Zirconium Complexes Containing Tetradentate O,P,P,O Ligands: Ethylene and Propylene Polymerization Studies

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The synthesis of a series of zirconium complexes bearing a linear diphosphanyl-bisphenoxide O,P,P,O ligand is described. The diphosphanyl-bisphenol proligand was prepared from $Ph(Cl)PC_2H_4P(Cl)Ph$ as a 1:1 mixture of *rac* and *meso* diastereomers, which could be separated as a result of their differing solubilities in methanol. A relatively low barrier to phosphine inversion ($\Delta G^{\ddagger}_{373K} = 28.02(3)$ kcal/mol) allows interconversion of the two isomers. The zirconium dichloride complex of each diastereomer was prepared via treatment of $ZrCl_4(THF)_2$ with the sodium (*rac*) or lithium (*meso*) salt of the respective bisphenol. Crystallographic and NMR analyses revealed a *cis*-α structure for the complex bearing the *rac*-O,P,P,O ligand and a seven-coordinate quasi-*cis*-*β* structure for the complex derived from the *meso*-O,P,P,O ligand. Dibenzyl complexes were synthesized by treatment of $Zr(CH_2Ph)_4$ with the *rac* and *meso* bisphenols; NMR evidence revealed *cis*-α and fluxional *cis*-*β* structures, respectively. Reactions of the dibenzyl complexes with $[CPh_3][B(C_6F_5)_4]$ afforded cationic alkyl derivatives in which the pre-existing ligand geometries were maintained. Ethylene polymerization studies afforded productivities up to 5450 and 116 g/mmol·h·bar for the *cis*-α and *cis*-*β* complexes, respectively, when using $[CPh_3][B(C_6F_5)_4]/Al(^iBu)_3$ as the activator. Under a propylene atmosphere, oligomeric products were obtained with low to moderate productivities.

Introduction

C_2-Symmetric *ansa*-metallocenes are capable of generating highly isotactic polyolefins. This is, in part, due to the rigid coordination sphere enforced by the bridge between the two cyclopentadienyl rings, which helps to maintain the catalyst geometry throughout the growth of a polymer chain. In the continuing search for new catalysts, linear tetradentate ligands offer a feasible alternative to cyclopentadienyl ligands, as they are capable of generating rigid chirality at a metal center[1] and hence have potential for stereoselective olefin enchainment. That said, there are still a number of structural isomers that can form, as shown in Figure 1. The binding mode depends *inter alia* upon the nature of the donors, the size of the metal ion, the nature of the interdonor linkages, and the spatial requirements of the ligand framework.

Bis-aryloxide ligands, with or without additional neutral donors, are well suited to group 4 metal catalysts and have been studied extensively.[2] Diimino-bisphenoxide, or salen-type, complexes typically give *trans* structures, although *cis* configurations can be accessed using less flexible N,N linkages.[3] Their saturated analogues, or salan-type ligands, are more flexible, and group 4 metal complexes have been shown to adopt the *cis*-α configuration.[4,5] **A** (Bn = CH_2Ph) is an example of the latter case and has been shown to give isotactic poly(α-olefins).

Nitrogen donors have been replaced by alternative hetereoatoms. The titanium dithioether-bisphenoxide complex **B** (R = R′ = H, B = C_2H_4) has been shown to possess a *cis*-*β* structure.[6a] However, ligand substituents can switch the coordination mode to *cis*-α, although Δ−Λ interconversion can occur for all but the bulkiest complexes (R = ^{t}Bu, cumyl).[5b−5m] These complexes are active for the isospecific polymerization of styrenes. It is of note that when B = C_3H_6 the coordination mode switches back to *cis*-*β*. Analogous diether-bisphenoxide complexes have not been extensively studied.[6a] However, a patent disclosure by Symyx Technologies reports that bridged biaryl O,O,O,O hafnium complexes **C** are capable of showing high isoselectivity for propylene polymerization, even at elevated temperature.[7]

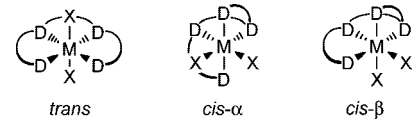

Figure 1. Structural isomers in octahedral complexes containing a linear tetradentate ligand.

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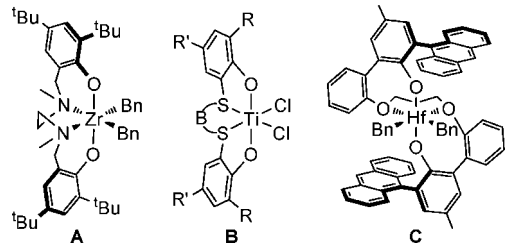
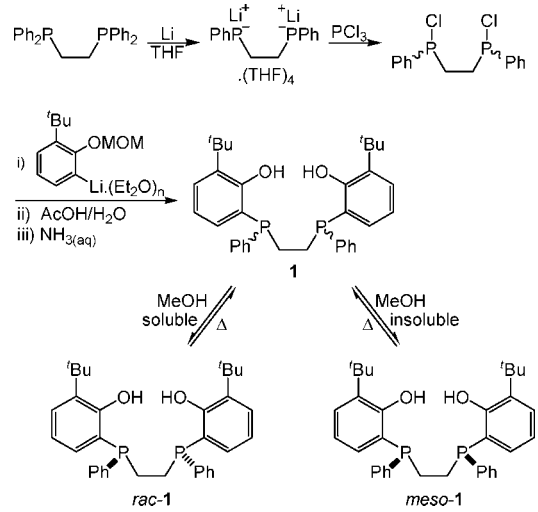


We have recently reported the synthesis and characterization of a series of group 4 metal complexes containing two bidentate O,P phosphanylphenoxide ligands and evaluated their capacity for olefin polymerization.[8] Of special note was a *tert*-butyl-substituted zirconium derivative, which gave excellent productivities for propylene polymerization, but essentially atactic polymer. NMR studies on cationic alkyl derivatives indicated that the active species is highly fluxional. Therefore, in order to enhance the potential for stereoselective insertion chemistry, we decided to target tetradentate ligands in which the O,P units are linked by an alkylene backbone. It was anticipated that the greater rigidity of the tetradentate ligand frame might allow a well-defined coordination environment to be maintained throughout the polymerization process.

Results and Discussion

Ligand Synthesis. The targeted diphosphanyl-bisphenol **1** (see Scheme 1) included *tert*-butyl groups *ortho* to the phenols and an ethylene bridge between the phosphines.[9] The synthetic pathway involved treating commercially available $Ph_2PC_2H_4PPh_2$ with an excess of lithium to give $[PhPC_2H_4PPh]^{2-}Li^{+}_2(THF)_4$,[10] which was then treated with PCl_3 at −78 °C to give $Ph(Cl)PC_2H_4P(Cl)Ph$ as a white solid.[11,12] Reaction of the latter with *ortho*-lithiated MOM-protected 2-*tert*-butylphenol gave the MOM-protected bisphenol *in situ*. Deprotection using AcOH/H_2O, followed by treatment with ammonia, afforded the desired diphosphanyl-bisphenol as a 1:1 mixture of *rac* and *meso* isomers ($^{31}P(CDCl_3)$ −43.3 and −43.5 ppm, respectively). Conveniently, the two diastereomers could be separated by their differing solubilities in methanol. The insoluble product was assigned as the *meso* isomer by X-ray crystallography (see Supporting Information).

Scheme 1. Synthesis of a Diphosphanyl-bisphenol



Since the maximum yield of either isomer using this route was limited to 50%, the temperature required to induce inversion at phosphorus, and hence interconversion of the isomers, was probed by heating a solution of *meso*-**1** in toluene/C_6D_6 (5:1) to 100 °C. After heating for 45 min a near 1:1 mixture of diastereomers was observed, indicating a relatively facile inversion of the phosphorus centers. Repeating the process over shorter time intervals gave a rate of inversion, k_{inv}, at 100 °C of $2.98(11) \times 10^{-4}$ s^{-1}, corresponding to a Gibbs free energy of activation ($\Delta G^{\ddagger}_{373K}$) of 28.02(3) kcal/mol, which is somewhat lower than in other biaryl-alkyl-phosphines (typically 29.1−30.8 kcal/mol at 403 K).[13] The fortuitous consequence of this accessible barrier is that, following isomer separation, the unwanted isomer can be recycled to a diastereotopic mixture, allowing further batches of the desired isomer to be isolated.

Complex Synthesis. The zirconium dichloride complex **2** was synthesized by treating *rac*-**1** with an excess of NaH followed by $ZrCl_4(THF)_2$ (Scheme 2). The disodium salt of *meso*-**1** was insoluble in THF; hence its zirconium complex **3** was synthe-

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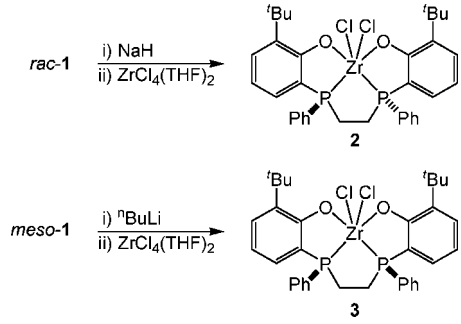
Scheme 2. Synthesis of Diphosphanyl-bisphenoxide Zirconium Dichloride Complexes



sized via reaction of the dilithium salt (generated using ^{n}BuLi) with $ZrCl_4(THF)_2$. Recrystallization from DCM/pentane gave analytically pure, air- and moisture-sensitive samples of both complexes. Crystals suitable for X-ray structure determinations were grown by slow diffusion of pentane into DCM solutions of the complexes.

The X-ray crystal structure of **2** (Figure 2) shows the metal center to have a distorted octahedral geometry (*cis* angles in the range 67.83(3)−109.63(4)°, Table 1), with the tetradentate ligand adopting a *cis*-α coordination mode, characterized by the two end donors [O(1) and O(2)] being mutually *trans*. This coordination mode gives approximate C_2 symmetry to the complex about an axis that passes through the metal center and bisects the Cl(1)−Zr−Cl(2) angle. The only notable feature of the bonding at the metal center is that the Zr−P(2) distance of 2.8602(10) Å is statistically significantly longer than that of Zr−P(1) [2.7865(10) Å]. This may be associated with the noticeably different folds of the two five-membered C_2OPZr chelate rings. For both the P(1)/O(1) and P(2)/O(2) rings, the $\{C_2OP\}$ atoms are coplanar to better than 0.01 Å, but whereas for the former the metal lies ca. 0.32 Å out of this plane [in the direction of P(2)], for the latter the metal lies only ca. 0.05 Å out of this plane [in the direction of P(1)]. The C_2P_2Zr ring has a twisted conformation, C(7) and C(8) lying ca. 0.44 and 0.28 Å "above" and "below" the $\{P_2Zr\}$ plane, respectively (in the structure shown in Figure 2 this ring has a λ-twist, but the crystal contains an equal number of complexes with a δ-twist).

The solid-state structure of **3** revealed an unexpected C_i-symmetric dinuclear complex with a pair of seven-coordinate zirconium centers bridged by two chlorine atoms (Figure 3). The geometry at the metal center is distorted pentagonal

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2

Zr−O(2)	1.989(3)	Zr−P(1)	2.7865(10)
Zr−Cl(1)	2.4001(10)	Zr−P(2)	2.8602(10)
Zr−O(1)	1.996(3)	Zr−Cl(2)	2.3981(10)
Cl(1)−Zr−Cl(2)	109.63(4)	Cl(1)−Zr−P(1)	151.78(4)
Cl(1)−Zr−P(2)	91.58(3)	Cl(1)−Zr−O(1)	93.31(8)
Cl(1)−Zr−O(2)	100.70(8)	Cl(2)−Zr−P(1)	95.59(4)
Cl(2)−Zr−P(2)	154.86(4)	Cl(2)−Zr−O(1)	98.21(8)
Cl(2)−Zr−O(2)	92.85(8)	P(1)−Zr−P(2)	67.83(3)
P(1)−Zr−O(1)	70.08(8)	P(1)−Zr−O(2)	90.16(8)
P(2)−Zr−O(2)	69.37(8)	P(2)−Zr−O(1)	93.71(8)
O(1)−Zr−O(2)	158.11(11)		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3

Zr−O(1)	2.0324(12)	Zr−Cl(2)	2.6234(5)
Zr−O(2)	2.0125(11)	Zr−Cl(2A)	2.6495(5)
Zr−P(1)	2.7425(5)	Cl(2)···Cl(2A)	3.1884(8)
Zr−P(2)	2.7746(5)	Zr···ZrA	4.1998(5)
Zr−Cl(1)	2.4437(5)		
Cl(1)−Zr−Cl(2)	91.814(17)	Cl(1)−Zr−P(1)	84.564(15)
Cl(1)−Zr−P(2)	85.072(18)	Cl(1)−Zr−O(1)	108.17(4)
Cl(1)−Zr−O(2)	154.59(3)	Cl(1)−Zr−Cl(2A)	91.776(18)
Cl(2)−Zr−P(1)	143.292(14)	Cl(2)−Zr−P(2)	146.858(14)
Cl(2)−Zr−O(1)	77.51(3)	Cl(2)−Zr−O(2)	111.09(3)
Cl(2)−Zr−Cl(2A)	74.409(16)	P(1)−Zr−P(2)	69.345(14)
P(1)−Zr−O(1)	69.15(3)	P(1)−Zr−O(2)	83.27(3)
P(1)−Zr−Cl(2A)	142.067(14)	P(2)−Zr−O(1)	134.69(3)
P(2)−Zr−O(2)	69.78(3)	P(2)−Zr−Cl(2A)	72.726(15)
O(1)−Zr−O(2)	88.11(5)	O(1)−Zr−Cl(2A)	145.90(3)
O(2)−Zr−Cl(2A)	84.33(3)	Zr−Cl(2)−ZrA	105.591(16)

bipyramidal with Cl(1) and O(2) in the axial sites [the Cl(1)−Zr−O(2) angle is 154.59(3)°]. Much of the distortion in the coordination geometry is in the equatorial plane, where O(1) lies ca. 0.71 Å out of the {Zr,P(1),P(2),Cl(2),Cl(2A)} plane, which is coplanar to within ca. 0.06 Å. Both of the five-membered C_2OPZr chelate rings have folded geometries, with the metal lying out of the associated $\{C_2OP\}$ plane which in each case is coplanar to within ca. 0.02 Å. For the O(1)/P(1) ring, the metal is displaced by ca. 0.88 Å towards O(2), while for the O(2)/P(2) ring the metal is displaced by ca. 0.32 Å in the direction of Cl(2a). The C_2P_2Zr ring again has a twisted conformation, C(7) and C(8) lying ca. 0.59 and 0.20 Å "below" and "above" the $\{P_2Zr\}$ plane, respectively (in the structure shown in Figure 3 this ring has a λ-twist, but because of the center of symmetry, the P(1A)/P(2A) ring has a δ-twist). The two Zr−P bonds are asymmetric, with that to P(2) [2.7746(5) Å] being ca. 0.03 Å longer than that to P(1) [2.7425(5) Å] (Table 2). This is probably caused by the differing *trans* environments. The Zr−O bonds are also different, with that to the equatorial oxygen O(1) [2.0324(12) Å] ca. 0.02 Å longer than that to its axial counterpart O(2) [2.0125(11) Å]. The central Zr_2Cl_2 ring is perfectly planar and has an asymmetric geometry, the two

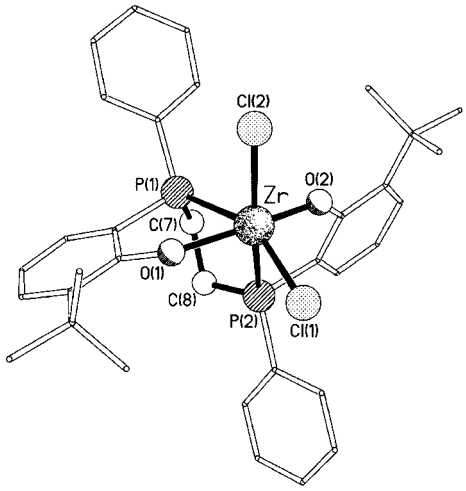


Figure 2. Molecular structure of **2**.

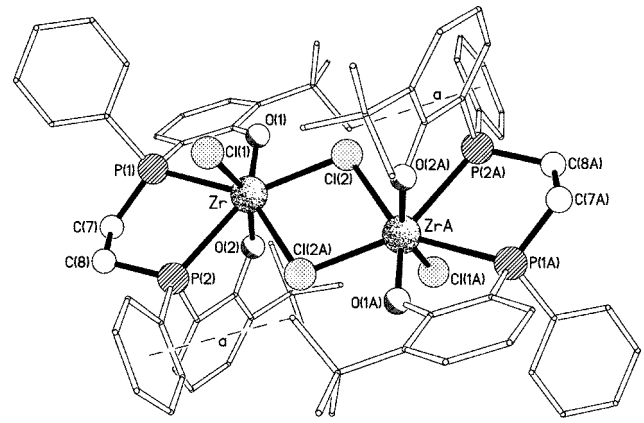


Figure 3. Molecular structure of **3**.

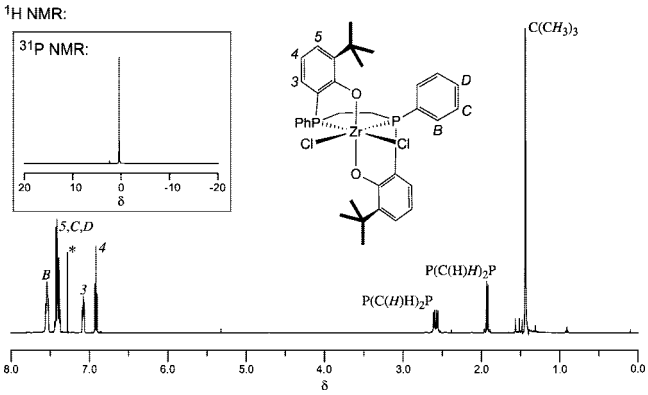


Figure 4. ^{1}H and ^{31}P NMR spectra of **2** in $CDCl_3$ (*).

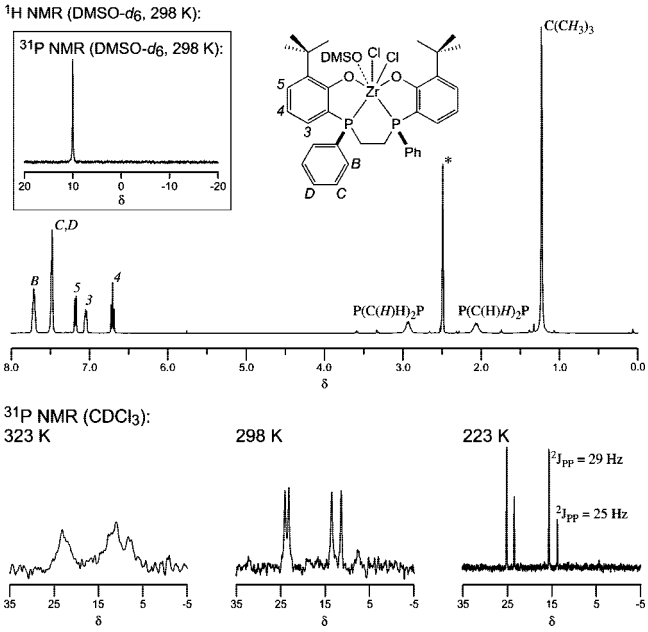
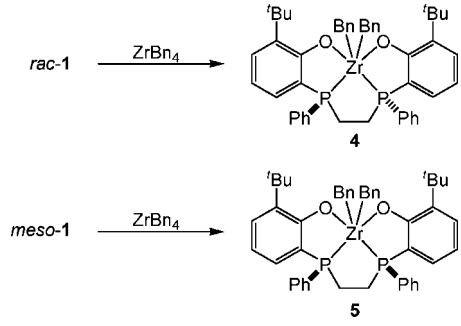


Figure 5. Variable-temperature ^{1}H and ^{31}P NMR spectra of **3** in $CDCl_3$ and DMSO-d_6 (*).

Scheme 3. Synthesis of Diphosphanyl-bisphenoxide Zirconium Dibenzyl Complexes (Bn = CH_2Ph)



Zr−Cl bonds differing by ca. 0.03 Å [Zr−Cl(2) 2.6234(5) Å, Zr−Cl(2A) 2.6495(5) Å]. The bond to the terminal chlorine Cl(1) is, unsurprisingly, much shorter at 2.4437(5) Å. The transannular Zr···ZrA and Cl(2)···Cl(2A) distances [4.1998(5) and 3.1884(8) Å, respectively] differ by more than 1 Å, and this disparity is reflected in the angles within the ring [Zr−Cl(2)−ZrA 105.591(16)°, Cl(2)−Zr−Cl(2A) 74.409(16)°]. The conformation of the complex is stabilized by a pair of C−H···π contacts (**a** in Figure 3), with one of the methyl protons of the O(1) *tert*-butyl unit approaching the centroid of the P(2) bound phenyl ring with an H···π separation of ca. 3.12 Å and a C−H···π angle of ca. 144°, the H···π vector being inclined by ca. 70° to the ring plane.

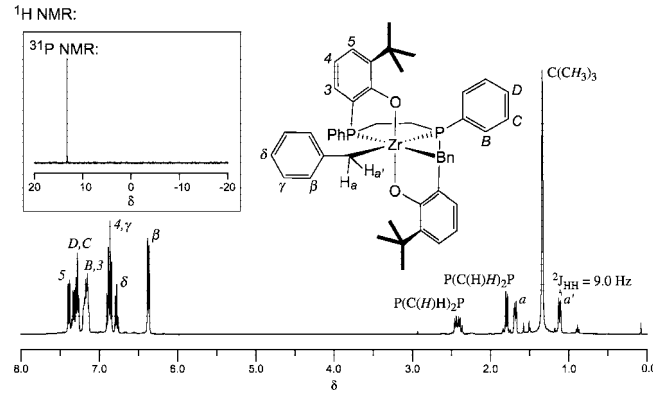


Figure 6. ^{1}H and ^{31}P NMR spectra of **4** in $CDCl_3$.

The solution-state structure of **2** is consistent with the C_2-symmetric *cis*-α structure found in the solid state. The ^{1}H NMR spectrum showed one set of aromatic signals and two resonances for the inequivalent protons of the ethylene bridge, while the ^{31}P NMR spectrum gave a single resonance (Figure 4). The behavior of **3** in solution is more complicated. The room temperature ^{31}P NMR ($CDCl_3$) spectrum at 323 K showed severely broadened signals (Figure 5), which resolve to two sets of doublets at 223 K, suggesting that two asymmetric species are present in solution. A solution equilibrium between the dimer species identified in the solid state and its monomeric relative, accompanied by intramolecular fluxional processes, may account for these observations. In DMSO-d_6 single, sharp peaks were observed in both the ^{1}H and ^{31}P NMR spectra, consistent with the donor solvent breaking up any aggregated species to give a monomeric complex. The observation of only one ^{31}P signal for **3** in DMSO suggests that the complex is highly fluxional on the NMR time scale in this solvent.

Reaction of *rac*-**1** and *meso*-**1** with $ZrBn_4$ at −78 °C afforded the zirconium dibenzyl complexes **4** and **5**, respectively (Scheme 3), as analytically pure yellow solids that were highly sensitive to air and moisture and also decomposed at room temperature in the presence of light. The geometries of these complexes was probed by NMR techniques. In addition to a single set of signals for the benzyl ligands, the ^{1}H and ^{31}P NMR spectra of **4** were comparable to those of its dichloro analogue **2**, pointing to a *cis*-α configuration (Figure 6). The ^{1}H-coupled ^{13}C NMR spectrum revealed a $^1J_{CH}$ coupling constant of 128 Hz for the benzylic carbon, indicating equivalent benzyl ligands coordinated in an undistorted η^1 fashion.[14] The ^{1}H and ^{31}P NMR spectra of **5** at room temperature showed single resonances for the *tert*-butyl groups and phosphorus donors, consistent with rapid exchange (Figure 7). At low temperature there was significant broadening in the ^{1}H NMR spectrum and two broad signals in the ^{31}P spectrum, consistent with a *cis*-β ground state.

(13) Baechler, R. D.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 3090.
(14) Values above 130 Hz indicate some distortion of the benzyl ligand. Examples of Zr complexes in which a solution state η^2-interaction has been confirmed by X-ray analysis include: (a) Tsurugi, H.; Matsuo, Y.; Yamsgata, T.; Mashima, K. *Organometallics* **2004**, *23*, 2797. (b) Shao, P.; Gendron, R. A. L.; Berg, D. J.; Bushnell, G. W. *Organometallics* **2000**, *19*, 509. (c) Bei, X. H.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3282. (d) Crowther, D. J.; Borkowsky, S. L.; Swenson, D.; Meyer, T. Y.; Jordan, R. F. *Organometallics* **1993**, *12*, 2897. (e) Jordan, R. F.; Lapointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. J. *Am. Chem. Soc.* **1987**, *109*, 4111. (f) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902.

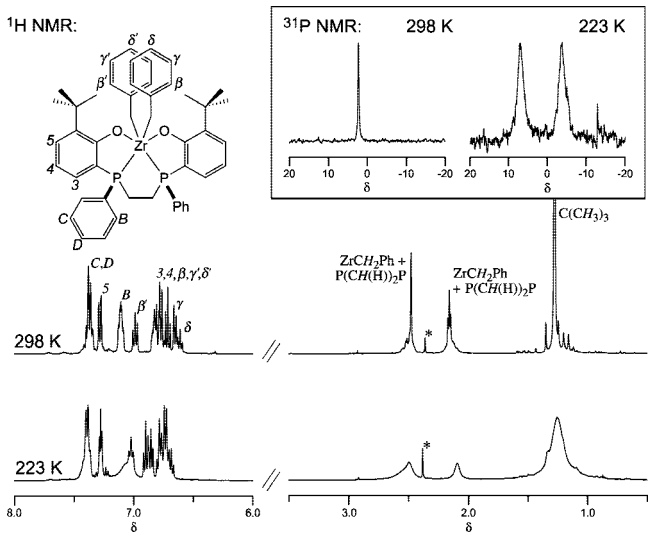


Figure 7. Variable-temperature ^{1}H and ^{31}P NMR spectra of **5** in $CDCl_3$. * = residual toluene.

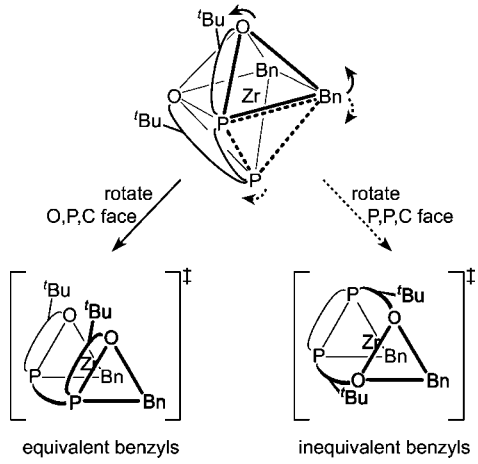


Figure 8. Transition states of O,P,C and P,P,C trigonal face rotation in **5**.

Significantly, since two sets of signals are observed for the benzyl ligands in the ^{1}H NMR spectrum at room temperature, P−P exchange must occur via rotation of a P,P,C trigonal face, not a O,P,C face, which would give equivalent benzyls in the transition state (see Figure 8).

Some insight into the nature of the catalytically active species derived from diphosphanyl-bisphenoxide complexes was obtained by treating **4** and **5** with $[CPh_3][B(C_6F_5)_4]$ at room temperature in NMR-scale reactions in C_6D_5Br. Included in the ^{1}H NMR spectrum of **4**/$[CPh_3][B(C_6F_5)_4]$ (Figure 9a) are two *tert*-butyl and four ethylene bridge signals. These, combined with the observation of two doublets in the ^{31}P spectrum, are consistent with a square-pyramidal structure in which the benzyl ligand does not migrate to and from the vacant site (although coordination of the solvent at this site cannot be ruled out).[15] The NMR spectra of **5**/$[CPh_3][B(C_6F_5)_4]$ (Figure 9b) were consistent with a highly fluxional complex with one *tert*-butyl and one phosphine signal in the ^{1}H and ^{31}P NMR spectra, respectively. Neither cationic species was sufficiently stable to obtain ^{1}H-coupled ^{13}C NMR spectra. However, the upfield shift of some of the aromatic signals in the ^{1}H NMR spectrum of **5**/$[CPh_3][B(C_6F_5)_4]$ suggests η^2-coordination of the remaining benzyl ligand.

(15) The ^{19}F NMR spectrum indicated no anion−cation interactions.

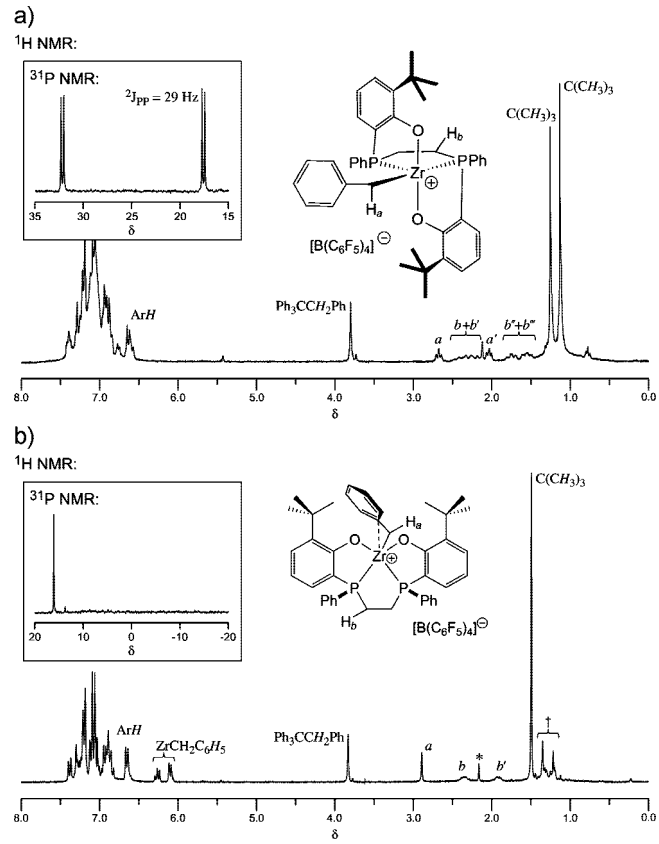


Figure 9. ^{1}H and ^{31}P NMR spectra of (a) **4**/$[CPh_3][B(C_6F_5)_4]$ and (b) **5**/$[CPh_3][B(C_6F_5)_4]$ in C_6D_5Br. * = residual toluene; † = residual pentane.

Olefin Polymerization. Ethylene polymerization studies using **2**−**5** were performed with either MAO or $[CPh_3][B(C_6F_5)_4]$ as the cocatalyst; the results are collected in Table 3. Conditions for **4** and **5** were optimized using *in situ* generated precatalysts (**4′** and **5′**) and then compared to catalysts generated from the isolated complexes. When MAO was used as the cocatalyst, the *rac*-O,P,P,O-containing complexes **2** and **4′** gave low productivities and a mixture of low molecular weight oligomers ($\leq C_{14}$) along with a high molecular weight polymeric fraction consistent with multiple propagating species. In contrast, activation of **4′** with $[CPh_3][B(C_6F_5)_4]$ gave a highly active, long-lived catalyst that exclusively gave the same oligomeric products as **4′**/MAO, suggesting that the active species responsible for the polymeric product is formed via a side reaction with the aluminoxane cocatalyst. Increasing the polymerization temperature to 50 °C improved the activity of **4′**/$[CPh_3][B(C_6F_5)_4]$ to 5570 g/mmol·h·bar (a comparable activity of 5450 g/mmol·h·bar was obtained with **4**/$[CPh_3][B(C_6F_5)_4]$). The GC trace of the liquid products is shown in Figure 10. In addition to linear α-olefins a large number of branched products are formed, indicative of efficient re-incorporation of the olefinic products. For instance, the C6 fraction contains 2-ethyl-1-butene, which is a dimerization product of ethylene and 1-butene.

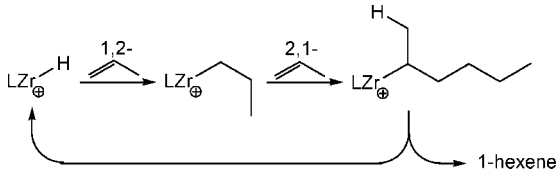
The *meso*-O,P,P,O-containing complexes **3** and **5′** also gave high molecular weight polymer when activated with MAO. Only a slight increase in activity (up to 116 g/mmol·h·bar) was observed by switching to the boron activator, although the molecular weight of the product dropped substantially to around 600 g/mol. Analysis of this product by ^{13}C NMR spectroscopy revealed a linear structure terminated by isobutyl and *n*-alkyl end-groups, consistent with chain transfer to Al^{i}Bu$_3$ acting as the sole termination mechanism.

Table 3. Ethylene Polymerization Using 2−5[a]

entry	precatalyst (loading (μmol))	cocatalyst	temp (°C)	liquid product[b] (g)	solid product[c] (g)	activity[d] (g/mmol·h·bar)	M_n[e] (kg/mol)	M_w[e] (kg/mol)	M_w/M_n
1	**2** (5)	MAO	25	0.30	0.11	41		>2000	
2	**4′** (5)	MAO	25	0.42	0.09	51		>2000	
3	**4′** (1)	$[CPh_3][B(C_6F_5)_4]$	25	2.75		1380			
4	**4′** (1)	$[CPh_3][B(C_6F_5)_4]$	50	11.14		5570			
5	**4** (1)	$[CPh_3][B(C_6F_5)_4]$	50	10.89		5450			
6	**3** (5)	MAO	25		0.11	11		>2000	
7	**5′** (5)	MAO	25		0.16	16		>2000	
8	**5′** (5)	$[CPh_3][B(C_6F_5)_4]$	25		0.80	80	0.5	1.1	2.2
9	**5′** (5)	$[CPh_3][B(C_6F_5)_4]$	50		1.07	107	0.4	0.7	1.8
10	**5** (5)	$[CPh_3][B(C_6F_5)_4]$	50		1.16	116	0.6	0.7	1.2

[a] Polymerization conditions: glass reactor with mechanical stirrer, MAO (2.5 mmol) or $[CPh_3][B(C_6F_5)_4]$ (1 equiv) with Al^iBu_3 (0.5 mmol), toluene (200 mL), 2 bar ethylene, 1 h. [b] Fraction analyzable by GC. [c] Obtained by precipitation with methanol. [d] Based on total yield. [e] Determined by high-throughput GPC.

Scheme 4. Dimerization of Propylene to 1-Hexene



Under a propylene atmosphere[16] at 50 °C, **4**/$[CPh_3][B(C_6F_5)_4]$ gave predominantly 1-hexene (84 wt %) with a productivity of 211 g/mmol·h·bar. The C6 product is presumed to arise via a 1,2-insertion of propylene into a zirconium hydride followed by a 2,1-insertion and finally β-hydrogen transfer (Scheme 4). Higher oligomer fractions (up to around C_{30}; see Supporting Information for GC traces) were obtained using **5**/$[CPh_3][B(C_6F_5)_4]$, although the productivity was notably reduced (43 g/mmol·h·bar at 50 °C).

The dramatic drop in productivity and molecular weight observed with these O,P,P,O catalysts compared to the previously reported bis(O,P) zirconium catalyst (up to 49 000 g/mmol·h·bar and $M_n = 8-17$ kg/mol)[9] is likely to be a consequence of a more open coordination sphere caused by tethering of the phosphine donors with the relatively short ethylene bridge. A more open coordination sphere can accelerate β-hydrogen termination reactions and allow unrestricted access to chain transfer agents. It is also consistent with the efficient incorporation of higher olefins seen from polymerizations using **4**/$[CPh_3][B(C_6F_5)_4]$.

Conclusions

A new diphosphanyl-bisphenoxide ligand has been introduced. Unlike their nitrogen donor relatives, i.e., the bis(amino)diphenoxide or salan ligand family, the large barrier to inversion at tertiary phosphorus, compared to those found in tertiary amines, allows the stabilization of *rac* and *meso* isomers. Differing solubilities for these isomers allowed for their convenient separation. The resultant zirconium dichloride and dibenzyl complexes selectively adopt a *cis*-α coordination mode for the *rac* isomer and *cis*-β for the *meso* isomer. Having the facility to change the coordination geometry of a complex without changing the ligand substituents is a unique feature of this class of tetradentate ligand, a facet that should readily lend itself to other areas of transition and main group metal catalysis.

The *cis*-α complex, when treated with $[CPh_3][B(C_6F_5)_4]$, showed good ethylene oligomerization and propylene dimerization activities. Less steric hindrance around the active metal center can explain the drop in molecular weight on tethering two bidentate O,P ligands to form one O,P,P,O ligand. Changing the size and electronic characteristics of the substituents attached to the *ortho* position of the phenoxide donors and the P donors, as well as modulating the length of the unit bridging the phosphorus centers, can be anticipated to have a marked affect on the productivities, product distribution, and stereoselectivities afforded by this catalyst system.

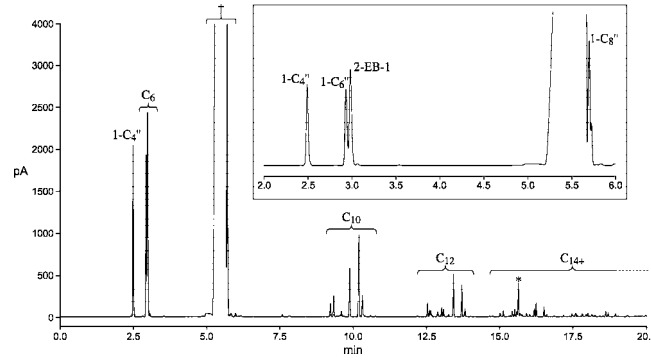


Figure 10. GC trace from **4**/$[CPh_3][B(C_6F_5)_4]$ and ethylene at 50 °C. 1-C_n'' = *n* carbon linear 1-alkene, C_n = *n* carbon product, 2-EB-1 = 2-ethyl-1-butene, * = GC reference, † = toluene eluent.

Experimental Methods

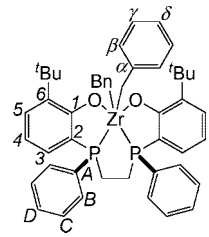
General Considerations. $ZrCl_4(THF)_2$ and $Zr(CH_2Ph)_4$ were synthesized according to a published procedures.[17] Air-sensitive procedures were performed under nitrogen using standard Schlenk techniques with solvents being distilled over standard drying agents and degassed before use. Deuterated solvents were dried and stored over 4 Å molecular sieves. Ethylene (CP grade) and propylene (instrument grade) were purified by passing them through an Oxytrap and a gas drier (Alltech Associates). Lithium wire (3.2 mm diam., ~0.01% Na) was purchased from Aldrich Chemical Co. Compounds were analyzed by NMR [Bruker AC-250, Bruker DRX-400, Bruker Avance-400, or Bruker Avance-500 spectrometer (referenced to solvent resonances for ^1H and ^{13}C NMR and externally to 85% $H_3PO_{4(aq)}$ and $CFCl_3$ for ^{31}P and ^{19}F NMR, respectively)]; IR [Perkin-Elmer 1760X FT-IR]; and mass spectrometry [Autospec Q spectrometer]. Elemental analyses were performed at London Metropolitan University. Liquid oligomers were analyzed by GC [Agilent 6890 gas chromatograph with a HP-5 column (30 m × 0.32 mm, film thickness 0.25 μm)] and quantified against a known mass of 2,2,4,4,6,8,8-heptamethylnonane. Solid oligomer/polymer samples were analyzed by ^{13}C NMR [Bruker Avance-400 spectrometer (in a 2:1 (by weight) mixture of 1,2,4-

(16) Conditions: Schlenk, magnetic stirring, 10 μmol of catalyst, heptane (100 mL), Al^iBu_3 (0.25 mmol), 2 bar of propylene, 50 °C, 1 h.

(17) (a) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135. (b) Felten, J. J.; Anderson, W. P. J. *Organomet. Chem.* **1972**, *36*, 87.

$C_6H_3Cl_3$/1,1,2,2-$C_2D_2Cl_4$ at 130 °C using a pulse delay of 15 s)] and GPC [Polymer Laboratories GPC-220 with PLgel HTS-B column (160 °C, 1,2,4-trichlorotoluene, run time = 6 min, PS standards)].

The numbering scheme below is used in the assignments of the O,P,P,O ligands and complexes:



$[PhPC_2H_4PPh]^{2-}Li^{+}_2(THF)_4$. A solution of 1,2-bis(diphenylphosphinoethane) (9.96 g, 25 mmol) in THF (100 mL) was added slowly to a rapidly stirred THF suspension of Li (1.75 g, 250 mmol). The mixture was allowed to warm to room temperature and stirred for 12 h. The mixture was decanted from the excess Li and the solvent reduced by half and cooled to −15 °C. The yellow precipitate was collected by filtration, washed with cold THF (30 mL) and pentane (2 × 25 mL), and then dried under vacuum (10.53 g, 19.3 mmol, 77% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.69 (d, $^3J_{HH}$ = 7.2 Hz, 4H, Ar-*H*), 7.12 (t, J_{HH} = 7.6 Hz, 4H, Ar-*H*), 6.72 (br, 2H, Ar-*H*), 3.36 (m, 16H, OCH_2CH_2), 3.10 (br, 4H, PCH_2), 1.25 (m, 16H, OCH_2CH_2). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ −71−(−86) (br m).

$Ph(Cl)PC_2H_4P(Cl)Ph$. To an ether (40 mL) solution of $[PhPC_2H_4PPh]^{2-}\cdot Li^{+}_2\cdot(THF)_4$ (3.63 g, 6.64 mmol) cooled to −78 °C was slowly added PCl_3 (2.9 mL, 33.2 mmol). The mixture was stirred for 30 min at −78 °C and 30 min at 25 °C. The suspension was filtered and the solvent removed from the filtrate. The resultant colorless product (50:50 mix of *rac* and *meso* diastereomers) was washed with cold pentane and dried under vacuum (1.38 g, 4.38 mmol, 66% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.41−7.36 (m, 4H, Ar-*H*), 7.02−6.95 (m, 6H, Ar-*H*), 2.19−1.83 (m, 4H, PCH_2). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 92.4 (s), 91.8 (s).

2-Methoxymethoxy-3-*tert*-butylphenyl lithium·$(Et_2O)_n$. To an ether solution (150 mL) of 1-*tert*-butyl-2-methoxymethoxybenzene (23.4 g, 120 mmol) cooled to 0 °C was added *n*-butyllithium (2.5 M in hexanes; 48 mL, 120 mmol). The mixture was stirred overnight at room temperature, giving a yellow solution and colorless precipitate. All volatiles were removed under vaccum. The product was triturated with pentane (50 mL) for 3 h and then filtered, washed with pentane (2 × 50 mL), and dried under vacuum (22.1 g, 80.5 mmol, 67% yield). ^{1}H NMR (250 MHz, C_6D_6): δ 7.92 (d, $^3J_{HH}$ = 5.0 Hz, 1H, Ar-*H*), 7.35 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ar-*H*), 7.25−7.18 (m, 1H, Ar-*H*), 5.33 (s, 2H, OCH_2O), 2.97 (q, $^3J_{HH}$ = 7.0 Hz, 4nH, OCH_2CH_3), 2.80 (s, 3H, OCH_3), 1.60 (s, 9H, $C(CH_3)_3$), 0.82 (t, $^3J_{HH}$ = 7.0 Hz, 6nH, OCH_2CH_3).

2,2′-[1,2-Ethanediylbis(phenylphosphinidene)]bis(6-*tert*-butyl)phenol, 1. An ether (10 mL) solution of 2-methoxymethoxy-3-*tert*-butylphenyl lithium·$(Et_2O)_n$ (n = 0.92; 0.867 g, 3.23 mmol) was added dropwise to a suspension of $Ph(Cl)PC_2H_4P(Cl)Ph$ (0.504 g, 1.60 mmol) in ether (15 mL) cooled to −78 °C. The mixture was stirred for 30 min at −78 °C and 30 min at 25 °C. The solvent was removed and the residue dissolved in 9:1 AcOH/H_2O (50 mL) and heated to 110 °C for 2 h. All volatiles were removed under vacuum and degassed EtOAc and $NH_{3(aq)}$ (25 mL) added. The mixture was stirred for 1 h, after which the organic fraction was separated and washed with $NH_{3(aq)}$ (25 mL) and H_2O (25 mL), dried ($MgSO_4$), and filtered. The solvent was removed to give a 1:1 diastereotopic mixture of the product as a white powder (0.746 g, 1.37 mmol, 86% yield).

***meso*-1.** A diastereotopic mixture of **1** was triturated with degassed methanol (25 mL) and then filtered to give insoluble *meso*-**1** as a colorless powder (44% yield). Anal. Calcd (%) for $C_{34}H_{40}O_2P_2$ (542.64): C, 75.26; H, 7.43. Found: C, 75.33; H, 7.34. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.29 (m, 12H, Ar-$H_{(5,B,C,D)}$). 7.16 (pt, J = 5.9 Hz, 2H, O*H*), 6.98−6.94 (m, 2H, Ar-$H_{(3)}$), 6.82 (pt, J = 7.6 Hz, 2H, Ar-$H_{(4)}$), 2.22−2.08 (m, 4H, PCH_2), 1.42 (s, 18H, $C(CH_3)_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 158.7 (pt, J_{CP} = 10.3 Hz, Ar-$C_{(1)}$), 136.5 (Ar-$C_{(6/A)}$), 136.0 (Ar-$C_{(6/A)}$), 131.8 (pt, J_{CP} = 8.6 Hz, Ar-$C_{(B)}$), 130.3 (Ar-$C_{(3)}$), 129.0 (Ar-$C_{(5)}$), 128.6 (d, $^3J_{CP}$ = 3.9 Hz, Ar-$C_{(C)}$), 128.6 (Ar-$C_{(D)}$), 120.9 (Ar-$C_{(2)}$), 120.4 (Ar-$C_{(4)}$), 34.9 ($C(CH_3)_3$), 29.5 ($C(CH_3)_3$), 22.8 (PCH_2). ^{31}P{^{1}H} NMR (101 MHz, $CDCl_3$): δ −43.5 (s). MS (FAB; *m*/*z*): 543 (15%) $[M]^+$, 285 (75%) $[M - P(Ph)(({}^t Bu)C_6H_3OH)]^+$, 77 (100%) $[Ph]^+$. IR (KBr; cm^{-1}): 3393br (OH). Crystals suitable for X-ray structural determination were grown from slow diffusion of pentane into a DCM solution.

***rac*-1.** A diastereotopic mixture of **1** was triturated with degassed methanol (25 mL) and then filtered. The filtrate was reduced in volume to ca. 10 mL, cooled, and filtered to give *rac*-**1** as a colorless powder (32% yield). Anal. Calcd (%) for $C_{34}H_{40}O_2P_2$ (542.64): C, 75.26; H, 7.43. Found: C, 75.39; H, 7.51. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.29 (m, 12H, Ar-$H_{(5,B,C,D)}$). 7.18 (pt, J = 5.9 Hz, 2H, O*H*), 6.94−6.91 (m, 2H, Ar-$H_{(3)}$), 6.82 (pt, J = 7.6 Hz, 2H, Ar-$H_{(4)}$), 2.21−2.04 (m, 4H, PCH_2), 1.41 (s, 18H, $C(CH_3)_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 158.9 (pt, J_{CP} = 10.4 Hz, Ar-$C_{(1)}$), 136.5 (Ar-$C_{(6/A)}$), 136.2 (Ar-$C_{(6/A)}$), 131.7 (pt, J_{CP} = 8.5 Hz, Ar-$C_{(B)}$), 130.3 (Ar-$C_{(3)}$), 129.0 (Ar-$C_{(5)}$), 128.6 (Ar-$C_{(C)}$ + Ar-$C_{(D)}$), 120.4 (Ar-$C_{(4)}$), 120.2 (Ar-$C_{(2)}$), 34.9 ($C(CH_3)_3$), 29.5 ($C(CH_3)_3$), 22.6 (PCH_2). ^{31}P{^{1}H} NMR (101 MHz, $CDCl_3$): δ −43.3 (s). MS (FAB; *m*/*z*): 543 (75%) $[M]^+$, 285 (100%) $[M - P(Ph)(({}^t Bu)C_6H_3OH)]^+$. IR (KBr; cm^{-1}): 3398br (OH).

[*rac*-2,2′-{1,2-Ethanediylbis(phenylphosphinidene)}bis(6-*tert*-butyl)phenoxide]zirconium dichloride, 2. A THF (20 mL) solution of *rac*-**1** (0.326 g, 0.60 mmol) was added dropwise to a suspension of NaH (36 mg, 1.5 mmol) in THF (10 mL) at 0 °C. The mixture was stirred at room temperature for 3 h and then filtered. The excess NaH was washed with THF, and the combined THF fractions were added dropwise to a THF (20 mL) solution of $ZrCl_4(THF)_2$ (0.226 g, 0.60 mmol) at −78 °C. The mixture was allowed to warm to room temperature over 12 h and the solvent then removed under vacuum. The residue was extracted with DCM (20 mL) and the filtrate reduced in volume to around 5 mL. Pentane (20 mL) was added and the resultant precipitate filtered, washed with pentane (10 mL), and dried under vacuum to give a colorless precipitate. Recrystallization from DCM/pentane gave **2** (0.309 g, 0.44 mmol, 74% yield). Anal. Calcd (%) for $C_{34}H_{38}Cl_2O_2P_2Zr$ (702.74): C, 58.11; H, 5.45. Found: C, 57.98; H, 5.54. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54−7.50 (m, 4H, Ar-$H_{(B)}$), 7.42−7.35 (m, 8H, Ar-$H_{(5,C,D)}$), 7.07−7.04 (m, 2H, Ar-$H_{(3)}$), 6.90 (pt, J = 7.5 Hz, 2H, Ar-$H_{(4)}$), 2.56 (dd, $^2J_{HH}$ = 19.8 Hz, $^3J_{HH}$ = 8.5 Hz, 2H, PC*H*(H)), 1.94−1.87 (m, 2H, PCH(*H*)), 1.42 (s, 18H, $C(CH_3)_3$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 168.8 (pt, J = 12.1 Hz, Ar-$C_{(1)}$), 138.7 (Ar-$C_{(6)}$), 131.7 (pt, J = 5.9 Hz, Ar-$C_{(B)}$), 130.8 (Ar-$C_{(5/D)}$), 130.5 (Ar-$C_{(5/D)}$), 129.9 (pt, J_{CP} = 18.0 Hz, Ar-$C_{(A)}$), 129.6 (Ar-$C_{(3)}$), 128.8 (pt, J_{CP} = 4.5 Hz, Ar-$C_{(C)}$), 121.4 (Ar-$C_{(4)}$), 120.7 (pt, J_{CP} = 18.5 Hz, Ar-$C_{(2)}$), 35.0 ($C(CH_3)_3$), 29.3 ($C(CH_3)_3$), 23.1 (pt, J_{CP} = 13.5 Hz, PCH_2). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 0.6 (s). Crystals suitable for X-ray structural determination were grown from slow diffusion of pentane into a DCM solution.

[*meso*-2,2′-{1,2-Ethanediylbis(phenylphosphinidene)}bis(6-*tert*-butyl)phenoxide]zirconium dichloride, 3. To a THF (20 mL) solution of *meso*-**1** (0.326 g, 0.60 mmol) cooled to −78 °C was added *n*-BuLi (2.5 M in hexanes; 0.48 mL, 1.20 mmol) dropwise. The mixture was allowed to warm to room temperature over 12 h and then filtered. The filtrate was added dropwise to a THF (20 mL) solution of $ZrCl_4(THF)_2$ (0.226 g, 0.60 mmol) at −78 °C. The mixture was allowed to warm to room temperature over 12 h and the solvent then removed under vacuum. The residue was extracted with DCM (20 mL) and the filtrate reduced in volume to around 5 mL. Pentane (20 mL) was added and the resultant precipitate filtered, washed with pentane (10 mL), and dried under vacuum to give a colorless precipitate. Recrystallization from DCM/pentane gave **3** (0.274 g, 0.39

mmol, 65% yield). Anal. Calcd (%) for $C_{34}H_{38}Cl_2O_2P_2Zr$ (702.74): C, 58.11; H, 5.45. Found: C, 58.04; H, 5.34. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.70−7.67 (m, 4H, Ar-$H_{(B)}$), 7.49−7.46 (m, 6H, Ar-$H_{(C,D)}$), 7.17 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, Ar-$H_{(5)}$), 7.05−7.02 (m, 2H, Ar-$H_{(3)}$), 6.69 (pt, J = 8.0 Hz, 2H, Ar-$H_{(4)}$), 2.94 (br, 2H, PCH(H)), 2.06 (br, 2H, PCH(H)), 1.22 (s, 18H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6): δ 168.7 (m, Ar-$C_{(1)}$), 136.7 (Ar-$C_{(6)}$), 132.0−131.8 (m, Ar-$C_{(A,B)}$), 129.9, 129.7, 128.6 (Ar-$C_{(3,5,6)}$), 128.6 (Ar-$C_{(C)}$), 123.7 (m, Ar-$C_{(2)}$), 119.6 (Ar-$C_{(4)}$), 34.5(C(CH$_3$)$_3$), 29.4 (C(CH_3)$_3$), 23.9 (m, PCH_2). ^{31}P{^{1}H} NMR (242 MHz, $CDCl_3$, 323 K): δ 22.2 (br), 10.9 (br), 8.3 (br). ^{31}P{^{1}H} NMR (242 MHz, $CDCl_3$, 298 K): δ 24.0 (s), 23.2 (s), 13.5 (s), 11.4 (s). ^{31}P{^{1}H} NMR (242 MHz, $CDCl_3$, 223 K): δ 25.1 (d, $^2J_{PP}$ = 29 Hz), 23.4 (d, $^2J_{PP}$ = 25 Hz), 15.6 (d, $^2J_{PP}$ = 29 Hz), 13.7 (d, $^2J_{PP}$ = 25 Hz). ^{31}P{^{1}H} NMR (202 MHz, DMSO-d_6): δ 10.0 (s).

[*rac*-2,2′-{1,2-Ethanediylbis(phenylphosphinidene)}bis(6-*tert*-butyl)phenoxide]zirconium dibenzyl, 4. [Reaction performed in the absence of light] To a mixture of *rac*-**1** (135 mg, 0.25 mmol) and $ZrBn_4$ (113 mg, 0.25 mmol) cooled to −78 °C was added toluene (10 mL) cooled to −78 °C. The reaction mixture was stirred for 1 h at −78 °C and 30 min at room temperature. The solvent was removed under vacuum and the yellow residue triturated with pentane at 0 °C. The mixture was filtered and dried under vacuum to give **4** as a yellow powder (123 mg, 0.15 mmol, 60% yield). Anal. Calcd (%) for $C_{48}H_{52}O_2P_2Zr$ (814.10): C, 70.82; H, 6.44. Found: C, 70.69; H, 6.33. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, Ar-$H_{(5)}$), 7.35−7.26 (m, 6H, Ar-$H_{(C,D)}$), 7.20−7.13 (m, 6H, Ar-$H_{(3,B)}$), 6.90−6.87 (m, 6H, Ar-$H_{(4,\gamma)}$), 6.77 (t, $^3J_{HH}$ = 7.2 Hz, 2H, Ar-$H_{(\delta)}$), 6.37 (d, $^3J_{HH}$ = 7.3 Hz, 4H, Ar-$H_{(\beta)}$), 2.42 (dd, $^2J_{HH}$ = 19.1 Hz, $^3J_{HH}$ = 8.0 Hz, 2H, PC(H)H), 1.80 (m, 2H, PC(H)H), 1.68 (d, $^2J_{HH}$ = 8.9 Hz, 2H, ZrC(H)HPh), 1.34 (s, 18H, C(CH_3)$_3$), 1.11 (d, $^2J_{HH}$ = 9.0 Hz, 2H, ZrC(H)HPh). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 169.3 (pt, J = 12.4 Hz, Ar-$C_{(1)}$), 143.9 (Ar-$C_{(\alpha)}$), 137.7 (Ar-$C_{(6)}$), 132.6 (pt, J = 16.8 Hz, Ar-$C_{(A)}$), 131.2 (pt, J = 5.6 Hz, Ar-$C_{(B)}$), 130.5 (Ar-$C_{(3)}$), 130.0 (Ar-$C_{(5)}$), 129.7 ((Ar-$C_{(\gamma)}$), 128.9 (Ar-$C_{(D)}$), 128.4 (pt, J = 4.2 Hz, Ar-$C_{(C)}$), 127.2 (Ar-$C_{(\beta)}$), 121.9 (Ar-$C_{(\delta)}$), 120.0 (pt, J = 16.7 Hz, Ar-$C_{(2)}$), 119.7 (Ar-$C_{(4)}$), 55.3 (ZrCH$_2$Ph), 34.9 (C(CH$_3$)$_3$), 29.3 (C(CH$_3$)$_3$), 25.1 (pt, J = 12.5 Hz, PCH$_2$). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 13.2 (s).

[*meso*-2,2′-{1,2-Ethanediylbis(phenylphosphinidene)}bis(6-*tert*-butyl)phenoxide]zirconium dibenzyl, 5. [Reaction performed in the absence of light] To a mixture of *meso*-**1** (136 mg, 0.25 mmol) and $ZrBn_4$ (115 mg, 0.25 mmol) cooled to −78 °C was added toluene (10 mL) cooled to −78 °C. The reaction mixture was stirred for 1 h at −78 °C and 30 min at room temperature. The solvent was removed under vacuum and the yellow residue triturated with pentane at 0 °C. The mixture was filtered and dried under vacuum to give **5** as a yellow powder (150 mg, 0.18 mmol, 73% yield). Anal. Calcd (%) for $C_{48}H_{52}O_2P_2Zr$ (814.10): C, 70.82; H, 6.44. Found: C, 70.74; H, 6.32. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.41−7.34 (m, 6H, Ar-$H_{(C,D)}$), 7.28 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, Ar-$H_{(5)}$), 7.12−7.08 (m, 4H, Ar-$H_{(B)}$), 6.98 (pt, J = 7.7 Hz, 2H, Ar-$H_{(\beta')}$), 6.89−6.74 (m, 7H, Ar-$H_{(3,\beta,\gamma',\delta')}$), 6.70 (t, $^3J_{HH}$ = 7.5 Hz, 2H, Ar-$H_{(4)}$), 6.65 (d, $^3J_{HH}$ = 7.3 Hz, 2H, Ar-$H_{(\gamma)}$), 6.60 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Ar-$H_{(\delta)}$), 2.55−2.45 (s + br, 4H, ZrCH_2Ph + PC(H)H), 2.17−2.13 (t + br, J = 4.8 Hz, 4H, ZrCH_2Ph + PC(H)H), 1.28 (s, 18H, C(CH_3)$_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 223 K): δ 7.43−7.32 (br m, 6H, Ar-H), 7.26 (d, J = 9.0 Hz, 2H, Ar-H), 7.15−6.95 (br + t, J = 9.0 Hz, 6H, Ar-H), 6.90−6.83 (m, 4H, Ar-H), 6.79−6.65 (m, 8H, Ar-H), 2.48 (br, 6H, 3 × CH_2), 2.08 (br, 2H, CH_2), 1.24 (br, 18H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 168.3 (br, Ar-$C_{(1)}$), 147.4 (Ar-$C_{(\alpha')}$), 142.7 (Ar-$C_{(\alpha)}$), 137.8 (Ar-$C_{(6)}$), 131.7 (pt, J = 6.0 Hz, Ar-$C_{(B)}$), 129.9 (Ar-$C_{(5)}$), 129.7 (Ar-$C_{(D)}$), 129.5 (Ar-$C_{(\beta')}$), 129.4 (Ar-$C_{(\beta)}$), 128.7 (pt, J = 4.3 Hz, Ar-$C_{(C)}$), 128.2 (Ar-$C_{(3)}$), 127.3 (Ar-$C_{(\gamma')}$), 126.9 (Ar-$C_{(\gamma)}$), 121.1 (Ar-$C_{(\delta')}$), 120.8 (Ar-$C_{(\delta)}$), 120.1 (Ar-$C_{(4)}$), 65.4−65.2 (m, ZrCH$_2$Ph), 61.8 (ZrCH$_2$Ph), 34.9 (C(CH$_3$)$_3$), 29.5 (C(CH$_3$)$_3$), 25.9−25.5 (m, PCH$_2$). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 298 K): δ 2.3 (s). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 223 K): δ 7.4 (br s), −3.6 (br s).

NMR Reactions Using [CPh$_3$][B(C$_6$F$_5$)$_4$]. In a nitrogen-filled glovebox, a C_6D_5Br solution of [CPh$_3$][B(C$_6$F$_5$)$_4$] (1 equiv) was added to a C_6D_5Br solution of **4** or **5** (1 equiv) at 25 °C. The orange solution was transferred to an NMR tube fitted with a Youngs tap valve. The NMR data were acquired immediately.

4/[CPh$_3$][B(C$_6$F$_5$)$_4$]. ^{1}H NMR (250 MHz, C_6D_5Br): δ 7.34−6.73 (m, 38H, Ar-H). 6.64−6.56 (m, 3H, Ar-H). 3.82 (s, 2H, Ph$_3$CCH_2Ph), 2.70 (t, J = 8.0 Hz, 1H, ZrC(H)HPh), 2.51−2.12 (m, 2H, PC(H)H), 2.18 (t, J = 7.5 Hz, 1H, ZrC(H)HPh), 1.79 (t, J = 15.0 Hz, 1H, PC(H)H), 1.58 (t, J = 14.7 Hz, 1H, PC(H)H), 1.28 (s, 9H, C(CH_3)$_3$), 1.15 (s, 9H, C(CH_3)$_3$). ^{31}P{^{1}H} NMR (101 MHz, C_6D_5Br): δ 32.5 (d, $^2J_{PP}$ = 29 Hz), 17.9 (d, $^2J_{PP}$ = 29 Hz). ^{19}F{^{1}H} NMR (235 MHz, C_6D_5Br): −136.0 (s, o-BC$_6F_5$), −166.4 (t, $^3J_{FF}$ = 21.1 Hz, p-BC$_6F_5$), −170.2 (pt, J = 17.9 Hz, m-BC$_6F_5$).

5/[CPh$_3$][B(C$_6$F$_5$)$_4$]. ^{1}H NMR (250 MHz, C_6D_5Br): δ 7.36 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Ar-H), 7.28−6.80 (m, 32H, Ar-H), 6.65−6.58 (m, 4H, Ar-H), 6.24 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Ar-H), 6.08 (d, $^3J_{HH}$ = 6.8 Hz, 2H, Ar-H), 3.81 (s, 2H, Ph$_3$CCH_2Ph), 2.87 (s, 2H, ZrCH_2Ph), 2.33 (br, 2H, PC(H)H), 1.89 (br, 2H, PC(H)H), 1.48 (s, 18H, C(CH_3)$_3$). ^{31}P{^{1}H} NMR (101 MHz, C_6D_5Br): δ 16.5 (s). ^{19}F{^{1}H} NMR (235 MHz, C_6D_5Br): δ −135.9 (s, o-BC$_6F_5$), −166.2 (t, $^3J_{FF}$ = 21.2 Hz, p-BC$_6F_5$), −170.0 (pt, J = 18.1 Hz, m-BC$_6F_5$).

Ethylene Oligo/polymerization. A 400 mL glass Fischer−Porter vessel was dried at 50 °C for 12 h. The Fischer−Porter head, equipped with an injection port (fitted with a rubber septum), pressure gauge, and mechanical stirrer was flame dried for 5 min and fitted to the glass vessel. The reactor was then purged with nitrogen for 45 min and then charged with solvent, purged with 1 bar of ethylene overpressure for 5 min (to give 2 bar total ethylene pressure), and placed in a water bath at the required temperature, allowing 10 min for the temperature to equilibrate. Scavenger (MAO or Al^{i}Bu$_3$) was then introduced at least 5 min before catalyst injection. A solution of precatalyst (for polymerizations using MAO) or activated catalyst (for polymerizations using [CPh$_3$][B(C$_6$F$_5$)$_4$]) in toluene was introduced via syringe to initiate the polymerization. The reaction mixture was rapidly stirred throughout. Polymerizations were terminated by venting of the overpressure followed by addition of 5 mL of 2 M HCl$_{(aq)}$. A sample of the reaction mixture was taken for GC analysis. The solid product was precipitated from the mixture by addition of MeOH (400 mL). After filtration the polymer was washed with a large quantity of MeOH and dried under vacuum at 60 °C for 12 h.

Propylene Oligomerization. A Schlenk, containing 100 mL of heptane and a magnetic stirrer and fitted with a rubber septum, was purged under 1 bar propylene overpressure for 5 min (to give 2 bar total propylene pressure). Al^{i}Bu$_3$ was added as a scavenger and the temperature of the vessel adjusted using a water bath to 50 °C. A toluene solution of precatalyst treated with [CPh$_3$][B(C$_6$F$_5$)$_4$] was introduced via syringe to initiate the polymerization. The reaction mixture was rapidly stirred throughout. Polymerizations were terminated by venting of the overpressure followed by addition of 5 mL of 2 M HCl$_{(aq)}$. A sample of the reaction mixture was taken for GC analysis.

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Supporting Information Available: Crystallographic data for *meso*-**1**, **2**, and **3**; kinetic data for phosphine inversion; GC traces for oligomeric products; and polymer NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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