Synthesis, Structure, Spectroscopic Properties, and Hydrolytic Chemistry of Organophosphonoyl Polyoxotungstates of Formula $[C_6H_5P(O)]_2X^{n+}W_{11}O_{39}^{(8-n)-}$ ($X^{n+} = P^{5+}, Si^{4+}$)

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Phenylphosphonoyl heteropolyundecatungstates of formula $[PhP(O)]_2X^{n+}W_{11}O_{39}^{(8-n)-}$ ($X^{n+} = P^{5+}, Si^{4+}$) have been prepared, purified, and characterized by elemental analysis, IR, and ^{1}H, ^{31}P, and ^{183}W NMR. The compound $[(n\text{-}C_4H_9)_4N]_2H[PhP(O)]_2PW_{11}O_{39}$ (**1**) offers the first X-ray structure of an organically modified lacunary or defect Keggin polyoxoanion that is not severely disordered (orthorhombic, *Pbcn*; $a = 19.680$ (11) Å, $b = 16.446$ (13) Å, $c = 23.398$ (13) Å, $V = 7573$ (8) Å^3, $Z = 4$, $R = 8.60\%$). Two equivalent $PhP(O)^{2+}$ groups in **1** each bridge two terminal oxygen atoms of the four that define the "hole" in the XM_{11} lacunary structure, thus connecting two W_3O_{13} triads and a W_2O_{10} diad. ^{1}H, ^{31}P, and ^{183}W NMR collectively establish that the same structure for **1** is maintained in anhydrous organic solutions. **1** converts cleanly to the partially hydrolyzed compound $[(n\text{-}C_4H_9)_4N]_2H_2[PhP(O)][PhP(O)(OH)]PW_{11}O_{39}$ (**2**) when dissolved in wet dimethyl sulfoxide. Potentiometric titrations of **1** and **2** with base in acetonitrile reveal one and three titratable protons for **1** and **2**, respectively. In a novel and clean transformation, **2** converts slowly back to **1** when dissolved in anhydrous acetonitrile. The analogous silicon compound does not show this kind of behavior in solution. A ^{183}W NMR study shows the $[PhP(O)]_2X^{n+}W_{11}O_{39}^{(8-n)-}$ compounds (X = P, Si) possess true C_s symmetry in either acetonitrile or chloroform solution and **2** shows C_1 symmetry in either acetonitrile or dimethyl sulfoxide. ^{31}P NMR shows that **2** decomposes slowly to several products in DMSO-d_6. The kinetics results reveal that the rate is dependent on the water concentration with the half-life, $\tau_{1/2}$, for **2** in dry DMSO and wet DMSO (with 10 equiv of water) at 296 K of 312 and 55 h, respectively.

Introduction

The focus of this paper is a new type of early transition metal–oxygen anion cluster (polyoxometalate) derivatized with organic groups, the title compounds, and their structural and solution chemistry. The impetus for this work is 2-fold. First, we wished to provide X-ray crystallographic structural information on the derivatives of the heteropolyundecametalates $X^{n+}M_{11}O_{39}^{(12-n)-}$, where X^{n+} = a transition metal or main group element (Figure 1a). To date all X-ray crystallographic structure determinations on these defect (lacunary) complexes and their numerous d-electron transition metal (TM) substituted derivatives, $(TM^{z+})X^{n+}M_{11}O_{39}^{(12-n-z)-}$, have been marginally useful at best, principally as a consequence of high levels (usually 12-fold) of disorder encountered in the solid state.[1-3] The fact that the $X^{n+}M_{11}O_{39}^{(12-n)-}$ complexes are the largest and most accessible class of reactive defect polyoxometalates underscores this first impetus.[1] One of the title complexes, $[(n\text{-}C_4H_9)_4N]_2H[PhP(O)]_2PW_{11}O_{39}$ (**1**) (Figure 1b), was amenable to structure elucidation by X-ray crystallography. Second, we wished to extend what is now a rich and well-documented chemistry on polyoxometalate complexes derivatized with organic groups.[4-11] Data for a large number of polyoxometalates with covalently attached organic and organometallic groups have been reported, including definitive X-ray crystal structure determinations on tetrametalate[10a] and hexametalate derivatives.[10c,d] However, no single X-ray structure has been reported on organic group-derivatized undecametalates so far. The appropriate organic groups on the surfaces of polyoxometalates could modify the solubility and other physical

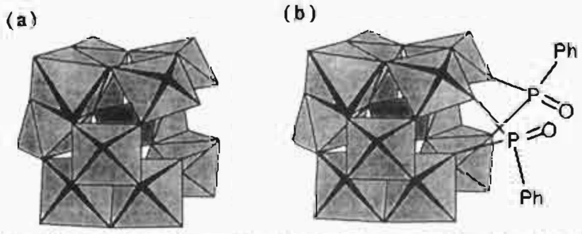

Figure 1. Polyhedral pictures of (a) lacunary $\alpha\text{-}X^{n+}W_{11}O_{39}^{(12-n)-}$ and (b) $\alpha\text{-}[PhP(O)]_2X^{n+}W_{11}O_{39}^{(8-n)-}$. Each octahedron denotes WO_6, and the central tetrahedron denotes XO_4 (X = Si, P).

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properties of the complexes that would increase their utility and versatility in catalysis (including asymmetric catalysis with chiral organic groups), film formation and microlithography, and various medical applications, including antiviral and antitumoral chemotherapy. In the last application covalently attached organic groups can alter activity, toxicity, and pharmacokinetic behavior of the compounds as well as aid in molecular recognition and targeting of the drugs.[12-14] Presented here is a thorough study encompassing the synthesis, solid-state and solution structures, and chemistry of these new title compounds.

Experimental Section

Methods and Materials. All chemicals purchased were reagent grade and were used without further purification. Infrared spectra were obtained as KBr pellets containing 2–5 wt % of the sample on either a Nicolet 510M FTIR or a Perkin-Elmer Model 1430 ratio recording spectrophotometer. Elemental analyses were conducted by Atlantic Microlab, Inc. (Norcross, GA), for C, H, and N and at E+R Microanalytical Lab., Inc. (Corona, NY), for all other elements. ^{1}H and ^{31}P NMR spectra were recorded with General Electric QE-300 and IBM WP-200SY FT NMR spectrometers at 300 and 81 MHz, respectively. ^{183}W NMR spectra were recorded with IBM WP-200SY and GE GN-500 spectrometers at 8.34 and 20.83 MHz, respectively. All NMR solvents were dried by storage over activated 3-Å molecular sieves for at least 1 week prior to use. ^{1}H, ^{31}P, and ^{183}W NMR chemical shifts were referenced to $(CH_3)_4Si$, 1.0% (v/v) trimethyl phosphate (TMP), and 2.0 M Na_2WO_4 in D_2O, respectively, unless otherwise noted. The chemical shift of the commonly used ^{31}P NMR external reference, 85% H_3PO_4, in the solvents used in this study, was consistently observed at δ −3.75 (±0.05) ppm relative to 1% TMP in the corresponding solvent using the IBM WP-200SY FT NMR spectrometer at room temperature. In the case of ^{31}P and ^{183}W NMR spectra, referencing was achieved by the substitution method. Chemical shifts downfield from the reference are reported as positive ($+\delta$), and multiplicity, numbers of the nuclei, and coupling constants (in hertz), as applicable, are given in parentheses. The probe temperature was 295 K in all NMR experiments unless otherwise stated. Potentiometric titrations of **1** and **2** in acetonitrile solution with 1.0 M methanolic $(n\text{-}C_4H_9)_4NOH$ to assess protonation states were carried out using a Corning Model 240 pH meter equipped with a combination micro glass electrode at room temperature.

Sodium and potassium salts of $X^{n+}W_{11}O_{39}{}^{(12-n)-}$ (X = P, Si) were prepared by following literature procedures.[15] The preparations of the two representative tetraalkylammonium salts are described below.

Synthesis of α-$[(n\text{-}C_4H_9)_4N]_4H_2NaPW_{11}O_{39}$. An aqueous solution of $Na_7PW_{11}O_{39}\cdot 13H_2O$[15a] was treated with a saturated aqueous solution of $(n\text{-}C_4H_9)_4NBr$ (15–20 equiv). The product was collected by filtration, washed with water, and air-dried to produce a white solid in 60–80% yield. IR (1300–400 cm^{-1}): 1151 (w), 1109 (m), 1055 (m), 958 (vs), 884 (s), 807 (vs), 752 (s), 596 (w), 517 (w). ^{31}P NMR (CD_3CN): δ −14.61. ^{183}W NMR (8.34 MHz, 0.21 M in DMSO-d_6): δ −81.9 (2W), −89.0 (2W), −104.2 (2W), −108.1 (2W), −113.2 (2W), −120.6 (1W).

Anal. Calcd for $C_{64}H_{146}N_4NaO_{39}PW_{11}$: C, 20.93; H, 4.01; N, 1.53; P, 0.84; Na, 0.63; W, 55.07. Found: C, 20.82; H, 3.93; N, 1.49; P, 1.22; Na, 0.52; W, 55.50.

Synthesis of α-$[(n\text{-}C_6H_{13})_4N]_{4.5}H_{2.5}NaSiW_{11}O_{39}$. To an aqueous solution of $Na_8SiW_{11}O_{39}\cdot 13H_2O$[15b,c] (9.05 g, 2.95 mmol in 150 mL of water) was added an acetonitrile solution of $(n\text{-}C_6H_{13})_4NBr$ (6.40 g in 40 mL, 5 equiv) with vigorous stirring. Upon mixing, an oily deposit was formed. A 350-mL portion of water was added, and the resulting mixture was stirred for 2 h. The turbid supernatant was decanted from the white sticky solid, which was washed with water and redissolved in 30 mL of acetonitrile. The solution was diluted with 200 mL of water, and the white sticky solid that formed was crushed with a spatula until it became powder. The solid was filtered off, washed with water, and air-dried overnight to give 6.9 g of white solid. A second crop (2.82 g) was harvested from the decanted supernatant. Total yield: 9.72 g (73%). IR (1300–300 cm^{-1}): 1157 (vw), 1009 (w), 967 (s), 908 (vs), 802 (s), 740 (sh), 547 (m), 387 (m), 350 (m). ^{183}W NMR (8.34 MHz, 0.21 M in CD_3CN): δ −76.1 (2W), −98.4 (2W), −112.1 (2W), −118.4 (5W). Instead of the expected 2:2:2:2:2:1 peak pattern, the three downfield peaks with a 2:2:1 ratio overlapped to give an overall 2:2:2:5 pattern. The full width at half-height (fwhh) is ≈11 Hz for the peaks.

Anal. Calcd for $C_{108}H_{236.5}N_{4.5}NaO_{39}SiW_{11}$: C, 30.20; H, 5.55; N, 1.47; Na, 0.54; Si, 0.65; W, 47.07. Found: C, 30.18; H, 5.50; N, 1.46; Na, 0.46; Si, 0.35; W, 46.19.

Synthesis of $[PhP(O)]_2PW_{11}O_{39}{}^{3-}$ and Related Compounds. Preparation of $[(n\text{-}C_4H_9)_4N]_2H[PhP(O)]_2PW_{11}O_{39}$ (1) from $[(n\text{-}C_4H_9)_4N]_4H_2NaPW_{11}O_{39}$ at Room Temperature. To α-$[(n\text{-}C_4H_9)_4N]_4H_2NaPW_{11}O_{39}$ (1.00 g, 0.27 mmol in 20 mL of acetonitrile) was added dropwise 0.08 mL of $PhP(O)Cl_2$ (2 equiv in 5 mL of acetonitrile) over a period of 10 min, during which the solution turned bright yellow. The flask was sealed with a septum stopper, and the mixture was stirred. After 67 h of stirring at room temperature, a pale yellow precipitate formed. The mixture was stirred for an additional 1 h, and the solid was collected on filter paper, washed with 20-mL of ether, and air-dried to give a pale yellow microcrystalline solid. The product was recrystallized from hot acetonitrile to give pale yellow elongated octahedral shaped crystals in 28% yield. The solubility of the compound in dry acetonitrile is approximately 2 mM. IR (1300–400 cm^{-1}): 1138 (m), 1119 (s), 1073 (m), 1063 (m), 1040 (w), 1024 (w), 991 (s), 977 (vs), 882 (s), 828 (vs), 744 (m, sh), 693 (w, sh), 594 (w), 575 (w), 528 (m), 514 (w). ^{1}H NMR (CD_3CN): δ 0.94 (t, 24H), 1.34 (sextet, 16H), 1.58 (quintet, 16H), 3.07 (t, 16H), 7.60 (m, 6H), 8.07 (quartet, 4H). ^{31}P NMR (CD_3CN): δ 17.20 (s), −15.94 (s). Compound **1** exhibited one titratable proton in acetonitrile consistent with the formula above (see Figure 9, Results and Discussion).

Anal. Calcd for $C_{44}H_{83}N_2O_{41}P_3W_{11}$: C, 15.49; H, 2.45; N, 0.82; P, 2.72; W, 59.28. Found: C, 15.57; H, 2.31; N, 0.81; P, 3.06; W, 59.04.

Preparation of 1 from $[(n\text{-}C_4H_9)_4N]_4H_2KPW_{11}O_{39}$ at 60 °C. To an acetonitrile solution of $[(n\text{-}C_4H_9)_4N]_4H_2KPW_{11}O_{39}$ (4.60 g in 30 mL) at 60 °C was added dropwise 2 equiv of $PhP(O)Cl_2$ in 15 mL of acetonitrile with stirring, and the flask was sealed with a septum stopper. The color of the solution changed from colorless to pale yellow over a period of 15 min. The solution was stirred for 3.5 h, during which time a pale yellow precipitate formed. The precipitate was filtered off, washed with 5 mL of acetonitrile, and air-dried to give 0.94 g (0.27 mmol) of a microcrystalline pale yellow solid in 22% yield. ^{1}H and ^{31}P NMR and IR spectra confirmed the product was **1**.

Preparation of 1 from $[(n\text{-}C_4H_9)_4N]_4H_2NaPW_{11}O_{39}$, $PhPCl_2$, and Ag^+. In situ generation of the phenylphosphonoyl moiety was accomplished by the addition of 4 equiv of $AgNO_3$ to 2 equiv of $PhPCl_2$ in 5 mL of acetonitrile. The yellow solution was quickly filtered from the white precipitate. This yellow solution was added to an acetonitrile solution of $[(n\text{-}C_4H_9)_4N]_4H_2NaPW_{11}O_{39}$ (4.06 g in 50 mL). The resulting solution was sealed and stirred overnight at room temperature. The pale yellow precipitate was filtered off, washed with 5 mL of acetonitrile, and air-dried to yield 0.67 g (0.20 mmol, 18% yield) of the product which was confirmed to be **1** by ^{1}H and ^{31}P NMR and IR spectroscopies.

Synthesis of $[(n\text{-}C_{10}H_{21})_4N]_2H[PhP(O)]_2PW_{11}O_{39}$. To a hot acetonitrile solution of $[(n\text{-}C_4H_9)_4N]_2H[PhP(O)]_2PW_{11}O_{39}$ (3.53 g in 200 mL) was added 3 equiv of $(n\text{-}C_{10}H_{21})_4NBr$ in 40 mL of chloroform. The solution volume was reduced to 50 mL using a rotary evaporator with a water bath

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of ~80 °C. While still spinning on the rotary evaporator, the solution was cooled to room temperature by removing the hot water bath. A heavy, yellow oily deposit isolated by decanting the supernatant was redissolved in 150 mL of a 1:2 (v/v) chloroform–acetonitrile solution. The solution volume was reduced to half of the original volume using a rotary evaporator with a water bath temperature of ~80 °C and cooled to room temperature again by removing the water bath. A heavy yellow amorphous deposit formed. The supernatant was decanted, and the thick, yellow oil was dried under vacuum to give a sticky solid (3.84 g). A second crop was harvested from the decanted solution by repeating the above procedure (0.55 g). Total yield: 4.39 g (~100%). IR (neat on CsI disk, 1200–500 cm^{-1}): 1156 (sh), 1135 (s), 1102 (vs), 1070 (s), 1058 (s), 1035 (s), 1021 (m), 986 (vs), 970 (vs), 900 (sh), 876 (vs), 825 (vs), 744 (s), 693 (m), 570 (m). ^{1}H NMR (CDCl$_3$): δ 8.13 (m, 4H), 7.53 (m, 6H), 3.15 (s, br, 16H), 1.61 (s, br, 16H), 1.26 (s, 96H), 0.86 (t, 24H). ^{183}W NMR (8.34 MHz, 0.17 M in CDCl$_3$): δ −83.0 (s, br, 2W), −99.5 (s, br, 3W), −111.0 (s, br, 2W), −190.0 (s, br, 2W, fwhh = 43 Hz), −215.3 (d, br, 2W, $^{2}J_{W\text{–}O\text{–}P} \approx 27$ Hz, fwhh = 58 Hz). The first three downfield peaks show fwhh = ~30 Hz. Due to the broad line shape and low S/N, the peak at δ −190.0 is not well resolved. The small peak observed at δ −87.9 was assigned to $PW_{12}O_{40}^{3-}$. This peak accounts for approximately 3 mol % of the product, as was deduced from the ^{183}W NMR peak integrations.

Synthesis of $[(n\text{-}C_4H_9)_4N]_2H_2[PhP(O)][PhP(O)(OH)]PW_{11}O_{39}$ (2). Compound **1** (0.73 g, 0.21 mmol) was dissolved in 5 mL of DMSO. Initially the mixture was turbid and orange yellow but within 5 min turned to a pale yellow homogeneous solution. The solution was diluted with 30 mL of methanol and 80 mL of anhydrous ether to give a white precipitate. The precipitate was isolated on a medium frit and slurried in anhydrous methanol, and the mixture was stirred for 30 min. The solid was filtered off, washed with 20 mL of anhydrous methanol, and vacuum-dried for 40 h at room temperature to give 0.62 g (84% yield) of a white powder. The solubility of the compound in dry acetonitrile was much higher than that of **1**. IR (1300–400 cm^{-1}): 1140 (m), 1114 (m), 1060 (sh), 971 (vs), 941 (sh), 881 (s), 830 (vs), 793 (sh), 695 (w,sh), 603 (w), 591 (w), 558 (w), 576 (w), 524 (m), 480 (vw). ^{1}H NMR (CD$_3$CN): δ 8.02 (m, 2H), 7.91 (m, 2H), 7.56 (m, 6H), ~4.8 (s, vbr, H$^+$ + H$_2$O), 3.08 (t, 16H), 1.58 (quintet, 16H), 1.35 (sextet, 16H), 0.96 (t, 24H). The position of the peak at δ 4.8 is dependent on the amount of water present and also on the presence of a protic solvent. When a trace of methanol-d_4 was added, this peak disappeared due to rapid exchange. ^{1}H NMR (DMSO-d_6): δ 7.87 (m, 2H, *o*-H), 7.85 (m, 2H, *o*-H), 7.48 (m, 4H, *m,p*-H), 7.40 (m, 2H, *m,p*-H), ~4.5 (s, vbr, H$^+$ + H$_2$O), 3.13 (t, 16H), 1.54 (quintet, 16H), 1.27 (sextet, 16H), 0.91 (t, 24H). ^{31}P NMR (DMSO-d_6): δ 12.99 (s, $^{2}J_{P\text{–}O\text{–}W}$ = 22.9 Hz), 8.45 (s, $^{2}J_{P\text{–}O\text{–}W}$ = 15.6 and 30.4 Hz), −15.18 (s). ^{31}P NMR (CD$_3$CN): δ 17.28 (s), 12.05 (s), −14.83 (s). 20.84-MHz ^{183}W NMR (0.16 M in DMSO-d_6): δ −50.2 (s, 1W), −84.7 (s, 1W), −86.6 (s, 1W), −97.8 (s, 1W), −98.3 (s, 1W), −119.9 (s, 1W), −122.4 (s, 1W), −133.1 (s, 1W), −185.7 (d, 1W, $^{2}J_{P\text{–}O\text{–}W}$ = 29.5 Hz), −205.5 (d, 1W, $^{2}J_{P\text{–}O\text{–}W}$ = 14.9 Hz), −218.1 (d, 1W, $^{2}J_{P\text{–}O\text{–}W}$ = 22.7 Hz). 8.34-MHz ^{183}W NMR (0.12 M in DMSO-d_6): δ −50.2 (s, 1W), −84.7 (s, 1W), −86.7 (s, 1W), −97.5 (s, 1W), −98.4 (s, 1W), −119.9 (s, 1W), −122.4 (s, 1W), −133.3 (s, 1W), −185.8 (d, 1W, $^{2}J_{P\text{–}O\text{–}W}$ = 32.9 Hz), −205.5 (d, 1W, $^{2}J_{P\text{–}O\text{–}W}$ = 16.7 Hz), −218.2 (d, 1W, $^{2}J_{P\text{–}O\text{–}W}$ = 22.1 Hz). For **2** the titration curve showed three well-defined inflection points which confirmed the presence of three titratable protons per formula unit: two protons for balancing the charge on the anion and the third one from the monoprotonated singly bound phenylphosphonoyl group, i.e., $[PhP(O)(O\underline{H})]^+$ (see Figure 9, Results and Discussion).

Anal. Calcd for $C_{44}H_{85}N_2O_{42}P_3W_{11}$: C, 15.41; H, 2.50; N, 0.82; P, 2.71; W, 58.97. Found: C, 16.36; H, 2.60; N, 0.97; P, 2.97; W, 58.61. The ^{1}H and ^{31}P NMR spectra of the isolated product in DMSO-d_6 are identical with those from the sample prepared in situ. The compound in both the solid and solution states is light sensitive. In the solid state the compound slowly changes from white to blue when subjected to the light. When the compound is stored in the dark, no color change occurs.

Synthesis of $[PhP(O)]_2SiW_{11}O_{39}^{4-}$. $[(n\text{-}C_4H_9)_4N]_3H[PhP(O)]_2SiW_{11}O_{39}$. (a) Preparation at Room Temperature. To $[(n\text{-}C_4H_9)_4N]_4H_3KSiW_{11}O_{39}$ (3.11 g, 0.82 mmol) in 50 mL of acetonitrile was slowly added dropwise 2 equiv of PhP(O)Cl$_2$ with vigorous stirring. The solution changed from colorless to pale yellow during the addition. The mixture was stirred for 4 days, and the solution was filtered through a fine glass frit. The pale yellow filtrate was diluted with 150 mL of water to form a pale yellow sticky solid. The supernatant was decanted and the solid redissolved in 50 mL of acetonitrile. Reprecipitation was effected by the addition of 200 mL of absolute ethanol. The solid isolated was reprecipitated again from 50 mL of acetonitrile solution by adding 250 mL of methanol to give 1.82 g (61% yield) of a white microcrystalline solid. IR (1300–400 cm^{-1}): 1139 (m), 1085 (m), 1069 (m, sh), 1041 (vw), 1011 (w), 976 (s), 914 (s), 812 (s), 741 (sh), 697 (sh), 648 (w), 593 (vw), 572 (w), 548 (w), 538 (w). ^{1}H NMR (CD$_3$CN): δ 8.08 (m, 2H, *o*-H), 7.55 (m, 3H, *m,p*-H), 3.12 (t, 12H), 1.61 (quintet, 12H), 1.40 (sextet, 12H), 0.96 (t, 18H). ^{31}P NMR (CD$_3$CN): δ 15.21 (s).

Anal. Calcd for $C_{60}H_{119}N_3O_{41}P_2SiW_{11}$: C, 19.74; H, 3.28; N, 1.15. Found: C, 20.10; H, 3.26; N, 1.21.

(b) Preparation at 65 °C. $[(n\text{-}C_4H_9)_4N]_4H_3NaSiW_{11}O_{39}$ (3.85 g, 1.03 mmol) was dissolved in 30 mL of acetonitrile, and the solution was heated to 65 °C. To this solution was added dropwise 2 equiv of PhP(O)Cl$_2$ dissolved in 10 mL of acetonitrile over a 12-min period, during which time the solution turned bright yellow. The mixture was stirred for 24 h at room temperature. The solution was filtered through a fine frit, and the filtrate was diluted with 200 mL of methanol to produce a white precipitate. The white precipitate was isolated by filtration, washed with 20 mL of methanol, and air-dried to give a 1.75 g of white solid. A second crop (1.07 g) was obtained from the filtrate by using the same procedure. Total yield: 2.82 g (75%). The identity of the product was confirmed by ^{1}H and ^{31}P NMR and IR spectroscopies.

$[(n\text{-}C_6H_{13})_4N]_3H[PhP(O)]_2SiW_{11}O_{39}$. $[(n\text{-}C_6H_{13})_{4.5}H_{2.5}NaSiW_{11}O_{39}$ (4.05 g, 0.090 mmol) was dissolved in 40 mL of acetonitrile, and the solution was heated to 60 °C. To this solution was added 0.34 mL (2.2 equiv) of PhP(O)Cl$_2$ dissolved in 10 mL of acetonitrile. The solution changed from colorless to bright yellow within 20 min. The mixture was stirred for 16 h at 40 °C. The solution was refluxed another 3 h and then concentrated on a rotary evaporator to give a pale yellow sticky gel. The gelatinous material was redissolved in 30 mL of acetonitrile, and the solution was diluted by adding 150 mL of water with vigorous stirring to give a pale yellow gel and a white turbid suspension. The solution was decanted, and 200 mL of water was added. The gelatinous material hardened with time. This solid was triturated to give a pale yellow powder, which was filtered off and air-dried to give a 3.30 g of a pale yellow solid (79% yield). IR (1300–400 cm^{-1}): 1138 (m), 1084 (m), 1040 (sh), 1012 (w), 980 (vs), 914 (vs), 893 (s), 812 (vs), 734 (s), 694 (m), 588 (sh), 572 (m), 549 (m), 516 (w). ^{1}H NMR (CD$_3$CN): δ 8.11 (m, 4H), 7.56 (m, 6H), 3.12 (t, 24H), 1.63 (quintet, 24H), 1.35 (s, 72H), 0.91 (t, 36H). ^{31}P NMR (CD$_3$CN): δ 15.14 (s, α-isomer, major species, intensity 8), 13.34 (s, one β-isomer, minor species, intensity 1). ^{31}P NMR (DMSO-d_6): δ 14.92 (s, α-isomer, major peak, intensity 3.5), 13.14 (s, β-isomer, minor peak, intensity 1), 10.52 (s, free PhP(O)(OH)$_2$, intensity 1). 20.83-MHz ^{183}W NMR (0.25 M in CD$_3$CN): δ −79.9 (s, 2W), −106.1 (s, 1W), −109.6 (s, 2W), −113.8 (s, 2W), −154.0 (d, 2W, $^{2}J_{P\text{–}O\text{–}W}$ = 14.4 Hz), −197.2 (d, 2W, $^{2}J_{P\text{–}O\text{–}W}$ = 26.4 Hz), along with smaller intensity peaks at −97.8 (s), −101.3 (s), −123.5 (s), −151.2 (d, $^{2}J_{P\text{–}O\text{–}W}$ = 14.4 Hz), −191.6 (d, $^{2}J_{P\text{–}O\text{–}W}$ = 26.4 Hz) with an approximate integration ratio of 2:2:2:2:2. A missing peak with intensity 1 was presumed to be hidden under one of the peaks with higher intensity. There was a 7 mol % impurity of $SiW_{12}O_{40}^{4-}$ (singlet at δ −90.6) in the starting material, as assessed by ^{183}W NMR integration.

Anal. Calcd for $C_{84}H_{167}N_3O_{41}P_2SiW_{11}$: C, 25.30; H, 4.22; N, 1.05; Si, 0.70; P, 1.55; W, 50.72. Found: C, 26.75; H, 4.26; N, 1.20; Si, 0.74; P, 1.81; W, 46.95. The poor analysis arises, in part, from the impurities including $SiW_{12}O_{40}^{4-}$, indicated by ^{183}W NMR spectroscopy.

X-ray Structure Determination on 1. Two pale yellow crystals of **1** were mounted on glass fibers and placed on a Siemens (formerly Nicolet) P3F diffractometer. The data for crystal A was collected at room temperature and showed very few observable reflections at $2\theta > 38°$ so data were collected on crystal B at −100 °C in order to obtain higher resolution data (a = 16.350 (3) Å, b = 19.521 (5) Å, c = 23.177 (7) Å, V = 7397 (3) Å^3). Of 3474 reflections collected ($2\theta_{max}$ = 40°), 2026 were observed ($I > 3\sigma(I)$), and the thermal parameters of isotropically refined atoms were no smaller than the room-temperature data set, the results of which are reported here. No intensity loss of the three check reflections (800, 0,12,0, and 008 measured every 126 reflections at approximately 2-h intervals) was observed. The data were corrected for Lp effects, and an empirical absorption correction based on azimuthal Ψ scans was applied to the data.

The structure was solved by a Patterson interpretation and expansion routine of SHELXS-86[16a] and refined by full-matrix least-squares techniques using the programs SHELXTL-PLUS.[16b] No hydrogens were included. Because of the limited data, only W and most of the O atoms were refined with anisotropic thermal parameters. The four disordered PO_4^{3-} oxygen atoms were assigned site occupancies of 0.5. The benzene

Table I. Crystallographic Data

empirical formula	$C_{44}H_{83}N_2O_{41}P_3W_{11}$
space group	*Pbcn* (No. 60)
unit cell dimens	$a = 19.680\ (11)$ Å
	$b = 16.446\ (13)$ Å
	$c = 23.398\ (13)$ Å
volume	7573 (8) Å^3
Z	4
density (calcd)	2.99 g/cm^3
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)
temperature	21 °C
no. of reflns collected	3990
no. of independent reflns	3557
no. of obsd reflns	1952 ($F \geq 6.0\sigma(F)$)
final R indices (obsd data)	$R = 8.60$, $R_w = 9.34$

ring was treated as a rigid body. Crystallographic data and final residual values are given in Table I.

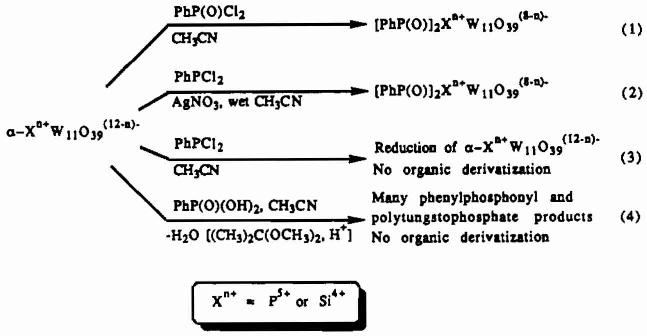
Stability of 1 in Wet CH_3CN at 60 °C. The stability of **1** was followed by ^{31}P NMR. A solution of **1** (6.2 mM) along with 100 equiv of H_2O in deuterated acetonitrile was prepared in a 10-mm-o.d. NMR tube and equilibrated in a water bath maintained at 60 ± 3 °C for 2 weeks. The ^{31}P NMR spectra at 296 K were obtained over this time. The spectra showed no conversion to **2**, but a ~5% decomposition to unknown products was observed after 2 weeks at 60 °C.

Decomposition of 2 in DMSO. ^1H NMR indicated that a solution of **2** in dry DMSO-d_6 showed a 30% decomposition after 8 days at room temperature. The peak intensity at δ 7.86 (two overlapped multiplets) decreased with time, with the appearance of a new multiplet peak at δ 7.63 with increasing intensity over time. Two additional samples were prepared by dissolving **2**, one in dry DMSO-d_6 with 10 equiv of D_2O added (12 mM solution of **2**) and the other in dry DMSO-d_6 (16 mM **2**). The percent decomposition of **2** was monitored as a function of time by ^{31}P NMR using the integrated peak areas for the two peaks at δ 12.99 and 8.45 as an indication of this decomposition. Analysis of the data indicated decomposition half-lives, $\tau_{1/2}$, of 55 and 312 h for wet and dry DMSO-d_6 solutions, respectively. A fourth sample of **2** (0.15 M solution in dry DMSO-d_6) was heated at 80 °C and showed total decomposition within several hours, the time necessary to observe the ^{183}W NMR signals. The ^{31}P NMR spectrum of the decomposed solution showed many peaks derived from the phenylphosphonoyl group (δ 19.4, 18.0, 16.5, 15.9, 10.9, 5.9, 5.6) as well as the polyoxotungstate PO_4 group (δ −12.5, −13.2, −14.2, −14.9, −15.9, −16.2, −17.9).

Re-Formation of 1 from 2 in Acetonitrile. Both the ^1H and ^{31}P NMR spectra of deuterated acetonitrile solutions of **2** showed the re-formation of **1** with time. After 1–2 days, pale yellow octahedral crystals formed in the solution. After 1 week, the ^1H NMR spectrum of the solution showed the appearance of a multiplet at δ 8.07 with the concomitant disappearance of the multiplet peaks at δ 8.02 and 7.91 characteristic of **2**. In addition, the multiplet peak pattern at δ 7.58, which is assigned to meta and para phenyl ring hydrogens, became more complex. Analysis of a series of spectra taken over a 1-month period, along with the product isolation, indicated ca. 50% conversion after 2 days and 75% after 1 month, with 60% crystallizing from the solution after 1 month. Approximately an equal mole percent mixture of **1** and **2** remained in the solution along with decomposition products which account for about 5 mol % after 1 month.

Results and Discussion

Synthesis. Synthetic reactions of pertinence to the generation of phenylphosphonoyl undecatungstophosphates are summarized in eqs 1–4. The compound $[(n\text{-}C_4H_9)_4N]_2H[PhP(O)]_2PW_{11}O_{39}$ (**1**) and the silicon analog, $[PhP(O)]_2SiW_{11}O_{39}^{4-}$, can be prepared by reaction of the lacunary complexes, α-$X^{n+}W_{11}O_{39}^{(12-n)-}$, with phenylphosphonoyl dichloride in acetonitrile solution (eq 1). The ranges for typical yields of isolated **1** and $[PhP(O)]_2SiW_{11}O_{39}^{4-}$ are 22–33 and 60–80%, respectively. This preparation of **1** generates more than 15 P-containing polyoxotungstates, including the parent Keggin complex, α-$PW_{12}O_{40}^{3-}$, which can also be isolated from the mixture. **1** can also be prepared by reaction of the lacunary precursor, $X^{n+}W_{11}O_{39}^{(12-n)-}$ ($X^{n+} = P^{5+}$, Si^{4+}), with the "$PhP(O)^{2+}$" synthetic equivalent prepared in situ by reaction of $PhPCl_2$ (P(III)) with a stoichiometric amount of the $AgNO_3$ in acetonitrile (eq 2). In this process, Ag^+ doubles as an agent to remove chloride and one to oxidize the P atom. In contrast, direct reaction of the lacunary precursor with $PhPCl_2$ in acetonitrile does not give any isolable product but results in a mixture of dark blue polytungstophosphate reduction products (eq 3).



The uncatalyzed direct reaction of alcohols with some polyoxometalates to generate organic esters of polyoxometalates[8h] and the direct reaction of a carboxylic acid (formic) and polyoxometalate to generate a surface acyl derivative (mixed organic–polyoxoanion anhydride)[8b] are precedented for particular polyoxometalates. In contrast, the reaction between the sodium or potassium salt of α-$PW_{11}O_{39}^{7-}$ with the $PhP(O)(OH)_2$ in water did not show any evidence for the attachment of the organic group; only unreacted $PW_{11}O_{39}^{7-}$ and a trace amount of $PW_{12}O_{40}^{3-}$ were isolated. Even under highly favorable conditions (removal of water with dimethoxypropane in anhydrous CH_3CN with a catalytic amount of a strong acid, e.g. triflic), no phenylphosphonoyl undecatungstates were formed (eq 4). Instead, a multitude of products containing both phenylphosphonoyl and polytungstophosphate moieties were generated. The data collectively indicate that a highly electrophilic phenylphosphonoyl moiety is needed for reaction with the lacunary polyoxotungstate.

X-ray Structure of 1. Although one structure of a Keggin-derived lacunary complex, $X^{n+}W_{11}O_{39}^{(12-n)-}$, shows only a 2-fold disorder, that of α-$[(CH_3)_4N]_4Na_2HPW_{11}O_{39}$,[2b] nearly all X-ray structures of this large and heavily cited class of heteropoly compounds and their d-electron transition metal (TM) substituted derivatives, $X^{n+}TM^{z+}W_{11}O_{39}^{(12-n-z)-}$, show 12-fold or high levels of disorder, making inferences about atom connectivities at unique sites questionable at best.[1,2] Pale yellow orthorhombic crystals of **1** were suitable for X-ray crystallography. The combined ball-and-stick and numbering diagram of the bis(phenylphosphonoyl)undecatungstophosphate anion is given in Figure 2. Although the ^{31}P and ^{183}W NMR and the chemistry of **1** given below establish that the polyanion has C_s symmetry in solution, and the X-ray structure effectively confirms this indirectly (Figure 2), the only crystallographically imposed symmetry on the complex is a 2-fold axis that goes through P1 (the central P atom), W1, and O1 (Figure 2). In the 2-fold-disordered structure of **1**, half the molecules in the crystal lattice are in the orientation shown in Figure 2 and half the molecules are in the orientation generated by the C_2 operation. The crystallographic imposition of inappropriate symmetries on the high-symmetry members of the Keggin family is a common feature of X-ray structures of this family of complexes. Pope and Evans have described the general problem of Keggin species (T_d symmetry) residing at inversion centers in crystals and a 2-fold model to describe this type of disorder.[17] This paper describes a second type of low-level disorder that is adequately delineated by a 2-fold-disorder model. Al-

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(16) (a) SHELXS-86: Sheldrick, G. M. A program for the solution of crystal structures. Institute für Anorganische Chemie der Universität, Göttingen, Germany, 1986. (b) SHELXTL-PLUS: Siemens Analytical X-ray Instruments, Inc. (Previously Nicolet Instrument Corp.), Madison, WI.

(17) Evans, H. T., Jr.; Pope, M. T. *Inorg. Chem.* **1984**, *23*, 501.

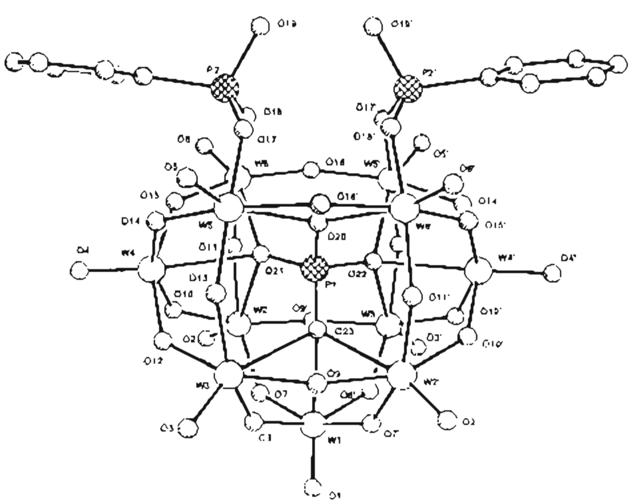


Figure 2. Combined ball-and-stick and numbering diagram of the polyanion in **1**, $[PhP(O)]_2PW_{11}O_{39}{}^{3-}$. The average W–W distance is 3.55 (0.02) Å due to the 2-fold disorder.

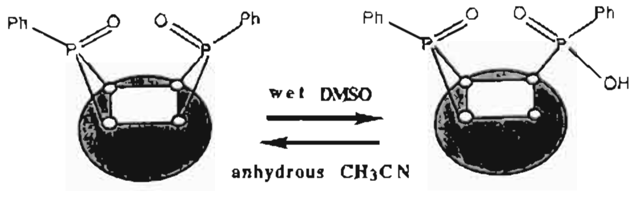
though the thermal ellipsoids of the atoms in **1** are larger than those in most small-molecule structures, they are typical of values seen in polyoxometalate X-ray structures. Furthermore, the 2-fold disorder contributes to the size of these thermal ellipsoids. Despite the disorder in the polyanion of **1**, the atom connectivity and mode of attachment of the organic groups to the lacunary anion are unequivocal. The doubly bonded groups each bridge two of the four terminal oxygen atoms that define the "hole" in the lacunary $PW_{11}O_{39}{}^{7-}$ polyanion. This is consistent with higher negative charge density on these oxygens versus the other external oxygens of the polyanion and considerably strengthens the structural proposal for the organometallic lacunary compounds $[(RY)_2O]X^{n+}W_{11}O_{39}{}^{(8-n)-}$ and $(RY)X^{n+}W_{11}O_{39}{}^{(9-n)-}$ (X = Si, P, Y = Si^{4+}, Ge^{4+}, Sn^{4+}; R = alkyl and aryl organic groups), first reported by the groups of Knoth[9a,b] and Pope.[10c] The latter compounds represent the largest class of lacunary derivatives with pendant organic or organometallic groups, and they remain under investigation at the present time.[6,13] All attempts thus far on the part of several research groups to grow low-disorder of disorder-free single crystals of any of these Knoth/Pope compounds have failed.

In both the title compounds and the Knoth/Pope $[(RY)_2O]$-$X^{n+}W_{11}O_{39}{}^{(8-n)-}$ compounds, the two organic groups bridging the terminal "hole" oxygens can bind in two configurations to preserve the C_s symmetry of all these complexes. The groups can bridge the oxygens such that both groups lie in the plane of symmetry and are inequivalent, or they can bridge the oxygens such that both groups lie across the plane of symmetry from one another and are equivalent. The X-ray structure of **1** clearly shows equivalent organic (phenylphosphonoyl) groups that are related by a crystallographic 2-fold axis in the latter mode. In this mode, the phenylphosphonoyl terminal oxygens are 2.43 Å apart while the sum of the van der Waals radii is 2 × 1.40 Å = 2.80 Å. In the other bonding mode, the phenylphosphonoyl terminal oxygens would be considerably closer together, generating energetically more unfavorable nonbonding interactions. The other notable dimensions are the nonbonded O···O distances of the four bridging oxygens which connect two $PhP(O)^{2+}$ groups to the PW_{11} moiety. The O···O separation of the two oxygens which bind to the same $PhP(O)^{2+}$ group (O17–O18 or O17′–O18′) is 2.60 Å. The other distance of two oxygens (O17–O18′ or O18–O17′) is 3.08 Å.

Generation of $[PhP(O)][PhP(O)(OH)]PW_{11}O_{39}{}^{4-}$. Solution Structures of 1 and 2. Compound **1** undergoes an unprecedented clean reversible partial hydrolysis[18] to $[(n\text{-}C_4H_9)_4N]_2H_2[PhP$-$(O)][PhP(O)(OH)]PW_{11}O_{39}$ (**2**), the complex where one and only one of the two bridging phenylphosphonoyl groups in **1** has been half-hydrolyzed. That is, one Ph(O)P–O–W bridge (Figure 2) has been cleaved. **1** converts to **2** in minutes when dissolved in wet dimethyl sulfoxide, and **2**, which has been isolated and thoroughly characterized (Experimental Section), reconverts to **1** when dissolved in dry acetonitrile (Figure 3). The interconversion can be followed by ^{31}P, ^1H, or ^{183}W NMR. An exemplary experiment, monitoring conversion of **2** back to **1**, by ^{31}P NMR is shown in Figure 4. The analogous interconversion of the silicon analog of **1** in DMSO solution was not observed. Instead, it slowly decomposes to $SiW_{11}O_{39}{}^{8-}$ and $PhPO_3{}^{2-}$.

The collective application of ^1H, ^{31}P, and ^{183}W NMR, IR, and other techniques provides several lines of evidence establishing that **1** has C_s symmetry in solution and the atom connectivity apparent from the X-ray structure, that **2** has C_1 symmetry in solution, and that neither **1** nor **2** is a mixture of isomers or a mixture of freely diffusing polytungstophosphate and phenylphosphonoyl species.

First, the title complexes, $[PhP(O)]_2XW_{11}O_{39}{}^{(8-n)-}$ (X = P^{5+}, Si^{4+}), the lacunary precursor complexes, α-$XW_{11}O_{39}{}^{(12-n)-}$, and



1 **2**

Figure 3. Schematic representation of interconversion of compounds **1** and **2** in organic media.

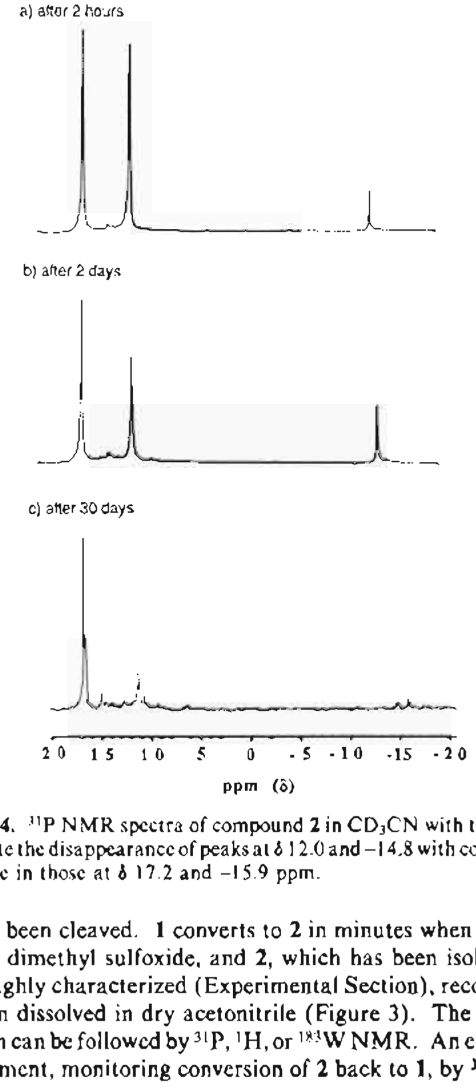


Figure 4. ^{31}P NMR spectra of compound **2** in CD_3CN with time at 296 K. Note the disappearance of peaks at δ 12.0 and −14.8 with concomitant increase in those at δ 17.2 and −15.9 ppm.

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[18] $(PhAs)_2Mo_6O_{24}{}^{4-}$ was reported to hydrolyze partially to $(PhAs)_2Mo_6O_{24}(H_2O)^{4-}$. However, in this case, the binding mode of the $PhAsO_3{}^{2-}$ group does not change (three oxygens of the group are still bound to three tungstens). Instead, skeletal rearrangement of the six MoO_6 octahedra takes place. This observation implies that the Mo_6 core of this compound is flexible in contrast to the rigid W_{11} core of **1**. See ref 10c for further details.

Table II. ^{183}W NMR Data for $X^{n+}W_{11}O_{39}{}^{(12-n)-}$ and Its Derivatives[a]

compound[b]	solvent	chemical shift, $-\delta$, ppm (no. of W, $^2J_{W-O-P}$)
		Complexes of C_s Symmetry
$[(n\text{-}C_{10}H_{21})_4N]_2H[PhP(O)]_2PW_{11}O_{39}$	$CDCl_3$	83.0 (2W), 99.5 (3W), 111.0 (2W), 190.0 (2W, ^2J[c]), 215.3 (2W, ^2J = 27 Hz)
$Q_4H_2NaPW_{11}O_{39}$	DMSO-d_6	81.9 (2W), 89.0 (2W), 104.2 (2W), 108.1 (2W), 113.2 (2W), 120.6 (1W)
$Q_4(CpTi)PW_{11}O_{39}$[d]	CD_3CN	78.3 (2W), 93.6 (1W), 94.8 (2W), 100.4 (2W), 112.3 (2W), 117.7 (2W)
$Li_7PW_{11}O_{39}$	D_2O	96.6 (2W), 97.5 (2W), 102.5 (2W), 120.2 (1W), 131.2 (2W), 151.0 (2W)
$[(n\text{-}C_6H_{13})_4N]_3H[PhP(O)]_2SiW_{11}O_{39}$[e]	CD_3CN	79.9 (2W), 106.1 (1W), 109.6 (2W), 113.8 (2W), 154.0 (2W, ^2J = 14 Hz), 197.2 (2W, ^2J = 26 Hz)
$[(n\text{-}C_6H_{13})_4N]_{4.5}H_{2.5}NaSiW_{11}O_{39}$	CD_3CN	76.1 (2W), 98.4 (2W), 112.1 (2W), 118.4 (5W)
$[(CH_3)_4N]_4[\{C_4H_7O_2Si\}_2O]SiW_{11}O_{39}$[f]	DMSO-d_6	103.7 (2W), 105.6 (2W), 110.2 (1W), 125.3 (2W), 169.8 (2W), 249.0 (2W)
		Complex of C_1 Symmetry
$Q_2H_2[PhP(O)][PhP(O)(OH)]PW_{11}O_{39}$	DMSO-d_6	50.2 (1W), 84.7 (1W), 86.6 (1W), 97.8 (1W), 98.3 (1W), 119.9 (1W), 122.4 (1W), 133.1 (1W), 186 (1W, ^2J = 30 Hz), 206 (1W, ^2J = 16 Hz), 218 (1W, ^2J = 23 Hz)

[a] For experimental conditions and data acquisition parameters, see Experimental Section. [b] Q = $(n\text{-}C_4H_9)_4N^+$. [c] Not resolved. [d] Reference 29. [e] Minor species assignable to β-isomer ($-\delta$): 97.8 (2W), 101.3 (2W), 123.5 (2W), 151.2 (2W, ^2J = 14 Hz), 191.6 (2W, ^2J = 26 Hz). [f] Reference 13.

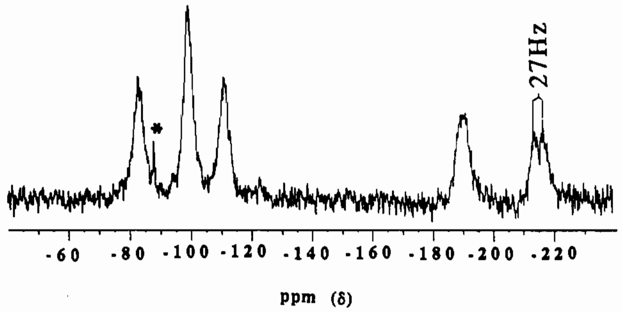

Figure 5. 8.34-MHz ^{183}W NMR spectrum of $[(n\text{-}C_{10}H_{21})_4N]_2H[PhP(O)]_2PW_{11}O_{39}$ in $CDCl_3$ (0.17 M, 33 500 scans, LB = 2 Hz). The asterisk denotes the $PW_{12}O_{40}{}^{3-}$ impurity accounting for approximately 3 mol % based on the integration.

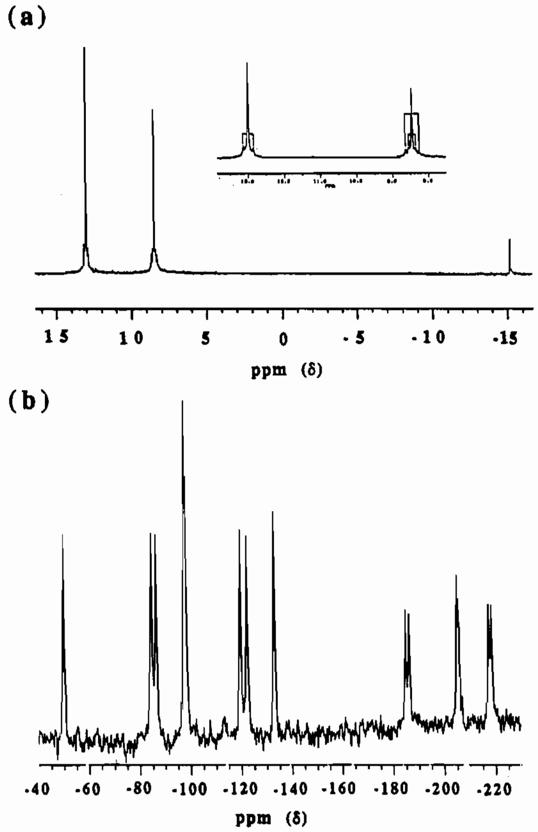

Figure 6. (a) ^{31}P NMR and (b) ^{183}W NMR spectra of **2** in DMSO-d_6. The inset in (a) shows the expanded portion of the phenylphosphonoyl region. Couplings due to $^2J_{P-O-W}$ are 23 Hz for the peak at δ 12.99 and 16 and 30 Hz for the peak at δ 8.45, respectively. For (b), concentration = 0.16 M, SF = 20.83 MHz, number of scans = 11 200, and LB = 1 Hz. Couplings due to $^2J_{W-O-P}$ are 23, 15, and 30 Hz, respectively, from the high-field side.

the literature organotransition metal lacunary complex, $(CpTi)PW_{11}O_{39}{}^{4-}$, all exhibit a 2:1:2:2:2:2 pattern (in some cases 2:3:2:2:2 as the peak of relative intensity 1 overlaps with one of the peaks with relative intensity 2 in their ^{183}W NMR spectra, consistent with C_s symmetry in all these cases (Table II; Figure 5). In contrast, **2** exhibits a 1:1:1:1:1:1:1:1:1:1:1 pattern, consistent with C_1 symmetry (Figure 6). Although **1** and the tetrahexylammonium and tetraphenylphosphonium salts of the title complex are not adequately soluble in CD_3CN for obtaining ^{183}W NMR spectra within a reasonable time interval, the tetradecylammonium salt of **1** is very soluble in $CDCl_3$ (see Experimental Section).

Second, the resonances in the ^{31}P NMR spectra of **1** and **2** (three resonances, two equal in intensity at δ 17 and 12 assignable to the phenylphosphonoyl groups and one at δ −14.8 for the central PO_4 unit of the polyoxotungstate portion) are all distinct from those of freely diffusing authentic $PhP(O)(OH)_2$ or its salts in the identical medium.

Third, **2**, like **1**, can be isolated in high yield and high purity, and the elemental analysis is consistent with the proposed structure.

Fourth, the hydrolytic chemistry of **2** in solution cited above (Figure 3) is consistent with the structures of both **1** and **2**. All the resonances of **1** and **2** during the conversion of **2** back to **1** in dry CH_3CN are correlated temporally. The time dependence of the ^{1}H NMR spectra, most cleanly indicated by the ortho phenyl proton resonances of the phenylphosphonoyl groups, and the ^{183}W NMR resonances of the compounds confirm the **1** to **2** interconversions.

The fifth line of evidence regarding the structures of **1** and **2** derives from the energies and splittings of the W–O and P–O stretching fundamentals in the mid-infrared region illustrated in Figure 7. The spectra of **1** and **2** show several extra peaks in the region of 1000–1150 cm^{-1} which arise from the P–O stretching modes of the phenylphosphonoyl group and central PO_4 moiety. It is possible to abstract the ν_3 stretching modes of the PO_4 unit (F_2)[19a] for **1** and **2** by comparing with the IR spectrum of the structurally identical $[PhP(O)]_2SiW_{11}O_{39}{}^{4-}$ anion. The IR assignments are summarized in Table III. There is no change in the splitting of the $\nu_3(PO_4)$ modes (~54 cm^{-1}) among the compounds. This observation is consistent with the fact that attachment of the phenylphosphonoyl groups structurally perturbs the central PO_4 unit, and, by inference, the entire C_s symmetry lacunary unit, minimally and definitely far less than when a d-electron transition metal ion is bound in the cavity. The splitting of the central PO_4 stretching modes is greatly influenced when the triply bridging oxygen of the PO_4 unit interacts with incoming species such as a d-electron transition metal ion.[19]

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[19] (a) Rocchiccioli-Deltcheff, C.; Thouvenot, R. *J. Chem. Res. Synop.* **1977**, 46. (b) Zonnevijlle, F.; Tourné, C. M.; Tourné, G. F. *Inorg. Chem.* **1982**, *21*, 2742.

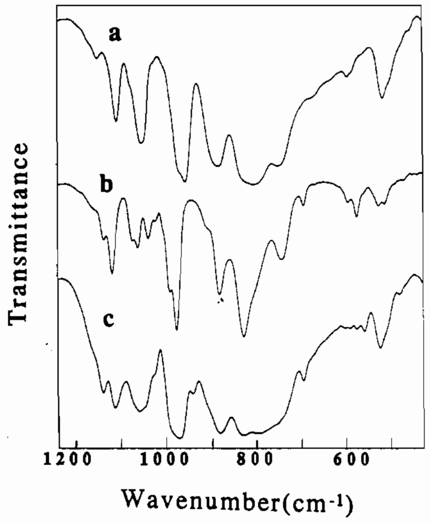

Figure 7. FTIR spectra of (a) $[(n\text{-}C_4H_9)_4N]_4H_2NaPW_{11}O_{39}$, (b) **1**, and (c) **2** in a KBr matrix.

Table III. Comparison of Infrared Stretching Frequencies

$Q_3PW_{12}O_{40}$[a]	Q_4H_2Na-$PW_{11}O_{39}$[a]	1	2	assign
1080	(1082)[b] 1109, 1055 (Δ = 54)[c]	(1091)[b] 1119, 1063 (Δ = 56)[c]	(1087)[b] 1114, 1060 (Δ = 54)[c]	ν(P—O)
977 (+19)	958 (0)	977 (+19)	971 (+13)	$\nu(W{=}O_t)$
896 (+12)	884 (0)	882 (−2)	881 (−3)	$\nu(W{-}O_b)$
830 (+2)	828 (0)	828 (0)	830 (+2)	$\nu(W{-}O_c)$
808 (+1)	807 (0)	803 (−4)	796 (−9)	$\nu(W{-}O_c)$
	752	744	752, 740	$\nu(W{-}O_c)$
596	596	594, 575	603, 591	δ(O—P—O)
513, 520	517	528, 514	524	δ(W—O—W)

[a] Q = $(n\text{-}C_4H_9)_4N^+$. [b] Average value. [c] Splitting.

The sixth and perhaps most definitive evidence regarding the structures and chemistry of **1** and **2** in solution comes from an analysis of the spin–spin coupling constants, $^2J_{W-O-P}$, exhibited by these complexes. Such two-bond P-to-W couplings are often not seen in polytungstophosphates,[20] but four independent lines of evidence indicate that this is what is being observed in this study. First, the numbers and types of the lines, second, the intensity of the satellite lines in the ^{31}P NMR spectra (coupling to ^{183}W nuclei in 14.4 atom % natural abundance), and third, the $^2J_{W-O-P}$ values apparent from both ^{31}P and ^{183}W NMR spectra (the same within experimental error) are all indicative of the determined (for **1**) and the proposed (for **2**) structures. The $^2J_{W-O-P}$ interactions in **1** under optimized conditions (maximum sample concentration, minimally viscous solvents, etc.) can be observed in the ^{183}W NMR spectrum but not in the ^{31}P NMR spectra. In contrast, the $^2J_{W-O-P}$ interactions in the more soluble **2** can be observed in both the ^{31}P and ^{183}W NMR spectra. The ^{31}P NMR peak at δ 12.99, from the singly bound phenylphosphonoyl group of **2**, shows one value ($^2J_{W-O-P}$ = 23 Hz), and the peak at δ 8.45, from the doubly bridging phenylphosphonoyl group, shows two values ($^2J_{W-O-P}$ = 16 and 30 Hz) (Figure 6).[21] The only atoms in the ^{183}W NMR spectrum of **2** that exhibit coupling are those bonded to the phenylphosphonoyl groups, the three most upfield resonances (see Table II and Figure 6). Fourth, the extra peaks in these upfield resonances were confirmed to be derived from spin–spin couplings, as the peak-to-peak separation (in hertz) for these resonances in the ^{183}W NMR of **2** at both 8.34 MHz (200 MHz for ^1H) and 20.83 MHz (500 MHz for ^1H) were the same while the peak-to-peak separations (in hertz) between all other narrowly placed peaks were changed by the appropriate amounts. The coupling constants are summarized in Figure 8. From these coupling constants, we can assign the most upfield peak in the ^{183}W NMR spectrum (δ −218 ppm, $^2J_{P-O-W}$ = 23 Hz) as the W atom bearing the singly bound $PhP(O)(OH)^+$ group; the other two pairs of peaks exhibiting coupling (δ −186 and −206 ppm, $^2J_{P-O-W}$ = 30 and 16 Hz, respectively) are assigned as the W atoms bearing the doubly bridging $PhP(O)^{2+}$ group. See Figures 6 and 8.

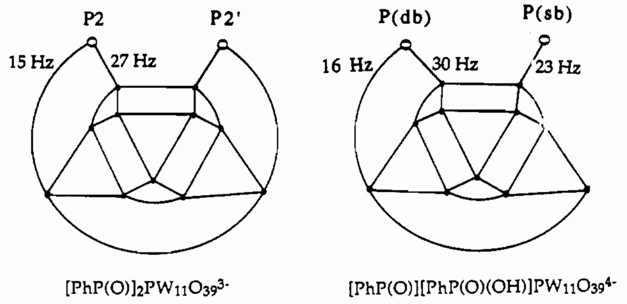

Figure 8. Diagram summarizing W atom connectivities and $^2J_{W-O-P}$ values in **1** and **2**. The black dots represent the 11 W atoms, and the equilateral triangles denote the W_3O_{13} triads.

Protonation States of 1 and 2 in Solution. With the structures of **1** and **2** confidently established, effort was turned to establishing the protonation state of the complexes. Proton counterions in polyoxoanions can be associated with the oxygens of the polyoxoanions themselves or with solvent molecules or the other species.[1,22-24] Klemperer, Day, and co-workers have reported the definitive location of polyoxoanion protons by application of X-ray crystallography, vapor pressure osmometry, and multinuclear NMR,[23] Finke and co-workers have reported the effective determination of the protonation state in aprotic media by potentiometric titrations,[24] and we have used multiple spectroscopic methods combined with kinetics to establish the polyoxoanion protonation state under dynamic conditions.[25] The most effective method for establishing the protonation states of **1** and **2** in the present study, however, proved to be titration of acetonitrile solutions of the complexes using methanolic $(n\text{-}C_4H_9)_4NOH$ followed potentiometrically (Figure 9).

Compound **1** exhibits one titratable proton, consistent with the formula implicated by the spectroscopic data and elemental analysis, while >1 equiv of OH^-/equiv of $[PhP(O)]_2PW_{11}O_{39}^{3-}$ induces the decomposition process in eq 5. Compound **2** exhibits

$$[PhP(O)]_2PW_{11}O_{39}^{3-} + 4OH^- \rightarrow PW_{11}O_{39}^{7-} + 2PhP(O)(OH)_2 \quad (5)$$

three titratable protons, consistent with cleavage of one PhP(O)–O–W bridge in **1** to generate PhP(O)OH and HO–W moieties in **2**. Two of the three protons in **2** are associated with the

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[20] (a) Thouvenot, R.; Tézé, A.; Constant, R.; Hervé, G. *Inorg. Chem.* **1988**, *27*, 524. (b) Acerete, R.; Server-Carrio, J.; Vegas, A.; Martinez-Ripoll, M. *J. Am. Chem. Soc.* **1990**, *112*, 9386. In $P_4W_{14}O_{58}^{12-}$, $^2J_{W-P}$ values of 10.2 and 18.0 Hz from the outer bound PO_4^{3-} were observed (both ^{183}W and ^{31}P NMR); 10.2 Hz was rigorously assigned to the P–O–W of the two W's of the W_3 triad, and 18.0 Hz was assigned to the W which does not belong to W_3 triad. There is no simple correlation of $^2J_{W-P}$'s with W–O bond lengths; in the above case, the W–O distances are all within 2.04 (±0.02) Å. In $P_6W_{18}O_{79}^{20-}$, $^2J_{W-P}$ = 30 Hz was observed for the most upfield ^{183}W peak (~−290 ppm; the rest of the peaks are in the range of −120 to −195 ppm). ^{31}P NMR shows the same coupling at 3.69 ppm, which is from tripod-bound $P(O)O_3^{3-}$.

[21] In contrast to this, the ^{31}P NMR spectrum of **2** in CD_3CN shows the reversed trend in chemical shift values for the two types of phosphorus, i.e., δ 17.3 for the doubly bound $PhP(O)^{2+}$ and δ 12.1 for the singly bound $PhP(O)(OH)^+$, as deduced from the spectral change of the conversion of **2** to **1** in CD_3CN (Figure 4). The reason is not clear.

[22] Hill, C. L.; Bouchard, D. A.; Kadkhodayan, M.; Williamson, M. M.; Schmidt, J. A.; Hilinski, E. F. *J. Am. Chem. Soc.* **1988**, *110*, 5471.

[23] Day, V. W.; Klemperer, W. G.; Maltbie, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 2991.

[24] Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947.

[25] Renneke, R. F.; Kadkhodayan, M.; Pasquali, M.; Hill, C. L. *J. Am. Chem. Soc.* **1991**, *113*, 8357.

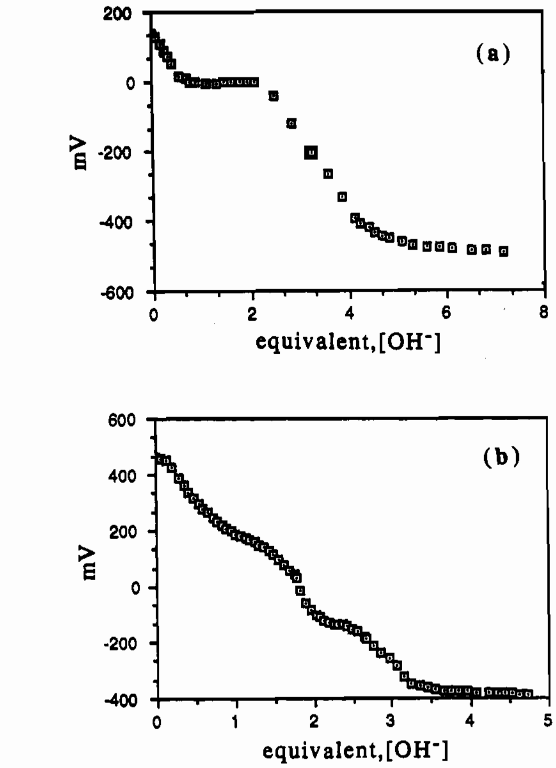

Figure 9. Potentiometric titration of (a) a 0.50 mM acetonitrile solution of **1** and (b) a 6.2 mM acetonitrile solution of **2** with methanolic 1.0 M $(n\text{-Bu})_4NOH$ solution.

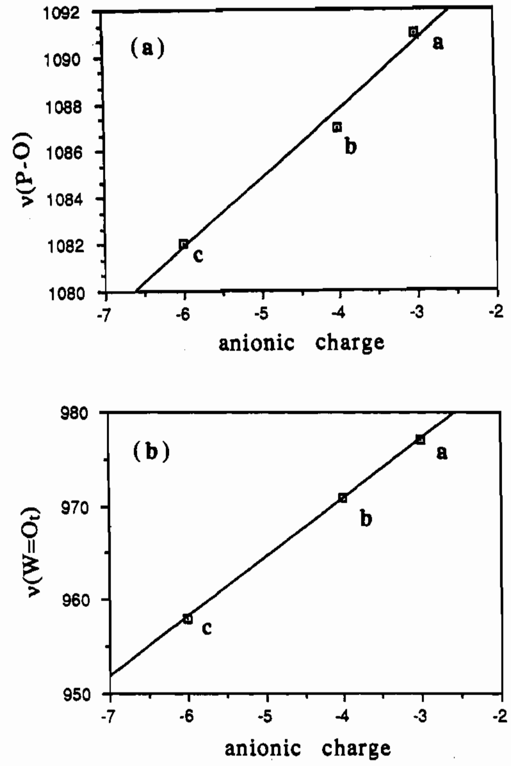

Figure 10. Correlation of (a) average IR stretching frequency ν(P—O) of PO_4^{3-} vs anionic charge and (b) $\nu(W{=}O_t)$ vs anionic charge. In the graphs a denotes **1**, b denotes **2**, and c denotes $[(n\text{-}C_4H_9)_4N]_4\text{-}H_2NaPW_{11}O_{39}$.

polytungstophosphate unit; the third is associated with the covalently attached and pendant phenylphosphonoyl group, $[PhP(O)(O\underline{H})]^+$ (see Experimental Section).

Effect of Organic Groups on Electronic Properties of the Lacunary Polytungstophosphate. It is clear that modulation of anionic charge density caused by binding of the phenylphosphonoyl groups in **1** and **2** is a dominant feature of this chemistry. First of all, charge dictates the sites of ligand binding. One model of merit for anionic charge densities in the common Keggin ion polyoxometalates, $X^{n+}W_{12}O_{40}{}^{(8-n)-}$, based primarily on bond distances and angles, is that the central charged tetrahedron, $X^{n+}O_4{}^{(8-n)-}$, is surrounded by a neutral $W_{12}O_{36}$ shell.[1b] Removal of the $(W{=}O)^{4+}$ unit produces the C_s lacunary complex, $X^{n+}M_{11}O_{39}{}^{(12-n)-}$, which contains three W_3O_{13} triads and one W_2O_{10} diad. If one makes the assumption that each triad or diad shares one-fourth of the negative charge of the central $X^{n+}O_4{}^{(8-n)-}$ unit, then the highest charge density will reside at the lacunary site.[26]

The trends in negative charge density also correlate with the chemical shifts in the ^{183}W and ^{31}P NMR spectra. The ^{31}P NMR chemical shifts of the central PO_4 group of $(Na)PW_{11}O_{39}{}^{6-}$, **2**, **1**, and $PW_{12}O_{40}{}^{3-}$, which have overall anionic charges of 6–, 4–, 3–, and 3–, respectively, all as tetrabutylammonium salts in acetonitrile under the same conditions, are δ −14.61, −14.83, −15.94 and −17.58.[27] It is of questionable wisdom to make strong arguments about the effects of charge density through the agency of ^{183}W NMR chemical shifts, however, as the origin of the latter, although reasonably modeled by the anisotropy of the electric field around the nucleus and the availability of excited states for mixing with the ground state,[28] is a complex matter that still defies quantitative delineation. Interestingly, the title complexes regardless of solvent show by far the largest chemical shift range in the ^{183}W NMR spectra of any of the Keggin lacunary derivatives (Table II), indicating the most severe perturbation of the magnetic environment of the W atoms in these particular compounds. The chemical shift range for both the precursor complexes (≤54 ppm) and $\alpha\text{-}(CpTi)PW_{11}O_{39}{}^{4-}$ (~40 ppm)[29] is substantially less than that for all the title complexes (over 100 ppm) regardless of solvent. The ^{183}W peak with $^2J_{W-O-P} = 27$ Hz for the tetradecylammonium salt of **1** and its tetrahexylammonium silicon analog can be assigned to the tungsten atoms in the W_2O_{10} unit with covalently attached phenylphosphonoyl groups. On the basis of this simple electronic consideration, the most upfield W peaks may be assigned to the W_2O_{10} unit and the next upfield peaks to the W atoms in the W_3O_{13} units bearing the phenylphosphonoyl groups.

Finally, negative charge density has a major effect on vibrational parameters of the title and related complexes. The energies of two of the purest modes in these compounds, the asymmetric stretch of the terminal W═O units, $\nu(W{=}O_t)$, and the split $\nu_3(PO_4)$ stretching mode, correlate with overall anionic charge density (Figure 10). Note the identical $\nu(W{=}O_t)$ value for compound **1** and $[(n\text{-}C_4H_9)_4N]_3PW_{12}O_{40}$, the limiting value of 977 cm^{-1} (Table III). This kind of correlation was observed for the Keggin type heteropolyanions of $XW_{12}O_{40}{}^{n-}$ in which the charges of the anions were systematically varied by changing the charge on the heteroatom, X.[30] The frequencies of the composite $\nu(W\text{–}O_b)$ mode (O_b denotes doubly bridging oxygen interconnecting W_3O_{13} units) are consistent with the fact that the parent Keggin structure, $[(n\text{-}C_4H_9)_4N]_3PW_{12}O_{40}$, has slightly higher

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(26) Each complete W_3 triad or incomplete W_2 unit shares one oxygen with PO_4^{3-}, each unit thereby sharing $-^3/_4$ formal negative charge. In each W_3O_{13} unit each tungsten shares $-^1/_4$ $(-^2/_8)$ formal negative charge; however, the incomplete W_2O_9 unit shares $-^3/_8$ formal negative charge, and hence is more negative compared to the W in W_3O_{13} triads.

(27) Alkali metal containing lacunary complexes are believed to retain an alkali metal cation in the vacant hole site. See ref 15a.

(28) For example, see: Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1982**, *104*, 5384.

(29) Gansow, O.; Ho, R. K. C.; Klemperer, W. G. *J. Organomet. Chem.* **1980**, *187*, C27.

(30) (a) Rocchiccioli-Deltcheff, C.; Thouvenot, R.; Frank, R. *Spectrochim. Acta* **1976**, *32A*, 587. (b) Rocchiccioli-Deltcheff, C.; Fournier, M.; Frank, R. *Inorg. Chem.* **1983**, *22*, 207.

W–O bond energies and is slightly more compact than **1**, **2**, and the lacunary precursor complex. The structural differences between the last three complexes are much less than those between any of them and the parent Keggin structure.

Hydrolytic Chemistry of the Title Complexes. The ^1H and ^{31}P NMR indicate that **1** is very stable to hydrolysis in acetonitrile even at ~60 °C in the presence of 100 equiv of water. (Note **2** reverts to **1** even in wet acetonitrile at room temperature, albeit slowly.) Approximately 5% of **1** is hydrolyzed after 2 weeks at this temperature. In contrast, **1** is not stable to hydrolysis in four other dipolar aprotic solvents, NMP, NMF, DMA, and DMSO that were not scrupulously dried. After the clean reversible partial hydrolysis of **1** to **2** discussed above takes place in fairly dry DMSO, **2** subsequently hydrolyzes slowly at 296 K in this medium to form at least six phosphorus-containing polyoxotungstates and $PhP(O)(OH)_2$, as indicated by ^{31}P NMR. The half-life, $\tau_{1/2}$, of **2** in wet DMSO-d_6 (containing 10 equiv of H_2O/equiv of **1**) is 55 h, whereas the half-life in dried DMSO-d_6 is 312 h.

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Supplementary Material Available: A textual presentation of the X-ray experimental details for **1**, stereoviews of **1** showing disorder of the PO_4^{3-} group (Figure S-1), full listings of crystal structure determination details (Table S-I), atomic coordinates and temperature factors (Table S-II), anisotropic temperature factors (Table S-III), and bond lengths and angles (Table S-IV), and ^{183}W NMR spectra of **1** and α-$[(n\text{-}C_4H_9)_4N]_4$-$H_2NaPW_{11}O_{39}$ in DMSO-d_6 (Figure S-2) and of $[(n\text{-}C_6H_{13})_4N]_3$-$H[PhP(O)]_2SiW_{11}O_{39}$ in CD_3CN (Figure S-3) (15 pages). Ordering information is given on any current masthead page.