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The C_s-Symmetric Aminoboranediyl-Bridged Zirconocene Dichloride [(η-9-$C_{13}H_8$)-BN(^{i}Pr)$_2$(η-C_5H_4)]$ZrCl_2$: Its Synthesis, Structure, and Behavior as an Olefin Polymerization Catalyst

Arthur J. Ashe, III,* Xinggao Fang, Andrea Hokky, and Jeff W. Kampf

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055

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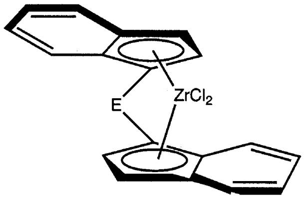
*Summary: The sequential reaction of 9-fluorenyllithium and CpNa with (^{i}Pr)$_2$NBCl$_2$ followed by the sequential treatment with LDA and ZrCl$_4$ afforded [(η^5-$C_{13}H_8$)BN(^{i}-Pr)$_2$(η^5-C_5H_4)ZrCl$_2$ (**2e**). The structure of **2e** was determined by X-ray diffraction, which shows that the molecule has C_s symmetry. On activation by excess methylaluminoxane (MAO) **2e** was converted to an active catalyst for polymerization of ethylene and propylene. The polypropylene is syndiotactic (81% rr triads).*

Introduction

Certain bridged or *ansa*-metallocenes of the group 4 metals are highly active and stereoselective catalysts for the polymerization of olefins.[1] By far the best known are the C_2-symmetric *ansa*-bis(indenyl) zirconium dihalides (**1**).[2] For example, on activation by a cocatalyst, usually methylaluminoxane (MAO), **1a** polymerizes propylene with high activity to yield isotactic polypropylene (i-PP).[3] Although a large number of different bridging groups have been studied, complexes with smaller bridges consisting of SiMe$_2$ (**1a**),[3] CH$_2$CH$_2$ (**1b**),[2] and CMe$_2$ (**1c**)[4] are most active. Stereoselectivity and molecular weight of the PP increases in the order Me$_2$C < C$_2$H$_4$ < Me$_2$Si.[5] It has recently been reported that boron-bridged zirconium and titanium complexes can be converted to olefin polymerization catalysts.[6−9] In particular, activated **1d**[8] and **1e**[9] seem to be comparable in activity and stereoselectivity to **1a**.

ansa-Zirconocenes based on the C_s-symmetric (cyclopentadienyl)(9-fluorenyl) bridged structure **2** polymerize propylene to give syndiotactic polypropylene (s-PP).[10] Again a large number of bridging groups have been studied. Interestingly, the influence of the bridge is rather different for **2** than for **1**. The single C-bridged compound **2c** is the most active, while stereoselectivity decreases in the order Me$_2$C (**2c**)[10] > C$_2$H$_4$ (**2b**)[11] > SiMe$_2$ (**2a**).[12] Thus, it was of interest to explore the boron-bridged analogues of **2** to find out how they might fit in the series.



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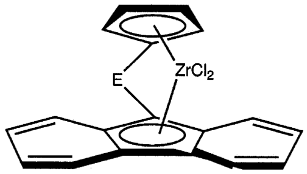

2

a, E = SiMe$_2$
b, E = CH$_2$CH$_2$
c, E = CMe$_2$
d, E = BPh(PMe$_3$)
e. E = BN(i-Pr)$_2$

The aminoboranediyl-bridged **1e** has a greater thermal stability than the borane donor-bridged complexes such as **1d**.[8,9] Thus we have only examined the former type. We report here on the synthesis, crystal structure, and polymerization activity of the new aminoboranediyl-bridged C_s-symmetric zirconocene **2e**.

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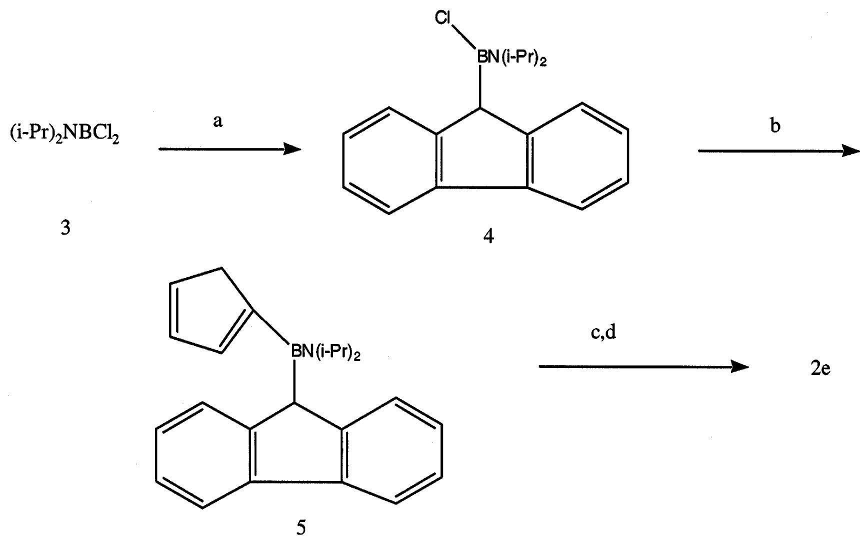
Scheme 1[a]



KEY: a, FluLi ; b, CpNa ; c, LDA ; d, ZrCl$_4$

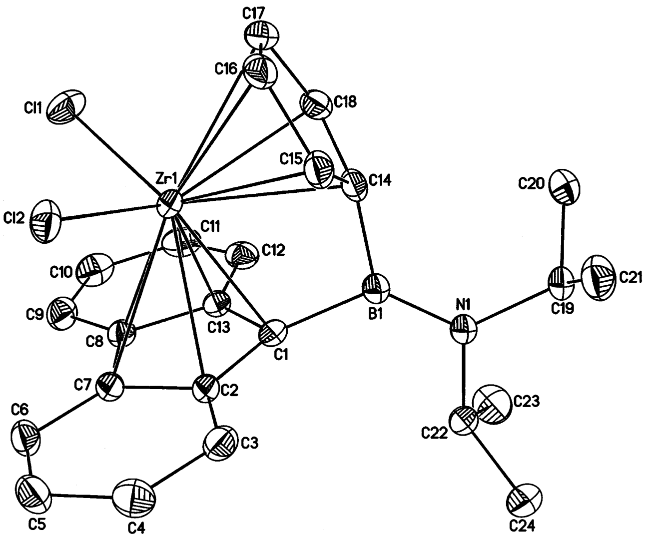


Figure 1. The molecular structure of **2e**.

Results and Discussion

The diisopropylaminoboranediyl-bridged zirconocene dichloride **2e** was prepared by the route indicated in Scheme 1. The addition of fluorenyllithium in THF to diisopropylaminoboron dichloride **3**[14] gave a near quantitative yield of **4**, a white crystalline solid. The ^{1}H NMR spectrum of **4** in CDCl$_3$ at 25 °C is consistent with the assigned structure. However, the signals assigned to the CH and CH$_3$ moieties of the ^{i}Pr groups are rather broad. On cooling the sample to −50 °C, the spectrum shows sharp signals, which are consistent with two nonequivalent ^{i}Pr groups. This behavior suggests that there is restricted rotation about the B−N bond at low temperatures due to its π-bond character.[15] The reaction of **4** with CpNa in THF afforded a 62% yield of **5**. The complex ^{1}H NMR spectrum of **5** is consistent with the compound existing as a mixture of double bond isomers. For this reason little attempt was made to purify **5**. Instead, it was treated with 2 equiv of LDA in THF followed by ZrCl$_4$ in toluene to afford **2e** as a red crystalline solid in 41% yield.

Table 1. Comparison of Selected Average Distances (Å) and Angles (deg) for 2a, 2c, and 2e

	2a,[a] E = SiMe$_2$	**2c**,[b] E = CMe$_2$	**2e**,[c] E = BN(^{i}Pr)$_2$
Zr−C$_i$(Cp)	2.478	2.436(7)	2.466(2)
Zr−C$_\alpha$(Cp)	2.464(7)	2.448(8)	2.461(2)
Zr−C$_\beta$(Cp)	2.527(1)	2.524(8)	2.529(2)
Zr−C$_i$(Flu)	2.426	2.401(8)	2.419(2)
Zr−C$_\alpha$(Flu)	2.553(2)	2.516(16)	2.525(4)
Zr−C$_\beta$(Flu)	2.739(7)	2.658(7)	2.688(2)
Zr−Cl	2.424(1)	2.424(3)	2.424(1)
C$_i$(Cp)−C$_\alpha$(Cp)	1.423(2)	1.42(1)	1.427(3)
C$_\alpha$(Cp)−C$_\beta$(Cp)	1.413(0)	1.40(1)	1.421(3)
C$_\beta$(Cp)−C$_\beta$′(Cp)	1.386	1.38(1)	1.392(3)
C$_i$(Flu)−C$_\alpha$(Flu)	1.452(1)	1.44(1)	1.440(2)
C$_\alpha$(Flu)−C$_\beta$(Flu)	1.443(2)	1.44(1)	1.438(3)
C$_\beta$(Flu)−C$_\beta$′(Flu)	1.442	1.43(1)	1.442(3)
C$_i$(Cp)−E	1.874	1.53(1)	1.585(3)
C$_i$(Flu)−E	1.874	1.53(1)	1.577(3)
B−N			1.377(3)
C$_i$(Cp)−E−C$_i$(Flu)	93.4	99.4	104.69(15)
Cl−Zr−Cl	96.6	98.2	96.44(2)
PL(Cp)−PL(Flu)	62.5	72.0	68.12(7)
Cp−M−Flu	127.9	118.6	122.15(2)

[a] Reference **12b**. [b] Reference **10b**. [c] This work.

The identity of **2e** was confirmed by its ^{1}H, ^{11}B, and ^{13}C NMR spectra, high-resolution mass spectrum, and X-ray crystal structure. It is noteworthy that the ^{1}H NMR spectrum of **2e** shows an identical pattern of signals for the Cp and Flu ring positions as the published spectra of **2c**.[10b]

The molecular structure of **2e** is illustrated in Figure 1. The molecule has an approximate C_s symmetry, which closely resembles that shown by **2a** and **2c**. Analogous structural parameters of **2a**, **2c**, and **2e** are compared in Table 1. In all three compounds the Cp and Flu groups are very similar with the average variation of the corresponding C−C bond distances of only ±0.01 Å between different compounds. As had previously been noted for **2a** and **2c**, the Zr atom of **2e** is slip distorted

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(13) Also see: Schaverien, C. J.; Terlouw, R. E. W.; Schut, P.; Sudmeijer, O.; Budzelaar, P. H. M. *J. Mol. Catal. A* **1998**, *128*, 245.

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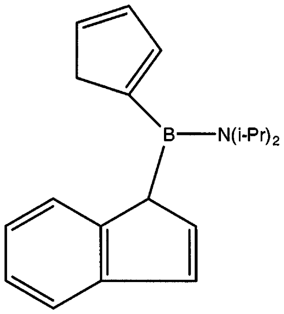
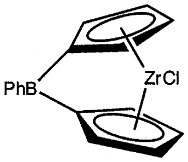
away from C_β toward C_α and C_{ipso} of the fluorenyl group. Thus the fluorenyl group coordination approaches η^3 coordination. Again for all three compounds there is a much smaller variation of the Zr−C distances in the Cp rings which are η^5-coordinated.

The major modification of the structure of analogous *ansa*-metallocenes with changes in the bridging groups is the change in the degree of canting of the coordinated rings. The dihedral angle between the Cp and Flu ring planes of the $SiMe_2$-bridged **2a** is 57°, which increases to 72° for the smaller bridging CMe_2 group of **2c**. The dihedral angle between the planes of **2e** is 68.2°. Thus the open wedge to the Zr of **2e** is intermediate in size between those of **2a** and **2c**.

The bridging of **2e** distorts the C−B−C angle (104.7°), which is reduced by 11.5° from that of nonbridged compound **6** (116.2°).[7d] The shortening of the B−N bond (1.377(3) Å) in comparison to that of **6** (1.402(4) Å) is consistent with strongerer B−N π-bonding.



6



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Strong B−N π-bonding is independently indicated by the high rotational barrier about the B−N bond. The ^{1}H NMR spectrum of **2e** in C_7D_8 at 25 °C shows signals at δ 1.36 and 1.58 and at δ 4.05 and 4.21 from the ^{i}Pr methyl and methine groups, respectively. When the temperature is raised to 200 °C, these signals neither broaden nor coalesce. On this basis, the rotational barrier about the B−N bond must be greater than 23.8 kcal/mol.[16] This strong B−N π-bonding exocyclic from the strained *ansa*-position of **2e** indicates that boron accepts substantial π-electron density from the $N(^iPr)_2$ group. This effect is analogous to the enhanced Lewis acidity found by Shapiro and co-workers for the structurally similar BPh bridge of compound **7**.[6b] We propose that the strong B−N π-bonding in **2e** and the bulky $N(^iPr)_2$ group are important for the high stability of **2e**.

When activated by a 10^3 molar excess of MAO as a cocatalyst **2e** is a highly active olefin polymerization catalyst. At 140 °C under typical conditions **2e** effects the copolymerization of mixtures of 1-octene/ethylene with an activity of 3.9×10^6 g of polymer/mol of Zr atm. The polymer has a density of 0.90 g/mL, which corresponds to the incorporation of 5.7 mol % of octene. At 70 °C the activity of **2e** toward the polymerization of propylene is 7.7×10^5 g of polymer/mol of Zr atm. The resulting PP was monodisperse with $M_w = 111 \times 10^3$ and PDI = 1.88. It had a melting point of 112 °C with triad ratio of 4:15:81 (mm/mr/rr). Thus the PP is modestly syndiotactic.

It is not possible to make precise comparisons of our data for polymerization using **2e** with the literature data for polymerizations using **2a**, **2b**, or **2c** because the polymerizations were run under somewhat different conditions. Qualitatively, the syndiotacticity resulting from the use of **2c** is clearly higher while that resulting from the use of **2a** is considerably lower. On the other hand, the syndiotacticity is in the same range as that reported with use of **2b**. Thus the order of stereoselectivity is **2c** (CMe_2) > **2e** ($BN(^iPr)_2$) ≈ **2b** (C_2H_4) > **2a** ($SiMe_2$). Qualitatively the decrease in the tacticity of the polymers formed from **2** correlates with the increase in the opening of the wedge to the metal as measured by the dihedral angles between the Cp and Flu planes.

The behavior of C_s-symmetric olefin polymerization catalysts **2**, particularly **2c**, have been extensively reviewed.[1,5] It is generally felt that the syndiotactity of the polymer derives from the regularly alternating insertion of propylene at the enantiotropic sites of the active complex. The steric interaction between the growing PP chain and the coordinated monomer is enforced by the ligand−metal geometry. A larger opening of the wedge to the metal implies a smaller steric interaction, which allows an occasional misinsertion of monomer and hence a lower stereoselectivity. The order of observed syndiotacitity of **2c** > **2e** ≈ **2b** > **2a** fits this picture.

The ethylene polymerization activity of **2e**/MAO is rather high as had previously been reported for **2a**/MAO. Indeed the activity of **2e** approaches that of constrained geometry catalysts which are used commercially for ethylene/α-olefin copolymerization.[17] Clearly the steric effects are minimal with the smaller ethylene.

In summary, we have prepared aminoboranediyl-bridged C_s zirconocene **2e**, which can produce syndiotactic PP. The $N(^iPr)_2$ pendant group appears to markedly stabilize the borane bridge of the catalyst.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of argon or nitrogen. Solvents were dried following standard procedures. The mass spectra were determined with a VG-70-S spectrometer. The NMR spectra were obtained on either a Bruker AM 300 or a Varian Inova-500 spectrometer. The ^{1}H NMR spectra and ^{13}C NMR spectra were calibrated by using signals from solvents referenced to Me_4Si. The ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$. The combustion analyses were determined by the analytical service department of the Department of Chemistry, The University of Michigan. Diisopropylaminoboron dichloride was prepared by a literature procedure.[14] All other compounds are commercially available.

$(^iPr)_2NBCl(9\text{-Flu})$ (4). A 2.5 M hexane solution of BuLi (46.6 mL, 116.6 mmol) was added to a solution of fluorene (17.65 g, 106 mmol) in 250 mL of THF at −78 °C. The resulting mixture was allowed to warm to 25 °C with stirring to give a red solution of fluorenyllithium. This solution was cooled to −78 °C and added dropwise to a solution of $(^iPr)_2NBCl_2$ (18.2 g, 100 mmol) in 100 mL of THF. The solution was allowed to warm to 25 °C and was stirred for 15 h. The volatile components were removed under reduced pressure and the residue was extracted with pentane, which was then filtered. Removal of the solvent afforded 22.4 g (72%) of product as a white solid, mp 139 °C. Anal. Calcd for $C_{10}H_{23}BClN$: C, 73.19; H, 7.38; N, 4.50. Found: C, 72.98; H, 7.45; N, 4.38. H RMS (EI) calcd for $C_{10}H_{23}{}^{11}B^{35}ClN$ 311.1612, found 311.1613. ^{1}H

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[16] Determined at 300 MHz for $\Delta\nu = 44$ Hz.

[17] Stevens, J. C. *Stud. Surf. Sci. Catal.* **1994**, *89*, 277.

NMR (300 MHz, CD Cl$_3$, $T = -50$ °C): δ 1.21 (br d, $J = 6.6$ Hz, 6H), 1.78 (d, $J = 6.8$ Hz, 6H), 3.75 (sept, $J = 6.6$ Hz, 1H), 4.55 (s, 1H), 4.65 (sept, $J = 6.6$ Hz, 1H), 7.30 (td, $J = 7.2$, 1.5 Hz, 2H), 7.38 (t, $J = 7.2$ Hz, 2H), 7.60 (br d, $J = 7.2$ Hz, 2H), 7.84 (d, $J = 7.4$ Hz, 2H). ^{13}C NMR (100.6 MHz, CDCl$_3$, $T = 25$ °C): δ 24.5 (br), 43.2 (br), 48.5 (br), 120.2, 124.4, 126.4, 126.9. Signals for C(4a), C(9), and C(9) were not observed. ^{11}B NMR (115.5 MHz, CDCl$_3$): δ 37.2.

$[(^i\mathrm{Pr}_2\mathrm{NB}(\eta^5\text{-}\mathrm{C}_5\mathrm{H}_4)(\eta^5\text{-}\mathrm{C}_{13}\mathrm{H}_8)\mathrm{ZrCl}_2]$ (2e). A solution of CpNa (26 mmol) in 63 mL of THF at −78 °C was added to a solution of **4** (8.1 g, 26 mmol) in 100 mL of THF at −78 °C. The resulting mixture was allowed to warm to 25 °C and was stirred for 15 h. The volatile components were removed under reduced pressure and the residue was extracted with pentane, which was then filtered. The pentane solution was cooled to −78 °C to afford the product as a white solid (5.58 g, 63%). The ^{1}H NMR and ^{13}C NMR spectra were very complicated, indicating that the product was a mixture of double bond isomers of $(^i\mathrm{Pr})_2$NBCp(9-Flu). ^{1}H RMS (EI): calcd for $\mathrm{C}_{24}\mathrm{H}_{28}{}^{11}$BN 341.2315, found 341.2329. A solution of LDA (18.46 mmol) in 25 mL of THF was added to a solution of **5** (3.15 g, 9.23 mmol) in 25 mL of THF at −78 °C. The resulting solution was allowed to warm slowly to 25 °C and was stirred for 15 h to give a dark red solution. Volatile components were removed under reduced pressure affording an orange residue, which was then dissolved in 75 mL of toluene. This solution was added to a suspension of ZrCl$_4$ (2.15 g, 9.23 mmol) in 75 mL of toluene at −78 °C. The mixture was allowed to warm slowly to 25 °C and was stirred for 15 h to afford a dark red solution. The volatile components were removed at reduced pressure and the residue was washed with pentane to afford a dark red solid (1.89 g, 41%), mp 280−282 °C. Anal. Calcd for $\mathrm{C}_{24}\mathrm{H}_{26}\mathrm{BCl}_2\mathrm{NZr}$: C, 57.49; H, 5.23; N, 2.79. Found: C, 57.07; H, 5.00; N, 2.52. H RMS (EI): calcd for $\mathrm{C}_{24}\mathrm{H}_{26}{}^{11}\mathrm{B}^{35}\mathrm{Cl}_2\mathrm{N}^{90}\mathrm{Zr}$ 499.0582, found 499.0570. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 0.99 (d, $J = 6.9$ Hz, 6H), 1.20 (d, $J = 6.9$ Hz, 6H), 3.68 (sept, $J = 6.7$ Hz, 1H); 3.78 (sept, $J = 6.9$ Hz, 1H), 5.28 (t, $J = 2.5$ Hz, 2H); 6.36 (t, $J = 2.5$ Hz, 2H), 7.03 (d, $J = 7.4$ Hz, 2H), 7.09 (td, $J = 7.0$, 1.2 Hz, 2H), 7.43 (td, $J = 7.0$, 1.2 Hz, 2H), 7.90 (d, $J = 8.2$ Hz, 2H). ^{11}B NMR (115.5 MHz, C$_6$D$_6$): δ 39.4. ^{13}C NMR (90.6 MHz, CDCl$_3$): δ 24.2, 25.4, 49.1, 49.8, 106.9, 122.2, 123.2, 125.4, 125.8, 129.0, 147.9, 157.1. (CB not observed.)

X-ray Structure Determination. Crystals of **2e** suitable for X-ray diffraction were obtained by recrystallization from THF/pentane. Crystallographic data are collected in Table 2. An ORTEP drawing of **2e** showing the numbering scheme used in the refinements is illustrated in Figure 1. Additional crystallographic data are available in the Supporting Information.

Ethylene/Octene Polymerization. The batch reactor ethylene polymerization was conducted in a 2-L Parr reactor with an electrical heating jacket, internal serpentine coil for cooling, and a bottom drain valve. Pressures, temperatures, and block valves were computer monitored and controlled. Isopar E (ca. 740 g) and 1-octene (ca. 118 g) were measured in a solvent shot tank. The contents of the reactor were stirred at 1200 rpm. Hydrogen was added by differential expansion (Δ 25 psi) from a 75-mL shot tank initially at 300 psig. The contents of the reactor were then heated to the desired run temperature, 140 °C, under 500 psig of ethylene pressure. The catalyst (1 micromol as a 0.0050 M solution in toluene) and MAO cocatalyst were combined in a 1:1000 molar ratio in the glovebox and transferred from the glovebox to the catalyst shot tank through 1/16 in. (0.16 cm) tubing, using toluene to aid in the transfer. The catalyst tank was then pressurized to 700 psig with nitrogen. After the contents of the reactor had stabilized at the desired run temperature of 140 °C, the catalyst was injected into the reactor via a dip tube. The temperature was maintained by allowing cold glycol to pass through the internal cooling coils. The reaction was allowed to proceed for 15 min with ethylene provided on demand. The contents of the reactor were then expelled into a 4-L nitrogen-purged vessel and quenched with isopropyl alcohol and antioxidant (67 mg of Irganox 1010) and stabilizer (133 mg of Irgafos 168) both in toluene. Volatile materials were removed from the polymers in a vacuum oven up to 140 °C overnight and cooled to at least 50 °C prior to removal from the oven. The polymer density was determined by the displacement technique with use of 2-butanone.

Table 2. Crystallographic Data Collection Parameters for 2e

	2e
empirial formula	$\mathrm{C}_{24}\mathrm{H}_{26}\mathrm{BCl}_2\mathrm{NZr}$
fw	501.39
temp, K	118(2)
wavelength, Å	0.71073
cryst syst	monoclinic
space group	P2(1)/C
unit cell dimens	
a, Å	8.1559(16)
b, Å	27.540(5)
c, Å	10.446(2)
β, deg	106.343(4)
V, Å^3; *Z*	2251.5(8); 4
calcd density, Mg/m^3	1.479
abs coeff, mm^{-1}	0.736
F(000)	1024
cryst size, mm	0.20 × 0.16 × 0.04
limiting indices	$-10 \le h \le 10$ $-36 \le k \le 36$ $-13 \le l \le 13$
no. of reflns collected	20208
no of indepent reflns	5585 (*R*(int) = 0.0352)
abs cor	semiempirical from equiv
refinement method	full-matrix least squares on F^2
no. of data/restrains/params	5585/0/266
GOF on F^2	1.031
final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0287$, w$R_2 = 0.0665$
R indices (all data)	$R_1 = 0.0397$, w$R_2 = 0.0705$
largest diff peak and hole, e/A^3	0.442 and −0.439

Propylene Polymerization. The polymerization of propylene was conducted in a similar manner, using 150 g of propylene in 650 g of Isopar E at a pressure of 350 psig and a temperature of 70 °C for 30 min. The M_w analyses was carried out on a Waters 150 °C high-temperature instrument. The sample (15 mg) was dissolved in 13 mL of 1,2,4-trichlorobenzene containing 300 ppm w/w Ional. The samples were shaken at 160 °C for 2 h. The hot solutions were filtered with use of a 0.5 μm stainless steel filter. The flow rate was set at 1.1 mL/min. The eluent was 1,2,4-trichlorobenzene with 200 ppm w/w Ionol. Injection was 150 μL with the injector set at 135 °C. The columns used were Polymer Laboratories 10 μm Mixed B-105-07, 105-08, and 105-92 heated to 138 °C. A refraction index detector was used. The molecular weight distribution was nondisperse (a single peak); PDI was 1.88 and $M_w = 1.11 \times 10^5$. The PP melting point was determined with DSC(TA Instruments 2910) to be 112 °C.

The ^{13}C NMR (150.81 MHz) spectra of the PP were recorded at 130 °C, using a GE Omega 600 spectrometer and a Z-spec 10 mm probe from Nalorac. Other acquisition parameters are the following: NA = 1400, AT = 0.852 s, 32 K points acquired, relaxation delay = 3.82 s, Waltz decoupling, full NOE. The NMR sample was prepared by dissolving 0.577 g of polymer in 3 mL of a 2:1 mixture of 1,2,4-trichlorobenzene/1,1,2,2-tetrachloroethylene-d_2. The sample was degassed with a nitrogen purge prior to heating to 150 °C to dissolve the polymer.

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Supporting Information Available: X-ray crystallographic data for the structure and a ^{1}H NMR spectrum of **2e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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