

Synthesis, Structure, and Olefin Polymerization Catalytic Behavior of Aryl-Substituted Zirconocene Dichlorides

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Standard ligand-substitution reactions afforded moderate yields of (PhC₅H₄)₂ZrCl₂ (**1**), (1,3-Ph₂C₅H₃)CpZrCl₂ (**2**), [1,3-(C₆F₅)₂C₅H₃]CpZrCl₂ (**5**), and [1,2,4-(C₆F₅)₂C₅H₃]CpZrCl₂ (**6**). Crystal structures of **1**, **2**, **6**, and [(C₆F₅)C₅H₄]₂HfMe₂ (**7**) were obtained. Physicochemical studies (CV, IR) show that C₆F₅ groups are strongly electron-withdrawing compared to phenyl groups. In ethylene-1-hexene copolymerization reactions using **1**, **2**, (C₆F₅C₅H₄)CpZrCl₂ (**3**), (C₆F₅C₅H₄)₂ZrCl₂ (**4**), and **5** (toluene solution, methylalumoxane cocatalyst), C₆F₅ substituents decrease catalytic activity but increase comonomer incorporation compared to phenyl substituents.

Introduction

Structure–activity relationships in olefin polymerization processes catalyzed by soluble group 4 metal complexes, especially zirconocene dichloride (Cp₂ZrCl₂, Cp = η⁵-C₅H₅) and its derivatives, have been analyzed extensively.^{1,2} Subtle changes in ancillary ligand structure can influence stereoregularity, comonomer distribution, and other polyolefin properties, in addition to catalytic activity.^{3,4} Empirical trends and theoretical modeling have illuminated the polymerization mechanism in considerable detail.^{5–13}

Electronic substituent effects in metallocene-catalyzed olefin polymerization are not as well understood.^{14–19} Strongly electron-donating (OMe, NMe₂)^{20–23} or electron-withdrawing substituents (e.g., F,^{22,24–27} CF₃,^{28–32}

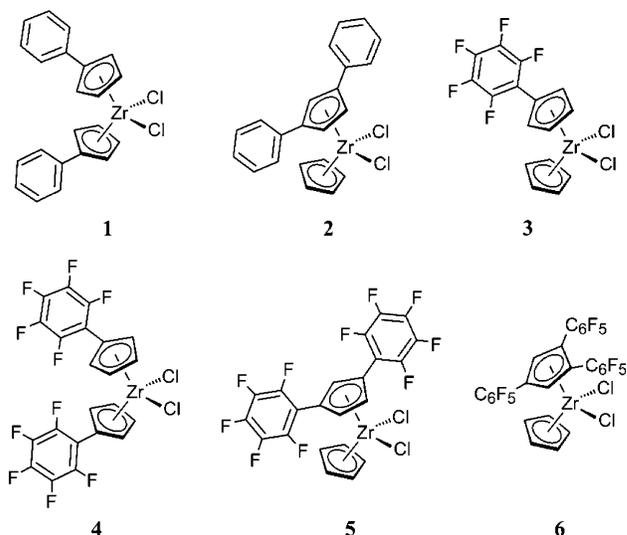
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 (1) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223–1252.
 (2) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143–1170.
 (3) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253–1345.
 (4) Thomas, E. J.; Chien, J. C. W.; Rausch, M. D. *Macromolecules* **2000**, *33*, 1546–1552.
 (5) Cruz, V. L.; Munoz-Escalona, A.; Martinez-Salazar, J. *J. Polym. Sci. Polym. Chem.* **1998**, *36*, 1157–1167.
 (6) Rappe, A. T.; Skiff, W. M.; Casewit, C. J. *Chem. Rev.* **2000**, *100*, 1435–1456.
 (7) Angermund, K.; Fink, G.; Jensen, V. R.; Kleinschmidt, R. *Chem. Rev.* **2000**, *100*, 1457–1470.
 (8) Vanka, K.; Chan, M. S. W.; Pye, C. C.; Ziegler, T. *Macromol. Symp.* **2001**, *173*, 163–177.
 (9) Xu, Z.; Vanka, K.; Firman, T.; Michalak, A.; Zurek, E.; Zhu, C.; Ziegler, T. *Organometallics* **2002**, *21*, 2444–2453.
 (10) Zubris, D. L.; Veghini, D.; Herzog, T. A.; Bercaw, J. E. *ACS Symp. Ser.* **2000**, *749*, 2–14.
 (11) Chen, E. Y. X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391–1434.
 (12) Nele, M.; Collins, S.; Dias, M. L.; Pinto, J. C.; Lin, S.; Waymouth, R. M. *Macromolecules* **2000**, *33*, 7249–7260.
 (13) Nele, M.; Mohammed, M.; Xin, S. X.; Collins, S.; Dias, M. L.; Pinto, J. C. *Macromolecules* **2001**, *34*, 3830–3841.

- (14) Blais, M. S.; Rausch, M. D. *Organometallics* **1994**, *13*, 3557–3563.
 (15) Blais, M. S.; Rausch, M. D. *J. Organomet. Chem.* **1995**, *502*, 1–8.
 (16) Witte, P.; Lal, T. K.; Waymouth, R. M. *Organometallics* **1999**, *18*, 4147–4155.
 (17) Lin, S.; Hauptman, E.; Lal, T. K.; Waymouth, R. M.; Quan, R. W.; Ernst, A. B. *J. Mol. Catal. A Chem.* **1998**, *136*, 23–33.
 (18) Reybuck, S. E.; Meyer, A.; Waymouth, R. M. *Macromolecules* **2002**, *35*, 637–643.
 (19) Kamigaito, M.; Lal, T. K.; Waymouth, R. M. *J. Polym. Sci. Polym. Chem.* **2000**, *38*, 4649–4660.
 (20) Leino, R.; Luttikhedde, H. J. G.; Langstedt, L.; Penninkangas, A. *Tetrahedron Lett.* **2002**, *43*, 4149–4151.
 (21) Leino, R.; Luttikhedde, H. J. G. *ACS Symp. Ser.* **2000**, *749*, 31–47.
 (22) Piccolrovazzi, N.; Pino, P.; Consiglio, G.; Sironi, A.; Moret, M. *Organometallics* **1990**, *9*, 3098–3105.
 (23) Lee, I. M.; Gauthier, W. J.; Ball, J. M.; Iyengar, B.; Collins, S. *Organometallics* **1992**, *11*, 2115–2122.
 (24) Curnow, O. J.; Hughes, R. P. *J. Am. Chem. Soc.* **1992**, *114*, 5895–5897.
 (25) Hughes, R. P.; Zheng, X.; Ostrander, R. L.; Rheingold, A. L. *Organometallics* **1994**, *13*, 1567–1568.
 (26) Richardson, D. E.; Lang, L.; Eyler, J. R.; Kircus, S. R.; Zheng, X. M.; Morse, C. A.; Hughes, R. P. *Organometallics* **1997**, *16*, 149–150.
 (27) Hughes, R. P.; Zheng, X. M.; Morse, C. A.; Curnow, O. J.; Lompfrey, J. R.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1998**, *17*, 457–465.
 (28) Baschky, M. C.; Sowa, J. R.; Gassman, P. G.; Kass, S. R. *J. Chem. Soc., Perkin Trans. 2* **1996**, 213–215.
 (29) Burk, M. J.; Arduengo, A. J.; Calabrese, J. C.; Harlow, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 8938–8940.
 (30) Gassman, P. G.; Ray, J. A.; Wenthold, P. G.; Mickelson, J. W. *J. Org. Chem.* **1991**, *56*, 5143–5146.
 (31) Gassman, P. G.; Mickelson, J. W.; Sowa, J. R. *J. Am. Chem. Soc.* **1992**, *114*, 6942–6944.

C_nF_{2n+1} ,³³ BR_2 ,^{34–36} and acetyl^{15,37–40}) are often difficult to attach to the cyclopentadienyl ligands, or they may be incompatible with the conditions of metallocene synthesis or olefin polymerization catalysis. For these reasons, electronic effects on metallocene reactivity are usually studied over a relatively narrow range in which the number of stable, weakly electron-donating substituents such as CH_3 or $SiMe_3$ is varied.^{41–47} The resulting trends are difficult to uncouple from the steric effects of increased ligand substitution.³¹ Steric effects are particularly important in determining comonomer incorporation and polymer tacticity. Recent reports have also pointed to the importance of ion pairing and solvation effects in polymerization processes.^{6,11,48,49}

We now report a controlled study of electronic substituent effects on the copolymerization of ethylene and 1-hexene catalyzed by a series of substituted zirconocene dichlorides and methylalumoxane (MAO).⁵⁰ Our approach uses pentafluorophenyl (C_6F_5) as a highly electron-withdrawing substituent, as in complexes **1–6** (Chart 1). We showed in earlier reports that C_6F_5 is readily attached to cyclopentadienyl (Cp) or indenyl ligands by nucleophilic aromatic substitution reactions of C_6F_6 and Cp or indenyl anions^{51–54} and that these ligands can be used to prepare a wide range of transition metal Cp complexes.^{55–60} Meanwhile, the phenyl (C_6H_5 or Ph) group is similar in overall size and shape to the

Chart 1



C_6F_5 group, but, as we will show, phenyl is weakly electron-donating. The phenyl substituent therefore serves as a “steric control”. This report describes the synthesis and characterization of C_6F_5 - and C_6H_5 -substituted group 4 metallocenes and the results of our copolymerization experiments. We find that electron-withdrawing substituents on the Cp ligands significantly increase the incorporation of 1-hexene while decreasing both activity and molecular weight of polyethylenes produced, compared to using Cp_2ZrCl_2/MAO .

Experimental Section

General Procedures. Standard inert-atmosphere techniques were used for all synthetic reactions. Solvents were purified according to established methods.⁶¹ “Hexane” in inert-atmosphere procedures and crystallizations refers to *n*-hexane. ($C_6F_5C_5H_4$)CpZrCl₂ (**3**),⁶² ($C_6F_5C_5H_4$)₂ZrCl₂ (**4**),⁵¹ ($C_6F_5C_5H_4$)₂HfMe₂ (**7**),⁶² ($C_6F_5C_5H_4$)Na,⁵¹ [1,3-(C_6F_5)₂C₅H₃]Na,⁵¹ 1,2,4-(C_6F_5)₃C₅H₂]Na,⁵⁴ ZrCl₄(THF)₂,⁶³ and CpZrCl₃(THF)⁶⁴ were prepared by published methods. Phenylcyclopentadiene⁶⁵ and 1,3-diphenylcyclopentadiene^{66,67} were prepared by published methods and converted to their corresponding sodium salts by treatment with NaH in THF. (The latter deprotonations were slow and proceeded with some decomposition; KH would probably have been a better reagent.) MAO was obtained as a 10% solution in toluene as a gift from Albemarle Corporation and dried under high vacuum (10^{-5} Torr, 15 h) to remove the solvent and “free” trimethylaluminum.^{68,69} NMR experiments used a Varian Unity 400 instrument. NMR solvents were

(32) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4228–4229.

(33) Hughes, R. P.; Trujillo, H. A. *Organometallics* **1996**, *15*, 286–294.

(34) Reetz, M. T.; Brummer, H.; Kessler, M.; Kuhnigk, J. *Chimia* **1995**, *49*, 501–503.

(35) Herberich, G. E.; Fischer, A.; Wiebelhaus, D. *Organometallics* **1996**, *15*, 3106–3108.

(36) Herberich, G. E.; Fischer, A. *Organometallics* **1996**, *15*, 58–67.

(37) Kunz, D.; Erker, G.; Fröhlich, R.; Kehr, G. *Eur. J. Inorg. Chem.* **2000**, 409–416.

(38) Rausch, M. D.; Lewison, J. F.; Hart, W. P. *J. Organomet. Chem.* **1988**, *358*, 161–168.

(39) Hart, W. P.; Macomber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 1196–1198.

(40) Rausch, M. D.; Mintz, E. A.; Macomber, D. W. *J. Org. Chem.* **1980**, *45*, 689–695.

(41) Wieser, U.; Babushkin, D.; Brintzinger, H. H. *Organometallics* **2002**, *21*, 920–923.

(42) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525–9546.

(43) Chirik, P. J.; Day, M. W.; Bercaw, J. E. *Organometallics* **1999**, *18*, 1873–1881.

(44) Mohring, P. C.; Coville, N. J. *J. Mol. Catal. A Chem.* **1995**, *96*, 181–195.

(45) Mohring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1–29.

(46) Mohring, P. C.; Vlachakis, N.; Grimmer, N. E.; Coville, N. J. *J. Organomet. Chem.* **1994**, *483*, 159–166.

(47) Grimmer, N. E.; Coville, N. J.; de Koning, C. B. *J. Organomet. Chem.* **2002**, *642*, 195–202.

(48) Chan, M. S. W.; Vanka, K.; Pye, C. C.; Ziegler, T. *Organometallics* **1999**, *18*, 4624–4636.

(49) Vanka, K.; Chan, M. S. W.; Pye, C. C.; Ziegler, T. *Organometallics* **2000**, *19*, 1841–1849.

(50) Maldanis, R. J.; Chien, J. C. W.; Rausch, M. D. *J. Organomet. Chem.* **2000**, *599*, 107–111.

(51) Deck, P. A.; Jackson, W. F.; Fronczek, F. R. *Organometallics* **1996**, *15*, 5287–5291.

(52) Deck, P. A.; Fronczek, F. R. *Organometallics* **2000**, *19*, 327–333.

(53) Thornberry, M. P.; Slobodnick, C.; Deck, P. A.; Fronczek, F. R. *Organometallics* **2001**, *20*, 920–926.

(54) Thornberry, M. P.; Slobodnick, C.; Deck, P. A.; Fronczek, F. R. *Organometallics* **2000**, *19*, 5352–5369.

(55) Wahren, R. *J. Organomet. Chem.* **1973**, *57*, 415–418.

(56) Lindsell, W. E. *J. Chem. Soc., Dalton Trans.* **1975**, 2548–2552.

(57) Roloff, A.; Meier, K.; Reidiker, M. *Pure Appl. Chem.* **1986**, *58*, 1267–1272.

(58) Klingert, B.; Roloff, A.; Urwyler, B.; Wirz, J. *Helv. Chim. Acta* **1988**, *71*, 1858–1867.

(59) Imrie, C.; Nonhebel, D. C.; Pauson, P. L. *J. Chem. Soc., Perkin Trans. 1* **1991**, *10*, 2555–2558.

(60) Ivushkin, V. A.; Sazonov, P. K.; Artamkina, G. A.; Beletskaya, I. P. *Russ. J. Org. Chem.* **1970**, *35*, 1640–1652.

(61) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

(62) Hawrelak, E. J.; Deck, P. A. *Organometallics* **2003**, *22*, 3558–3565.

(63) Manzer, L. E. *Inorg. Synth.* **1987**, *21*, 135.

(64) Lund, E. C.; Livinghouse, T. *Organometallics* **1990**, *9*, 2426–2427.

(65) Singh, P.; Rausch, M. D.; Bitterwolf, T. E. *J. Organomet. Chem.* **1988**, *352*, 273–282.

(66) Farnum, D. G.; Mostashari, A.; Hagedorn, A. A., III. *J. Org. Chem.* **1971**, *36*, 698–702.

(67) Kang, Y. K.; Lee, H.-K.; Lee, S. S.; Chung, Y. K.; Carpenter, G. *Inorg. Chim. Acta* **1997**, *261*, 37–44.

(68) Imhoff, D. W.; Simeral, L. S.; Sangokoya, S. A.; Peel, J. H. *Organometallics* **1998**, *17*, 1941–1945.

Table 1. Crystallographic Data

	1	2	6	7
empirical formula	C ₂₂ H ₁₈ Cl ₂ Zr	C ₂₂ H ₁₈ Cl ₂ Zr	C ₂₈ H ₇ Cl ₂ F ₁₅ Zr	C ₂₄ H ₁₄ F ₁₀ Hf
fw	444.48	444.48	790.46	670.84
diffractometer	Nonius Kappa CCD	Nonius Kappa CCD	Nonius Kappa CCD	Siemens P4
cryst dimens (mm)	0.03 × 0.08 × 1.00	0.10 × 0.25 × 0.35	0.20 × 0.23 × 0.28	0.30 × 0.30 × 0.30
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic
a (Å)	11.5690(13)	14.8140(2)	11.2970(2)	10.0776(2)
b (Å)	23.3310(18)	29.8600(9)	14.0810(3)	10.4687(2)
c (Å)	6.755(3)	8.6230(3)	16.4470(4)	10.6314(2)
α (deg)	90	90	90	86.6088(6)
β (deg)	90	99.7980(14)	90.6920(14)	74.0965(4)
γ (deg)	90	90	90	80.2345(7)
V (Å ³) ^s	1823.3(8)	3758.71(18)	2616.08(10)	1062.95(4)
space group	<i>Fmm2</i> (No. 42)	<i>P2₁/n</i> (No. 14)	<i>P2₁/n</i> (No. 14)	<i>P1</i> (No. 2)
Z	4	8	4	2
D _{calc} (Mg m ⁻³)	1.619	1.571	2.007	2.096
abs coeff (mm ⁻¹)	0.9	0.9	0.8	5.0
F ₀₀₀	896	1792	1536	640
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
temp (K)	150	120	150	198
θ range	3.5–30.3	2.6–30.0	2.6–35.0	2.0–28.4
no. of reflns coll'd	9620	18 512	20 309	6958
no. of indep reflns	1308	10 906	11 399	4587
abs corr method	multiscan	multiscan	multiscan	DIFABS
no. of data/params	1308/64	10 906/451	11 399/415	4587/316
R [I > 2σ(I)]	0.061	0.033	0.032	0.045
R _w [I > 2σ(I)]	0.16	0.074	0.081	0.120
GoF on F ²	1.09	0.87	0.98	0.97
peak, hole (e Å ⁻³)	0.94, -1.07	0.75, -0.73	0.48, -0.84	1.41, -1.85

vacuum-transferred from appropriate drying agents. ¹⁹F NMR spectra were referenced to external C₆F₆ in CDCl₃ (−163 ppm). Quantitative ¹³C experiments were conducted using Randall's published method.⁷⁰ GPC analyses were carried out at Dow Chemical Company (Midland, Michigan) using a Waters 150C instrument. Elemental analyses were performed by Desert Analytics (Tucson, AZ) or Oneida Research Services (Whitesboro, NY). The Cambridge Structural Database (CSD) was searched using the ConQuest software package provided by Cambridge.

Crystallographic Studies. Colorless prisms of **1** were obtained by cooling a concentrated solution of **1** in hexane/toluene to 25 °C. Cooling a hexane/toluene solution of **2** to 25 °C afforded colorless crystals that were coated with an unidentified dark residue. Pale yellow crystals of **6** were obtained by cooling a warm toluene/hexane solution slowly to −10 °C. Colorless crystals of **7** were discovered in a hexane solution of the complex in a Schlenk flask that had been left in a refrigerator for several months. Relevant crystallographic data are assembled in Table 1. Complete data tables are included in the Supporting Information. The crystals used for the structural characterization of **1** (and the ensuing data set) were of marginal quality, and an ambiguity arose in the assignment of the space group. We initially solved the structure in *C2* (monoclinic), but systematic absences were equally consistent with *Fmm2* (orthorhombic), so we defaulted to the higher symmetry. Thermal ellipsoids looked about the same in both solutions. We deduce that even if **1** does not have crystallographic *mm2* symmetry, the molecular geometry must still be very close to *C_{2v}*. An initial structure of **2** obtained at 200 K showed only one molecule per asymmetric unit, but some of the ellipsoids for the carbon atoms of the unsubstituted Cp ligand were elongated, suggesting a positional disorder. A superior data set was subsequently obtained at 120 K, showing two molecules per independent unit, differing most notably by rotation about the Cp–Zr axis of the unsubstituted Cp ligand. The solutions and refinements of the structures of **6** and of **7** were routine.

Polymerization Studies. The reactor used for polymerization experiments was a 1.5 L flanged glass kettle equipped

with a thermocouple, an ethylene inlet-port, a septum-sealed injection port, and a Teflon-sealed overhead paddle stirrer fitted through a condenser. After drying in an oven for several hours, the reactor was evacuated to below 0.1 Torr while still warm and then flushed thoroughly with nitrogen. Purified^{61,71} toluene (400 mL) was added, followed by 50 mg of MAO to scavenge adventitious moisture. Comonomer (1-hexene, 20 mL, freshly distilled from calcium hydride) was then added using a syringe. The reactor was lowered into a vigorously agitated water bath interfaced to an Omega temperature controller. After establishing an internal temperature of 50 °C, the stirred reactor was purged for 5 min with ethylene (purified by passage over Engelhard Q5 oxygen scavenger and Davison 10X molecular sieves) through an immersed gas dispersion tube, allowing the exhaust to escape via the condenser to a mineral oil bubbler. During reactor temperature equilibration, a cocktail containing MAO (300 mg) and metallocene precatalyst (2.6 μmol) in 10 mL of toluene was stirred for about 20 min at 25 °C to preactivate the catalyst. An aliquot of the catalyst cocktail (typically 1–5 mL depending on anticipated activity) was injected into the reactor to commence polymerization. Reactions in which the internal temperature varied by more than 1 °C were quenched and discarded. After 5 min, 20 mL of acidified methanol (prepared by diluting 50 mL of concentrated hydrochloric acid to 1 L with methanol) was added to quench the reaction. The reactor was vented, and the contents were poured into 200 mL of rapidly stirred acidified methanol. The solvent volume was reduced to about 20 mL by evaporation, and another 200 mL of acidified methanol was added to induce precipitation. The polymer was collected on a filter, washed with methanol, and dried in a vacuum oven at 60 °C for at least 12 h. We conducted several control experiments with zirconocene dichloride to ensure that activity (g_{PE} mol⁻¹ atm⁻¹ h⁻¹) was invariant with metallocene concentration and with a 2-fold increase in reaction time.

1,1'-Diphenylzirconocene Dichloride (1). A solution of ZrCl₄ (0.29 g, 1.2 mmol) and sodium phenylcyclopentadienide (0.40 g, 2.4 mmol) in THF (50 mL) was stirred at room temperature for 24 h. After evaporating the solvent, the green residue was recrystallized from hot toluene to afford 0.25 (0.56 mmol, 47%) of green-yellow needles. A second crystallization

(69) Imhoff, D. W.; Simeral, L. S.; Blevins, D. R.; Beard, W. R. *ACS Symp. Ser.* **2000**, *749*, 177–191.

(70) Hsieh, E. T.; Randall, J. C. *Macromolecules* **1982**, *15*, 1402–1406.

(71) Evans, W. J.; Pedersen, S.; Farina, J.; Meyer, J.; Staunton, G. *Chem. Eng. News* **2002**, *80*, 8–12.

from hexane/toluene afforded colorless needles. ^1H NMR (CDCl_3): δ 7.53 (m, 4 H), 7.15 (t, $^3J_{\text{HH}} = 7.6$ Hz, 4 H), 7.32 (tt, $^3J_{\text{HH}} = 7.4$ Hz, $^4J_{\text{HH}} = 1.5$ Hz, 2 H), 6.71 (t, $^3J_{\text{HH}} = 4J_{\text{HH}} = 2.8$ Hz, 4 H), 6.29 (t, $^3J_{\text{HH}} = 4J_{\text{HH}} = 2.6$ Hz, 4 H). ^{13}C NMR (CDCl_3): δ 133.0, 129.2, 128.4, 128.3, 126.3, 115.8, 115.6. Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{Cl}_2\text{Zr}$: C, 59.45; H, 4.08. Found: C, 59.33; H, 3.76.

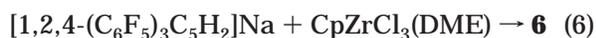
1,3-Diphenylzirconocene Dichloride (2). A mixture of $\text{CpZrCl}_3(\text{DME})$ (0.514 g, 1.46 mmol), sodium 1,3-diphenylcyclopentadienide (0.30, 1.2 mmol), and toluene (50 mL) was stirred at reflux for 20 h. The reaction mixture was cooled and filtered through a glass frit. The toluene was stripped, and the crude solid was recrystallized from toluene/hexane to afford 0.13 g (0.29 mmol, 23%) of gray needles. ^1H NMR (CDCl_3): δ 7.69 (m, 4 H), 7.46 (t, $^3J_{\text{HH}} = 7.8$ Hz, 4 H), 7.34 (tt, $^3J_{\text{HH}} = 7.4$ Hz, $^4J_{\text{HH}} = 1.4$ Hz, 2 H), 7.24 (t, $^4J_{\text{HH}} = 2.6$ Hz, 1 H), 6.88 (d, $^4J_{\text{HH}} = 2.4$ Hz, 2 H), 6.18 (s, 5 H). ^{13}C NMR (CDCl_3): δ 133.1, 129.2, 128.5, 127.3, 126.2, 117.2, 113.8, 112.9. Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{Cl}_2\text{Zr}$: C, 59.45; H, 4.08. Found: C, 59.13; H, 3.85.

1,3-Bis(pentafluorophenyl)zirconocene Dichloride (5). A mixture of CpZrCl_3 (1.04 g, 3.97 mmol), sodium 1,3-bis(pentafluorophenyl)cyclopentadienide (1.72 g, 4.09 mmol), and toluene (100 mL) was stirred at 110°C for 2 h. The hot mixture was filtered, and the precipitate was washed with an additional 50 mL of hot toluene. The filtrate was cooled to 25°C , and the resulting microcrystalline precipitate was collected on a filter, washed with pentane (25 mL), and dried under vacuum to afford 1.91 g (3.06 mmol, 77%) of a white solid. ^1H NMR (CDCl_3): δ 7.35 (s, 1 H), 6.93 (s, 2 H), 6.55 (s, 5 H). ^{19}F NMR (CDCl_3): δ -139.65 (m, 4 F), -153.51 (tt, $^3J_{\text{FF}} = 21$ Hz, $^4J_{\text{FF}} = 2.6$ Hz, 2 F), -161.65 (m, 4 F). Anal. Calcd for $\text{C}_{22}\text{H}_8\text{Cl}_2\text{F}_{10}\text{Zr}$: C, 42.32; H, 1.29. Found: C, 42.55; H, 1.03.

1,2,4-Tris(pentafluorophenyl)zirconocene Dichloride (6). A mixture of $\text{CpZrCl}_3(\text{DME})$ (0.138 g, 0.391 mmol), $[\text{1,2,4-(C}_6\text{F}_5)_3\text{C}_5\text{H}_2]\text{Na}$ (0.222 g, 0.379 mmol), and toluene (25 mL) was stirred at 22°C for 20 h and then filtered. The filtrate was evaporated, and the residue was triturated with hexane (15 mL, 0°C) to afford 0.132 g (0.167 mmol, 44%) of a tan solid. An analytically pure sample was obtained by crystallization from toluene/hexane. ^1H NMR (CDCl_3): δ 7.35 (s, 2 H), 6.42 (s, 5 H). ^{19}F NMR (CDCl_3): δ -134.98 (d, $^3J_{\text{FF}} = 19$ Hz, 4 F), -138.96 (d, $^3J_{\text{FF}} = 18$ Hz, 2 F), -151.77 (tt, $^3J_{\text{FF}} = 21$ Hz, $^4J_{\text{FF}} = 2.8$ Hz, 2 F), -152.46 (tt, $^3J_{\text{FF}} = 21$ Hz, $^4J_{\text{FF}} = 3.0$ Hz, 1 F), -160.50 (m, 2 F), -160.93 (m, 4 F). Anal. Calcd for $\text{C}_{28}\text{H}_7\text{Cl}_2\text{F}_{15}\text{Zr}$: C, 42.55; H, 0.89. Found: C, 42.77; H, 0.77.

Results

Metalloocene Synthesis. Several metallocenes (**1**–**6**) desired for the catalytic studies described here were prepared in moderate yields by standard ligand-substitution reactions (eqs 1–6). Complexes **3** and **4** were reported earlier.⁵¹ The synthesis and purification of the thermally unstable triarylated metallocene (**6**) were carried out below 25°C . We speculate that poor ligand basicity accounts for the thermal instability of **6**.



Analysis of Electronic Substituent Effects. Numerous methods have been developed for quantifying the effects of ligand substituents, and differences among these methods are notable. Using oxidation potentials of arylated ferrocenes, one would conclude that *both* C_6F_5 and C_6H_5 are electron-withdrawing, although the effect of C_6H_5 is much smaller in magnitude (about 5 mV per C_6H_5 group compared to 170 mV per C_6F_5 group).⁷² Using infrared spectroscopic analysis of arylated $\text{CpMn}(\text{CO})_3$ complexes, C_6F_5 is strongly electron-withdrawing, increasing $\nu_{\text{CO}}(\text{A})$ by 4 cm^{-1} per C_6F_5 group, whereas each C_6H_5 group has a roughly opposite effect.⁶⁷ Core electron binding energies are arguably the most direct probe of metal-centered electron deficiency,^{73–76} especially for complexes lacking useful ligands for IR spectroscopy (such as carbonyl)^{77,78} or highly metal-centered HOMOs needed for voltammetric measurements.⁴² Unfortunately, the XPS method also suffers from poor sensitivity and resolution, and we lack the special equipment needed to mount air-sensitive samples. However, iron core electron (Fe 2p) binding energies correlated well with δ_{Cp} for a series of $[(\eta^6\text{-arene})\text{FeCp}][\text{PF}_6]$ complexes,⁷⁹ and in that series, the C_6H_5 substituent (arene = biphenyl) is about as electron-donating as two methyl groups. We likewise thought of using the chemical shifts (δ_{Cp}) of the *unsubstituted* Cp ligands of the unsymmetrical metallocenes (**2**, **3**, **5**, and **6**) to probe relative metal-centered electrophilicities. An upfield shift of about 0.16 ppm in δ_{Cp} was observed for each of two phenyl groups in **1** (relative to Cp_2ZrCl_2), signifying a relatively strong electron-donating effect of the phenyl groups. In contrast, each C_6F_5 group in **3** and **5** effected a downfield shift in δ_{Cp} of only about 0.03 ppm. The triarylated complex (**6**) deviated significantly from this trend, showing an *upfield* shift in δ_{Cp} of 0.07 ppm relative to Cp_2ZrCl_2 . However, with increasing arylation, more conformations bring the aryl groups in close proximity to the opposing Cp ligand, which could result in transannular local magnetic field anisotropies (“ring currents”). In the case of **6**, structural distortions may also be significant. These issues are much less important in metallocenes having parallel ligands. In summary, we do not yet have an independent *quantitative* measure of the electronic effects of Ph versus C_6F_5 in group 4 complexes, but where good comparisons can be made in other complexes, the Ph group appears to be neutral or weakly electron-donating, whereas C_6F_5 is moderately electron-withdrawing. Importantly C_6F_5 is always found to be more electron-withdrawing than C_6H_5 , which probably surprises no one.

Structural Studies. Three metallocene dichlorides (**1**, **2**, and **6**) were structurally characterized. We also

(72) Lu, S.; Strelets, V. V.; Ryan, M. F.; Pietro, W. J.; Lever, A. B. *Inorg. Chem.* **1996**, *35*, 1013–1023.

(73) Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470–1472.

(74) Gassman, P. G.; Winter, C. H. *Organometallics* **1991**, *10*, 1592–1598.

(75) Gassman, P. G.; Deck, P. A.; Winter, C. H.; Dobbs, D. A.; Cao, D. H. *Organometallics* **1992**, *11*, 959–960.

(76) Lichtenberger, D. L.; Elkadi, Y.; Gruhn, N. E.; Hughes, R. P.; Curnow, O. J.; Zheng, X. M. *Organometallics* **1997**, *16*, 5209–5217.

(77) Duplooy, K. E.; Ford, T. A.; Coville, N. J. *J. Organomet. Chem.* **1992**, *441*, 285–294.

(78) Graham, P. B.; Rausch, M. D.; Taschler, K.; Vonphilipsborn, W. *Organometallics* **1991**, *10*, 3049–3052.

(79) Gassman, P. G.; Deck, P. A. *Organometallics* **1994**, *13*, 2890–2894.

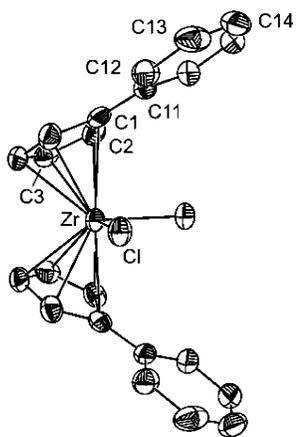


Figure 1. Thermal ellipsoid plot of **1** shown at 50% probability. Hydrogen atoms were removed for clarity.

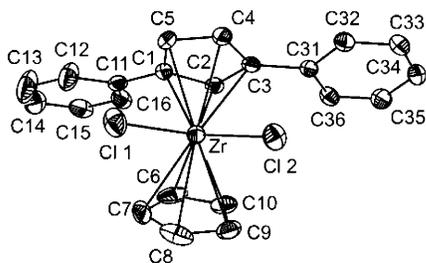


Figure 2. Thermal ellipsoid plot of **2** showing one of two nearly identical molecules in the asymmetric unit at 50% probability. Hydrogen atoms were removed for clarity.

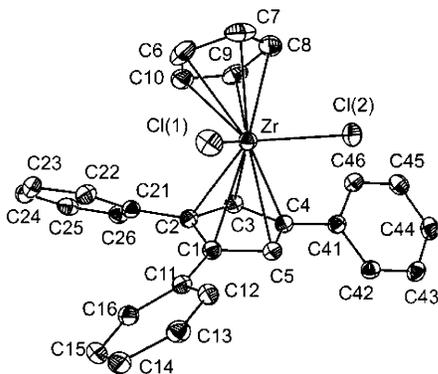


Figure 3. Thermal ellipsoid plot of **6** shown at 50% probability. Hydrogen and fluorine atoms were removed for clarity. Fluorine atoms are numbered the same as the carbons to which they are attached.

discovered crystals of the hafnocene dimethide **7** in a flask that had been abandoned in a refrigerator for several months. Crystallographic data are collected in Table 1. Thermal ellipsoid plots are shown in Figures 1–4. The metric data for the metallocene cores of **1** and **2** (Table 2, entries 1 and 2) were nearly identical to corresponding data previously reported for Cp_2ZrCl_2 (entry 4).⁸⁰ The triarylated zirconocene complex (**6**) showed a lengthening of the Cp–Zr distance for the substituted Cp ligand and widening of the Cp–Zr–Cp angle in **6** (Table 2, entry 3 vs entry 4). In an effort to understand the thermal instability of **6**, we also examined the Zr–C bond distances for the triarylated Cp ligand for “slip” distortions.^{81–85} The triarylated Cp

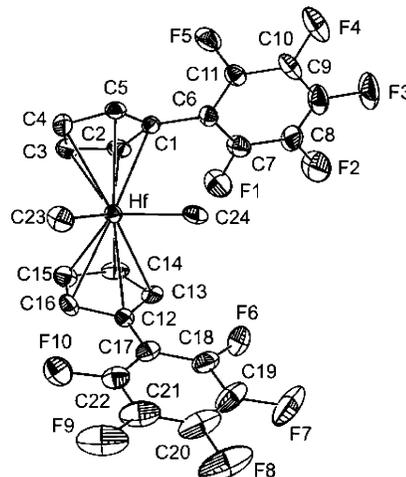


Figure 4. Thermal ellipsoid plot of **7** shown at 50% probability. Hydrogen atoms were removed for clarity.

ligand of **6** shows a “slip” distance (Δ , defined according to ref 81) of 0.074 Å, whereas the corresponding parameter for the unsubstituted Cp ligand of **6** is 0.023 Å. As a reference, the Cp ligands of Cp_2ZrCl_2 show $\Delta = 0.031\text{--}0.036$ Å.⁸⁰ We conclude that the “slip” distortions observed for **6** are not especially noteworthy and may not contribute substantially to the instability of this complex. The Zr–Cl bond lengths in the zirconocenes were invariant to ancillary ligand substitution (entries 1–4).

A search of the Cambridge Structural Database (CSD) revealed several crystallographically characterized group 4 metallocene complexes bearing *isolated* aryl substituents. We are interested in the native conformational preferences of aryl substituents, so we excluded from our analysis several structures having vicinal rather than isolated aryl groups.^{86–88} Aryl conformational preferences may be described by two parameters (Figure 5, Table 2): the absolute Cp–aryl interplanar angle ($0^\circ < \alpha < 90^\circ$) and the absolute C(aryl)–Cp(centroid)–M–X₂(centroid) conformational angle ($0^\circ < \beta < 180^\circ$). In the symmetrical, 1,1-diarylated metallocene (**1**), both C_6H_5 groups are directed exactly between the two chloro ligands, although the ambiguity in the space group assignment means that the trivial torsion angle ($\beta = 0^\circ$) may be inexact. Both C_6H_5 groups of **1** are nearly coplanar with their respective Cp ligands ($\alpha = 5^\circ$), although the deviation from coplanarity is mostly due to a slight splaying of the phenyl substituents away from the chlorine atoms. Ten zirconocene dichloride structures in the CSD having aryl substituents with only hydrogens in the positions adjacent to the aryl

(81) Marder, T. B.; Calabrese, J. C.; Roe, D. C.; Tulip, T. H. *Organometallics* **1987**, *6*, 2012–2014.

(82) Westcott, S. A.; Kakkar, A. K.; Stringer, G.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1990**, *394*, 777–794.

(83) Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929–935.

(84) Carl, R. T.; Hughes, R. P.; Rheingold, A. L.; Marder, T. B.; Taylor, N. J. *Organometallics* **1988**, *7*, 1613–1624.

(85) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839–845.

(86) Zhang, F.; Mu, Y.; Zhao, L.; Zhang, Y.; Bu, W.; Chen, C.; Zhai, H.; Hong, H. *J. Organomet. Chem.* **2000**, *613*, 68–76.

(87) Zhang, F.; Mu, Y.; Wang, J.; Shi, Z.; Bu, W.; Hu, S.; Zhang, Y.; Feng, S. *Polyhedron* **2000**, *19*, 1941–1947.

(88) Greene, D. L.; Chau, A.; Monreal, M.; Mendez, C.; Cruz, I.; Wenj, T.; Tikkanen, W.; Schick, B.; Kantardjiev, K. *J. Organomet. Chem.* **2003**, *682*, 8–13.

(80) Repo, T.; Klinga, M.; Mutikainen, I.; Su, Y. C.; Leskela, M.; Polamo, M. *Acta Chem. Scand.* **1996**, *50*, 1116–1120.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Several Metallocene Complexes

entry	complex	Cp ^a -M	M-X ^b	Cp-M-Cp	X-M-X	α ^c	β ^c
1 ^d	1	2.22(1)	2.45	129.3(2)	95.2(1)	5.0(7)	0.0(8)
2 ^e	2	2.21(1), 2.19(1)	2.42, 2.46	129.8(1)	98.0(1)	15.2(2), 3.4(2)	123.0(2), 92.1(2)
		2.22(1), 2.21(1)	2.42, 2.46	129.9(1)	99.6(2)	12.4(2), 4.7(2)	128.2(2), 87.1(2)
3	6	2.29, 2.20	2.41, 2.40	131.7(1)	98.7(1)	36.9(2), 38.6(2), 39.6(2)	59.2(2), 131.9(2), 84.2(2)
4 ^{e,f}	Cp ₂ ZrCl ₂	2.20(1), 2.20(1)	2.44, 2.45	129.5(1)	97.0(1)		
		2.21(1), 2.20(1)	2.45, 2.45	129.1(1)	97.1(1)		
5	7	2.22, 2.24	2.25(1), 2.23(1)	132.1(2)	94.8(3)	24.2(5), 3.4(5)	74.9(5), 10.2(5)

^a Cp refers to the cyclopentadienyl ligand centroid. Cp-M distance errors are estimated from M-C distance errors. ^b X refers to Cl or the methyl carbon atom, where X = Cl; M-X distance errors were typically 0.001 Å or less. ^c Conformational angles (absolute values) defined in Figure 5. Errors are estimates. ^d Molecule exhibits ambiguously characterized crystallographic *mm*2 symmetry. ^e Two essentially identical independent molecules in the asymmetric unit. ^f Data from ref 100.

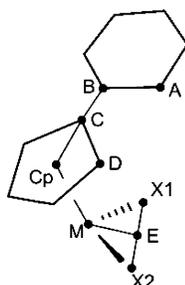


Figure 5. Definitions of conformational parameters for arylated group 4 metallocene complexes. α is the torsion angle between the C₆ and C₅ planes (\sim ABCD), and β is the torsion angle C-Cp-M-E, where E is the centroid of X1 and X2.

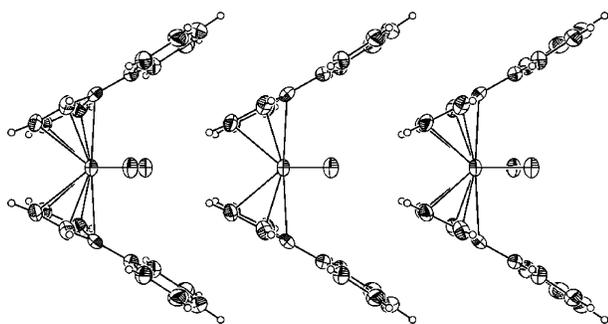


Figure 6. Thermal ellipsoid plot of a partial packing diagram of **1** (50% probability) viewed along the crystallographic *a* axis.

groups showed an average Cp-aryl interplanar angle of $\alpha = 12(6)^\circ$. A partial packing diagram of **1** (Figure 6) shows how the molecules are arrayed in a head-to-tail fashion along the crystallographic axis. However the distance between the phenyl mean plane and the Cp mean plane of a neighboring molecule is 3.34 Å (distance between centroids = 3.82 Å), probably too long to be considered a true stacking interaction.

In the structure of **7** (Figure 4), one aryl substituent is directed into the center of the metallocene wedge, while one substituent is directed toward the side. The Cp-aryl interplanar angles in **7** are small (nearly coplanar). We speculate that the p- π donating ability of the aryl fluorides is maximized when $\alpha = 0^\circ$, so smaller values of α should be expected with increasing electron demand. In C₆F₅-substituted Re(I) and Fe(II) Cp complexes that we have characterized, the torsion angle α typically ranges from 20 to 50°, and metal-centered electron demand in these systems is arguably lower. However much more data would be needed to establish a clear trend in α . Examination of packing diagrams for **7** does not reveal any specific interactions

Table 3. Data for Ethylene Homopolymerization and Ethylene-1-hexene Copolymerization Reactions

entry	catalyst ^a	[1-hexene] (M)	activity, ^b Mg mol ⁻¹ atm ⁻¹ h ⁻¹	M _w (kD)	PDI	mol % hexene
1	Cp ₂ ZrCl ₂		53(10)	524	2.2	
2	1		53(10)	730	2.1	
3	4		14(2)	432	2.4	
4	Cp ₂ ZrCl ₂	0.4	26(4)	130	2.5	6
5	1	0.4	26(4)	230	3.0	7
6	2	0.4	26(6)	265	2.2	5
7	3	0.4	12(6)	114	3.1	7
8	4	0.4	10(3)	38	2.6	13
9	5	0.4	7(1)	17	2.4	19

^a Catalysts were preactivated with MAO for 20 min at 25 °C. Reaction volume = 400 mL of toluene. T_p = 50(1) °C. Al:Zr = 2300. P(C₂H₄) = 1.0 atm. [1-Hexene] = 0.40 M. Reaction time = 5 min. ^b Standard deviations obtained from at least three runs.

such as arene stacking or C-H \cdots F-C interactions that might influence the conformational disposition of the C₆F₅ groups. However these relatively soft conformational parameters could still be influenced by general-weak packing interactions.

In the structures of **2** (Figure 2) positioning an aryl substituent in the center of the metallocene wedge ($\beta \approx 0^\circ$) is prevented by transannular steric repulsions, so the aryl groups are directed instead toward the "sides" of the molecule. The Cp and aryl groups are nearly coplanar. According to the CSD, when the 3- and 4-positions of a 1-aryl-substituted Cp ligand are occupied by methyl groups or by benzo ring fusion (2-aryllindenyl complexes), the aryl group is also usually directed toward the side or into the Cp₂M hemisphere of the complex,^{16,89-93} and values of α are still around 15°. Thus the two parameters α and β are not strongly correlated.

Polymerization Results. Table 3 summarizes our polymerization results. The observed trend in activity comparing Cp₂ZrCl₂ and its fluoroarylated congener **4** (entries 1 and 3; 4 and 9) is qualitatively consistent with the results of Maldanis et al.,⁵⁰ who showed that **4** has slightly lower activity than Cp₂ZrCl₂ in ethylene homopolymerization at 50 °C.⁵⁰ Because of the roughly

(89) Kimura, K.; Takaishi, K.; Matsukawa, T.; Yoshimura, T.; Yamazaki, H. *Chem. Lett.* **1998**, 571-572.

(90) Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 11586-11587.

(91) Tagge, C. D.; Kravchenko, R. L.; Lal, T. K.; Waymouth, R. M. *Organometallics* **1999**, *18*, 380-388.

(92) Bruce, M. D.; Coates, G. W.; Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 11174-11182.

(93) Petroff, J. L. M.; Bruce, M. D.; Waymouth, R. M.; Masood, A.; Lal, T. K.; Quan, R. W.; Behrend, S. J. *Organometallics* **1997**, *16*, 5909-5916.

isosteric relationship of C_6F_5 and C_6H_5 , one could infer that the retarding (steric-encumbering) effect of C_6H_5 is offset by electron-donating character, whereas the difference in activity between corresponding C_6H_5 - and C_6F_5 -substituted catalysts is largely due to electronic effects alone.

The data in Table 3 also reveal a pronounced effect of aryl substituents on molecular weight and on the incorporation of 1-hexene. The electron-releasing C_6H_5 groups effect slightly higher molecular weights relative to zirconocene dichloride (entries 2, 5, and 6), whereas C_6F_5 groups effect a dramatic decrease in molecular weight (entries 3 and 7–9). The PDI values ranged from 2.2 to 3.1, suggesting that the polymerizations remained orderly despite the large variations in activity and molecular weight. Because C_6H_5 groups do not lead to increased 1-hexene incorporation, however, the increased molecular weight cannot be attributed to a comonomer effect,⁹⁴ but rather the increase must derive from steric and electronic features of the catalyst site. In contrast, electron-withdrawing C_6F_5 groups lead to significant increases in the incorporation of 1-hexene (entries 1 and 4–6).

Importantly, *previously reported attempts to measure electronic effects on α -olefin incorporation either were ambiguous or reached the opposite conclusion.* Yano et al. found that alkylating the Cp moiety of $[Ph_2C(C_{13}H_8)(C_5H_4)]ZrCl_2/MAO$ catalysts increased 1-hexene incorporation,⁹⁵ but no correction for steric factors was possible. In reviewing composite trends, Karol and Kao concluded simply that electron-donating substituents increased comonomer incorporation.⁹⁶ Mohring and Coville studied copolymerization *activities* using a series of ring-substituted Cp_2ZrCl_2/MAO catalysts and found no useful correlation of activity to either steric or electronic factors. Instead they attributed the *difference* between copolymerization and ethylene homopolymerization activities primarily to electronic effects. However the substituents used ($R = H, Me, Et, iPr, tBu, Me_3Si, CMe_2Ph$) give only a narrow range of electronic variation.⁴⁴

(94) Pietikainen, P.; Seppälä, J. V. *Macromolecules* **1994**, *27*, 1325–1328.

(95) Yano, A.; Hasegawa, S.; Kaneko, T.; Sone, M.; Sato, M.; Akimoto, A. *Macromol. Chem. Phys.* **1999**, *200*, 1542–1553.

(96) Karol, F. J.; Kao, S. C. *New J. Chem.* **1994**, *18*, 97–103.

We surmise that the observed increase in 1-hexene incorporation contributes partly to the decrease in molecular weight, as the rate of chain transfer to monomer (β -hydride elimination) is known to be higher after insertion of 1-hexene. Although the frequently cited “comonomer effect” predicts that increasing 1-hexene incorporation should lead to increased activity,^{97–99} others have found that 1-hexene decreases the activity significantly and that the decrease is substituent dependent.⁴⁴ Again, much of the work uses a range of substituents that offers little electronic variation. Work is underway in our laboratories to develop further control experiments that will extend the range of electronic effects in group 4 metallocene olefin polymerization catalysts in order to understand the influence of steric, electronic, and comonomer factors more fully.

Conclusions. Electron-withdrawing substituents (a) decrease the activity of zirconocene dichloride as a catalyst for MAO-cocatalyzed ethylene polymerization and (b) increase the amount of 1-hexene comonomer that is incorporated into an ethylene-1-hexene copolymer.

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Supporting Information Available: Tables of crystallographic data for **1** (Tables S1–S8), **2** (Tables S9–S16), **6** (S17–S24), and **7**. Information is available free of charge via the Internet at <http://pubs.acs.org>.

OM034280D

(97) Quijada, R.; Dupont, J.; Miranda, M. S. L.; Scipioni, R. B.; Galland, G. B. *Macromol. Chem. Phys.* **1995**, *196*, 3991–4000.

(98) Koivumäki, J.; Seppälä, J. V. *Macromolecules* **1993**, *26*, 5535–5538.

(99) Chien, J. C. W.; Nozaki, T. *J. Polym. Sci. Polym. Chem.* **1993**, *31*, 227–237.

(100) Corey, J. Y.; Zhu, X. H.; Brammer, L.; Rath, N. P. *Acta Crystallogr.* **1995**, *C51*, 565–567.