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Combining Hard and Soft Donors in Early-Transition-Metal Olefin Polymerization Catalysts

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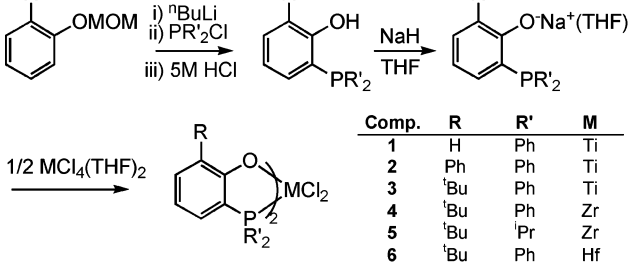
Bis(phosphanylphenoxide) complexes of the group 4 metals, upon activation by methylaluminoxane, are highly active for ethylene and propylene polymerization; a zirconium derivative possesses one of the highest propylene polymerization activities found to date for a nonmetallocene system.

Following the ground-breaking advances provided by *ansa*-metallocenes in solution-based stereoselective olefin polymerizations,[1] attention has more recently turned toward the development of nonmetallocene systems with the capacity to control polyolefin tacticity.[2−11] Among the more significant recent developments are bis(phenoxyimine) complexes of the group 4 metals,[2−5] bridged bis(biaryl) O,O,O,O complexes of hafnium,[10] and cyclometalated N,N,C ligands attached to hafnium.[11] These catalyst systems employ hard phenoxide and amido donors coupled with relatively hard first-row donors. Recent discoveries have suggested that there may be a surprising advantage to using ligands that contain softer second-row donors in early-transition-metal-based catalysts.[12] With this in mind, we decided to investigate group 4 metal complexes containing two bidentate ligands combining phenoxide and tertiary phosphine donors. Such bis-ligand complexes would parallel the highly active group 4 metal phenoxyimine systems introduced by Fujita and co-workers and offer the possibility of a new class of early-transition-metal polymerization catalysts with the potential to influence tacticity.

Using known methodology, the *o*-phosphanylphenols shown in Scheme 1 were synthesized from the corresponding ortho-substituted phenols.[13] These were then converted to sodium salts using NaH and reacted with MCl$_4$(THF)$_2$ (M = Ti, Zr, and Hf; THF = tetrahydrofuran) to give the desired complexes **1**−**6** (Scheme 1).

Scheme 1. Synthesis of Bis(*o*-phosphanylphenoxide)M(IV) Dichloride Complexes (OMOM = OCH$_2$OCH$_3$)



Comp.	R	R'	M
1	H	Ph	Ti
2	Ph	Ph	Ti
3	^{t}Bu	Ph	Ti
4	^{t}Bu	Ph	Zr
5	^{t}Bu	^{i}Pr	Zr
6	^{t}Bu	Ph	Hf

Single-crystal X-ray structures of **1**, **5**, and **6** (Figure 1) show the metal center in each case to possess a distorted octahedral coordination geometry with cis angles in the ranges 74.57(11)−102.22(12)° (**1**), 69.33(4)−119.70(4)° (**5**), and 69.66(10)−103.34(4)° (**6**); in each case, the most acute

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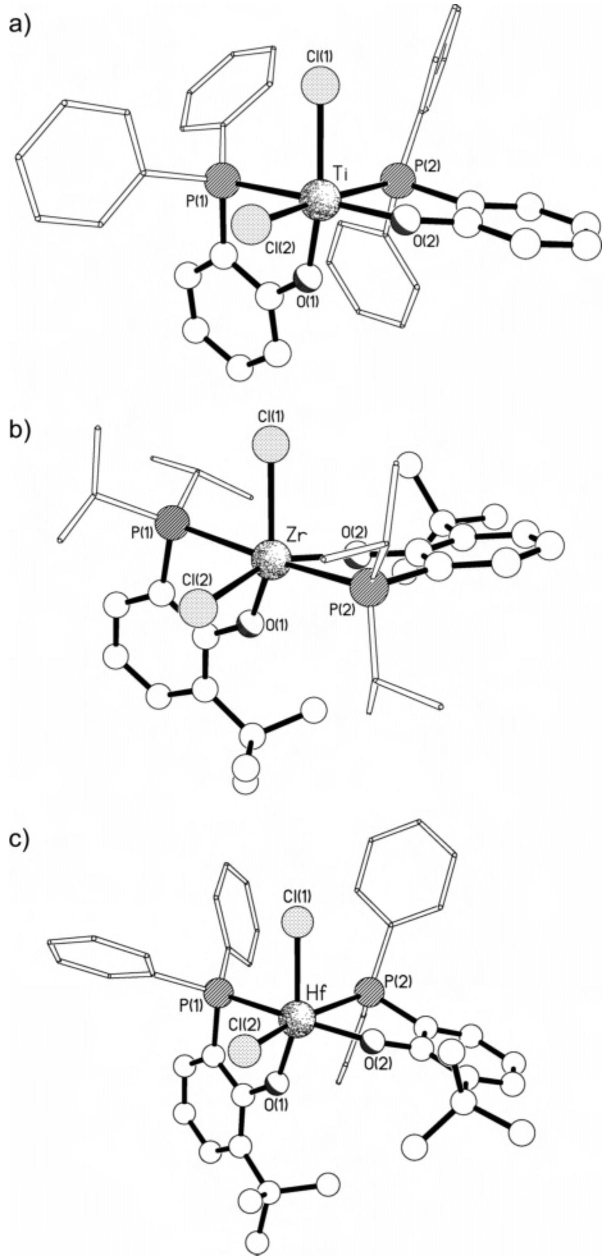


Figure 1. Molecular structures of (a) **1**, (b) **5**, and (c) **6**, showing the differing ligand displacements (H atoms omitted for clarity). Key bond lengths are given in Table 1.

Table 1. Selected Bond Lengths (Å) for **1**, **5**, and **6**

	1 (M = Ti)	**5** (M = Zr)	**6** (M = Hf)
M−Cl(1)	2.3192(16)	2.4422(6)	2.4060(12)
M−Cl(2)	2.2707(16)	2.4378(8)	2.4058(11)
M−P(1)	2.6527(16)	2.8005(6)	2.7954(11)
M−P(2)	2.7293(15)	2.8156(7)	2.8628(11)
M−O(1)	1.869(4)	1.9965(12)	1.989(3)
M−O(2)	1.839(4)	1.9988(12)	1.956(3)

angles correspond to the bite of the chelating phosphanylphenoxide ligand.

Of most interest is the arrangement of the ligands around the metal centers. While in all three complexes the chloro ligands lie mutually cis, the two chelating phosphanylphenoxide ligands adopt differing relative positions. In **1** and **6**, P(1) is trans to oxygen and O(1) is trans to chlorine, while P(2) is trans to chlorine and O(2) trans to phosphorus, affording molecular C_1 symmetry. By contrast, in **5** the two P,O ligands have identical chemical environments, with the structure having molecular C_2 symmetry. However, rather than an *O*,*O*-trans configuration, as seen in the bis(phenoxy-imine) metal systems, a *P*,*P*-trans configuration is observed with the phenoxy donors trans to the chlorines. The bond distances for the three structures (Table 1) reflect the differing ionic radii for Ti^{IV}, Zr^{IV}, and Hf^{IV} (0.68, 0.79, and 0.78 Å, respectively) and the different trans environments of the donor atoms but do not reveal any obvious cause for the change in the coordination geometry.

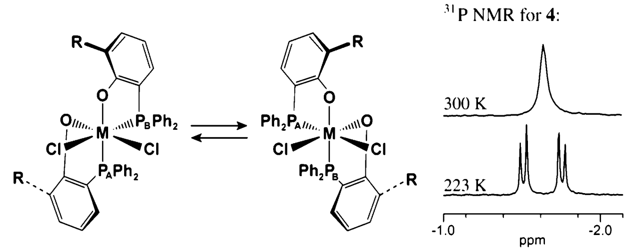
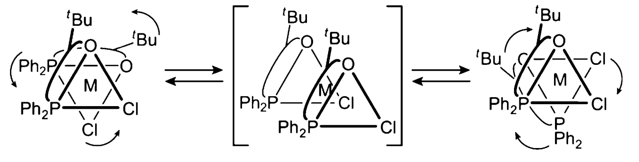


Figure 2. Scheme illustrating P−P exchange in **1**−**4** and **6**. The ^{31}P NMR spectrum (toluene-d_8) of **4** is shown at ambient and low temperatures.



	3	**4**	**6**
$\Delta H^{\ddagger}$ (kcal/mol)	12.3(2)	11.5(2)	10.8(1)
$\Delta S^{\ddagger}$ (cal/K.mol)	-12.6(5)	-3.4(6)	-8.3(5)
$\Delta G^{\ddagger}_{298K}$ (kcal/mol)	16.1(3)	12.5(3)	13.3(3)

Figure 3. Key activation parameters for the P−P exchange process in **3**, **4**, and **6** and illustration of the proposed nondissociative pathway.

^{31}P NMR spectroscopy provides a convenient method of assessing the geometries of these and other $(P,O)_2MCl_2$ complexes in solution. For a C_1-symmetric, all-cis complex, two doublets would be anticipated for the two inequivalent but coupled phosphorus environments. However, only **3** gave this pattern; ^{31}P NMR spectra of **1**, **2**, and **4**−**6** all showed a single ^{31}P resonance suggestive of an averaging process in solution.

To investigate this further, variable-temperature ^{31}P NMR spectra were recorded. At low temperatures, **1**−**4** and **6** afforded two coupled doublets consistent with a C_1-symmetric ground state, whereas **5** still afforded a sharp singlet in accordance with the ground-state structure established by crystallography. At ambient temperature, the single ^{31}P resonances for **1**−**4** and **6** must arise from a rapid P−P exchange process (Figure 2), the energetics of which were probed for **3**, **4**, and **6** using ^{31}P NMR data measured over the temperature range 203−363 K in toluene-d_8; the activation parameters are tabulated in Figure 3.[14] Negative $\Delta S^{\ddagger}$ values are found in all cases, indicating transition states that are more ordered than their ground states and implying a nondissociative mechanism. It is thus likely that a series of

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(14) Rates of P−P exchange were obtained by line-shape analysis using WINDNMR v7.1.6 © 2002 Hans J. Reich. For full kinetic data and plots, see the Supporting Information.

Table 2. Ethylene Polymerization Results for Complexes **1**−**6**^{a}

precatalyst (loading/μmol)	MAO loading (mmol)	yield PE (g)	activity^{b}	M_n^{c} (kg/mol)	M_w^{c} (kg/mol)	M_w/M_n
1 (5.0)	2.50	0.41	41	1.9	529	278^{d}
2 (5.0)	2.50	6.15	615	19.2	44.5	2.32
3 (5.0)	2.50	3.90	390	782	1370	1.75
4 (0.1)	2.50	2.24	11200	8.2	21.0	2.56
4 (0.1)	1.25	5.34	26700	12.0	71.8	5.98
5 (5.0)	2.50	0.35	35	1.0^{e}	109^{e}	109^{e}
6 (1.0)	2.50	1.10	550	1.0^{f}	8.3^{f}	8.3^{f}
6 (1.0)	1.25	2.13	1070	2.0^{g}	228^{g}	114^{g}

[a] Conditions: 400-mL Fisher-Porter glass reactor, mechanical stirring, toluene (200 mL), 2 bar ethylene, 25 °C, 1 h. [b] Activities in gPE/mmol·h·bar. [c] Determined by high-throughput GPC versus PS standards. [d] Multimodal distribution. [e] Bimodal distribution, $M_{pk} = 0.50$ and 25.9 kg/mol. [f] Bimodal distribution, $M_{pk} = 0.55$ and 10.5 kg/mol. [g] Trimodal distribution, $M_{pk} =$ 1.10, 18.6, and 562 kg/mol.

Bailar twists[15] occur via a trigonal-prismatic C_{2v} transition state in which both phosphorus atoms are equivalent. A general schematic of this process is shown in Figure 3. The barrier to the exchange process is likely to be strongly influenced by the steric congestion arising when the bulky *tert*-butyl groups pass close to each other in the trigonal-prismatic transition state.

Complexes **1**−**6**, upon activation with methylaluminoxane (MAO), are active for ethylene polymerization (Table 2). A bulky ortho substituent in the phenoxide donor is clearly beneficial to the activity of the titanium-based catalysts (**1**−**3**/MAO) as well as the molecular weight of the resultant polyethylene. Replacing a proton substituent by phenyl or *tert*-butyl groups affords order of magnitude increases in the molecular weight with concurrent decreases in the polydispersity index (PDI). The zirconium-based catalyst, **4**/MAO, was found to be highly active (26 700 gPE/mmol·h·bar; PE = polyethylene), with sub-micromolar quantities of catalyst required to prevent excessive exotherms and polymer yields. At reduced precatalyst loadings, the concentration of the cocatalyst also had to be reduced to achieve optimal activity. Altering the phosphine substituents from phenyl to isopropyl gave rise to a dramatic lowering of activity and molecular weight. Although care must be taken when extrapolating metal−ligand geometries from precatalysts to the active species, the differing configurations of **4** (all-cis) and **5** (P-trans) may be responsible for this change in performance. The hafnium-based catalyst **6**/MAO showed good activity (1070 gPE/mmol·h·bar) but somewhat lower than its zirconium analogue.

4/DMAO and **6**/DMAO[16] also afforded high activities for propylene polymerization (Table 3). At 20 °C, **4** gave a viscous oil of moderate molecular weight and low PDI with an activity of 5340 gPP/mmol·h·bar (PP = polypropylene). Analysis of the polymer by ^{13}C NMR spectroscopy showed it to have a slight syndiotactic bias ([*rr*] = 39.8%, compared to [*rr*] = 25.0% for an atactic polymer). The activity could be further increased, to 7010 gPP/mmol·h·bar, by lowering the polymerization temperature to −20 °C, accompanied by an increase in the molecular weight. To our knowledge, **4**/DMAO is among the most active homogeneous, non-cyclopentadienyl catalysts for the polymerization of propylene reported to date. Consistent with the results found for ethylene polymerization, **6**/DMAO (772 gPP/mmol·h·bar) gave a somewhat lower activity than **4**/DMAO, but this could be increased, to 949 gPP/mmol·h·bar, by raising the polymerization temperature to 50 °C. Attempts to improve tacticity control using **4** by running polymerizations in liquid propylene at −50 °C resulted in only a minor increase in the syndiotactic bias ([*rr*] = 44.1%).

Table 3. Propylene Polymerizations Using **4** and **6**^{a}

precatalyst (loading/μmol)	temp (°C)	activity^{b}	M_n^{c} (kg/mol)	M_w^{c} (kg/mol)	M_w/M_n	[*rr*]^{d} (%)
4 (2.5)	20	5340	37.0	62.7	1.70	39.8
4 (2.5)	−20	7010	52.9	79.1	1.49	41.9
4 (2.5)	−30	4500	58.4	95.5	1.63	42.4
6 (10.0)	50	949	14.9	34.4	2.30	34.0
6 (10.0)	25	772	18.2	35.1	1.93	36.4
6 (10.0)	0	112	7.79	12.7	1.63	37.7

[a] Conditions: Schlenk, magnetic stirring, DMAO (2.5 mmol), TIBAL (125 μmol), heptane (100 mL), 2 bar propylene, 30 min (**4**)/1 h (**6**). [b] Activities in gPP/mmol·h·bar. [c] Determined by GPC versus PS standards. [d] Determined by ^{13}C NMR.

The impressive activities seen for these phosphanylphenoxide ligands, and especially the remarkable activity of a zirconium derivative for propylene polymerization, indicate that there is significant scope for incorporating soft donors into early-transition-metal-based polymerization catalysts, a finding that may have relevance for other areas of early-transition-metal-mediated catalysis. Our efforts are now directed toward improving tacticity control by linking the P,O ligands to give configurationally rigid tetradentate O,P,P,O and P,O,O,P ligands.

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Supporting Information Available: Experimental and spectroscopic details (including variable-temperature NMR data), crystal structures, and polymer NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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