unencumbered end, viz., on the metal atom bonded to the four fhp oxygen atoms. The question of why this arrangement is so preferred by this ligand whereas it has not been observed for any other similar ligand is still unanswered, but attention is now directed toward the properties of the ligand itself as well as the properties of the dimetal unit itself.

One possible explanation might be the following. Of the four ligands **1a–1d**, the fhp ligand may be unique in its steric requirements. Ligand **1a** has been relatively little studied, but it is certainly clear, by example ($Os_2(hp)_4Cl_2$[10]), that four of these may be arranged in a two-vs.-two (i.e., two pointing one way and two the other) fashion and still leave room at each end for an axial ligand. The H atoms at the 6-positions are too small to block these positions in a major way. Thus, an $M_2(hp)_4L_2$ species is possible in which the symmetrical arrangement of bridging ligands (assuming that this is inherently favorable) and the formation of two axial M–L bonds can be achieved at the same time. For all other type **1** ligands, **1b–d**, the size of the substituents at the 6-position is such that, in a two-vs.-two arrangement, no axial M–L bonds could be formed. In the case of fhp the unidirectional arrangement is possible since four fluorine atoms can fit at one end without repulsive contact, as noted earlier. It is then possible to form a good M–L axial bond at the other end. On the other hand, for **1b** and **1c**, a unidirectional arrangement would result in large repulsive interactions between methyl groups or chlorine atoms. A simple graphical estimate shows that adjacent pairs of these groups would make contacts that are 0.3–0.5 Å less than the sums of van der Waals radii.

This analysis still leaves open a possibility that merits experimental study. If the axial ligand molecules could be removed and the remaining $M_2(fhp)_4$ compound dissolved in a noncoordinating solvent, would rearrangement to a two-vs.-two structure take place? Preliminary experiments have been done on all of the $M_2(fhp)_4L$ systems but have not yielded any clean-cut results.

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**Registry No.** $Rh_2(fhp)_4(Me_2SO)$, 93426-94-9; $Rh_2(fhp)_4(C_4H_8O)$, 93426-95-0; $Rh_2(fhp)_4(C_2H_5OH)$, 93426-96-1; Rh, 7440-16-6.

**Supplementary Material Available:** Tables of general temperature factor expressions (*B*'s and *U*'s), refined temperature factor expressions (*B*'s), root-mean-square amplitudes of thermal vibration, bond lengths, bond angles, final atomic coordinates, and structure factors for all observed data (26 pages). Ordering information is given on any current masthead page.

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Contribution No. 3471 from the Central Research
& Development Department, Experimental Station,
E. I. du Pont de Nemours & Company,
Wilmington, Delaware 19898

# Esters of Phosphotungstic Acid. Anhydrous Phosphotungstic Acid

W. H. Knoth* and R. D. Farlee

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Preparations of the neutral methyl and ethyl esters of phosphotungstic acid were undertaken following the earlier preparations of $CH_3OW_{12}PO_{39}{}^{2-}$ and $C_2H_5OW_{12}PO_{39}{}^{2-}$ reported from this laboratory.[1] The route chosen was vacuum thermolysis of the corresponding trialkyloxonium salts, $[(CH_3)_3O]_3W_{12}PO_{40}$ and $[(C_2H_5)_3O]_3W_{12}PO_{40}$. The desired esters, in slightly impure form, were obtained at 150 °C. Unfortunately, these esters do not sublime, and no inert solvent for them has been found, so that characterization had to be done on the crude products.

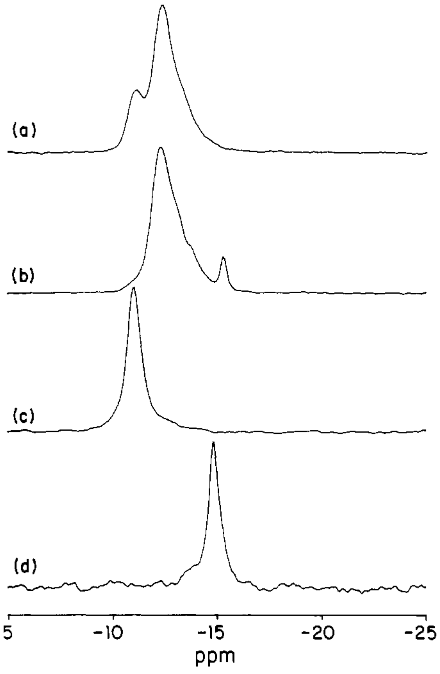

**Figure 1.** $^{31}P$ MAS NMR spectra: (a) $(C_2H_5O)_3W_{12}PO_{37}$ (90° pulse, 10-s recycle, 32 scans); (b) $(CH_3O)_3W_{12}PO_{37}$ (30° pulse, 10-s recycle, 52 scans); (c) $(HO)_3W_{12}PO_{37}$ (90° pulse, 10-s recycle, 4 scans); (d) $[(C_2H_5)_3O]_3W_{12}PO_{40}$ (90° pulse, 4-s recycle, 1375 scans).

The 150 °C thermolysate of $[(C_2H_5)_3O]_3W_{12}PO_{40}$ analyzed satisfactorily for $(C_2H_5O)_3W_{12}PO_{37}$. The $^{31}P$ MAS (magic-angle-spinning) NMR spectrum (Figure 1a) consisted of a major line at −12.3 ppm, assigned to the ester, and a minor line at −11.0 ppm, which is assigned to a small amount of anhydrous phosphotungstic acid, discussed in more detail below. The $^{31}P$ MAS spectrum of the 150 °C thermolysate of $[(CH_3)_3O]_3W_{12}PO_{40}$ (Figure 1b) also included a major line at −12.3 ppm, assigned to $(CH_3O)_3W_{12}PO_{37}$, but analysis showed an unsatisfactorily high carbon content. This is rationalized by the two minor lines at −15.2 and −13.7 ppm that are assigned to residual $[(CH_3)_3O]_3W_{12}PO_{40}$ and $[(CH_3)_3O]_2CH_3OW_{12}PO_{39}$, respectively. We find a $^{31}P$ MAS NMR line at −14.8 ppm for $[(C_2H_5)_3O]_3W_{12}PO_{40}$, consistent with assignment of the −15.2 ppm line; assignment of the −13.7 ppm line is based on earlier work[1] that reported a $^{31}P$ chemical shift of −13.9 ppm for $[(n\text{-}C_6H_{13})_4N]_2CH_3OW_{12}PO_{39}$ in dichloroethane.

Thermolysis of either of the tris(trialkyloxonium) salts or their 150 °C thermolysates at 215 °C under vacuum gave anhydrous phosphotungstic acid, $(HO)_3W_{12}PO_{37}$.[2] These samples all had a major $^{31}P$ MAS NMR line at −11.0 ppm and minor lines at −12.5 and/or −13.7 and/or −15.2 ppm, which are assigned as discussed above.

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(2) (a) Characterization (GC/MS) of the volatile products from the 215 °C thermolysis of crude $(CH_3O)_3W_{12}PO_{37}$ revealed trace amounts of ethylene and propylene, larger amounts of $C_3$–$C_7$ hydrocarbons (butanes dominant), and dimethyl ether. These results correlate roughly with reported studies[2b] on the conversion of methanol and dimethyl ether to hydrocarbons by heteropolyacids. (b) Ono, Y.; Baba, T.; Sakai, J.; Keii, T. *J. Chem. Soc., Chem. Commun.* **1981**, 400. Hayashi, H.; Moffat, J. B. *J. Catal.* **1982**, *77*, 473–484. Okuhara, T.; Hibi, T.; Takahashi, K.; Tatematsu, S.; Misono, M. *J. Chem. Soc., Chem. Commun.* **1984**, 697–698.

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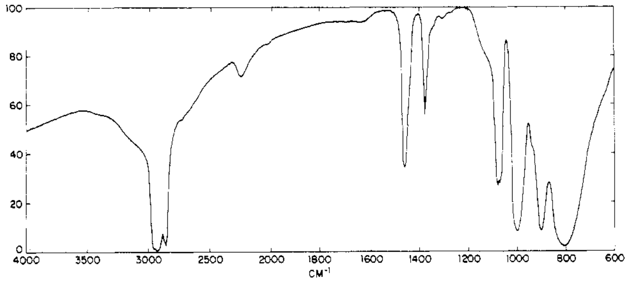

**Figure 2.** Infrared spectrum (mineral oil mull) of $(HO)_3W_{12}PO_{37}$.

Pure anhydrous phosphotungstic acid, exhibiting only the −11.0 ppm $^{31}P$ MAS NMR line (Figure 1c) was easily prepared by thermolysis of the hydrated acid ($^{31}P$, δ −14.7) at 215 °C under vacuum. The infrared spectrum of this material (Figure 2) is the same as that of the 215 °C thermolysis products of the alkyloxonium salts or the neutral esters referred to above.

Anhydrous phosphotungstic acid has been reported previously, and portions of its infrared spectra have been discussed.[3-5] One report[4] states that there is no appreciable difference between the anion absorption of the hydrated and dehydrated acids; another[3] reports that frequency changes occur in the 600–1100-cm$^{-1}$ region upon dehydration. We agree with the latter except that we also note loss of degeneracy of the P–O stretching band, which would be expected upon protonation of the anion, and a new weak band at 2246 cm$^{-1}$. We have been unable to assign this band. It would be unreasonable to expect an O–H band at this frequency; nevertheless, we prepared $D_3W_{12}PO_{40}\cdot nD_2O$ and converted it to $(DO)_3W_{12}PO_{37}$ at 215 °C. The 2246-cm$^{-1}$ band did not shift. We also observe a similar band in the spectrum of silicotungstic acid that has been thermolyzed at 205 °C under vacuum.

Other features of note in the infrared spectrum of $(HO)_3W_{12}PO_{37}$ are the absence of a normal water deformation band in the 1700-cm$^{-1}$ region and a very broad band for hydrogen-bonded OH extending from about 3600 to 2400 cm$^{-1}$. The latter is more easily seen in a hexachlorobutadiene mull spectrum than in Figure 2, which is a mineral oil mull spectrum. It has also been discussed extensively by others.[3,4] $(HO)_3W_{12}PO_{37}$ dissolves easily in water, and normal $W_{12}PO_{40}{}^{3-}$ salts can be precipitated quantitatively from the solutions.

The infrared spectra of the $(RO)_3W_{12}PO_{37}$ esters are similar to that of $(HO)_3W_{12}PO_{37}$ except they lack the OH absorption as well as the band at 2246 cm$^{-1}$.

The question as to whether or not anhydrous phosphotungstic acid is truly anhydrous $(HO)_3W_{12}PO_{37}$ or is a partially hydrated species such as $H_3O(HO)_2W_{12}PO_{38}$ cannot be answered by analysis. We prefer the anhydrous formulation because of the preparation of the acid by thermolysis of the trialkyloxonium salts. These salts show no evidence of hydration and would not be expected to be hydrated because the excess trialkyloxonium cations present during their preparation (note that $[(CH_3)_3O]_3W_{12}PO_{40}$ was prepared from $[(Hex)_4N]_3W_{12}PO_{40}$ and $(CH_3)_3OBF_4$ in dichloroethane[1]) should serve as effective dehydrating agents. It is difficult to see how α- or β-elimination reactions from these anhydrous salts could lead to a hydrated acid.

### Experimental Section

Hydrated phosphotungstic and silicotungstic acids were obtained from Fisher Scientific Co. The preparation of $[(CH_3)_3O]_3W_{12}PO_{40}$ has been reported previously.[1] Infrared spectra were determined on a Perkin-Elmer 983 as mineral oil mulls unless otherwise noted. Solid-state $^{31}P$ NMR spectra were obtained at 121.4 MHz on a Bruker CXP-300 spectrometer. A Bruker MAS probe with 9-mm Delrin rotors was used. The observe coil was replaced with 3 $^1/_2$ turns of 14 gauge Au-plated Cu wire (11 mm i.d., 8 mm long). Magic-angle spinning at 4 kHz produces spectra free of detectable spinning sidebands, indicating that the chemical shift anisotropy is small, as expected for nearly symmetrical $PO_4{}^{3-}$ groups.[6] Quantitative spectra were obtained with 30–90° pulses with a 4–10-s recycle delay, depending on the $^{31}P$ $T_1$ of the sample. Proton decoupling ($\gamma H_2 = 40$ kHz) was employed. Proton cross-polarization was not used to obtain the quantitative spectra shown here but yields nonquantitative spectra more quickly (5-ms cross-polarization, 2-s recycle). Chemical shifts are reported in ppm downfield from external 85% phosphoric acid with an estimated precision of ±0.2 ppm. It is expected that the $^{31}P$ chemical shifts of the central phosphate groups in these compounds are well shielded from solvent effects so can be directly compared to solution values.

**$[(C_2H_5)_3O]_3W_{12}PO_{40}$.** Triethyloxonium tetrafluoroborate (6.0 g, 31.6 mmol) was added to a solution of phosphotungstic acid (14 g, 4.7 mmol) in acetonitrile (50 mL) in a nitrogen atmosphere. The mixture was stirred for 15 min and then filtered to obtain 12 g (80%) of $[(C_2H_5)_3O]_3W_{12}PO_{40}$, which was washed three times with acetonitrile and dried under vacuum at room temperature. The infrared spectrum was normal for a salt of $W_{12}PO_{40}{}^{3-}$. Anal. Calcd for $[(C_2H_5)_3O]_3W_{12}PO_{40}$: C, 6.78; H, 1.42. Found: C, 6.88, 6.86; H, 1.50, 1.47.

**$(C_2H_5O)_3W_{12}PO_{37}$.** One gram of $[(C_2H_5)_3O]_3W_{12}PO_{40}$ was heated at 150 °C under vacuum (nominal 0.1 mm) for 16 h to leave $(C_2H_5O)_3W_{12}PO_{37}$. Anal. Calcd for $(C_2H_5O)_3W_{12}PO_{37}$: C, 2.43; H, 0.51; O, 21.6; W, 74.4; P, 1.04. Found: C, 2.70, 2.76; H, 0.66; 0.66; O, 21.8, 22.0; W, 74.1, 74.9; P, 1.70, 1.60.

The infrared and $^{31}P$ MAS spectra and the slight contamination by $(HO)_3W_{12}PO_{37}$ they reveal are discussed above.

**$(CH_3O)_3W_{12}PO_{37}$.** $[(CH_3)_3O]_3W_{12}PO_{40}$ (4.8 g) was heated as above to leave 4.4 g of a solid residue that was primarily $(CH_3O)_3W_{12}PO_{37}$ by spectroscopic characterization as discussed above.

**$(HO)_3W_{12}PO_{37}$.** Hydrated phosphotungstic acid (20 g) was heated at 215 °C under vacuum (nominal 0.1 mm) for 16 h to leave a solid residue of $(HO)_3W_{12}PO_{37}$. Anal. Calcd for $(HO)_3W_{12}PO_{37}$: W, 76.6; O, 22.2. Found: W, 76.3, 76.0; O, 23.0, 23.2. Samples of $[(C_2H_5)_3O]_3W_{12}PO_{40}$ and $[(CH_3)_3O]_3W_{12}PO_{40}$ were thermolyzed similarly at 215 °C. The infrared spectra of the products were identical with that of $(HO)_3W_{12}PO_{37}$. The 215 °C thermolysis product from $[(C_2H_5)_3O]_3W_{12}PO_{40}$ (4.5 g) was stirred in water (15 mL) and filtered to remove 0.18 g of insoluble material. Addition of cesium chlorde to the filtrate precipitated $Cs_3W_{12}PO_{40}$ (4.5 g (97%)), identified by infrared analysis.

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Contribution from the Department of Chemistry,
The University of Texas at Austin, Austin, Texas 78712

## Unsymmetrical, Chelating Ligands. Synthesis of 1-Mercapto-2-phosphinobenzenes with a Variety of Substituents on the Ligating Sites

Evan P. Kyba* and Clyde N. Clubb

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The synthesis of *o*-phenylenebis(ligand) (where L and L$^1$ contain heteroatoms such as phosphorus, arsenic, sulfur, ni-

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