Synthesis, Structure, and Reactivity of C_2-Symmetric Bis(phospholyl)zirconium and Bis(phospholyl)hafnium Complexes

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Several C_2-symmetric bis(phospholyl) adducts of group 4 metals, including the first example of an η^5-phospholyl complex of hafnium, have been synthesized and structurally characterized. These complexes undergo rac/meso isomerization in a process that is accelerated by Lewis bases. A C_2-symmetric bis(phospholyl)zirconium dichloride binds as a bidentate ligand to Mo(CO)$_4$. In the presence of methylalumoxane, bis(phospholyl)zirconium complexes serve as active catalysts for ethylene−hexene copolymerization reactions.

A few years ago, we initiated a program directed at the development of applications of planar-chiral heterocycles as ligands for enantioselective transition metal-catalyzed processes.[2,3] As part of this effort, in 1998 we reported the synthesis and resolution of C_2-symmetric 1,1′-diphosphaferrocene **1**, a potentially useful chiral bidentate ligand.[4,5] Of course, the essentially parallel relationship between the two phospholyl rings of complex **1** (6° deviation from coplanarity) is not the ideal geometry for bidentate complexation to a transition metal.[6] On the other hand, we felt that the bent geometry of a bis(phospholyl) complex of a group 4 metal (**2**) might be better predisposed for chelation.[7] In 1999, we therefore initiated an investigation of the chemistry of such complexes, the results of which we describe in this article.

(−)-**1** **2** M = Ti, Zr, Hf
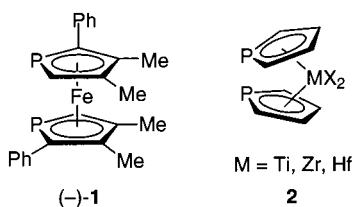
Results and Discussion

Synthesis of Bis(phospholyl) Complexes of Group 4 Metals. We chose to synthesize 2-phenyl-3,4-di-

methyl-substituted phospholyl complexes, because of the ready accessibility of precursor phospholide **4** by the procedure of Mathey.[8] Treatment of ZrCl$_4$ with **4** furnishes racemic bis(phospholyl)zirconium complex **5** in 39% yield after recrystallization from pentane (eq 1).[9] The same procedure provides the corresponding C_2-symmetric bis(phospholyl)hafnium adduct (**6**) in 25% yield after recrystallization from pentane/Et$_2$O; to the best of our knowledge, complex **6** is the first example of an η^5-phospholyl complex of hafnium. Attempts to apply this route to the synthesis of the corresponding titanium adduct instead afforded 3,3′,4,4′-tetramethyl-2,2′-diphenylbiphosphole, which was fully characterized, including an X-ray structure determination.[10]

(1)

M = Zr: *rac*-**5**
   Hf: *rac*-**6**
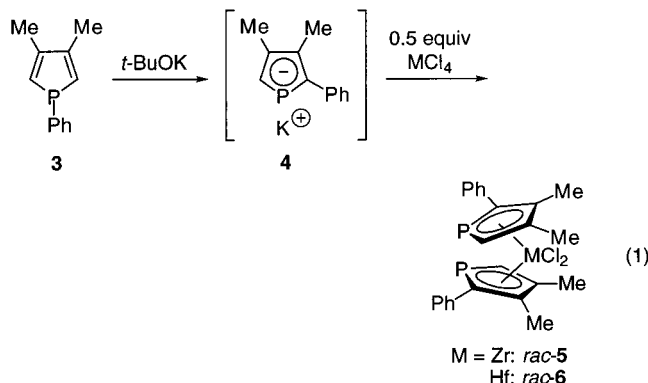
We have obtained an X-ray crystal structure of zirconium complex *rac*-**5**, which is illustrated in Figure

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(1) Correspondence concerning the X-ray crystal structures should be directed to M.M.-C.L.
(2) For ligands based on phosphorus heterocycles, see: (a) Shintani, R.; Lo, M. M.-C.; Fu, G. C. *Org. Lett.* **2000**, *2*, 3695−3697. (b) Tanaka, K.; Qiao, S.; Tobisu, M.; Lo, M. M.-C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 9870−9871. (c) Qiao, S.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 4168−4169.
(3) For ligands based on nitrogen heterocycles, see: (a) Lo, M. M.-C.; Fu, G. C. *Tetrahedron* **2001**, *57*, 2621−2634. (b) Rios, R.; Liang, J.; Lo, M. M.-C.; Fu, G. C. *Chem. Commun.* **2000**, 377−378. (c) Lo, M. M.-C.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 10270−10271. (d) Dosa, P. I.; Ruble, J. C.; Fu, G. C. *J. Org. Chem.* **1997**, *62*, 444−445.
(4) Qiao, S.; Hoic, D. A.; Fu, G. C. *Organometallics* **1998**, *17*, 773−774.
(5) For an overview of phospholyl chemistry, see: Mathey, F. *Coord. Chem. Rev.* **1994**, *137*, 1−52.

(6) Chelation by a 1,1′-diphosphaferrocene is rare. (a) For an example of complexation of the phosphorus atoms to two different metals, see: de Lauzon, G.; Deschamps, B.; Mathey, F. *Nouv. J. Chim.* **1980**, *4*, 683−685. (b) For an example of complexation to the same metal, see: Atwood, D. A.; Cowley, A. H.; Dennis, S. M. *Inorg. Chem.* **1993**, *32*, 1527−1528.
(7) For a pioneering study with an achiral bis(phospholyl)zirconium complex, see: Nief, F.; Mathey, F.; Ricard, L. *J. Organomet. Chem.* **1990**, *384*, 271−278.
(8) Holand, S.; Jeanjean, M.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 98−100. Phosphole **3** can be synthesized in one step from commercially available PhPCl$_2$ and 2,3-dimethyl-1,3-butadiene: Breque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983−985.
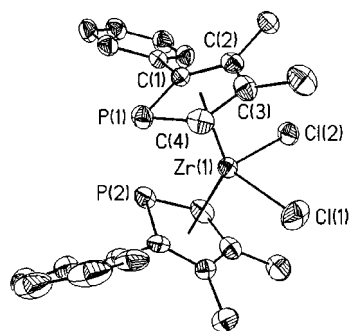
Figure 1. ORTEP representation of *rac*-**5**, with thermal ellipsoids drawn at the 35% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for *rac*-5

Zr(1)−Cl(1)	2.423(2)	Cl(1)−Zr(1)−Cl(2)	95.32(7)
Zr(1)−P(1)	2.728(2)	C(4)−P(1)−C(1)	88.8(3)
Zr(1)−C(1)	2.592(5)	P(1)−C(1)−C(2)	112.5(4)
Zr(1)−C(2)	2.655(5)	C(1)−C(2)−C(3)	112.1(5)
Zr(1)−C(3)	2.618(5)	C(2)−C(3)−C(4)	111.9(5)
Zr(1)−C(4)	2.550(5)	C(3)−C(4)−P(1)	114.4(4)
P(1)−C(1)	1.780(5)		
C(1)−C(2)	1.421(7)		
C(2)−C(3)	1.415(7)		
C(3)−C(4)	1.402(8)		
C(4)−P(1)	1.752(6)		
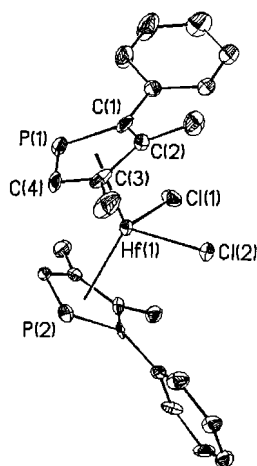
Figure 2. ORTEP representation of *rac*-**6**, with thermal ellipsoids drawn at the 35% probability level.

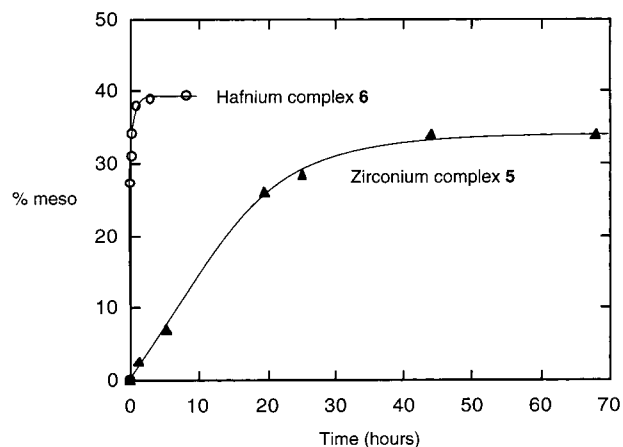**1** (for selected bond lengths and bond angles, see Table 1). The dihedral angle between the pholpholyl planes is 46.7°. The overall structure is similar to Cp_2ZrCl_2 (dihedral angle between Cp's: 53.4°), with a centroid−Zr−centroid angle of 135.4° (vs 129.2° for Cp_2ZrCl_2) and a Cl−Zr−Cl angle of 95.3° (vs 97.0° for Cp_2ZrCl_2).[11] The phosphorus atoms of *rac*-**5** are located at the back of the wedge formed by the two rings, in good positions for bidentate complexation to a metal.

The crystal structure of C_2-symmetric hafnium complex **6** (Figure 2; Table 2) reveals comparable values for the centroid−metal−centroid angle (Hf, 132.1°; Zr, 135.4°) and the Cl−metal−Cl angle (Hf, 94.1°; Zr, 95.3°).

Figure 3. Percentage of the meso isomer, as a function of time, for bis(pholpholyl) complexes **5** and **6** (benzene-d_6 at room temperature; c = 0.010 mol/L).
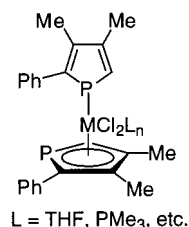
Table 2. Selected Bond Lengths (Å) and Angles (deg) for *rac*-6

Hf(1)−Cl(1)	2.409(3)	Cl(1)−Hf(1)−Cl(2)	94.08(10)
Hf(1)−P(1)	2.690(3)	C(4)−P(1)−C(1)	87.9(5)
Hf(1)−C(1)	2.669(10)	P(1)−C(1)−C(2)	112.9(9)
Hf(1)−C(2)	2.697(10)	C(1)−C(2)−C(3)	113.2(10)
Hf(1)−C(3)	2.592(10)	C(2)−C(3)−C(4)	110.4(10)
Hf(1)−C(4)	2.508(9)	C(3)−C(4)−P(1)	115.6(8)
P(1)−C(1)	1.806(11)		
C(1)−C(2)	1.382(15)		
C(2)−C(3)	1.450(15)		
C(3)−C(4)	1.387(14)		
C(4)−P(1)	1.767(12)		

The angle between the pholpholyl planes is larger for the hafnium adduct than for the zirconium complex (Hf, 57.5°; Zr, 46.8°).
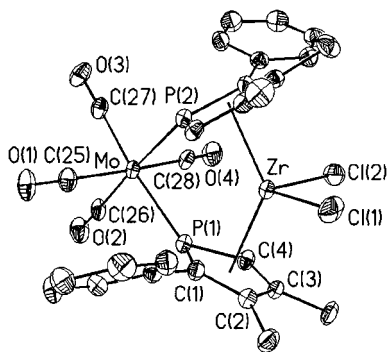
Isomerization of Bis(pholpholyl) Complexes of Zirconium and Hafnium. In the course of characterizing zirconium complex *rac*-**5**, we discovered that, in solution, diastereomerically pure *rac*-**5** converts to a mixture of racemic and meso isomers. A subsequent study established that *rac*-**5** equilibrates to a 1.9:1.0 rac/meso ratio with a $t_{1/2}$ of 12 h in benzene at room temperature (Figure 3). This isomerization process occurs much more rapidly with the hafnium complex, *rac*-**6**, which reaches a 1.5:1.0 equilibrium mixture of rac/meso with a $t_{1/2}$ of 10 min (Figure 3).

We have determined that the isomerization of zirconium complex *rac*-**5** proceeds at a significantly faster rate in THF than in benzene ($t_{1/2}$ [THF] = 30 min; $t_{1/2}$ [benzene] = 12 h).[12] The addition of 1 equiv of PMe_3 also markedly accelerates the equilibration process (in benzene, $t_{1/2} \ll 10$ min). Polar, Lewis-basic species probably facilitate isomerization by stabilizing ring-slipped intermediates (e.g., see **7**).[13,14]

L = THF, PMe₃, etc.

7

(9) For a crystal structure of Cp_2ZrCl_2, see: Repo, T.; Klinga, M.; Mutikainen, I.; Su, Y.; Leskelä, M.; Polamo, M. *Acta Chem. Scand.* **1996**, *50*, 1116−1120.

(10) For the first example of a bis(pholpholyl) complex of a group 4 element, see: Meunier, P.; Gautheron, B. *J. Organomet. Chem.* **1980**, *193*, C13−C16. See also: Nief, F.; Mathey, F.; Ricard, L.; Robert, F. *Organometallics* **1988**, *7*, 921−926.

(11) Bis(pholpholyl)titanium complexes have been synthesized through reaction of $TiCl_4$ with a stannylated phosphole: Nief F.; Ricard L.; Mathey F. *Organometallics* **1989**, *8*, 1473−1477.

(12) The rates of isomerization in DME and in acetonitrile are also faster than in benzene.

Figure 4. ORTEP representation of *rac*-**8**, with thermal ellipsoids drawn at the 35% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for *rac*-8

Zr−Cl(1)	2.423(2)	Cl(2)−Zr−Cl(1)	96.15(7)
Zr−Cl(2)	2.413(2)	P(1)−Mo−P(2)	78.70(5)
Mo−P(1)	2.501(2)	P(1)−Mo−C(25)	91.5(2)
Mo−P(2)	2.512(2)	P(1)−Mo−C(26)	94.3(2)
Mo−C(25)	2.053(7)	P(1)−Mo−C(27)	176.8(2)
Mo−C(26)	1.984(7)	P(1)−Mo−C(28)	94.5(2)
Mo−C(27)	1.987(7)		
Mo−C(28)	2.049(7)		

Zirconium Complex *rac*-5 as a Bidentate Ligand. Treatment of $(CO)_4Mo(nbd)$[15] with *rac*-**5** in toluene at 75 °C for 5 h furnishes molybdenum complex **8** in nearly quantitative yield (97%; eq 2).[16] Although the rac and
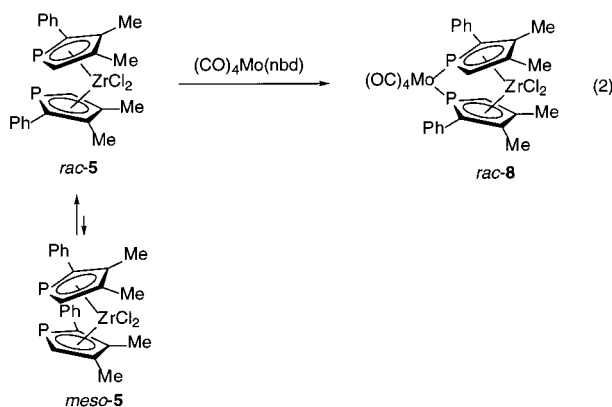
the meso isomers of **5** are interconverting under these conditions, only one diastereomeric complex is isolated.[17] An X-ray crystallographic study established that it is the C_2-symmetric rac isomer of the metallocene that is bound to molybdenum, in a bidentate mode (Figure 4; Table 3). The geometry around molybdenum is pseudo-octahedral.

Synthesis of the Corresponding Dialkyl Complexes. Alkylzirconium complexes have found widespread application in organometallic chemistry, e.g., as

olefin polymerization catalysts.[18] We have synthesized dimethylzirconocene derivative *rac*-**9** in good yield through the reaction of *rac*-**5** with MeMgBr (85%; eq 3).[19] The dimethyl derivative of bimetallic complex *rac*-**8** can be generated by an analogous procedure (34%; eq 4).

Ethylene−Hexene Copolymerizations.[18,20] We have examined the activity of the rac form of complexes **5**, **6**, **8**, **9**, and **10** as ethylene−hexene copolymerization catalyst precursors (hexane slurry in a 1 L stirred autoclave reactor operated under a constant ethylene pressure of 85 psi and maintained at 75 °C). The polymerization experiments were conducted with methylalumoxane (with **5**, **6**, **8**, **9**, and **10**) and triphenylcarbenium tetrakis(pentafluorophenyl)borate (with **9**) as cocatalysts. Of the five catalyst precursors tested, only *rac*-**5** and *rac*-**9** display polymerization activity.[21]

Polymerization data for *rac*-**5** are presented in Table 4. The polymerization activities range between 5000 and 42 000 g PE (mmol Zr)$^{-1}$ (h)$^{-1}$ (100 psi C_2H_4)$^{-1}$, with a strong dependence on the Al/Zr ratio (entries 1−3) and on the reaction temperature (entries 3−5). Using the designations suggested by Gibson, *rac*-**5** exhibits "very high" activity for ethylene polymerization.[18] The apparent maximum in polymerization activity observed between 65 and 85 °C appears to be consistent with the kinetic profile for ethylene consumption. Under polymerization conditions at 75 °C, the catalyst is short-lived, with a half-life of ∼4−6 min. At higher temperature, the rate of propagation and the rate of catalyst decomposition both increase.

Analysis of the polymer samples by GPC, IR, and ^{13}C NMR reveals number average molecular weight (M_n) values between 40 000 and 94 000, with polydispersity indices (PDI) in the range 2.71−3.32, indicating normal single-site behavior. The M_n shows a strong dependence on the polymerization temperature, increasing with decreasing temperature (entries 3−5), but it appears to

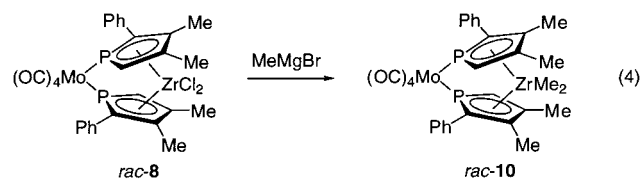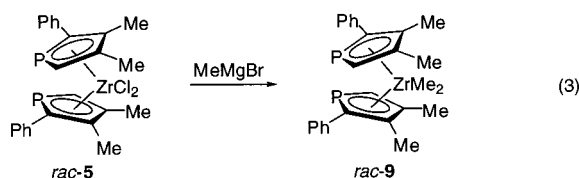(13) For a review of ring slippage, see: O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307−318.

(14) For a study of the low barrier to inversion in phospholes, see: Egan, W.; Tang, R.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 1442−1444.

(15) Bennett, M. A.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 2037−2044.

(16) For the first synthesis of a metal-bridged *ansa*-metallocene that involves a bis(phospholyl)zirconium complex, see: Nief, F.; Mathey, F.; Ricard, L. *J. Organomet. Chem.* **1990**, *384*, 271−278.

(17) Use of a mixture of *rac*- and *meso*-**5** also furnishes *rac*-**8** as a single diastereomer in almost quantitative yield.

(18) For a recent review of the search for new olefin polymerization catalysts, see: Britovsek G. J. P.; Gibson V. C.; Wass D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447.

(19) After 1 day in benzene-d_6 at room temperature, *rac*-**9** isomerizes to an equilibrium mixture (1:1) of *rac*- and *meso*-**9**.

(20) For previous studies of bis(phospholyl)zirconium complexes as catalyts for Ziegler−Natta polymerization, see: (a) Janiak, C.; Lange, K. C. H.; Versteeg, U.; Lentz, D.; Budzelaar, P. H. M. *Chem. Ber.* **1996**, *129*, 1517−1529. (b) de Boer, E. J. M.; Gilmore, I. J.; Korndorffer, F. M.; Horton, A. D.; van der Linden, A.; Royan, B. W.; Ruisch, B. J.; Schoon, L.; Shaw, R. W. *J. Mol. Catal. A* **1998**, *128*, 155−165. (c) Janiak, C.; Versteeg, U.; Lange, K. C. H.; Weimann, R.; Hahn, E. *J. Organomet. Chem.* **1995**, *501*, 219−234.

(21) We speculate that complexes **8** and **10** may decompose under the polymerization conditions.

Table 4. Effect of Temperature and Al/Zr on the Polymerization Performance of *rac*-5

entry	temp (°C)	Al/Zr	g PE (mmol Zr)$^{-1}$ (h)$^{-1}$ (100 psi C$_2$H$_4$)$^{-1}$	M_n	M_w	PDI	BBF (per 1000 C)
1	75	250	5365	51846	166 458	3.21	2.0
2	75	500	9682	40050	133 209	3.32	1.5
3	75	1000	41 964	49261	159 448	3.23	3.0
4	65	1000	23 647	93773	254 547	2.71	2.7
5	85	1000	13 624	41335	127 310	3.10	2.0

be insensitive to changes in the Al/Zr ratio (entries 1−3). Interestingly, endgroup analysis of the samples by ^{13}C NMR reveals no detectable levels of unsaturation in the polymer, suggesting that chain transfer to aluminum (either the alumoxane or the triisobutylaluminum scavenger) is the dominant mechanism for chain termination. 1-Hexene comonomer incorporation into the polymer is relatively low, with butyl branch frequencies (BBF) in the range 1.5−3.0 per 1000 carbon atoms. Changes in the polymerization temperature and alumoxane level have no significant effect on comonomer incorporation.

The dimethyl derivative *rac*-**9** also exhibits high polymerization activity when methylalumoxane is used as a cocatalyst. At 75 °C with an Al/metal ratio of 1000, activities in the range 38 000−41 000 g PE (mmol Zr)$^{-1}$ (h)$^{-1}$ (100 psi C$_2$H$_4$)$^{-1}$ are observed. No polymerization occurs when the reaction is carried out at 95 °C (see above). As might be expected, the properties of the polymers produced by *rac*-**9** are essentially identical to those furnished by *rac*-**5**. When the polymerization is carried out in the absence of 1-hexene comonomer, the catalytic activity decreases, as expected, to 15 000 g PE (mmol Zr)$^{-1}$ (h)$^{-1}$ (100 psi C$_2$H$_4$)$^{-1}$. Polymerization also occurs when triphenylcarbenium tetrakis(pentafluorophenyl)borate is employed as a cocatalyst; in two separate experiments, activities were measured to be 4300 and 5200 g PE (mmol Zr)$^{-1}$ (h)$^{-1}$ (100 psi C$_2$H$_4$)$^{-1}$.

Summary

We have synthesized and structurally characterized new bis(phospholyl) adducts of group 4 metals, including the first example of an η^5-phospholyl complex of hafnium. In addition, we have determined that these metallocenes undergo rac/meso isomerization in a process that is accelerated by Lewis bases. Furthermore, we have shown that a bis(phospholyl)zirconium complex can serve as an effective bidentate ligand for Mo(CO)$_4$ and that the C_2-symmetric, rather than the meso, isomer binds preferentially. Finally, we have converted bis(phospholyl)zirconium dichloride complexes into the corresponding dimethyl adducts through reaction with MeMgBr, and we have established that, in the presence of MAO, both bis(phospholyl)zirconium dichloride and dimethyl complexes are active catalysts for ethylene−hexene copolymerizations.

Experimental Section

General Procedures. Solvents were distilled from the indicated drying agents: CH$_2$Cl$_2$ (CaH$_2$), Et$_2$O (Na), THF (Na), benzene (Na), and pentane (NaH). All other reagents were used as received. ^{1}H, ^{13}C, and ^{31}P nuclear magnetic resonance spectra were recorded on a Varian XL-300 spectrometer at ambient temperature. ^{1}H NMR spectra are referenced to solvent: 7.16 (C$_6$D$_6$), 7.27 (CDCl$_3$), 5.32 (CD$_2$Cl$_2$). ^{13}C NMR spectra are referenced to solvent: 54.00 (CD$_2$Cl$_2$). ^{31}P spectra

are referenced to an external standard (85% H$_3$PO$_4$, δ 0). ^{1}H data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration. All ^{13}C and ^{31}P spectra were determined with complete proton decoupling. Infrared spectra were obtained on a Perkin-Elmer Series 1600 FT-IR spectrophotometer. High-resolution mass spectra were recorded on a Finnegan MAT System 8200 spectrometer. All manipulations were performed in a nitrogen-filled glovebox or with standard Schlenk procedures under argon.

3,3′,4,4′-Tetramethyl-2,2′-diphenyl-1,1′-diphosphazirconocene Dichloride (*rac*-5). A mixture of 3,4-dimethyl-1-phenylphosphole (**3**)^{22} (0.66 g, 3.5 mmol) and *t*-BuOK (0.40 g, 4.2 mmol) in THF (3.5 mL) was heated (140 °C) with stirring in a closed Schlenk tube for 12 h. The resulting yellow solution was evaporated to dryness, and the yellow solid was then dissolved in THF (4.5 mL) and added to a precooled (−30 °C) suspension of ZrCl$_4$ (0.37 g, 1.6 mmol) in THF (9 mL), resulting in a deep green mixture. After 30 min, the reaction mixture, which had turned orange, was evaporated to dryness and then extracted with Et$_2$O (30 mL). The Et$_2$O extracts were filtered through a glass frit and evaporated to dryness. The residue was taken up in pentane (60 mL) and filtered through a bed of Celite. The eluant was evaporated to a volume of 30−35 mL; crystallization furnished 150 mg of orange crystals that were suitable for single-crystal X-ray diffraction. A second crop (180 mg) was obtained after concentrating the filtrate to 25 mL. Total yield: 0.33 g (39%).

^{1}H NMR (300 MHz, C$_6$D$_6$): 7.37 (d, 4H, J = 7.2 Hz), 7.16−7.05 (m, 6H), 6.25 (apparent dd, 2H, J = 12.9 Hz, J = 24.9 Hz), 2.22 (s, 6H), 2.06 (s, 6H). ^{13}C NMR (75 MHz, CD$_2$Cl$_2$): 153.7, 145.2, 144.4, 137.2 (apparent t, J_{C-P} = 9.1 Hz), 134.6 (m), 130.4 (apparent t, J_{C-P} = 5.2 Hz), 128.6, 128.4, 18.9, 16.2. ^{31}P (122 MHz, C$_6$D$_6$): 83.3. IR (NaCl, Nujol): 3050, 3021, 2921, 2854, 1681, 1596, 1574, 1494, 1443, 1413, 1357, 1317, 1233, 1182, 1101, 1081, 1020, 1004, 986, 946, 920, 856, 842, 821, 758, 701, 663, 630 cm^{-1}. HRMS calcd for C$_{24}$H$_{24}$Cl$_2$P$_2$Zr 534.9761, found 534.9770. Anal. Calcd: C, 53.73; H, 4.51. Found: C, 53.76; H, 4.49.

Data for the meso isomer: ^{1}H NMR (300 MHz, C$_6$D$_6$): 7.53 (d, 4H, J = 6.9 Hz), 7.16−7.05 (m, 6H), 6.67 (apparent dt, 2H, J = 39.0 Hz), 2.16 (s, 6H), 2.00 (s, 6H). ^{31}P (122 MHz, C$_6$D$_6$): 85.3.

3,3′,4,4′-Tetramethyl-2,2′-diphenyl-1,1′-diphosphahafnocene Dichloride (*rac*-6). A mixture of 3,4-dimethyl-1-phenylphosphole (**3**)^{22} (0.66 g, 3.5 mmol) and *t*-BuOK (0.40 g, 4.2 mmol) in THF (3.5 mL) was heated (140 °C) with stirring in a closed Schlenk tube for 12 h. The resulting yellow solution was evaporated to dryness, and the yellow solid was then dissolved in THF (4.5 mL) and added to a precooled (−30 °C) suspension of HfCl$_4$ (0.53 g, 1.65 mmol) in THF (9 mL), resulting in a deep green mixture. After 1 h, the reaction mixture was evaporated to dryness and then extracted with Et$_2$O (30 mL). The Et$_2$O extracts were filtered through a glass frit and evaporated to dryness. The residue was taken up in pentane (80 mL) and filtered through a bed of Celite. The eluant was evaporated to a volume of 40 mL, and Et$_2$O (20 mL) was added; crystallization furnished 250 mg (25%) of yellow crystals that were suitable for single-crystal X-ray diffraction.

(22) Breque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983−985.

^{1}H NMR (300 MHz, C$_6$D$_6$): 7.40 (d, 4H), 7.20−7.05 (m, 6H), 6.27 (apparent dd, 2H, J = 12.6 Hz, J = 24.8 Hz), 2.24 (s, 6H), 2.05 (s, 6H). ^{31}P (122 MHz, C$_6$D$_6$): 73.7. IR (NaCl, Nujol): 3053, 2923, 2856, 1598, 1577, 1496, 1455, 1402, 1314, 1173, 1160, 1082, 1034, 1008, 990, 966, 939, 913, 890, 880, 840, 824, 756, 700, 694, 661, 637 cm^{-1}. HRMS calcd for C$_{24}$H$_{24}$Cl$_2$HfP$_2$ 624.0196, found 624.0209. Anal. Calcd: C, 46.21; H, 3.88. Found: C, 46.42; H, 4.01.

Data for the meso isomer: ^{1}H NMR (300 MHz, C$_6$D$_6$): 7.57 (d, 4H), 7.20−7.05 (m, 6H), 6.65 (apparent dt, 2H, J = 38.9 Hz), 2.18 (s, 6H), 2.04 (s, 6H). ^{31}P (122 MHz, C$_6$D$_6$): 72.2.

(3,3′,4,4′-Tetramethyl-2,2′-diphenyl-1,1′-diphosphazirconocene dichloride)molybdenum(CO)$_4$ (*rac*-8). A solution of *rac*-5 (260 mg, 0.48 mmol) in benzene (10 mL) was added to (CO)$_4$Mo(nbd)[15] (145 mg, 0.48 mmol), resulting immediately in a red solution. After 10 min at room temperature, the solution was heated (75 °C) with stirring for 5.0 h in a closed Schlenk tube. Then, CH$_2$Cl$_2$ (2 mL) was added (to help dissolve the red solid), and the solution was filtered through a bed of Celite. Evaporation of the solvents furnished a deep red powder that was washed with cold pentane (2 × 1 mL). The solid was dried under vacuum overnight to provide 350 mg (97%) of *rac*-8. Crystals of *rac*-8 suitable for single-crystal X-ray diffraction were obtained through crystallization from a mixture of CH$_2$Cl$_2$ and acetonitrile.

^{1}H NMR (300 MHz, C$_6$D$_6$): 7.38 (d, 4H, J = 7.5 Hz), 7.22−7.02 (m, 6H), 5.69 (app. dd, 2H, J = 9.3 Hz, J = 20.4 Hz), 2.01 (m, 12H). ^{13}C (75 MHz, CD$_2$Cl$_2$): 213.1, 206.3 (m), 154.0 (m), 146.7, 143.3, 134.1 (apparent t, J_{C-P} = 7.1 Hz), 132.1 (m), 131.1 (apparent t, J_{C-P} = 5.2 Hz), 129.1, 129.0, 19.1, 16.1. ^{31}P (122 MHz, C$_6$D$_6$): 65.0. IR (NaCl, Nujol): 3063, 2954, 2922, 2854, 2032, 1939, 1923, 1899, 1866, 1462, 1179, 1156, 1080, 1019, 915, 867, 842, 828, 754, 697, 605, 572, 537 cm^{-1}. HRMS calcd for C$_{28}$H$_{24}$Cl$_2$MoO$_4$P$_2$Zr 743.8628, found 743.8612. Anal. Calcd: C, 45.17; H, 3.25. Found: C, 45.48; H, 3.28.

3,3′,4,4′-Tetramethyl-2,2′-diphenyl-1,1′-diphosphazirconocenedimethyl (*rac*-9). MeMgBr in Et$_2$O (3.0 M; 0.27 mL, 0.81 mmol) was added to a precooled (−30 °C) solution of *rac*-5 (195 mg, 0.36 mmol) in Et$_2$O (10 mL). The solution turned from orange to yellow and became cloudy. After 15 min, 1,4-dioxane (2 mL) was added. The suspension was filtered through a bed of Celite, and the filtrate was evaporated to dryness. Et$_2$O (2 mL) was added to the resulting yellow oil, followed by pentane (4 mL). The solution was concentrated until precipitation occurred (∼3 mL). The resulting yellow powder was collected, washed with cold pentane (2 mL), and dried in vacuo to yield 150 mg of *rac*-9 (84%).

^{1}H NMR (300 MHz, C$_6$D$_6$): 7.20−6.90 (m, 10H), 5.72 (app. dd, 2H, J = 12.3 Hz, J = 24.9 Hz), 2.13 (s, 6H), 1.96 (s, 6H), −0.37 (s, 6H). ^{13}C (75 MHz, CD$_2$Cl$_2$): 150.1, 149.5, 139.9 (apparent t, J_{C-P} = 3.1 Hz), 138.6 (apparent t, J_{C-P} = 9.5 Hz), 135.5, 129.5 (apparent t, J_{C-P} = 5.2 Hz), 128.5, 127.4, 38.6 (ZrMe$_2$), 18.6, 15.7. ^{31}P (122 MHz, C$_6$D$_6$): 62.6. IR (NaCl, Nujol): 3053, 2955, 2923, 2853, 1595, 1462, 1409, 1309, 1184, 1152, 1110, 1080, 1030, 986, 950, 912, 844, 827, 757, 699 cm^{-1}. HRMS calcd for C$_{26}$H$_{30}$P$_2$Zr 494.0870, found 494.0862.

Data for the meso isomer: ^{1}H NMR (300 MHz, C$_6$D$_6$): 7.46 (d, 4H), 7.15−6.90 (m, 6H), 5.91 (apparent dt, 2H, J = 39.0 Hz), 2.07 (s, 6H), 1.89 (s, 6H), −0.25 (s, 3H), −0.29 (s, 3H). ^{31}P (122 MHz, C$_6$D$_6$): 71.4.

(3,3′,4,4′-Tetramethyl-2,2′-diphenyl-1,1′-diphosphazirconocenedimethyl)molybdenum(CO)$_4$ (*rac*-10). MeMgBr in Et$_2$O (3.0 M; 0.22 mL, 0.66 mmol) was added to a precooled (−30 °C) solution of *rac*-8 (219 mg, 0.29 mmol) in Et$_2$O (10 mL). The solution turned from red to dark brown and became cloudy. After 1 h, 1,4-dioxane (2 mL) was added. The suspension was filtered through a bed of Celite, and the resulting brown solution was concentrated to ∼5 mL and cooled at −30 °C overnight. Orange-brown crystals were collected, washed quickly with cold pentane, and dried in vacuo to yield 70 mg of *rac*-10 (34%).

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): 7.45−7.27 (m, 10H), 5.92 (apparent dd, 2H), 2.35 (s, 6H), 2.32 (s, 6H), −0.27 (s, 6H). ^{31}P (122 MHz, CD$_2$Cl$_2$): 31.0. IR (NaCl, Nujol): 3063, 2953, 2923, 2854, 2032, 1927, 1896, 1877, 1866, 1598, 1495, 1404, 1263, 1182, 1156, 1120, 1081, 1035, 986, 917, 872, 820, 758, 740, 702, 610, 572 cm^{-1}. HRMS calcd for C$_{30}$H$_{30}$MoO$_4$P$_2$Zr 703.9720, found 703.9708.

X-ray Data Collection and Reduction. X-ray quality crystals of *rac*-5, *rac*-6, and *rac*-8 were obtained as described above. The crystals were mounted under STP and transferred to the diffractometer. A preliminary unit cell was determined for each crystal by harvesting reflections $I > 20\sigma(I)$ from three sets of 15 10-s frames.

A hemisphere of data was then collected using ω scans of 0.30°. A measure of decay was obtained by re-collecting the first 50 frames of each data set, and no statistically significant changes in the intensities of the reflections were observed in any case. The raw data frames were integrated using the program SAINT[23] with constant spot sizes of 1.6° in the detector plane and 0.6° in ω. The data were corrected for Lorentz and polarization effects, and absorption was corrected as described in Table 5.

Structure Solution and Refinement. All aspects of the solution and refinement were handled by SHELXTL NT version 5.10.[24] The structure was solved by the Patterson method for *rac*-6 and by direct methods for *rac*-5 and *rac*-8. The refinement was carried out using standard difference Fourier techniques. To distinguish between the centrosymmetric space group C2/c and the non-centrosymmetric space group Cc, *rac*-6 and *rac*-8 were solved under both space groups. Subsequent refinement of the structures showed that C2/c gave solutions with better statistics and well-behaved anisotropic thermal parameters.

All non-hydrogen atoms were located and refined anisotropically. All hydrogen atoms were included in calculated positions and refined isotropically on a riding model. The location of the largest peaks in the final difference Fourier map calculation and the magnitude of the residual electron densities in each case were of no chemical significance.

The relevant crystallographic data are summarized in Table 5.

General: Polymerizations. Methylalumoxane (4.00 M in Al in toluene) was purchased from Akzo Nobel. Triphenylcarbenium tetrakis(pentafluorophenyl)borate was purchased from Boulder Scientific and was used as received. All solvents were purified by successive passage through a bed of activated alumina and supported copper chromite deoxo catalyst (Q-5, Engelhardt Corp.).

Representative Procedure for Activation of *rac*-5 with Methylalumoxane (500:1 Al/Zr). In a glovebox, a stock solution of catalyst precursor was prepared by dissolving *rac*-5 (8.0 mg, 15 μmol) in toluene (10 mL). A 2.0 mL (3.0 μmol) aliquot of the stock solution was removed and placed in a scintillation vial, and 0.19 mL of a 4.00 M methylalumoxane solution in toluene (760 μmol) was added via syringe. After stirring at ambient temperature for 25 min, a 0.8 mL aliquot of activated catalyst (1.0 μmol Zr) was removed via syringe and injected into an autoclave reactor to which the remaining methylalumoxane had already been added.

Representative Procedure for Activation of *rac*-9 with Triphenylcarbenium Tetrakis(pentafluorophenyl)borate. Catalyst activation with triphenylcarbenium tetrakis(pentafluorophenyl)borate was carried out by dissolving a mixture of *rac*-9 (5.0 mg, 10 μmol) and triphenylcarbenium tetrakis(pentafluorophenyl)borate (9.3 mg, 10 μmol) in fluorobenzene (2 mL). A 0.50 mL aliquot of this solution (2.5 μmol)

(23) *SAINT*; Siemens Industrial Automation, Inc.: Madison, WI, 1995.
(24) *SHELXTL NT* version 5.10; Bruker AXS, Inc.: Madison, WI, 1998.

Table 5. Crystallographic Data for Complexes *rac*-5, *rac*-6, and *rac*-8[a]

	rac-5	*rac*-6	*rac*-8
empirical formula	$C_{24}H_{24}Cl_2P_2Zr$	$C_{24}H_{24}Cl_2HfP_2$	$C_{28}H_{24}Cl_2MoO_4P_2Zr$
fw	536.49	623.76	744.47
cryst size (mm)	$0.33 \times 0.24 \times 0.24$	$0.33 \times 0.09 \times 0.06$	$0.24 \times 0.12 \times 0.09$
color/shape	orange/block	yellow/plate	red/block
cryst system	monoclinic	monoclinic	monoclinic
temp (K)	177(2)	152(2)	177(2)
space group	$P2_1$/c	$C2$/c	$C2$/c
a (Å)	25.573(6)	22.7285(4)	33.050(7)
b (Å)	8.6736(13)	13.53160(10)	11.214(2)
c (Å)	22.082(6)	18.2118(4)	16.829(3)
β (deg)	104.594(14)	123.7610(10)	109.98(3)
V (Å^3)	4739.9(18)	4656.54(14)	5861(2)
Z	8	8	8
μ (mm^{-1})	0.833	4.856	1.107
abs corr	empirical	SADABS[25]	empirical
θ range (deg)	1.91–23.26	1.85–23.28	2.19–23.26
index ranges	$-24 \le h \le 26$	$-22 \le h \le 25$	$-34 \le h \le 36$
	$-8 \le k \le 9$	$-13 \le k \le 15$	$-12 \le k \le 11$
	$-17 \le l \le 24$	$-20 \le l \le 20$	$-18 \le l \le 16$
no. of reflns	14 535	9327	11 794
no. of indep reflns	6485	3343	4203
R indices $(I > 2\sigma(I))$[b,c]	R1 = 0.0484	R1 = 0.0525	R1 = 0.0482
	wR2 = 0.1048	wR2 = 0.0991	wR2 = 0.0928
R indices (all data)[b,c]	R1 = 0.0716	R1 = 0.0778	R1 = 0.0525
	wR2 = 0.1169	wR2 = 0.1085	wR2 = 0.0941
GooF[d]	1.128	1.096	1.351

[a] All data were collected on a Bruker/AXS SMART/CCD three-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). [b] R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] wR2 = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [d] GooF = $[\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$.

was placed in a stainless steel bomb for transfer into the pressurized reactor.

General Procedure for Slurry-Phase Ethylene−1-Hexene Copolymerization in a 1 L Stirred-Autoclave Reactor Using Methylalumoxane as a Cocatalyst. Dry hexane (600 mL) was added to a 1 L stirred autoclave reactor (maintained at a temperature 10 °C below the run temperature) under a nitrogen purge. 1-Hexene (43 mL), triisobutylaluminum (0.20 mL of 1.0 M solution in hexane, 200 μmol), and one-half of the designated amount of alumoxane were added successively via syringe. After stirring for approximately 10 min, a solution containing 1−10 μmol of activated catalyst was injected into the reactor via syringe, and the reactor was pressurized to 85 psi with ethylene and brought to the run temperature. Polymerization experiments were conducted with maintenance of the set temperature and pressure (85 psi) for a period of 30 min. Polymerization activities were calculated as g PE (mmol Zr)$^{-1}$ (h)$^{-1}$ (100 psi C$_2$H$_4$)$^{-1}$.

General Procedure for Slurry-Phase Ethylene−1-Hexene Copolymerization in a 1 L Stirred-Autoclave Reactor Using Triphenylcarbenium Tetrakis(pentafluorophenyl)borate as a Cocatalyst. Dry hexane (600 mL) was added to a 1 L stirred autoclave reactor (maintained at 75 °C) under a nitrogen purge. 1-Hexene (43 mL) and triisobutylaluminum (0.20 mL of 1.0 M solution in hexane, 200 μmol) were added successively via syringe. After stirring for approximately 10 min, the reactor was pressurized to 85 psi with ethylene. A

stainless steel bomb containing 2−5 μmol of activated catalyst solution was pressurized to 250 psi with nitrogen, and the solution was injected into the reactor through a dip tube. Polymerization experiments were conducted with maintenance of the set temperature (75 °C) and pressure (85 psi) for a period of 30 min. Polymerization activities were calculated as PE (mmol Zr)$^{-1}$ (h)$^{-1}$ (100 psi C$_2$H$_4$)$^{-1}$.

Note Added in Proof: After we completed this work (February 2000), in an independent study, Hollis discovered the same isomerization reaction for zirconium complex **5** and the same rate acceleration in the presence of Lewis bases. Hollis cleverly exploited this isomerization process to effect a dynamic resolution of **5** with (*R*-BINAP)Rh$^+$.[26]

Supporting Information Available: Molecular structures and numbering schemes for *rac*-5, *rac*-6, and *rac*-8. Tables describing crystal data and structure refinement, fractional atomic coordinates, bond distances and angles, anisotropic displacement parameters, hydrogen coordinates, and torsional angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010256T

(25) *SADABS*: Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38.

(26) Hollis, T. K.; Wang, L.-S.; Tham, F. *J. Am. Chem. Soc.* **2000**, *122*, 11737−11738.