2,6-diisopropylphenyl)-aminopent-2-en-4-(phenyl)imine (200 mg, 0.45 mmol) in 5 mL of CH_2Cl_2 was added to trichloro(η^5 -allylcyclopentadienyl)zirconium-dme (dme = dimethoxyethane; 177 mg, 0.45 mmol) in CH_2Cl_2 . The reaction mixture was stirred for 4 h at room temperature. 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 yellow powder corresponding to compound **7** was isolated in 85% yield (230 mg). Single crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of pentane into CH_2Cl_2 at room temperature. Anal. Calcd for $(\text{C}_{31}\text{H}_{38}\text{Cl}_2\text{N}_2\text{Zr})_3\text{CH}_2\text{Cl}_2$ ($M = 2488.04$): C, 59.82; H, 6.20; N, 4.45. Found: C, 59.40; H, 6.14; N, 4.46. ^1H NMR (500 MHz, CD_2Cl_2 , 298 K): δ /ppm 7.46 (m, 2H, *m*-Ph), 7.32 (m, 2H, *m*-, *p*-Ar), 7.30 (m, 1H, *p*-Ph), 7.22 (br, 2H, *o*-Ph), 7.20 (m, 1H, *m*'-Ar), 6.32 (m, 1H, 2-H), 6.26 (m, 1H, 5-H), 6.02 (ddt, $^3J_{\text{H,H}} = 16.9$, 10.2, 6.5 Hz, 1H, 7-H), 5.88 (m, 1H, 4-H), 5.74 (m, 1H, 3-H), 5.67 (s, 1H, CH), 5.03 (dm, $^3J_{\text{H,H}} = 16.9$ Hz, 1H, 8-H), 5.01 (dm, $^3J_{\text{H,H}} = 10.2$ Hz, 1H, 8-H), 3.63 (hept, $^3J = 6.6$ Hz, 1H, $\text{HC}^{\text{ipr}(\text{o})}$), 3.61 (m, 2H, 6-H), 2.69 (hept, $^3J = 6.8$ Hz, 1H, $\text{HC}^{\text{ipr}(\text{o})}$), 2.06 (s, 3H, Me^{Ar}), 2.03 (s, 3H, Me^{Ph}), 1.35 (d, $^3J = 6.6$ Hz, 3H, $\text{Me}^{\text{ipr}(\text{o})}$), 1.20 (d, $^3J = 6.6$ Hz, 3H, $\text{Me}^{\text{ipr}(\text{o})}$), 1.14 (d, $^3J = 6.8$ Hz, 3H, $\text{Me}^{\text{ipr}(\text{o})}$), 0.92 (d, $^3J = 6.8$ Hz, 3H, $\text{Me}^{\text{ipr}(\text{o})}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 298 K): δ /ppm 168.3 ($\text{C}=\text{N}^{\text{Ar}}$), 161.7 ($\text{C}=\text{N}^{\text{Ph}}$), 150.0 (*i*-Ph), 144.6 (*i*-Ar), 143.6 (*o*-Ar), 141.6 (*o*'-Ar), 137.7 (C7), 134.2 (C1), 129.4 (*m*-Ph), 127.8, 126.4 (*p*-Ar, *p*-Ph), 125.8 (*m*-Ar), 124.6 (br, *o*-Ph), 124.3 (*m*'-Ar), 118.0 (C2), 117.4 (C5), 117.1 (C3), 115.8 (C8), 115.5 (C4), 90.4 (CH), 35.4 (C-6), 27.8 ($\text{HC}^{\text{ipr}(\text{o})}$), 27.7 ($\text{HC}^{\text{ipr}(\text{o})}$), 25.8 ($\text{Me}^{\text{ipr}(\text{o})}$), 25.0 ($\text{Me}^{\text{ipr}(\text{o})}$), 24.6 ($\text{Me}^{\text{ipr}(\text{o})}$), 24.1 (Me^{Ar}), 23.29 (Me^{Ph}), 23.27 ($\text{Me}^{\text{ipr}(\text{o})}$).

Compound 7. One equivalent of bis(pentafluorophenyl)borane (58 mg in 1 mL of toluene, 0.17 mmol) was added to a toluene suspension of **6** (100 mg, 0.17 mmol). The reaction mixture was stirred for 4 h, and then the volatiles were removed under vacuum and the residue washed with pentane. A 137 mg amount of a light yellow solid corresponding to compound **7** was collected in 87% yield. ^1H NMR (500 MHz, C_6D_6 , 298 K): δ /ppm 7.29 (br, 2H, *o*-Ph), 7.16 (m, 2H, *m*-Ph), 7.13 (dd, $^3J = 7.7$ Hz, $^4J = 1.6$ Hz, 1H, *m*-Ar), 7.07 (t, $^3J = 7.7$ Hz, 1H, *p*-Ar), 6.99 (m, 1H, *p*-Ph), 6.95 (dd, $^3J = 7.7$ Hz, $^4J = 1.6$ Hz, 1H, *m*'-Ar), 6.50 (m, 1H, 2-H), 6.38 (m, 1H, 5-H), 5.92 (m, 1H, 4-H), 5.79 (m, 1H, 3-H), 5.22 (s, 1H, CH), 3.90 (hept, $^3J = 6.7$ Hz, 1H, $\text{HC}^{\text{ipr}(\text{o})}$), 3.21 (m, 2H, 6-H), 2.72 (hept, $^3J = 6.8$ Hz, 1H, $\text{HC}^{\text{ipr}(\text{o})}$), 2.03/1.96 (each m, each 1H, 7-H), 1.96 (m, 2H, 8-H), 1.76

(s, 3H, Me^{Ph}), 1.56 (s, 3H, Me^{Ar}), 1.44 (d, $^3J = 6.7$ Hz, 3H, $\text{Me}^{\text{ipr}(\text{o})}$), 1.18 (d, $^3J = 6.7$ Hz, 3H, $\text{Me}^{\text{ipr}(\text{o})}$), 1.01 (d, $^3J = 6.8$ Hz, 3H, $\text{Me}^{\text{ipr}(\text{o})}$), 0.72 (d, $^3J = 6.8$ Hz, 3H, $\text{Me}^{\text{ipr}(\text{o})}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): δ /ppm 168.0 ($\text{C}=\text{N}^{\text{Ar}}$), 161.3 ($\text{C}=\text{N}^{\text{Ph}}$), 150.3 (*i*-Ph), 144.7 (*i*-Ar), 143.7 (*o*-Ar), 141.3 (*o*'-Ar), 135.7 (C1), 129.1 (*m*-Ph), 127.7 (*p*-Ar), 126.2 (*p*-Ph), 125.8 (*m*-Ar), 124.5 (br, *o*-Ph), 124.0 (*m*'-Ar), 117.2 (C2), 116.8 (C5), 116.6 (C3), 114.8 (C4), 90.9 (CH), 33.7 (C-6), 32.2 (br, C-8), 27.6 ($\text{HC}^{\text{ipr}(\text{o})}$), 27.4 ($\text{HC}^{\text{ipr}(\text{o})}$), 26.1 (C-7), 25.9 ($\text{Me}^{\text{ipr}(\text{o})}$), 24.8 ($\text{Me}^{\text{ipr}(\text{o})}$), 24.5 ($\text{Me}^{\text{ipr}(\text{o})}$), 23.4 (Me^{Ar}), 23.2 ($\text{Me}^{\text{ipr}(\text{o})}$), 22.9 (Me^{Ph}) (C_6F_5 not listed). ^{19}F NMR (470 MHz, C_6D_6 , 298 K): δ /ppm -130.1 (m, 2F, *o*-(C_6F_5)), -147.8 (t, $^3J_{\text{FF}} = 19.4$ Hz, 1F, *p*-(C_6F_5)), -161.1 (m, 2F, *m*-(C_6F_5)) ($\Delta\delta(^{19}\text{F}_{\text{m.p.}}) = 13.4$).

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 (**2–7**) 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. The reactor was attached to an ethylene line, and the gas was fed continuously into the reactor to a pressure of 178 psi. The pressurized reaction mixture was stirred at 75 °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.

Polymer Characterization. Polymers were dried overnight under vacuum, and the polymerization activities were calculated from the mass of product obtained. These values were to within 5% of the calculated mass determined by measuring the ethylene consumed by use of a mass flow controller. The polymers were characterized by gel permeation chromatography (GPC). GPC analysis was performed on a Waters Alliance GPC 2000 system equipped with a refractive index detector. Samples were run at 150 °C in spectrophotometric grade 1,2,4-trichlorobenzene (TCB), stabilized with BHT (0.5 g of BHT/4 L of solvent). Molecular weights were calculated by using a universal calibration from narrow polystyrene standards in the molecular weight range of 580–7 500 000. 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 2920) at a rate of 10 °C/min for two cycles in the temperature range 25–200 °C.

Solid-State MAS NMR Spectroscopy. ^{11}B and $^{13}\text{C}\{^1\text{H}\}$ CPMAS spectra were recorded at resonance frequencies of 160.5 MHz (128.4 MHz) and 100.6 MHz, respectively, on Bruker DSX 500 and BRUKER Avance DSX 400 spectrometers, equipped with a 4 mm NMR double-resonance probe operating at MAS rotation frequencies of 4–14 kHz. Typical acquisition parameters for single-pulse and CPMAS measurements: 0.6 μs (30° flip angle) for ^{11}B and 5 μs for ^1H (90° flip angle) with a contact time of 5 ms within the CP step; recycle delay 4 s for ^{11}B and 5 s in the $^{13}\text{C}\{^1\text{H}\}$ CPMAS experiments. ^1H decoupling was achieved by applying the TPPM-15 decoupling scheme.²⁴ ^{11}B and $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts are referenced to a $\text{BF}_3\cdot\text{Et}_2\text{O}$ standard and to TMS, respectively, in the latter case using adamantane ($\delta(\text{CH}_2)$ 38.56 ppm for the methylene resonance as a secondary standard). For more experimental details see the Supporting Information.

DFT Calculations. All computations have been performed using the program packages TURBOMOLE²⁵ and GAUSSIAN.²⁶ ^{13}C magnetic shieldings and CSA tensor elements were calculated on a GGA level of theory by using the BP-86 functional²⁷ and the def2-TZVP²⁸ basis set (for zirconium the all-electron basis set TZVPPals2²⁹ was applied). EFGs were calculated with the B97-D³⁰ functional and a slightly modified def2-TZVP basis set. For more technical details of the computations see the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, and CIF files giving further experimental and spectroscopic details and crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

[†]X-ray crystal structure analyses.

Author Contributions

[‡]Solid-state NMR.

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