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Synthesis and Structure of Organic-Soluble Binuclear Molecular Phosphonates of Tantalum, Molybdenum, and Tungsten

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The reaction of (η^5-C_5Me_5)$TaMe_4$ with *tert*-butylphosphonic acid leads to the formation of a mixture of compounds: {[(η^5-C_5Me_5)TaMe][*t*-BuP(O)(OH)][*t*-BuP(O)$(OH)_2$]}$_2$(*t*-$BuPO_3$)$_2$ (**1**) and {[(η^5-C_5Me_5)Ta][*t*-BuP(O)$(OH)_2$]}$_2$(*t*-$BuPO_3$)$_2$(μ-O)$_2$ (**2**). Compound **2** was also obtained by recrystallization of **1** from a THF/hexane mixture. Reaction of (η^5-C_5Me_5)MCl_4 (M = Mo, W) with PhP(O)$(OH)_2$ yields the binuclear phosphonates {[(η^5-C_5Me_5)M][PhP(O)$(OH)_2$]}$_2$($PhPO_3$)$_2$(μ-O)$_2$ (M = Mo (**3**); M = W (**4**)). Compounds **2**·THF and **3**·2.5THF were characterized by single-crystal X-ray studies. The tantalum and molybdenum phosphonates **2**·THF and **3**·2.5THF have different structures as compared to those of the previously reported titanophosphonate cages.

Introduction

The chemistry of groups 5 and 6 transition metal phosphate and phosphonate complexes attracts permanent attention because of their catalytic properties.[1−3] Furthermore, these compounds are well-known as ion exchange reagents and building blocks for the preparation of supramolecular assemblies.[4−8] The usual synthetic route to these systems affords hydrothermal synthesis as well as reactions of acetylacetonato complexes or metal chlorides with the appropriate phosphonic acids in organic solutions.[3,6,9−12]

On the other hand, the soluble organometallic phosphonates are attracting the attention of chemists because of their structural peculiarities as well as their ability to serve as models for many heterogeneous transition metal doped catalysts. The synthetic methodology employed for the synthesis has been commonly the reaction of metal alkyls with phosphonic acids because of the facile elimination of an alkane as a side product.[13−15]

In our previous work we established different synthetic methods for organic soluble organometallic titanophosphonates with $Ti_4O_{14}P_4$ and $Ti_3O_{10}P_3$ cage frameworks.[14] The direct reaction of (η^5-C_5Me_5)$TiCl_3$ with phosphonic acids in the presence of Et_3N as a base resulted in the formation of tetranuclear phosphonate cages. These systems were similarly obtained using (η^5-C_5Me_5)$TiMe_3$ as a precursor. Herein, we report on synthetic routes to tantalum, molybdenum, and tungsten phosphonates using the organometallic precursors (η^5-C_5Me_5)$TaMe_4$, (η^5-C_5Me_5)$MoCl_4$, and (η^5-C_5Me_5)WCl_4, respectively.

Results and Discussion

Reaction of (η^5-C_5Me_5)$TaMe_4$ and *tert*-Butylphosphonic Acid. (η^5-C_5Me_5)$TaMe_4$ reacts with *t*-BuP(O)$(OH)_2$ in a ratio of 1:3 in ether at room temperature with evolution of methane and precipitation of a pale-yellow solid. The resulting product of composition, {[(η^5-C_5Me_5)TaMe][*t*-BuP(O)(OH)][*t*-BuP(O)$(OH)_2$]}$_2$(*t*-$BuPO_3$)$_2$ (**1**; Scheme 1) was characterized by ^1H, ^{13}C NMR, IR, and analytical methods.

The ^1H NMR spectrum of **1** in $CDCl_3$ shows two doublets for the protons of the *t*-Bu groups (1.11 and 1.24 ppm) and a singlet for the methyl groups of the C_5Me_5 ligand (2.20 ppm) with the correct integration (12:6:10). This indicates that compound **1** contains four terminal and two bridging phosphonate moieties. Moreover, a singlet with the correct integration at 0.47 ppm can be assigned to the methyl groups on the tantalum atoms. The appearance of a signal at 59.08 ppm for this group in the ^{13}C NMR confirms this finding.[16] The protons for the OH groups on phosphorus are downfield-shifted, giving a broad signal (13.00 ppm). The ^{31}P NMR spectrum exhibits two signals, a broad signal (46.29 ppm) for terminal and a singlet (39.81 ppm) for bridging phosphorus nuclei. The mass spectroscopic studies show no formation of a molecular ion in the gas phase. However, fragmentation peaks with high molecular weights (up to 1200 *m*/*e*) are observed. The elemental analysis of **1** is consistent with the proposed structure.

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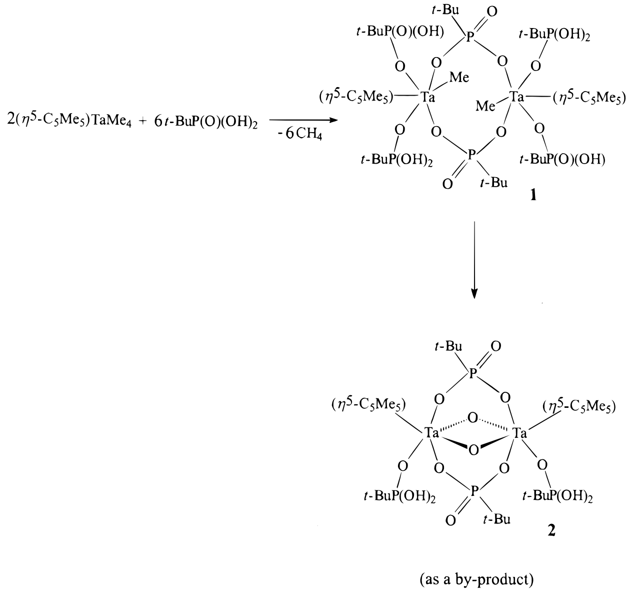
(16) For comparison, NMR data of compound [(η^5-C_5Me_5)$TaMe_3$]$_2$(μ-O) were taken. Jernakoff, P.; de Bellefon, C. M.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1987,** *6*, 1362.

10.1021/ic990966f CCC: $19.00

Scheme 1



Storing the filtrate of the previous reaction at −26 °C leads to the precipitation of the colorless compound **2**, $\{[(\eta^5\text{-}C_5Me_5)Ta][t\text{-}BuP(O)(OH)_2]\}_2(t\text{-}BuPO_3)_2(\mu\text{-}O)_2$. Compound **2** contains only two terminal t-BuP(O)(OH)$_2$ molecules coordinated to the tantalum atoms. Moreover, single crystals of **2**·THF were obtained by recrystallization of **1** from a THF/hexane (1:1) mixture. The ^{1}H NMR spectrum of compound **2** in $CDCl_3$ gives two doublets for the protons of the t-Bu groups (1.09 and 1.20 ppm) and a singlet for the C_5Me_5 protons (2.25 ppm) with the integration 6:6:10, and a broad signal for the OH groups (11.10 ppm). The ^{31}P NMR spectrum shows two sharp resonances (47.75 and 29.86 ppm).

The by-products formed during the conversion of **1** to **2** were not isolated. Studying the filtrate after the recrystallization of **1** from THF/hexane by ^{1}H and ^{31}P NMR shows a mixture of phosphorus-containing products. Compound **2**·THF was characterized by single-crystal X-ray analysis.

X-ray Crystal Structure of 2·THF. Compound $\{[(\eta^5\text{-}C_5Me_5)Ta][t\text{-}BuP(O)(OH)_2]\}_2(t\text{-}BuPO_3)_2(\mu\text{-}O)_2$ (**2**) crystallizes with one molecule of THF from a solution of THF/hexane (1:1). The crystal structure of compound **2**·THF is shown in Figure 1, and selected bond lengths and angles are listed in Table 2. Compound **2**·THF crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell (Figure 1). To the best of our knowledge, compound **2**·THF represents the first example of a tantalum phosphonate compound. The molecule has a central four-membered Ta_2O_2 ring with an average Ta−O bond distance of 1.960 Å. There are two additional bridges connecting the two tantalum centers by t-BuPO$_3$ groups and forming an eight-membered $Ta_2O_4P_2$ ring vertical to the plane of the Ta_2O_2 ring. The Ta−O bond lengths within the eight-membered $Ta_2O_4P_2$ ring are longer (av 2.082 Å) than the Ta−O bond distances in the four-membered Ta_2O_2 ring. The terminal P=O bond lengths of the t-BuPO$_2$ groups forming the eight-membered ring are 1.525(5) Å (P1−O5) and 1.558(6) Å (P2−O8).

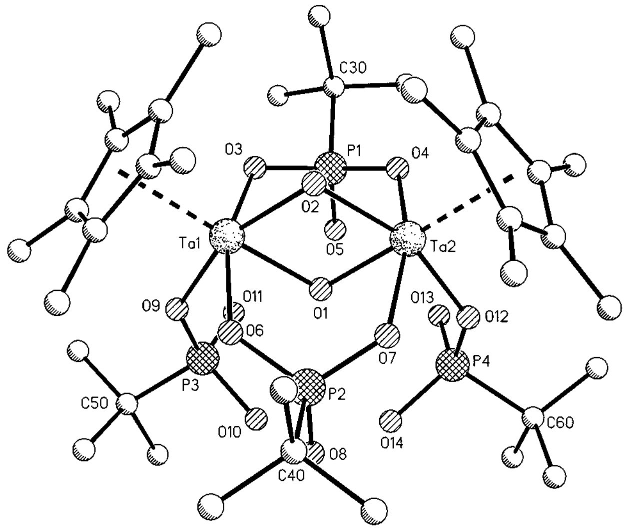


Figure 1. Molecular structure of **2**·THF in the solid state. THF molecules and hydrogen atoms are omitted for clarity.

Table 1. Crystallographic Data for Compounds **2**·THF and **3**·2.5THF

	2·THF	**3**·2.5THF
chemical formula	$C_{36}H_{68}O_{14}P_4Ta_2\cdot C_4H_8O$	$C_{44}H_{52}Mo_2O_{14}P_4\cdot 2.5(C_4H_8O)$
fw	1282.79	1300.94
space group	$P2_1/c$	$P2_1/n$
a (Å)	11.875(3)	16.992(2)
b (Å)	42.072(9)	20.189(3)
c (Å)	10.394(2)	18.107(4)
α, γ (deg)	90	90
β (deg)	106.09(3)	98.24(3)
V (Å^3)	4989.5(19)	6147.5(18)
Z	4	4
ρ_{calcd} (g cm^{-3})	1.708	1.406
temp (°C)	−140(2)	−100(2)
μ (cm^{-1})	4.572	0.575
R1^a	0.0501	0.0546
wR2^b	0.0958	0.1288

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**·THF

Ta1−O1	1.967(5)	P1−O4	1.543(5)
Ta1−O2	1.964(5)	P1−O5	1.525(5)
Ta2−O1	1.972(5)	P2−O6	1.542(5)
Ta2−O2	1.938(5)	P2−O7	1.544(5)
Ta1−O3	2.069(5)	P2−O8	1.558(6)
Ta1−O6	2.085(5)	P3−O9	1.520(6)
Ta1−O9	2.096(5)	P3−O10	1.522(8)
Ta2−O4	2.084(5)	P3−O11	1.557(7)
Ta2−O7	2.088(5)	P4−O12	1.513(5)
Ta2−O12	2.110(5)	P4−O13	1.555(7)
P1−O3	1.554(5)	P4−O14	1.518(7)
Ta1−O1−Ta2	102.8(2)	O3−Ta1−O6	160.9(2)
Ta1−O2−Ta2	104.2(2)	O4−Ta2−O7	160.9(2)
Ta1−O3−P1	124.6(3)	O3−P1−O4	110.7(3)
Ta2−O4−P1	124.5(3)	O6−P2−O7	111.7(3)
Ta1−O6−P2	124.8(3)	Ta1−O9−P3	137.8(3)
Ta2−O7−P2	124.2(3)	Ta2−O12−P4	139.5(3)

Reactions of $(\eta^5\text{-}C_5Me_5)MoCl_4$ and $(\eta^5\text{-}C_5Me_5)WCl_4$ with Phenylphosphonic Acid. Reaction of $(\eta^5\text{-}C_5Me_5)MoCl_4$ and $(\eta^5\text{-}C_5Me_5)WCl_4$ with 2 equiv of phenylphophonic acid in the presence of 4 equiv of triethylamine afforded the diamagnetic Mo and W phosphonates of composition $\{[(\eta^5\text{-}C_5Me_5)M][PhP(O)(OH)_2]\}_2(PhPO_3)_2(\mu\text{-}O)_2$ (M = Mo (**3**); M = W (**4**); Scheme 2). The compounds were characterized using analytical and spectroscopic techniques and in the case of **3**·2.5THF by means of single-crystal X-ray crystallographic studies.

The IR spectra of the phosphonates **3** and **4** clearly reveal broad bands in the region of 3400 and 2700 cm^{-1}, indicating the presence of OH groups at a phosphorus center. The analysis of the ^{1}H NMR spectra shows broad signals at 12.30 ppm (**3**)

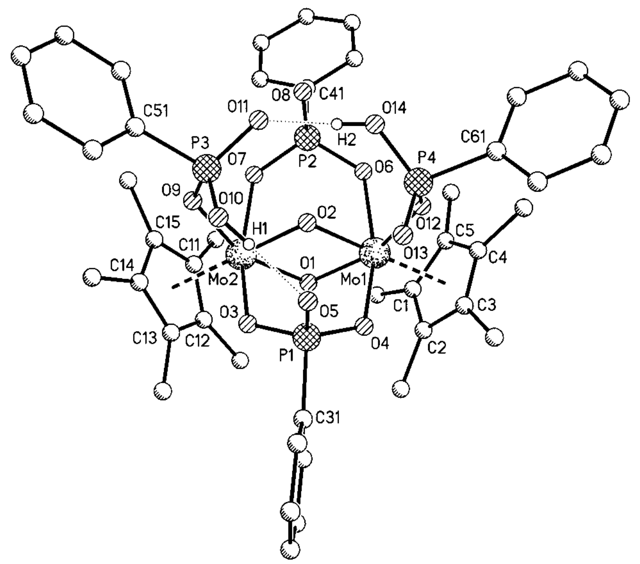
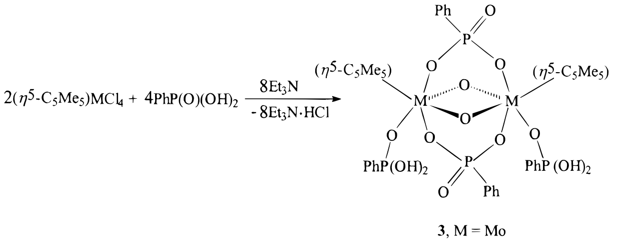


Figure 2. Molecular structure of $\mathbf{3}\cdot 2.5$THF in the solid state. THF molecules and hydrogen atoms of organic groups are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $\mathbf{3}\cdot 2.5$THF

Mo(1)−O(1)	1.934(3)	P(4)−O(13)	1.532(4)
Mo(1)−O(2)	1.937(3)	P(4)−O(14)	1.535(4)
Mo(2)−O(1)	1.920(3)	P(2)−O(8)	1.563(4)
Mo(2)−O(2)	1.942(3)	P(1)−O(5)	1.540(4)
Mo(1)−O(4)	2.139(4)	H(1)···O(5)	1.73(2)
Mo(1)−O(6)	2.121(4)	H(2)···O(11)	1.70(2)
Mo(2)−O(3)	2.109(4)		
Mo(2)−O(7)	2.126(3)	Mo(1)−O(1)−Mo(2)	104.46(15)
Mo(1)−Mo(2)	3.047(10)	Mo(1)−O(2)−Mo(2)	103.51(14)
Mo(1)−O(12)	2.127(3)	O(1)−Mo(1)−O(2)	75.91(13)
Mo(2)−O(9)	2.129(3)	O(1)−Mo(2)−O(2)	76.12(13)
P(3)−O(10)	1.546(4)	O(10)−H(1)···O(5)	175(6)
P(3)−O(11)	1.518(4)	O(14(−H(2)···O(11)	173(8)

Scheme 2



3, M = Mo

4, M = W

and 13.12 ppm (**4**) according to unreacted OH groups as expected. At 1.86 ppm (**3**) and 2.09 ppm (**4**) the signals for the protons of the (η^5-C_5Me_5) group appear.

The ^{31}P NMR spectrum shows in both cases two signals of equal intensity, indicating that the phosphorus atoms in the molecules have different environments as documented by the crystal structure of **3**. The chemical shifts (18.41 ppm (**3**) and 14.84 ppm (**4**)) could be assigned to the two terminal phosphorus atoms, while the signals at 16.43 ppm (**3**) and 13.66 ppm (**4**) correspond to the bridging ones. Compound $\mathbf{3}\cdot 2.5$THF was characterized by single-crystal X-ray analysis.

X-ray Crystal Structure of $\mathbf{3}\cdot 2.5$THF. Single crystals of compound $\{[(\eta^5\text{-}C_5Me_5)Mo][PhP(O)(OH)_2]\}_2(PhPO_3)_2(\mu\text{-}O)_2\cdot 2.5$THF were grown from a solution in THF/hexane (3:1). The crystal structure of compound $\mathbf{3}\cdot 2.5$THF is shown in Figure 2, and selected bond lengths and angles are listed in Table 3.

Compound $\mathbf{3}\cdot 2.5$THF crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell (Figure 2). The central core of $\mathbf{3}\cdot 2.5$THF consists of two molybdenum atoms connected via two μ-oxo bridges, forming a four-membered Mo_2O_2 ring with an average Mo−O bond length of 1.933 Å. The ability of the μ-oxo bridges in transition metal complexes in mediating strong antiferromagnetic coupling probably accounts for the diamagnetism of this molybdenum(V) complex, as well as for its tungsten analogue **4**. A comparable phenomenon was previously observed for the structurally characterized chromium(V) μ-oxo-bridged $[(\eta^5\text{-}C_5Me_5)Cr(O)Me]_2(\mu\text{-}O)$ complex.[17]

The Mo−O bond lengths in the eight-membered $Mo_2O_4P_2$ ring are longer (av 2.124 Å) than those in the four-membered Mo_2O_2 ring. The P═O bond lengths are found to be in the range 1.540−1.563 Å for the $PhPO_2$ forming the eight-membered ring and 1.518−1.532 Å for the external ligands. Refinement of the X-ray data shows the presence of strong hydrogen bonds between external $PhPO_3H_2$ groups (1.73 Å) and between an external $PhPO_3H_2$ group and a core P═O moiety (1.75 Å).

Conclusions

We have thus demonstrated a facile synthetic approach to the first organic-soluble organometallic tantalum, molybdenum, and tungsten phosphonates. Compounds $\mathbf{2}\cdot$THF and $\mathbf{3}\cdot 2.5$THF show frameworks different from those of the previously characterized group 4 compounds.

Experimental Section

General Methods and Materials. All experimental manipulations were carried out either using Schlenk tube techniques or in a drybox under an inert atmosphere. Solvents were dried by standard methods and freshly distilled prior to use. Triethylamine was dried over CaH_2 and distilled under a nitrogen atmosphere. (η^5-C_5Me_5)$TaMe_4$, (η^5-C_5Me_5)$MoCl_4$, and (η^5-C_5Me_5)WCl_4 were prepared using literature procedures.[18−20] *Tert*-butyl- and phenylphosphonic acids (Aldrich) were dried under high vacuum prior to use. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AS 400 instrument. The chemical shifts are reported in ppm relative to external $SiMe_4$ (for ^{1}H and ^{13}C) and to external 85% H_3PO_4 (for ^{31}P). IR spectra were recorded on a Bio-Rad Digilab FTS 7 spectrometer. Melting points were obtained on a HWS-SG 3000 instrument and are reported uncorrected. Elemental analyses were performed at the analytical laboratory of the Institute of Inorganic Chemistry, University of Göttingen.[21]

Preparation of $\{[(\eta^5\text{-}C_5Me_5)TaMe][t\text{-}BuP(O)(OH)][t\text{-}BuP(O)(OH)_2]\}_2(t\text{-}BuPO_3)_2$ (1) and $\{[(\eta^5\text{-}C_5Me_5)Ta][t\text{-}BuP(O)(OH)_2]\}_2(t\text{-}BuPO_3)_2(\mu\text{-}O)_2$ (2). A solution of *t*-BuP(O)(OH)$_2$ (1.2 g, 8.7 mmol) in ether (50 mL) was added dropwise to a stirred solution of (η^5-C_5Me_5)$TaMe_4$ (1.1 g, 2.9 mmol) in ether (30 mL). After complete addition the reaction mixture was stirred for 24 h at room temperature. The precipitate was filtered off and dried in vacuo. Yield of **1**: 1.65 g (76%). Storing the filtrate for 48 h at −26 °C led to precipitation of **2** (0.110 g, 6% yield). Spectroscopic and analytical data for **1**. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.47 (s, 6H, CH_3), 1.11 (d, 36H, CH_3(*t*-Bu), *J*(PH) = 16.85 Hz), 1.24 (d, 18H, CH_3(*t*-Bu), *J*(PH) = 16.69 Hz), 2.20 (s, 30H, CH_3 (C_5Me_5)), 13.00 (br, 6H, O*H*). ^{13}C NMR (63 MHz, $CDCl_3$): δ 11.79 (s, CH_3 (C_5Me_5)), 25.31 (m, CH_3(*t*-Bu)), 31.81 (d, *C*(CH_3)$_3$, *J*(PC) = 147.13 Hz), 32.09 (d, *C*(CH_3)$_3$, *J*(PC) = 136.87 Hz), 59.08 (d, Ta−CH_3, *J*(PC) = 5.57 Hz), 126.31 (s, C_5Me_5). ^{31}P NMR

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(21) Analytical and spectroscopic data are reported for solvent-free compounds. Compounds **1**−**4** were dried for 2 h in high vacuum in order to remove all volatile residues.

(100 MHz, $CDCl_3$): δ 39.81, 46.29. IR (KBr, cm^{-1}): ν 3400, 2300, 1480, 1463, 1444, 1397, 1377, 1366, 1296, 1150, 1030, 995, 931, 923, 830, 727, 679, 660, 645, 662, 608, 548, 491, 476, 428, 368. Anal. Calcd for $C_{46}H_{96}O_{18}P_6Ta_2$: C, 37.2; H, 6.5; P 12.5. Found: C, 37.6; H, 6.5; P 12.3. Spectroscopic and analytical data for **2**. ^1H NMR (200 MHz, $CDCl_3$): δ 1.09 (d, 18H, CH_3(*t*-Bu), J(PH) = 16.12 Hz), 1.20 (d, 18H, CH_3(*t*-Bu), J(PH) = 16.91 Hz), 2.25 (s, 30H, CH_3 (C_5Me_5)), 11.00 (br, 4H, O*H*). ^{31}P NMR (100 MHz, $CDCl_3$): δ 29.86, 47.75. IR (KBr, cm^{-1}): ν 3500, 2400, 1310, 1262, 1225, 1194, 1134, 1088, 1041, 1015, 997, 983, 934, 908, 825, 721, 678, 652, 619, 601, 548, 498, 484. EI MS (70 eV): *m/e* (%) [$M^+ - 2H_2O$], 1176 (10), [$M^+ - 2H_2O - C_5Me_5$], 1041 (100). Anal. Calcd for $C_{36}H_{70}O_{14}P_4Ta_2$: C, 35.7; H, 5.8; P, 10.2. Found: C, 35.6; H, 6.1; P, 10.1.

Preparation of $\{[(\eta^5\text{-}C_5Me_5)Mo][PhP(O)(OH)_2]\}_2(PhPO_3)_2(\mu\text{-}O)_2$ (3). A mixture containing phenylphosphonic acid (0.85 g, 5.4 mmol) and triethylamine (1.11 g, 11 mmol) in THF (50 mL) was prepared. To the resulting stirred suspension was slowly added at room temperature a suspension of (η^5-C_5Me_5)$MoCl_4$ (1.00 g, 2.7 mmol) in THF (30 mL), whereby the reaction mixture immediately turned dark-green. After addition of (η^5-C_5Me_5)$MoCl_4$ the suspension was stirred for 2 h at room temperature and the mixture was then filtered. All volatiles were removed from the filtrate in vacuo, and the residue was extracted with a mixture of THF/hexane (2:1, 80 mL). Removal of solvent in vacuo yielded **3** as a dark-green solid. Yield: 1.02 g (68%). The solid was crystallized from a THF/hexane (3:1) mixture at − 30 °C over 7 days to obtain analytically pure **3**. ^1H NMR (250 MHz, $CDCl_3$): δ 1.86 (s, 30H,CH_3 (C_5Me_5)), 7.38, 7.78, and 7.91 (m, 20H, arom C*H*), 12.30 (br, 4H, P−O*H*). ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.43, 18.41. IR (KBr, cm^{-1}): ν 3430, 3055, 3002, 2962, 2911, 2727, 2312, 1596, 1496, 1439, 1371, 1132, 1065, 975, 944, 751, 715, 696, 646, 581, 535, 395, 354. Anal. Calcd for $C_{44}H_{54}Mo_2O_{14}P_4$: C, 47.1; H, 4.8; P, 11.0. Found: C, 47.3; H, 5.1; P, 10.6.

Preparation of $\{[(\eta^5\text{-}C_5Me_5)W][PhP(O)(OH)_2]\}_2(PhPO_3)_2(\mu\text{-}O)_2$ (4). To a stirred suspension of phenylphosphonic acid (0.82 g, 5.2 mmol) and triethylamine (1.16 g, 11.5 mmol) in THF (40 mL) a suspension of (η^5-C_5Me_5)WCl_4 (1.20 g, 2.6 mmol) in THF (20 mL) was added slowly at room temperature. The color of the mixture slowly turned green, and after being stirred for 12 h a dark-green solution containing a white solid was obtained. After the reaction mixture was filtered and all volatiles were removed in vacuo, the resulting solid was extracted with a THF/hexane (2:1, 80 mL) mixture. The solvent was removed under reduced pressure leaving **4** as a dark-green solid. Yield: 0.76 g (45%). Recrystallization from THF/hexane (2:1) mixture at −30 °C gave analytically pure **4**. ^1H NMR (250 MHz, $CDCl_3$): δ 2.09 (s, 30H, CH_3 (C_5Me_5)), 7.92 and 7.42 (m, 20H, arom C*H*), 13.12 (s, 4H, P−O*H*). ^{31}P NMR (100 MHz, $CDCl_3$): δ 14.84, 13.66. IR (KBr, cm^{-1}): ν 3420, 3053, 3000, 2963, 2914, 2717, 2312, 1596, 1499, 1439, 1374, 1131, 1067, 950, 753, 716, 697, 661, 588, 530, 386, 358. Anal. Calcd for $C_{44}H_{54}O_{14}P_4W_2$: C, 40.7; H, 4.2; P, 9.5. Found: C, 40.4; H, 4.5; P, 9.6.

Crystal Structure Solution and Refinement for 2·THF and 3·2.5THF (Table 1). Data for structures **2**·THF and **3**·2.5THF were collected on a Stoe−Siemens−Huber four-circle diffractometer coupled with a Siemens CCD area detector by the use of φ and ω scans. A semiempirical absorption correction was applied. All structures were solved by direct methods (SHELXS-97)[22] and refined against F^2 using SHELXL-97.[23] All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms a riding model was employed. During the refinement of the structure of **2**·THF, SIMU, DELO, and SAME restrains were applied (THF disorder). For the structure of **3**·2.5THF, SAME, SIMO, DELU, FLAT (phenyl groups disorder), and SIMU, DELU, SAME, DFIX (THF disorder) restrains were used.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of **2**·THF and **3**·2.5THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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