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Metal Alkoxides as Versatile Precursors for Group 4 Phosphonates: Synthesis and X-ray Structure of a Novel Organosoluble Zirconium Phosphonate[†]

Debashis Chakraborty, Vadapalli Chandrasekhar, Manish Bhattacharjee, Ralph Krätzner, Herbert W. Roesky,* Mathias Noltemeyer, and Hans-Georg Schmidt

Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4,
D-37077 Göttingen, Germany

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Reactions of $Ph_2P(O)(OH)$ and t-$BuP(O)(OSiMe_3)(OH)$ with $Ti(O$-i-$Pr)_4$ in equimolar ratios gave titanium phosphonates of the type $[(O$-i-$Pr)_3Ti(\mu$-$O)_2PR^1R^2]_2$ (**1**, $R^1 = R^2 =$ Ph; **2**, $R^1 = t$-Bu, $R^2 = OSiMe_3$) as colorless crystalline solids in moderate yields. Reactions of $Ph_2P(O)(OH)$ and the isopropoxides of zirconium and hafnium resulted in products of the composition $[(O$-i-$Pr)_3M(\mu$-O-i-$Pr)_2(\mu$-$OPOPh_2)M(O$-i-$Pr)_2]Ph_2P(O)(OH)$ (M = Zr (**3**), Hf (**4**)) in high yields. The compounds were characterized by ^1H, ^{31}P, and ^{29}Si NMR, infrared (IR), and mass spectroscopic (MS) techniques. The molecular structures of **2** and **3** were confirmed by X-ray crystallography.

Introduction

Organophosphonates and phosphates have received considerable attention owing to their structural chemistries, intercalation behaviors, ion exchange properties, and catalytic applications. Early attempts have revealed the possibility of incorporating transition metals such as V, Zr, and Zn into phosphate frameworks.[1,2] Titanium phosphates containing alkali metals have shown useful applications as ion exchangers,[3] fast-ion conductors,[4] low-thermal-expansion ceramics,[5] and nonlinear optic materials.[6] The conceptual view of molecular titanium phosphates as precursors to solid-state materials is recent.[7] Extensive research focusing on the applications of zirconium phosphates has made these materials of vital importance in the area of structurally mediated interlayer transport[8] in addition to areas where their microporous and mesoporous properties are utilized.[9] In the past few years, there has been widespread success in devising *molecular routes* for the synthesis of advanced materials.[10] With regard to soluble phosphonates containing transition metals, our first success emerged upon employing the reactions of various $RP(O)(OH)_2$ systems with Cp^*TiCl_3 or Cp^*TiMe_3 as the counterpart organometallic precursor.[11] Since then, our constant goal has been to devise rational synthetic routes to synthesize other transition metal phosphonates. Complementary synthetic strategies employed for the zirconium and hafnium systems proved to be a failure. The applicability of the titanium alkoxide $Ti(O$-i-$Pr)_4$ as a useful synthon for the generation of titanium phosphonates[12] prompted us to explore the possibility of group 4 metal alkoxides in general as phosphonate-producing precursors. To the best of our knowledge, there have been no earlier reports on the synthesis or structural characterization of soluble phosphonate systems of Zr and Hf. In this report, we wish to contribute our investigations concerning the reactivity of group 4 metal alkoxides and $R_2P(O)(OH)$ systems. While this study was in progress, a few interesting examples were contributed by Tilley,[12] Mutin,[13] and their co-workers.

Results and Discussion

Our recent experience in conducting the investigations with dialkylaluminum halides and phosphate esters of the type

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[†] Dedicated to Professor Arndt Simon on the occasion of his 60th birthday.

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$(R_3SiO)_3PO$ has been that the most favorable product is an eight-membered ring containing suitable substituents on the metal as well as on the phosphorus centers where the phosphate ester could be considered as an $R_2P(O)(OH)$ analogue.[14] This is in accord with the observations of Mason and co-workers[15] and the earlier investigations reported on the reactions of group 13 metal alkyls and $Ph_2P(O)(OH)$.[16] On this basis, it could be easily surmised that reactions of titanium alkoxides with $R_2P(O)(OH)$ systems should generate a product possessing an eight-membered ring as the core with appropriate substituents on the Ti and P centers. This was first reported by Tilley et al.[12] We have carried out a systematic investigation into the reactivity of various titanium alkoxides with the $R_2P(O)(OH)$ systems.

Reactions of $Ph_2P(O)(OH)$ and t-BuP(O)(OSiMe$_3$)(OH) with Ti(O-i-Pr)$_4$ in equimolar ratios in hydrocarbon solvents give titanium phosphonates of the type $[(O\text{-}i\text{-}Pr)_3Ti(\mu\text{-}O)_2PR^1R^2]_2$ (**1**, $R^1 = R^2 = Ph$; **2**, $R^1 = t\text{-}Bu$, $R^2 = OSiMe_3$) as colorless crystalline solids in moderate yields (eq 1).

$$2Ti(O\text{-}i\text{-}Pr)_4 + 2HO(O)PR^1R^2 \xrightarrow{-2\ i\text{-}PrOH} [(O\text{-}i\text{-}Pr)_3Ti(\mu\text{-}O)_2PR^1R^2]_2 \quad (1)$$

$$\mathbf{1}\text{: } R^1 = R^2 = Ph$$
$$\mathbf{2}\text{: } R^1 = t\text{-}Bu,\ R^2 = OSiMe_3$$

In the case of $Ph_2P(O)(OH)$, the reactions were carried out in toluene, while for t-BuP(O)(OSiMe$_3$)(OH), the reactions were carried out in pentane. The starting material t-BuP(O)(OSiMe$_3$)(OH) was prepared from an equimolar reaction between t-BuP(O)(OH)$_2$ and Me$_3$SiCl in the presence of triethylamine employing high-dilution techniques.

In the case of **1**, the ^{1}H NMR spectrum recorded in benzene-d_6 revealed two sets of resonances for the O-i-Pr groups in a 3:1 ratio for each set, while the phenyl moieties were observed as two sets of poorly resolved resonances in the prescribed range. The ^{31}P NMR spectrum showed the presence of three distinct resonances. The spectral characteristics remained unchanged after several recrystallizations. EI-MS could not provide further insight. Furthermore, we prepared the ester t-BuP(O)(OSiMe$_3$)(OH) with the view of having the OSiMe$_3$ group as an extra-ring NMR probe. The reactions were carried out under identical conditions in pentane to obtain **2** in moderate yields. The ^{1}H NMR spectrum of **2** displayed signals for the various moieties in the required ratio of integration. The ^{31}P NMR spectrum revealed numerous signals in the range 17−35 ppm. The ^{29}Si NMR spectrum revealed prominent signals at 16.8 and 19.7 ppm in addition to signals at 14.7 and 18.7 ppm. Temperature-dependent NMR studies in the range −50 to +40 °C were carried out. No significant changes were observed in the ^{1}H NMR spectrum. However, at −40 °C, in the ^{31}P NMR spectrum major signals were observed at 14.7, 20.8, 22.9, and 32.2 ppm whereas in the ^{29}Si NMR spectrum the signals at 14.7 and 19.7 ppm diminished in intensity. The NMR characteristics imply dynamic behavior of **2** in the solution state. These observations are in agreement with those reported by Tilley et al. for the corresponding (t-BuO)$_2$P derivatives.[12]

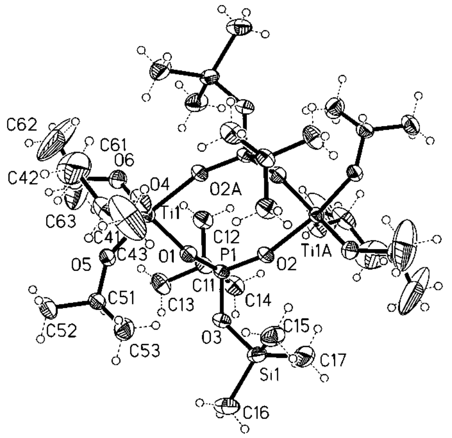

Figure 1. Molecular structure of $[(O\text{-}i\text{-}Pr)_3Ti(\mu\text{-}O)_2P(OSiMe_3)(t\text{-}Bu)]_2$.

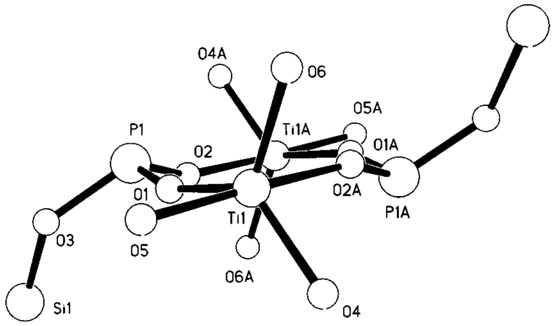

Figure 2. Shape of the $Ti_2P_2O_4$ core revealing the chair conformation.

Similar investigations carried out with Ti(OMe)$_4$ did not lead to any isolable products.

The spectroscopic conclusions were corroborated by an X-ray diffraction study of **2**. Single crystals of **2** were grown from pentane over a 15 day period at −80 °C. **2** crystallizes as a centrosymmetric dimer in the monoclinic space group $P2_1/n$ with the titanium centers assuming a five-coordinated trigonal bipyramidal geometry (Figure 1). The t-Bu and the OSiMe$_3$ substituents present on each phosphorus center are trans to each other. The central $Ti_2P_2O_4$ core assumes a chair conformation in the solid state (Figure 2). The intra-ring Ti−O and P−O bond lengths are nearly identical [Ti(1)−O(1) = 1.891(2) Å, Ti(1)−O(2A) = 2.031(2) Å; P(1)−O(1) = 1.444(2) Å, P(1)−O(2) = 1.494(2) Å] and are in close agreement with the literature precedents.[12]

In contrast to the monomeric titanium alkoxides, the isopropoxides of zirconium and hafnium are dimeric alcoholates[17] of the general formula $[M(O\text{-}i\text{-}Pr)_4(i\text{-}PrOH)]_2$ (M = Zr, Hf). Through our experience in the previous investigations with titanium alkoxides, it was realized that the use of low initial temperatures and hydrocarbon solvents is the ideal initial condition necessary for analogous reactions. A 2:1 reaction between $Ph_2P(O)(OH)$ and the corresponding isopropoxide of either zirconium or hafnium at −60 °C in toluene resulted in a product of the composition $[(O\text{-}i\text{-}Pr)_3M(\mu\text{-}O\text{-}i\text{-}Pr)_2(\mu\text{-}OPOPh_2)\text{-}M(O\text{-}i\text{-}Pr)_2]Ph_2P(O)(OH)$ (M = Zr (**3**), Hf (**4**)) in high yield (eq 2). A 1:1 reaction between the above-mentioned starting materials also yielded **3** and **4**, in addition to the unreacted isopropoxide, thereby indicating that these are the most favorable products under the reaction conditions employed.

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$$[\mathrm{M(O\text{-}\mathit{i}\text{-}Pr)_4(\mathit{i}\text{-}PrOH)}]_2 + 2\mathrm{Ph_2P(O)(OH)} \xrightarrow{-3\ \mathit{i}\text{-PrOH}}$$
$$[\mathrm{(O\text{-}\mathit{i}\text{-}Pr)_3M(\mu\text{-}O\text{-}\mathit{i}\text{-}Pr)_2(\mu\text{-}OPOPh_2)M(O\text{-}\mathit{i}\text{-}Pr)_2}]\mathrm{Ph_2P(O)(OH)}$$
$$\mathrm{M} = \mathrm{Zr}\ (\mathbf{3}),\ \mathrm{Hf}\ (\mathbf{4}) \qquad (2)$$

In the case of **3** and **4**, the ^{1}H NMR spectra recorded in benzene-d_6 reveal three distinct sets of doublets (in the range 1.2−1.6 ppm) and three distinct sets of multiplets (in the range 4.5−4.9 ppm), indicating three different O-*i*-Pr environments in the molecule. The phenyl moieties are observed as two different sets of multiplets (8.1−8.3 ppm) in the aromatic region. Also, a singlet was observed in each case (ca. 11.9 ppm) which is characteristic of an OH group associated with hydrogen-bonding interactions present on a phosphorus center. On the basis of the ^{1}H NMR data, it could be assumed that one $Ph_2P(O)O$ moiety provides a bridge between two metal centers and the other molecule could just be associated coordinatively through the oxygen center present as P═O. This assumption was supported by the ^{31}P NMR spectra in which two distinct signals were observed (18.8, 26.9 ppm for **3**, 20.1, 28.5 ppm for **4**).

The IR spectra of **3** and **4** reveal the presence of broad bands (ca. 2380 and ca. 1670 cm^{-1}, respectively) which could be additional support for the presence of intra- or intermolecular hydrogen bonding in these molecules. These absorptions are also present in the IR spectra of $Ph_2P(O)(OH)$ and in *t*-BuP(O)(OSiMe$_3$)(OH). Besides, the absorption at ca. 1260 cm^{-1} is characteristic for ν(P═O) as evidenced in metal phosphates.[11,14] In the spectrum of **4**, the band at 430 cm^{-1} is typical for ν(Hf−OR).[17b] The EI-MS spectra of **3** and **4** reveal a peak due to the $[M^+ - 2PrOH]$ fragment (*m/e* 911 for **3** and 1086 for **4**) of 100% intensity.

Since **3** and **4** have identical spectroscopic properties, their solid-state structures could also be anticipated to be isomorphous. Hence, we proceeded with the structural characterization of only the zirconium compound. Single crystals of **3** were grown from toluene over a period of 2 days at −32 °C. **3** crystallizes in the monoclinic space group $P2_1/n$. The two zirconium centers are connected through two O-*i*-Pr bridges, forming a four-membered ring with an average Zr−O bond distance of 2.170 Å (Figure 3), which resembles that of the starting material.[17a] The Zr(1)−O(3) and Zr(2)−O(4) bond lengths are similar with 2.142 Å as the average value. However, the Zr(2)−O(5) bond distance is slightly shorter (2.077(3) Å). Also, there is an intramolecular hydrogen-bonding interaction between the OH group linked to the phosphorus center P(2) and one of the O-*i*-Pr moieties connected to the zirconium center Zr(1) (H(67)- - -O(31) = 2.064 Å).

Through the above-mentioned investigations, we have demonstrated the use of metal alkoxides as viable precursors to group 4 metallaphosphonates. Under the conditions employed, the titanium systems yield an eight-membered ring, containing titanium and phosphorus centers. Interestingly, the presence of a reactive P−OH moiety in the zirconium and hafnium compounds suggests their potential as building blocks for macromolecular assemblies. Also, these are the first examples of organosoluble zirconium and hafnium phosphonates produced by employing molecular routes.

Experimental Section

General Information. All experimental manipulations were carried out under a dry, prepurified argon atmosphere, using Schlenk techniques and rigorously excluding moisture and air.[18] The samples for spectral measurements were prepared in a drybox. Solvents were dried over an Na/K alloy and freshly distilled prior to use. ^{1}H, ^{31}P, and ^{29}Si NMR spectra were measured on Bruker MSL-400, AM-250, and AM-200 instruments. The chemical shifts are reported in ppm with reference to $SiMe_4$ (external) for ^{1}H and ^{29}Si nuclei and to 85% H_3PO_4 (external) for the ^{31}P nucleus. IR spectra were recorded on a Bio-Rad Digilab FTS 7 spectrometer. Mass spectra were obtained on a Finnigan MAT 8230 or a Varian MAT CH 5 spectrometer. Elemental analyses were performed at the analytical laboratory of the Institute of Inorganic Chemistry, University of Göttingen.

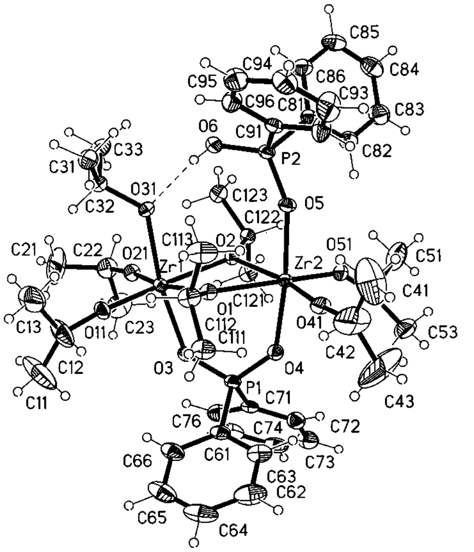

Figure 3. Molecular structure of $[(O\text{-}i\text{-}Pr)_3Zr(\mu\text{-}O\text{-}i\text{-}Pr)_2(\mu\text{-}OPOPh_2)\text{-}Zr(O\text{-}i\text{-}Pr)_2]Ph_2P(O)(OH)$.

Starting Materials. *t*-BuP(O)(OH)$_2$ was prepared using a literature procedure.[19] Me_3SiCl (Aldrich) was distilled prior to use. Triethylamine was dried over calcium dihydride and freshly distilled before use. $Ph_2P(O)(OH)$ (Acros) was dried under high vacuum. Titanium isopropoxide (Aldrich), zirconium isopropoxide (Strem), and hafnium isopropoxide (Strem) were used as received without further purification.

Preparation of *t*-BuP(O)(OSiMe$_3$)(OH). To a stirred solution containing *t*-BuP(O)(OH)$_2$ (20 g, 0.14 mol) and Et_3N (14.7 g, 0.14 mol) in THF (300 mL) at −10 °C was added dropwise Me_3SiCl (15.7 g, 0.14 mol) diluted in THF (50 mL) with the aid of a dropping funnel over a period of 1 h. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The amine hydrochloride formed was filtered off using a frit of medium porosity, and the solvent was removed in vacuo from the filtrate. The solid obtained was extracted with hexane (100 mL), and the extract was filtered to remove the residual amine hydrochloride. After the solvent was removed in vacuo, a waxy solid was obtained, which was subsequently dried overnight. Yield: 21 g (71%, 0.1 mol). Anal. Calcd for $C_7H_{19}O_3PSi$: C, 39.98; H, 9.11; P, 14.73; Si, 13.36. Found: C, 39.54; H, 8.92; P, 14.7; Si, 13.2. MS (EI, 70 eV): *m/e* 211 (100, M^+). IR (Nujol), cm^{-1}: 2721 w, 2338 br, 1677 br, 1480 vs, 1421 m, 1395 m, 1365 m, 1255 s, 1224 w, 1189 vs, 1033 w, 1015 w, 976 w, 853 s, 830 s, 761 vs, 723 w, 689 m, 644 vs, 598 m, 502 vs. ^{1}H NMR (250 MHz, benzene-d_6): δ 0.22 (s, $(CH_3)_3Si$, 9H), 1.20 (d, $C(CH_3)_3$, 9H, $^3J_{PH} = 16.6$ Hz), 13.60 (s, P−OH). ^{31}P NMR (101 MHz, benzene-d_6): δ 32.4 (s). ^{29}Si NMR (49.7 MHz, benzene-d_6): δ 21.1 (d, $^2J_{PSi} = 10.4$ Hz).

Preparation of $[(O\text{-}i\text{-}Pr)_3Ti(\mu\text{-}O)_2PPh_2]_2$ (1). To a stirred suspension of $Ph_2P(O)(OH)$ (220 mg, 1 mmol) in toluene (25 mL) at −60 °C was slowly added Ti(O-*i*-Pr)$_4$ (280 mg, 1 mmol) diluted in toluene (10 mL). The reaction mixture was allowed to warm slowly to room temperature and stirred for an additional period of 6 h. After removal of the solvent in vacuo, an oily solid was obtained, which was subsequently crystallized from toluene at −30 °C to obtain **1** as a white crystalline solid. Yield: 200 mg (45.2%, 0.22 mmol). Anal. Calcd for

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$C_{42}H_{62}O_{10}P_2Ti_2$: C, 57.02; H, 7.06; P, 7.00. Found: C, 56.58; H, 7.09; P, 6.8. IR (Nujol), cm^{-1}: 1593 w, 1261 w, 1160 m, 1199 w, 1160 m, 1128 vs, 1068 m, 1043 s, sh, 1021 s, sh, 848 m, 800 w, 751 m, 725 s, 694 m, 611 m, sh, 531 w, sh, 466 w. ^{1}H NMR (200 MHz, benzene-d_6): δ 1.21 (d, $OCH(CH_3)_2$), 1.35 (d, $OCH(CH_3)_2$), 4.53 (m, $OCH(CH_3)_2$), 5.12 (m, $OCH(CH_3)_2$), 6.91 (m, C_6H_5), 7.90 (m, C_6H_5). ^{31}P NMR (81 MHz, benzene-d_6): δ 19.2 (s), 21.0 (s), 24.3 (s).

Preparation of [(O-*i*-Pr)$_3$Ti(μ-O)$_2$P(OSiMe$_3$)(*t*-Bu)]$_2$ (2). To a stirred solution of *t*-BuP(O)(OSiMe$_3$)(OH) (500 mg, 2.38 mmol) in pentane (30 mL) at −60 °C was added dropwise a solution containing Ti(O-*i*-Pr)$_4$ (680 mg, 2.38 mmol) in pentane (20 mL). The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The solvent was removed in vacuo, and prolonged pumping yielded a waxy solid, which was subsequently dissolved in pentane (10 mL). The solution was stored at −80 °C over a period of 15 days to give analytically pure **2**. Yield: 620 mg (60%, 0.71 mmol). Anal. Calcd for $C_{32}H_{78}O_{12}P_2Si_2Ti_2$: C, 44.24; H, 9.05; P, 7.13. Found: C, 43.9; H, 9.0; P, 7.0. IR (Nujol), cm^{-1}: 1590 w, 1365 s, sh, 1331 w, 1255 s, 1211 m, 1159 m, sh, 1125 vs, 1074 m, 1009 s, 852 s, 801 w, 690 w, 507 w. ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.21 (s, $(CH_3)_3Si$, 18H), 1.22 (d, $C(CH_3)_3$, 18H, $^3J_{PH} = 12.51$ Hz), 1.31 (d, $OCH(CH_3)_2$, 36H), 3.98 (m, $OCH(CH_3)_2$, 6H). ^{31}P NMR (101 MHz, CDCl$_3$): δ 17−35 (numerous signals). ^{29}Si NMR (49.7 MHz, CDCl$_3$): δ 14.7 (s), 16.8 (d), 18.7 (d), 19.7 (d).

Preparation of [(O-*i*-Pr)$_3$Zr(μ-O-*i*-Pr)$_2$(μ-OPOPh$_2$)Zr(O-*i*-Pr)$_2$]-Ph$_2$P(O)(OH) (3). A solution of [Zr(O-*i*-Pr)$_4$(*i*-PrOH)]$_2$ (387 mg, 0.5 mmol) in toluene (10 mL) was added dropwise to a stirred suspension of Ph$_2$P(O)(OH) (220 mg, 1 mmol) in toluene (35 mL) at −60 °C. The reaction mixture was allowed to warm slowly to room temperature. The solvent was reduced (to 10 mL) in vacuo, and the resultant solution was stored at −30 °C overnight to yield analytically pure **3**. Yield: 410 mg (79.5%, 0.39 mmol). Anal. Calcd for $C_{45}H_{70}O_{11}P_2Zr_2$: C, 52.40; H, 6.84; P, 6.01. Found: C, 52.30; H, 6.60; P, 5.9. MS (EI, 70 eV): *m*/*e* 911 (100, M$^+$ − 2PrOH). IR (Nujol), cm^{-1}: 2619 w, 2377 br, 1676 br, 1440 s, sh, 1359 vs, 1337 s, sh, 1261 m, 1130 vs, 1086 s, sh, 997 vs, 940 m, 844 m, 820 s, 753 m, 725 s, 696 s, 558 vs, 457 m, 418 w. ^{1}H NMR (200 MHz, benzene-d_6): δ 1.16 (d, $OCH(CH_3)_2$, 12H), 1.42 (d, $OCH(CH_3)_2$, 12H), 1.51 (d, $OCH(CH_3)_2$, 18H), 4.5 (m, $OCH(CH_3)_2$, 2H), 4.71 (d, $OCH(CH_3)_2$, 2H), 4.84 (m, $OCH(CH_3)_2$, 3H), 8.10 (m, C_6H_5, 10H), 8.26 (m, C_6H_5, 10H), 11.81 (s, P−OH, 1H). ^{31}P NMR (101 MHz, benzene-d_6): δ 18.8 (s), 26.9 (s).

Preparation of [(O-*i*-Pr)$_3$Hf(μ-O-*i*-Pr)$_2$(μ-OPOPh$_2$)Hf(O-*i*-Pr)$_2$]-Ph$_2$P(O)(OH) (4). A procedure similar to that for **3** was followed. Yield: 487 mg (81%, 0.40 mmol). Anal. Calcd for $C_{45}H_{70}Hf_2O_{11}P_2$: C, 44.82; H, 5.85; P, 5.14. Found: C, 44.50; H, 6.03; P, 5.1. MS (EI, 70 eV): *m*/*e* 1086 (100, M$^+$ − 2PrOH). IR (Nujol), cm^{-1}: 2623 w, 2381 br, 1679 br, 1441 s, sh, 1358 vs, 1336 s, sh, 1261 m, 1133 vs, 1045 s, sh, 997 vs, 937 m, 844 m, 820 s, 754 m, 723 s, 696 s, 555 vs, 454 m, 430 w. ^{1}H NMR (200 MHz, benzene-d_6): δ 1.18 (d, $OCH(CH_3)_2$, 12H), 1.43 (d, $OCH(CH_3)_2$, 12H), 1.52 (d, $OCH(CH_3)_2$, 18H), 4.59 (m, $OCH(CH_3)_2$, 2H), 4.73 (d, $OCH(CH_3)_2$, 2H), 4.86 (m, $OCH(CH_3)_2$, 3H), 8.15 (m, C_6H_5, 10H), 8.29 (m, C_6H_5, 10H), 11.89 (s, P−OH, 1H). ^{31}P NMR (101 MHz, benzene-d_6): δ 20.1 (s), 28.5 (s).

X-ray Structure Determination. Crystal data for **2** were collected on a Stoe-Siemens-AED four-circle diffractometer using a learned-profile method.[20] The data for **3** were collected on a Stoe-Siemens-Huber four-circle diffractometer equipped with a Siemens CCD area detector using the ψ-scan mode. The structures were solved by direct methods (SHELXS-90/96)[21] and refined on all data by full-matrix least-squares on F^2.[22] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added in idealized positions and refined using a riding model. The crystal data and structure refinement details for **2** and **3** are given in Table 1.

Table 1. Crystal Data and Structure Refinement Details for **2** and **3**

	2	**3**
empricial formula	$C_{32}H_{78}O_{12}P_2Si_2Ti_2$	$C_{52}H_{78}O_{11}P_2Zr_2$ incl.toluene
fw	868.86	1123.52
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	11.296(13)	9.944(3)
b (Å)	17.403(3)	22.096(9)
c (Å)	12.241(2)	25.878(10)
α (deg)	90	90
β (deg)	90.217(15)	96.472(11)
γ (deg)	90	90
V (Å^3)	2406.4	5650
T (°C)	−70	−130
λ (Å)	0.710 73	0.710 73
D_{calcd} (g cm^{-3})	1.199	1.321
μ (mm^{-1})	0.496	0.479
F(000)	936	2352
cryst size (mm)	0.90 × 0.70 × 0.60	0.50 × 0.50 × 0.20
θ range (deg)	3.53−23.00	2.26−25.99
index ranges	$-12 \le h \le 12$	$-11 \le h \le 11$
	$-18 \le k \le 18$	$0 \le k \le 27$
	$-13 \le l \le 13$	$0 \le l \le 30$
no. of reflns collcd	8874	10 043
no. of indep reflns	3291	10 043
R(int)	0.0251	0.0000
no. of data	3290	10 043
no. of params	238	607
no. of restraints	0	59
goodness-of-fit on F^2	1.030	1.051
$R1[I > 2\sigma(I)]$[a]	0.0411	0.0424
$wR2$(all data)	0.1139	0.1164
largest diff peak and hole (e Å^{-3})	0.531, −0.368	0.869, −0.736

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

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Supporting Information Available: Tables of the X-ray crystal structure determination data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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