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Biphenolate Phosphine Complexes of Group 4 Metals

Lan-Chang Liang,*,† Yu-Ning Chang,† and Hon Man Lee‡

Department of Chemistry and Center for Nanoscience & Nanotechnology, National Sun Yat-sen University, Kaohsiung 80424, Taiwan, and Department of Chemistry, National Changhua University of Education, Changhua 50058, Taiwan

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The preparation and structural characterization of a series of group 4 complexes supported by 2,2′-phenylphosphinobis(4,6-di-*tert*-butylphenolate) ($[OPO]^{2-}$) are described. The reaction of either $H_2[OPO]$ with $Ti(OR)_4$ (R = Et, ^{i}Pr) or $Li_2[OPO]$ with $TiCl_4(THF)_2$ produced yellowish-orange crystals of $Ti[OPO]_2$, regardless of the stoichiometry of the starting materials employed. Comproportionation of the bis-ligand complex $Ti[OPO]_2$ with 1 equiv of $TiCl_4(THF)_2$ led to the formation of $[OPO]TiCl_2(THF)$ as brownish-red crystals. Surprisingly, treatment of $H_2[OPO]$ with $[(Me_3Si)_2N]_2MCl_2$ (M = Zr, Hf), irrespective of the molar ratio, generated colorless crystals of the corresponding bis-ligand complex $[OPO]_2M(OH_2)$ as an aqua adduct. The solution and solid-state structures of these group 4 complexes were all characterized by multinuclear NMR spectroscopy and X-ray crystallography, respectively.

Introduction

Group 4 complexes of chelating biphenolate ligands are currently receiving considerable attention largely because of their potential use as homogeneous catalyst precursors for polymerization of terminal olefins and ring-opening polymerization of heterocyclic molecules.[1−6] The chelating biphenolate ligands are versatile in view of a large number of possible substituents potentially available for the two phenolate rings, from which the electronic and steric properties of the derived metal complexes may be finely tailored. The two phenolate rings may be either directly connected to each other in the ortho position[7−9] or bridged by a donor atom[6,9−16] or a hydrocarbon linkage.[9,14,16−20] As a result, a rich structural variety of biphenolato group 4 complexes has evolved. It has been demonstrated that the reactivity of these compounds may be altered significantly by careful modification of the biphenolate linkage. For instance, the titanium complexes of the sulfide-bridged 2,2′-thiobis(6-*tert*-butyl-4-methylphenolate) ligand (**1**; Figure 1) are active catalyst precursors for α-olefin polymerization,[9,15,21−23] the catalytic activity of

* To whom correspondence should be addressed. E-mail: lcliang@mail.nsysu.edu.tw.
† National Sun Yat-sen University.
‡ National Changhua University of Education.

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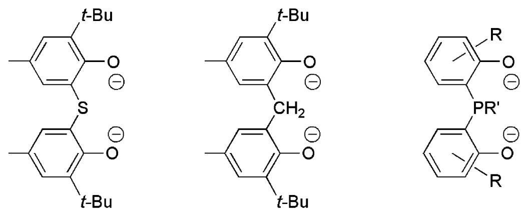

Figure 1. Representative examples of chelating biphenolate ligands.

which has been found to be higher than that of the methylene-bridged 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolate) (**2**) analogues.[18−20] The increased reactivity of the former complexes has been ascribed to sulfur coordination to the electrophilic titanium center in the catalytically active species, although likely in a hemilabile fashion, thereby leading to a lower activation barrier for olefin insertion than that found for the latter.[15,24,25] These results, along with our general interests in metal complexes of mismatched hard−soft donor−acceptor pairs,[26−36] prompt us to investigate the coordination chemistry of group 4 complexes of chelating biphenolates that contain a soft phosphine linkage (**3**). We note that although ligands of this type have been known since 1980,[37] group 4 complexes incorporating a biphenolate phosphine ligand are extremely rare.[38] In this contribution, we aim to demonstrate the synthetic possibility and establish the structural characterization of group 4 complexes of 2,2′-phenylphosphinobis(4,6-di-*tert*-butylphenolate) ($[OPO]^{2-}$). It is worth noting that compounds described herein represent an intriguing addition to the family of rarely encountered triarylphosphine complexes of group 4 metals that are structurally characterized to date.[38−44]

Results and Discussion

The reactions of $Li_2[OPO]$[45] with 1 equiv of $TiCl_4(THF)_2$[46] in a variety of solvents such as toluene or tetrahydrofuran (THF) at −35 °C produced a mixture of $[OPO]TiCl_2(THF)$ (vide infra), $Ti[OPO]_2$, and some unidentified materials, as indicated by $^{31}P\{^1H\}$ NMR spectroscopy. The formation of a significant amount (ca. 25%) of minor $Ti[OPO]_2$ accompanied with major $[OPO]TiCl_2(THF)$ is suggestive of a comparable reactivity of $[OPO]TiCl_2(THF)$ and $TiCl_4(THF)_2$ with respect to $Li_2[OPO]$ under the conditions employed. Attempts to selectively isolate the anticipated $[OPO]TiCl_2(THF)$ from these reaction mixtures led instead to bis-ligand complex $Ti[OPO]_2$ as yellowish-orange crystals after standard workup procedures. The selective isolation of $Ti[OPO]_2$ rather than $[OPO]TiCl_2(THF)$ is ascribed to the higher crystallinity of the former complex. Similar results were also obtained from reactions of $H_2[OPO]$ with $TiCl_4(THF)_2$ in the presence of 2 equiv of triethylamine, a phenomenon that is reminiscent of what has been reported for reactions involving **1** and **2**.[9] Surprisingly, protonolysis of $Ti(OR)_4$ (R = Et, ^{i}Pr) or $[(Me_3Si)_2N]_2TiCl_2$[4747] with 1 equiv of $H_2[OPO]$ in toluene or pentane at −35 °C generated $Ti[OPO]_2$ exclusively, as indicated by $^{31}P\{^1H\}$ NMR spectroscopy.

On the basis of the aforementioned results, analytically pure bis-ligand complex $Ti[OPO]_2$ is thus readily prepared in high yield from reactions of either $H_2[OPO]$ with $Ti(OR)_4$ (R = Et, ^{i}Pr) or $Li_2[OPO]$ with $TiCl_4(THF)_2$ in a 2:1 ratio (Scheme 1). The solution NMR spectroscopic data of $Ti[OPO]_2$ are all consistent with a C_2-symmetric geometry for this molecule. The ^1H NMR spectrum reveals four well-resolved singlet resonances for the *tert*-butyl groups. A variable-temperature ^1H NMR study indicated that the four singlet resonances do not tend to coalesce upon heating up to 100 °C (toluene-d_8), suggesting that both soft phosphorus donors in $Ti[OPO]_2$ likely remain bound, even at elevated temperatures, to the hard, six-coordinate, tetravalent titanium center. The two phosphorus donors are observed as one singlet resonance at 20 ppm in the $^{31}P\{^1H\}$ NMR spectroscopy, a value that is markedly shifted downfield from those of $H_2[OPO]$ (−50 ppm)[48] and $Li_2[OPO]$ (−32 ppm).[45]

Yellowish-orange crystals of $Ti[OPO]_2$ suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at −35 °C. Crystallographic details are summarized in Table 1. As depicted in Figure 2, $Ti[OPO]_2$ is a C_2-symmetric, six-coordinate species, consistent with the solution structure determined by NMR spectroscopy. The C_2 axis lies approximately on the mean P(1)−O(1)−O(3)−P(2) plane and bisects the P(2)−Ti(1)−P(1) angle. The

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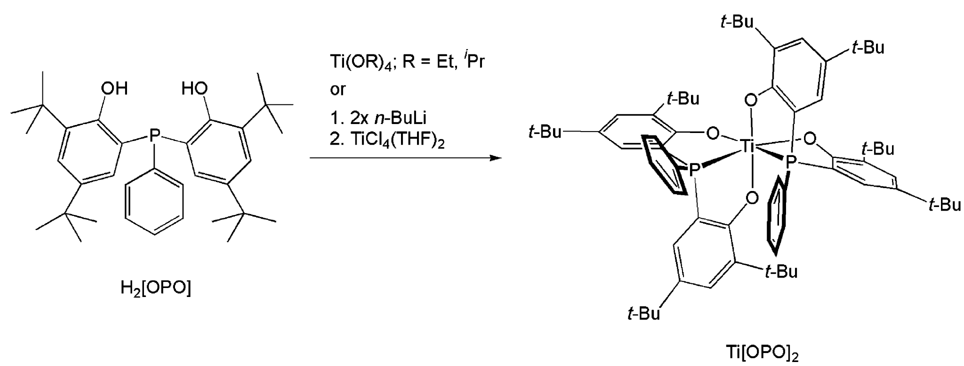
Table 1. Crystallographic Data for Ti[OPO]$_2$, [OPO]$TiCl_2$(THF), [OPO]$_2$Zr(OH_2), and [OPO]$_2$Hf(OH_2)

compound	{Ti[OPO]$_2$}(Et_2O)$_2$	{[OPO]$TiCl_2$(THF)}$_2$(C_6H_6)$_3$	{[OPO]$_2$Zr(OH_2)}(Et_2O)	[OPO]$_2$Hf(OH_2)
formula	$C_{76}H_{110}O_6P_2Ti$	$C_{94}H_{124}Cl_4O_6P_2Ti_2$	$C_{72}H_{102}O_6P_2Zr$	$C_{68}H_{92}HfO_5P_2$
fw	1229.48	1649.47	1216.70	1229.85
cryst size (mm^3)	0.32 × 0.3 × 0.16	0.11 × 0.08 × 0.02	0.36 × 0.24 × 0.14	0.10 × 0.10 × 0.10
D_{calc} (Mg/m^3)	1.081	1.194	1.129	1.200
cryst syst	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	15.7888(3)	11.2340(8)	13.0543(9)	13.328(5)
b (Å)	19.1122(4)	13.267(1)	15.800(1)	15.052(6)
c (Å)	25.3020(6)	16.535(1)	19.508(2)	18.924(7)
α (deg)	90	78.436(6)	108.855(7)	67.765(6)
β (deg)	98.396(1)	76.747(5)	104.769(7)	75.820(7)
γ (deg)	90	75.310(3)	97.517(5)	81.975(8)
V (Å^3)	7553.3(3)	2293.7(3)	3580.6(5)	3402(2)
Z	4	1	2	2
T (K)	293(2)	200(2)	150(2)	150(2)
diffractometer	Kappa CCD	Kappa CCD	SMART APEX II	SMART APEX II
radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
2θ range (deg)	4.16−50.68	4.18−49.98	2.32−52.50	3.38−50.50
h, k, l ranges	$-19 \le h \le 18$ $-22 \le k \le 22$ $-30 \le l \le 27$	$-13 \le h \le 13$ $-15 \le k \le 15$ $-19 \le l \le 18$	$-16 \le h \le 16$, $-19 \le k \le 19$, $-24 \le l \le 24$	$-15 \le h \le 15$, $-18 \le k \le 17$, $-22 \le l \le 16$
total no. of reflns	54831	26859	25330	18831
no. of indep reflns	13705	7524	14283	11839
R_{int}	0.1011	0.2362	0.0864	0.1650
abs coeff (mm^{-1})	0.202	0.375	0.244	1.624
no. of data/ restraints/param	13705/0/791	7524/0/488	14283/32/734	11839/48/698
GOF	1.037	1.068	0.932	0.836
final R indices [$I > 2\sigma(I)$]	R1 = 0.0800 wR2 = 0.2165	R1 = 0.1313 wR2 = 0.2970	R1 = 0.0896 wR2 = 0.2157	R1 = 0.0829 wR2 = 0.1830
R indices (all data)	R1 = 0.1639 wR2 = 0.2613	R1 = 0.2760 wR2 = 0.3855	R1 = 0.1850 wR2 = 0.2679	R1 = 0.2569 wR2 = 0.2352
residual density (e/Å^3)	−0.584 to +0.771	−0.531 to +0.567		

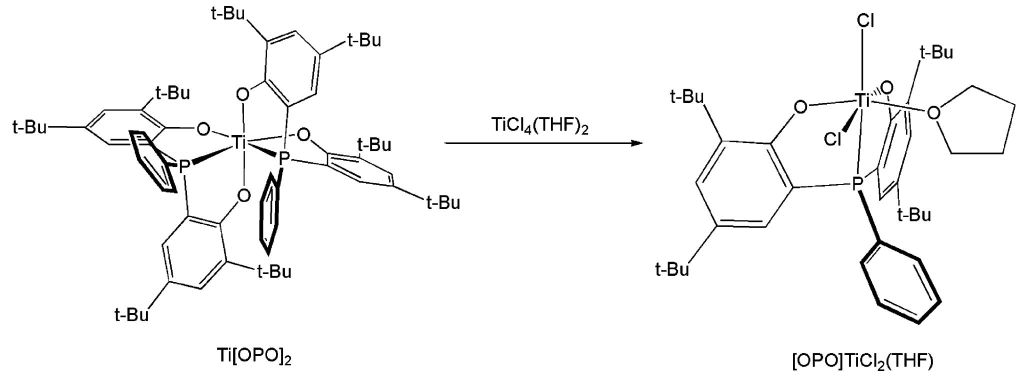
Scheme 1



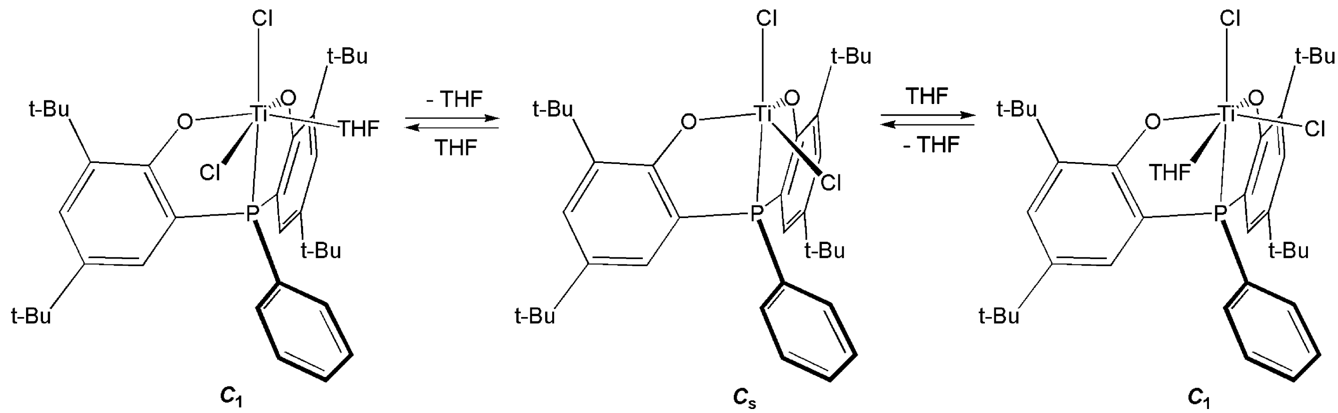
geometry of the titanium center is best described as a distorted octahedron in which both [OPO]$^{2-}$ ligands adopt a facial coordination mode. The facial geometry of [OPO]$^{2-}$ is anticipated in view of the inherent pyramidal structure of the phosphorus donor. The two phosphorus donors are mutually cis with the P(2)−Ti(1)−P(1) angle of 89.93(4)°. The chirality of this molecule shown in Figure 2 is ΔΛΛ on the basis of the handedness of nonadjacent and noncoplanar chelate ring pairs. We suggest that possible stereoisomers other than this absolute configuration and its enantiomer be virtually not present in the reaction mixture on the basis of the nearly quantitative isolated yield and the solution NMR studies that display only one set of signals for the reaction aliquots. The Ti−O distances (1.896 Å average) are within the expected values for those found in six-coordinate titanium phenolate complexes such as $TiCl_2$(2-$OC_6H_4PPh_2$)$_2$ (1.854 Å average),[44] Ti(OPr)$_2$[(2-O-3,5-$Cl_2C_6H_2$)CH_2N(Me)CH_2CH_2N(Me)CH_2(2-O-3,5-$Cl_2C_6H_2$)] (1.911 Å average),[12] and {(^{i}PrO)$_2$Ti(μ^3-O)TiCl(^{i}PrO)[(2-OC_6H_4)$_2$PPh]}$_2$ (2.044 Å average).[38] Interestingly, the Ti−P distances (2.551 Å average) are slightly shorter than those of titanium complexes supported by bidentate phenolate phosphine ligands such as (η^5-C_5H_5)$TiCl_2$(2-O-3-t-BuC_6H_3-PPh_2) [2.624(3) Å][42] and $TiCl_2$(2-$OC_6H_4PPh_2$)$_2$ (2.691 Å average)[44] but comparable to that of tridentate biphenolate phosphine derived {(^{i}PrO)$_2$Ti(μ^3-O)TiCl(^{i}PrO)[(2-OC_6H_4)$_2$-PPh]}$_2$ [2.563(1) Å].[38] More significantly, the Ti−P distances of Ti[OPO]$_2$ are notably shorter than the Ti−S distances found for Ti[**1**]$_2$ (2.765 Å average),[15] a result that is somewhat surprising in view of the relatively larger atomic size of the phosphorus donor than the sulfur but likely indicative of a stronger chemical bonding for the former to bind titanium than the latter.

After unsuccessful attempts to isolate [OPO]$TiCl_2$(THF) under various conditions as described above, we found that comproportionation of Ti[OPO]$_2$ with $TiCl_4$(THF)$_2$ in toluene

Scheme 2



Scheme 3



at room temperature effectively generates [OPO]TiCl$_2$(THF) cleanly (Scheme 2). The ^{1}H NMR spectrum of [OPO]TiCl$_2$-(THF) exhibits 1 equiv of a coordinated THF molecule. The α- and β-CH_2 groups of the titanium-bound THF are observed as two triplet resonances in C_6D_6 at 4.05 and 0.99 ppm, respectively. In the presence of an excess amount (e.g., 10 equiv) of THF, solutions of [OPO]TiCl$_2$(THF) exhibit only one set of resonances for the THF protons, a result that is ascribed to a facile exchange process between the coordinated and free THF molecules. The coordinated THF in [OPO]TiCl$_2$(THF) is thus presumably labile and tends to dissociate from the titanium center. Interestingly, a variable-temperature ^{1}H NMR study (toluene-d_8) revealed two doublet of triplets resonances with equal intensity at 4.16 and 3.87 ppm for the α-CH_2 groups of the coordinated THF at −50 °C, a result that is reflective of the diastereotopic nature of the α-CH_AH_B moieties at low temperatures. The four *tert*-butyl groups in [OPO]TiCl$_2$(THF) are observed as four well-resolved singlet resonances at −50 °C but two sharp singlet resonances at temperatures higher than 0 °C, consistent with a fluxional exchange between molecules that are C_1-symmetric and C_s-symmetric, respectively. These results suggest that the coordinated THF in the static structure of [OPO]TiCl$_2$(THF) cannot be trans to the phosphorus donor, assuming that the geometry of [OPO]TiCl$_2$(THF) is octahedral. Scheme 3 illustrates a plausible mechanism for this fluxional process on the basis of the labile nature of the coordinated THF molecule, in which the THF likely dissociates from the six-coordinate titanium center, thereby generating a five-coordinate, trigonal-bipyramidal [OPO]-TiCl$_2$, followed by recoordination of the freed THF molecule. The phosphorus donor of [OPO]$^{2-}$ in [OPO]TiCl$_2$(THF) appears as a singlet resonance at 18 ppm in the ^{31}P{^{1}H} NMR spectrum.

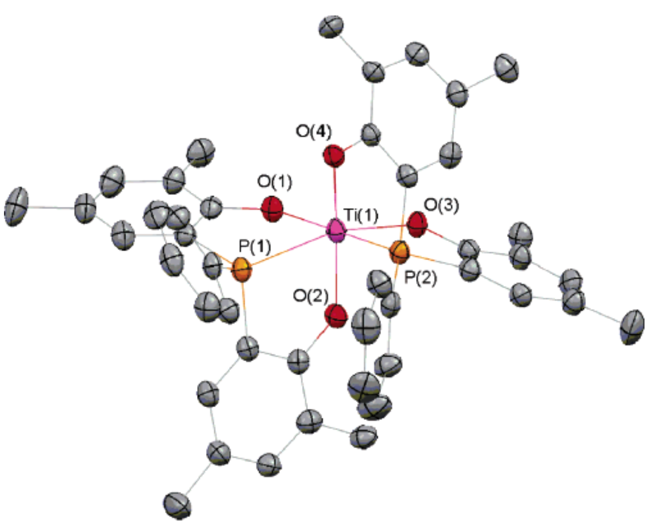


Figure 2. Molecular structure of Ti[OPO]$_2$ with thermal ellipsoids drawn at the 35% probability level. The methyl groups in [OPO]$^{2-}$ and two unbound diethyl ether molecules found in the asymmetric unit cell are omitted for clarity. Selected bond distances (Å) and angles (deg): Ti(1)−O(1) 1.871(3), Ti(1)−O(3) 1.880(3), Ti(1)−O(2) 1.912(3), Ti(1)−O(4) 1.919(3), Ti(1)−P(2) 2.542(1), Ti(1)−P(1) 2.560(1); O(1)−Ti(1)−O(3) 120.4(1), O(1)−Ti(1)−O(2) 97.5(1), O(3)−Ti(1)−O(2) 91.0(1), O(1)−Ti-(1)−O(4) 93.6(1), O(3)−Ti(1)−O(4) 96.5(1), O(2)−Ti(1)−O(4) 161.2(1), O(1)−Ti(1)−P(2) 163.1(1), O(3)−Ti(1)−P(2) 74.91(9), O(2)−Ti(1)−P(2) 88.70(9), O(4)−Ti(1)−P(2) 76.73(9), O(1)−Ti(1)−P(1) 76.44(9), O(3)−Ti(1)−P(1) 160.5(1), O(2)−Ti(1)−P(1) 76.22(9), O(4)−Ti(1)−P(1) 91.75-(9), P(2)−Ti(1)−P(1) 89.93(4).

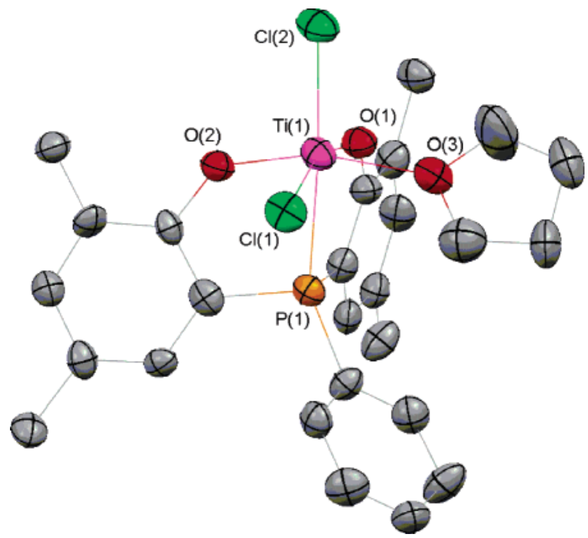


Figure 3. Molecular structure of [OPO]$TiCl_2$(THF) with thermal ellipsoids drawn at the 35% probability level. The methyl groups in $[OPO]^{2-}$ and unbound benzene molecules found in the asymmetric unit cell are omitted for clarity. Selected bond distances (Å) and angles (deg): Ti(1)−O(2) 1.848(8), Ti(1)−O(1) 1.858(7), Ti(1)−O(3) 2.128(9), Ti(1)−Cl(2) 2.281(3), Ti(1)−Cl(1) 2.340(3), Ti(1)−P(1) 2.596(3); O(2)−Ti(1)−O(1) 96.0(3), O(2)−Ti(1)−O(3) 163.3(3), O(1)−Ti(1)−O(3) 86.1(3), O(2)−Ti(1)−Cl(2) 99.9(2), O(1)−Ti(1)−Cl(2) 96.0(2), O(3)−Ti(1)−Cl(2) 96.3(2), O(2)−Ti(1)−Cl(1) 88.7(2), O(1)−Ti(1)−Cl(1) 159.3(2), O(3)−Ti(1)−Cl(1) 83.8(2), Cl(2)−Ti(1)−Cl(1) 103.0(1), O(2)−Ti(1)−P(1) 73.7(2), O(1)−Ti(1)−P(1) 75.6(2), O(3)−Ti(1)−P(1) 91.0(2), Cl(2)−Ti(1)−P(1) 168.5(1), Cl(1)−Ti(1)−P(1) 86.5(1).

Brownish-red crystals of [OPO]$TiCl_2$(THF) suitable for X-ray diffraction analysis were grown by slow evaporation of a concentrated benzene solution at room temperature. As illustrated in Figure 3, [OPO]$TiCl_2$(THF) is a six-coordinate, C_1-symmetric species that contains a coordinated THF molecule trans to one of the phenolate oxygen donors, consistent with what has been observed from solution NMR spectroscopic studies. The Ti−O, Ti−P, and Ti−Cl distances are all within the expected values for a six-coordinate titanium(IV) complex.[44,49,50] The Ti(1)−Cl(2) distance [2.281(3) Å] is slightly shorter than Ti(1)−Cl(1) [2.340(3) Å] likely because of the lower trans influence of phosphine than the phenolate oxygen anion. Similar to what has been observed for the bis-ligand complexes of titanium that contain $[OPO]^-$ and $[\mathbf{1}]^-$ (vide supra), the Ti−P distance of 2.596(3) Å in [OPO]$TiCl_2$(THF) is shorter than the Ti−S distances in sulfide-bridged biphenolate complexes of titanium such as $[(\mathbf{1})TiCl_2]_2$ [2.664(2) Å],[49] $[(\mathbf{1})Ti(O^iPr)_2]_2$ [2.719(1) Å],[15] and $[(\mathbf{1})Ti(CH_2Ph)_2]_2$($\mu$-1,4-dioxane) [2.8699(6) Å].[51] Although inconsistent with the relative atomic size and hardness of the donor atoms, the presumably stronger chemical bonding of Ti−P than Ti−S found in this study is reminiscent of that of Ti−Te[49] than of Ti−S[49] of dimeric titanium dichloride complexes that contain the corresponding chalcogenide-bridged biphenolate ligands. Such enhanced interaction between tetravalent titanium and the phosphorus donor, as compared to the sulfur in the biphenolate complexes, is beneficial in view of the decreased insertion barrier for catalytic α-olefin polymerization as suggested by theoretical calculation studies.[24,25]

In contrast to what has been observed for titanium chemistry, reactions of Li_2[OPO][45] with $MCl_4(THF)_2$ (M = Zr, Hf)[46] in a number of solvents such as Et_2O, THF, or toluene led to intractable materials regardless of the molar ratio of the starting materials employed. Treatment of H_2[OPO][48] with $[(Me_3Si)_2N]_2MCl_2$ (M = Zr, Hf),[52] irrespective of the molar ratio, generated colorless crystals of the corresponding bis-ligand complex $[OPO]_2M(OH_2)$ as an aqua adduct (Scheme 4). The incorporation of a water molecule in $[OPO]_2M(OH_2)$ is presumably due to the trace amount of moisture present in the solvent employed. The formation of seven-coordinate $[OPO]_2Zr(OH_2)$ and $[OPO]_2Hf(OH_2)$ rather than six-coordinate $Zr[OPO]_2$ or $Hf[OPO]_2$ that has been found for $Ti[OPO]_2$ is consistent with the relative atomic sizes of these metals. The putative six-coordinate $Zr[OPO]_2$ and $Hf[OPO]_2$ are thus presumably highly electrophilic. The coordinated water molecule in $[OPO]_2M(OH_2)$ (M = Zr, Hf) at room temperature appears as an extremely broad singlet resonance in the ^1H NMR spectrum at ca. 2.6 ppm, which gradually sharpens upon cooling to temperatures lower than −73 °C (in toluene-d_8) to give a sharp singlet resonance (see the Supporting Information). These results are indicative of a fast equilibrium involving $[OPO]_2M(OH_2)$, $M[OPO]_2$, and free water (eq 1). In contrast to those of $Ti[OPO]_2$ (vide

$$[OPO]_2M(OH_2) \rightleftarrows M[OPO]_2 + H_2O \qquad (1)$$
$$M = Zr, Hf$$

supra), the *tert*-butyl groups of $[OPO]_2M(OH_2)$ (M = Zr, Hf) in ^1H NMR spectroscopy at room temperature are observed as two sharp singlet resonances, which do not tend to broaden or resolve until the temperature is lowered to −73 °C, indicating a rapid fluxional process that exchanges the *tert*-butyl groups in the latter complexes. It is likely that a facile turnstile rearrangement occurs for the putative six-coordinate $Zr[OPO]_2$ and $Hf[OPO]_2$ on the basis of the nondissociative nature observed for the phosphorus donors in $Ti[OPO]_2$. In accordance with the relative atomic sizes of the group 4 metals, a much higher exchange barrier is anticipated for $Ti[OPO]_2$ to undergo such a turnstile rearrangement because of the steric repulsion imposed by the two $[OPO]^-$ ligands. As a result, the static structure of $[OPO]_2Zr(OH_2)$ and $[OPO]_2Hf(OH_2)$ is likely C_2-symmetric. Consistent with the conformation discrepancies in these bis-ligand complexes, the ^{31}P NMR chemical shift of ca. 3 ppm for both $[OPO]_2Zr(OH_2)$ and $[OPO]_2Hf(OH_2)$ is notably different from that of $Ti[OPO]_2$.

Colorless crystals of $[OPO]_2Zr(OH_2)$ and $[OPO]_2Hf(OH_2)$ suitable for X-ray diffraction analysis were grown from a concentrated pentane solution at −35 °C. Figures 4 and 5 illustrate the molecular structures of these compounds. Both are isostructural. The geometries of $[OPO]_2Zr(OH_2)$ and $[OPO]_2Hf(OH_2)$ are best described as a distorted pentagonal

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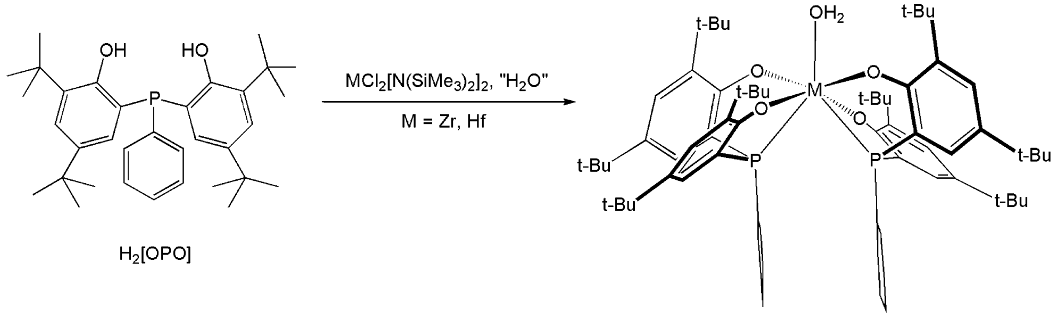
Scheme 4



$H_2[OPO]$

$[OPO]_2M(OH_2)$
M = Zr, Hf

bipyramid, with O(1) and O(4) atoms being at the apical positions. The O(1)−M−O(4) angle is 156.6(2)° for $[OPO]_2Zr(OH_2)$ and 155.0(3)° for $[OPO]_2Hf(OH_2)$. The mean deviation of the equatorial pentagon is 0.268 and 0.216 Å for $[OPO]_2Zr(OH_2)$ and $[OPO]_2Hf(OH_2)$, respectively. Nevertheless, the metal center lies approximately on the mean equatorial plane with a negligible displacement of 0.002 Å for Zr and 0.009 Å for Hf. The M−P distances of 2.776 Å (average) for $[OPO]_2Zr(OH_2)$ and 2.709 Å (average) for $[OPO]_2Hf(OH_2)$ are comparable to those found for zirconium and hafnium complexes of triarylphosphines such as [NPN]-$ZrCl_2$ (2.7229(8) Å, [NPN] = [(2,4,6-$Me_3C_6H_2$)N-2-(5-MeC_6H_3)]$_2$PPh),[41] [NP]$_2ZrCl_2$ (2.801 Å average, $[NP]^-$ = *N*-(2-diphenylphosphinophenyl)-2,6-dimethylanilide),[40] $ZrCl_2$-(2-O-3-*t*-$BuC_6H_3P^iPr_2)_2$ (2.808 Å average),[44] [NP]$_2HfCl_2$ (2.7736(9) Å, $[NP]^-$ = *N*-(2-diphenylphosphinophenyl)-2,6-dimethylanilide),[40] and $HfCl_2$(2-O-3-*t*-$BuC_6H_3PPh_2)_2$ (2.829 Å average).[44] Consistent with the intramolecular steric congestion of these seven-coordinate species, the M−O(phenolate) distances of 2.063 Å (average) and 2.038 Å (average) for $[OPO]_2Zr(OH_2)$ and $[OPO]_2Hf(OH_2)$, respectively, are slightly longer than the corresponding values of six-coordinate group 4 phenolate complexes such as $ZrCl_2$(2-O-3-*t*-$BuC_6H_3P^iPr_2)_2$ (1.998 Å average),[44] {[(2-O-3,5-*t*-$Bu_2C_6H_2)CH_2]_2NCH_2CH_2NMe_2$}$ZrBn_2$ (1.995 Å average),[53] $HfCl_2$(2-O-3-*t*-$BuC_6H_3PPh_2)_2$ (1.973 Å average),[44] and {[(2-O-3,5-*t*-$Bu_2C_6H_2)CH_2]_2NCH_2CH_2NMe_2$}$HfBn_2$ (1.978 Å average).[53] As anticipated, the M−O(water) distances [2.329(5) Å for Zr and 2.19(1) Å for Hf] are significantly longer than the corresponding M−O(phenolate) values. In agreement with the solution structure determined by NMR spectroscopic studies, both $[OPO]_2Zr(OH_2)$ and $[OPO]_2Hf(OH_2)$ are C_2-symmetic in the solid state. The C_2 axis coincides with the M−O(5) bond.

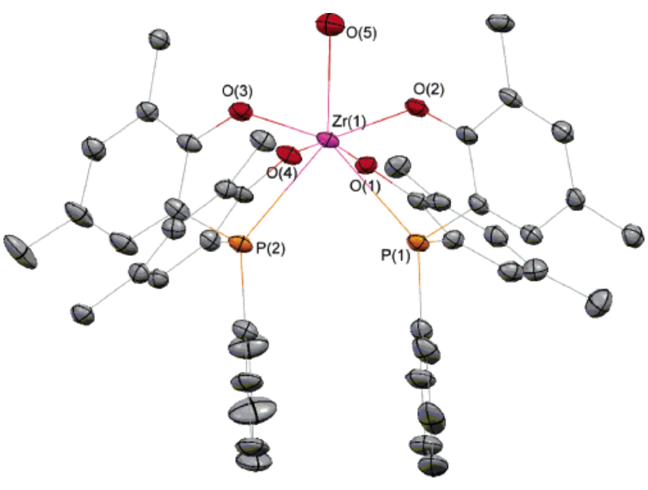


Figure 4. Molecular structure of $[OPO]_2Zr(OH_2)$ with thermal ellipsoids drawn at the 35% probability level. The methyl groups in $[OPO]^{2-}$ and one unbound diethyl ether molecule found in the asymmetric unit cell are omitted for clarity. Selected bond distances (Å) and angles (deg): O(2)−Zr(1) 2.103(4), O(1)−Zr(1) 2.035(4), O(4)−Zr(1) 2.033(4), O(3)−Zr(1) 2.079(4), O(5)−Zr(1) 2.329(5), P(1)−Zr(1) 2.795(2), P(2)−Zr(1) 2.757(2); O(4)−Zr(1)−O(1) 156.6(2), O(4)−Zr(1)−O(3) 97.6(2), O(1)−Zr(1)−O(3) 89.1(2), O(4)−Zr(1)−O(2) 89.7(2), O(1)−Zr(1)−O(2) 97.1(2), O(3)−Zr(1)−O(2) 146.5(2), O(4)−Zr(1)−O(5) 101.0(2), O(1)−Zr(1)−O(5) 102.4(2), O(3)−Zr(1)−O(5) 74.4(2), O(2)−Zr(1)−O(5) 72.1(2), O(4)−Zr(1)−P(2) 70.8(1), O(1)−Zr(1)−P(2) 90.9(1), O(3)−Zr(1)−P(2) 69.4(1), O(2)−Zr(1)−P(2) 142.8(1), O(5)−Zr(1)−P(2) 141.1(1), O(4)−Zr(1)−P(1) 91.3(1), O(1)−Zr(1)−P(1) 71.0(1), O(3)−Zr(1)−P(1) 144.3(1), O(2)−Zr(1)−P(1) 67.5 (1), O(5)−Zr(1)−P(1) 137.6(1), P(2)−Zr(1)−P(1) 81.29(5).

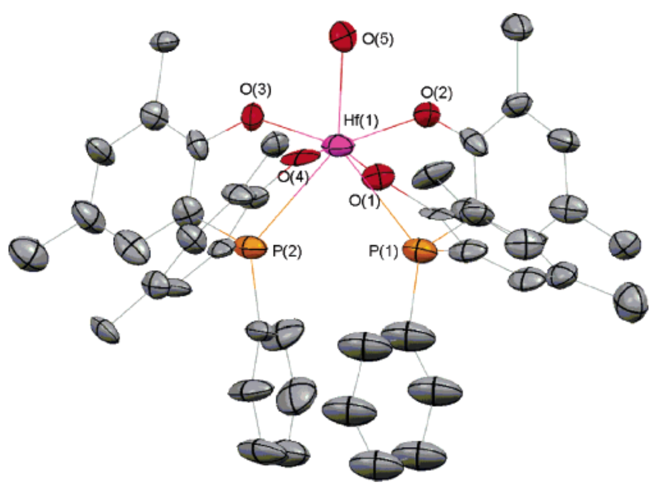


Figure 5. Molecular structure of $[OPO]_2Hf(OH_2)$ with thermal ellipsoids drawn at the 35% probability level. The methyl groups in $[OPO]^{2-}$ are omitted for clarity. Selected bond distances (Å) and angles (deg): Hf(1)−O(4) 1.996(9), Hf(1)−O(1) 2.028(9), Hf(1)−O(2) 2.05(1), Hf(1)−O(3) 2.08(1), Hf(1)−O(5) 2.19(1), Hf(1)−P(2) 2.695(4), Hf(1)−P(1) 2.723(5); O(4)−Hf(1)−O(1) 155.0(3), O(4)−Hf(1)−O(2) 90.2(4), O(1)−Hf(1)−O(2) 95.4(4), O(4)−Hf(1)−O(3) 99.5(4), O(1)−Hf(1)−O(3) 89.5(4), O(2)−Hf(1)−O(3) 145.9(4), O(4)−Hf(1)−O(5) 103.3(4), O(1)−Hf(1)−O(5) 101.7(4), O(2)−Hf(1)−O(5) 72.8(4), O(3)−Hf(1)−O(5) 73.1(4), O(4)−Hf(1)−P(2) 72.1(3), O(1)−Hf(1)−P(2) 89.7(3), O(2)−Hf(1)−P(2) 144.1(3), O(3)−Hf(1)−P(2) 69.4(3), O(5)−Hf(1)−P(2) 140.6(3), O(4)−Hf(1)−P(1) 86.7(3), O(1)−Hf(1)−P(1) 73.0(3), O(2)−Hf(1)−P(1) 68.1(3), O(3)−Hf(1)−P(1) 144.5(3), O(5)−Hf(1)−P(1) 139.7(3), P(2)−Hf(1)−P(1) 79.7(1).

Conclusions

In summary, we have prepared a series of group 4 complexes of the tridentate biphenolate phosphine ligand $[OPO]^{2-}$ and established the solution and solid-state structures of these molecules by means of multinuclear NMR spectroscopy and X-ray crystallography. These compounds represent the rarely encountered triarylphosphine complexes of group 4 metals that have been structurally characterized to date. Of particular note is perhaps the somewhat stronger chemical bond of the soft phosphorus donor in $[OPO]^{2-}$ to hard tetravalent titanium than that of the sulfur in **1**.[15,49] Such enhanced interaction is likely advantageous for the development of highly active catalysts for α-olefin polymerization. Studies directed to delineate the reactivity of these compounds are currently underway.

Experimental Section

General Procedures. Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques. All solvents were reagent-grade or better and were purified by standard methods. The NMR spectra were recorded on Varian Unity or Bruker AV instruments. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane and coupling constants (J) in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C_6D_6 and δ 2.09 for toluene-d_8 (the most upfield resonance). ^{13}C NMR spectra are referenced using the residual solvent peak at δ 128.39 for C_6D_6. The assignment of the carbon atoms is based on the DEPT ^{13}C NMR spectroscopy. ^{31}P NMR spectra are referenced externally using 85% H_3PO_4 at δ 0. Routine coupling constants are not listed. All NMR spectra were recorded at room temperature in specified solvents unless otherwise noted. Elemental analysis was performed on a Heraeus CHN−O Rapid analyzer.

Materials. Compounds H_2[OPO],[48] Li_2[OPO],[45] $TiCl_4(THF)_2$,[46] and $[(Me_3Si)_2N]_2MCl_2$ (M = Zr, Hf)[52] were prepared according to the literature procedures. All other chemicals were obtained from commercial vendors and used as received.

X-ray Crystallography. Table 1 summarizes the crystallographic data for Ti[OPO]$_2$, [OPO]TiCl$_2$(THF), [OPO]$_2$Zr(OH$_2$), and [OPO]$_2$-Hf(OH$_2$). Data were collected on a Bruker-Nonius Kappa CCD diffractometer or a SMART APEX II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Structures were solved by direct methods and refined by full-matrix least-squares procedures against F^2 using the WinGX crystallographic software package or *SHELXL-97*. All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. In Ti[OPO]$_2$, three *tert*-butyl groups are disordered, with the methyl substituents being in the ratio of ca. 50:50 over two conformations. The crystals of [OPO]TiCl$_2$(THF) were of poor quality but sufficient to establish the identity of this molecule. In [OPO]TiCl$_2$(THF), three *tert*-butyl groups are disordered, with the methyl substituents being in the ratio of either ca. 70:30 or 49:51 over two conformations. In [OPO]$_2$Zr(OH$_2$), one *tert*-butyl group is disordered, with the methyl substituents being in the ratio of ca. 53:47 over two conformations.

Synthesis of Ti[OPO]$_2$. Method 1: Solid 2,2′-phenylphosphinobis(4,6-di-*tert*-butylphenol) (H$_2$[OPO]; 500 mg, 0.97 mmol) was dissolved in toluene (5 mL) and cooled to −35 °C. To this was added dropwise a prechilled solution of Ti(OEt)$_4$ (110 mg, 0.48 mmol) in toluene (1 mL) at −35 °C. The reaction mixture was stirred at room temperature for 10 h and evaporated to dryness under reduced pressure. The resulting yellowish-orange solid was dissolved in diethyl ether (8 mL), and the ether solution was filtered through a pad of Celite. The extraction and filtration procedures were repeated again, and the filtrates were combined. Evaporation of the diethyl ether solution under reduced pressure afforded the product as a yellowish-orange solid; yield 507 mg (97%). Employment of Ti(O^{i}Pr)$_4$ in place of Ti(OEt)$_4$ gave the same result. **Method 2**: Solid H$_2$[OPO] (100 mg, 0.19 mmol) was dissolved in toluene (4 mL) and cooled to −35 °C. To this was added *n*-BuLi (0.24 mL, 1.6 M in hexane, Aldrich, 0.38 mmol, 2 equiv) dropwise. The reaction mixture was stirred at room temperature for 1 h. The resultant suspension was cooled to −35 °C again and added in portions to prechilled TiCl$_4$(THF)$_2$ (31.8 mg, 0.095 mmol, 0.5 equiv) suspended in toluene (4 mL) at −35 °C. The reaction mixture was stirred at room temperature for 16 h and evaporated to dryness under reduced pressure. The brown solid thus obtained was dissolved in diethyl ether (6 mL × 2). The diethyl ether solution was filtered through a pad of Celite and evaporated to dryness to afford the product as a yellowish-orange solid; yield 98 mg (94%). Yellowish-orange crystals suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at −35 °C. ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 7.47 (d, 2, Ar), 7.39 (d, 2, Ar), 7.34 (m, 4, Ar), 7.26 (dd, 2, Ar), 7.19 (dd, 2, Ar), 6.92 (m, 6, Ar), 1.68 (s, 18, C*Me*$_3$), 1.52 (s, 18, C*Me*$_3$), 1.12 (s, 18, C*Me*$_3$), 1.09 (s, 18, C*Me*$_3$). ^{1}H NMR (toluene-d_8, 500 MHz): δ 7.44 (d, 2, Ar), 7.36 (d, 2, Ar), 7.26 (m, 4, Ar), 7.19 (dd, 2, Ar), 7.12 (td, 2, Ar), 6.92 (m, 6, Ar), 1.66 (s, 18, C*Me*$_3$), 1.48 (s, 18, C*Me*$_3$), 1.13 (s, 18, C*Me*$_3$), 1.10 (s, 18, C*Me*$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 202.31 MHz): δ 20.36 ($\Delta\upsilon_{1/2}$ = 1.83 Hz). ^{31}P{^{1}H} NMR (toluene-d_8, 80.95 MHz): δ 20.33. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.70 MHz): δ 169.66 (d, J_{CP} = 27.15, C), 167.90 (d, J_{CP} = 8.04, C), 167.70 (d, J_{CP} = 7.04, C), 144.71 (d, J_{CP} = 6.03, C), 142.12 (d, J_{CP} = 6.03, C), 137.15 (d, J_{CP} = 6.03, C), 136.54 (d, J_{CP} = 9.05, C), 133.52 (d, J_{CP} = 11.19, CH), 130.23 (s, CH), 129.26 (d, J_{CP} = 4.02, C), 128.85 (s, CH), 128.77 (s, CH), 127.86 (s, CH), 127.72 (s, CH), 126.62 (d, J_{CP} = 12.07, CH), 122.38 (d, J_{CP} = 44.25, C), 36.00 (s, *C*Me$_3$), 35.99 (s, *C*Me$_3$), 35.00 (s, *C*Me$_3$), 34.80 (s, *C*Me$_3$), 31.94 (s, C*Me*$_3$), 31.91-(s, C*Me*$_3$), 30.31 (s, C*Me*$_3$), 30.02 (s, C*Me*$_3$). Anal. Calcd for C$_{68}$H$_{90}$O$_4$P$_2$Ti: C, 75.53; H, 8.39. Found: C, 75.56; H, 8.30.

Synthesis of [OPO]TiCl$_2$(THF). Toluene (5 mL) was added to a solid mixture of Ti[OPO]$_2$ (100 mg, 0.09 mmol) and TiCl$_4$(THF)$_2$ (30.7 mg, 0.09 mmol) at room temperature. After being stirred at room temperature for 6 h, the reaction mixture was filtered through a pad of Celite, which was further washed with toluene (1 mL). The filtrates were combined and concentrated under reduced pressure until the volume became ca. 1 mL. Cooling the concentrated toluene solution to −35 °C afforded the product as a brownish-red solid; yield 82 mg (63%). Brownish-red crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a concentrated benzene solution at room temperature. ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 7.90 (t, 2, Ar), 7.49 (d, 2, Ar), 7.38 (dd, 2, Ar), 7.13 (td, 2, Ar), 7.07 (m, 1, Ar), 4.05 (t, 4, OC*H*$_2$CH$_2$), 1.61 (s, 18, C*Me*$_3$), 1.13 (s, 18, C*Me*$_3$), 0.99 (t, 4, OCH$_2$C*H*$_2$). ^{1}H NMR (toluene-d_8, 500 MHz): δ 7.86 (t, 2, Ar), 7.47 (d, 2, Ar), 7.32 (dd, 2, Ar), 7.15 (td, 3, Ar), 4.01 (t, 4, OC*H*$_2$CH$_2$), 1.60 (s, 18, C*Me*$_3$), 1.15 (s, 22, C*Me*$_3$ + OCH$_2$C*H*$_2$). ^{1}H NMR (toluene-d_8, 500 MHz, −50 °C): δ 7.93 (dd, 2, Ar), 7.60 (s, 1, Ar), 7.50 (dd, 1, Ar), 7.44 (s, 1, Ar), 7.30 (dd, 1, Ar), 7.12 (td, 2, Ar), 7.03 (t, 1, Ar), 4.16 (td, 2, OC*H*$_A$H$_B$CH$_2$), 3.87 (td, 2, OCH$_A$*H*$_B$CH$_2$), 1.72 (s, 9, C*Me*$_3$), 1.59 (s, 9, C*Me*$_3$), 1.16 (s, 9, C*Me*$_3$), 1.14 (s, 9, C*Me*$_3$),

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0.80 (t, 4, OCH_2CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz): δ 18.06. $^{31}P\{^1H\}$ NMR (toluene, 80.95 MHz): δ 16.89. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.70 MHz): δ 169.07 (d, J_{CP} = 27.90, C), 145.88 (d, J_{CP} = 5.02, C), 136.98 (d, J_{CP} = 6.41, C), 133.09 (d, J_{CP} = 10.06, CH), 131.24 (s, CH), 129.53 (d, J_{CP} = 9.68, CH), 128.93 (d, J_{CP} = 7.79, C), 128.68 (s, CH), 127.25 (d, J_{CP} = 1.89, CH), 126.03 (s, C), 75.25 (s, OCH$_2$CH$_2$), 36.01 (d, J_{CP} = 1.38, CMe$_3$), 35.13 (s, CMe$_3$), 31.86 (s, CMe_3), 30.18 (s, CMe_3), 25.36 (s, OCH$_2$$CH_2$). Anal. Calcd for $C_{38}H_{53}Cl_2O_3PTi$: C, 64.50; H, 7.55. Found: C, 64.37; H, 7.55.

Synthesis of $[OPO]_2Zr(OH_2)$. Pentane (6 mL) was added to a solid mixture of H_2[OPO] (445 mg, 0.86 mmol) and $[(Me_3Si)_2N]_2ZrCl_2$ (207 mg, 0.43 mmol, 0.5 equiv) at room temperature. The reaction solution was stirred at room temperature for 3 h and filtered through a pad of Celite. The Celite pad was further washed with pentane (2 mL $\times$ 2), and the filtrates were combined. The pentane solution was concentrated under reduced pressure until the volume became ca. 1 mL. Cooling the concentrated pentane solution to −35 °C overnight afforded colorless crystals suitable for X-ray diffraction analysis; yield 191 mg (73%). ^1H NMR (C_6D_6, 500 MHz): δ 7.41 (d, 4, Ar), 7.25 (m, 4, Ar), 7.12 (t, 4, Ar), 6.88 (t, 2, Ar), 6.81 (t, 4, Ar), 2.52 (br s, 2, H_2O), 1.54 (s, 36, CMe_3), 1.15 (s, 36, CMe_3). ^1H NMR (toluene-d_8, 500 MHz): δ 7.38 (d, 4, Ar), 7.18 (m, 4, Ar), 7.05 (t, 4, Ar), 6.88 (t, 2, Ar), 6.82 (t, 4, Ar), 2.69 (br s, 2, H_2O), 1.53 (s, 36, CMe_3), 1.16 (s, 36, CMe_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz): δ 2.99 ($\Delta\upsilon_{1/2}$ = 13.73 Hz). $^{31}P\{^1H\}$ NMR (toluene-d_8, 80.95 MHz): δ 3.51. $^{31}P\{^1H\}$ NMR (pentane, 80.95 MHz): δ 4.28. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.70 MHz): δ 167.98 (m, C), 141.24 (s, C), 136.48 (s, C), 133.42 (t, J_{CP} = 5.97, CH), 131.56 (m, C), 128.77 (s, CH), 128.68 (m, CH), 127.15 (s, CH), 126.81 (s, CH), 125.06 (m, C), 35.71 (s, CMe$_3$), 34.74 (s, CMe$_3$), 32.02 (s, CMe_3), 30.38 (s, CMe_3). Anal. Calcd for $C_{68}H_{92}O_5P_2Zr$: C, 71.48; H, 8.12. Found: C, 71.72; H, 8.34.

Synthesis of $[OPO]_2Hf(OH_2)$. Pentane (3 mL) was added to a solid mixture of H_2[OPO] (100 mg, 0.19 mmol) and $[(Me_3Si)_2N]_2HfCl_2$ (55 mg, 0.096 mmol, 0.5 equiv) at room temperature. The reaction solution was stirred at room temperature for 9 h and filtered through a pad of Celite. The Celite pad was further washed with pentane (2 mL $\times$ 2), and the filtrates were combined. The pentane solution was concentrated under reduced pressure until the volume became ca. 1 mL. Cooling the concentrated pentane solution to −35 °C overnight afforded colorless crystals suitable for X-ray diffraction analysis; yield 77 mg (71%). ^1H NMR (C_6D_6, 500 MHz): δ 7.43 (d, 4, Ar), 7.26 (m, 4, Ar), 7.12 (m, 4, Ar), 6.87 (t, 2, Ar), 6.80 (t, 4, Ar), 2.67 (br s, 2, H_2O), 1.53 (s, 36, CMe_3), 1.15 (s, 36, CMe_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz): δ 2.62 ($\Delta\upsilon_{1/2}$ = 8.41 Hz). $^{31}P\{^1H\}$ NMR (pentane, 80.95 MHz): δ 4.35. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.70 MHz): δ 168.11 (t, J_{CP} = 14.20, C), 141.12 (t, J_{CP} = 2.26, C), 137.11 (t, J_{CP} = 1.76, C), 133.43 (t, J_{CP} = 5.91, CH), 131.78 (dd, J_{CP} = 14.71 and 17.35, C), 128.68 (s, CH), 128.62 (m, CH), 127.21 (s, CH), 126.84 (s, CH), 124.78 (dd, J_{CP} = 20.11 and 22.00, C), 35.65 (s, CMe$_3$), 34.71 (s, CMe$_3$), 32.04 (s, CMe_3), 30.41(s, CMe_3). Anal. Calcd for $C_{68}H_{92}HfO_5P_2$: C, 66.41; H, 7.54. Found: C, 66.80; H, 7.79.

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Supporting Information Available: Variable-temperature ^1H NMR spectra of $[OPO]_2Zr(OH_2)$ and X-ray crystallographic data in CIF format for Ti$[OPO]_2$, [OPO]$TiCl_2$(THF), $[OPO]_2Zr(OH_2)$, and $[OPO]_2Hf(OH_2)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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