during the tenure of which this paper was written.

Registry No. 1, 61059-04-9; 6, 55227-55-9; 8, 92671-61-9; 9, 60890-82-6; 10, 64588-24-5; 11, 92014-16-9; 12, 64588-25-6; 13, 64588-26-7; 15, 92671-62-0; 16, 92671-63-1; 17, 88296-48-4; 18, 16109-39-0; 19, 64588-17-6; $Me_3SiC{\equiv}CSiMe_3$, 14630-40-1; $(Ph_3P)_2PdCl_2$, 13965-03-2; phenylacetylene, 536-74-3; isopropenylacetylene, 78-80-8; *tert*-butylacetylene, 917-92-0; acetylene, 74-86-2; allene, 463-49-0; (*E*)-2,4-pentadienyltrimethylsilane, 72952-73-9; 2,3-dimethyl-1,3-butadiene, 513-81-5.

Anions of the Type $(RMOH_2)_3W_{18}P_2O_{68}{}^{9-}$ and $[H_2OCo]_3W_{18}P_2O_{68}{}^{12-}$. A Reinvestigation of "B,β-$W_9PO_{34}{}^{9-}$"†,‡

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$Na_8HW_9PO_{34}$ reacts with $RMCl_3$ (RM = PhSn, $CpFe(CO)_2Sn$, CpTi) to form the corresponding $(RMOH_2)_3W_{18}P_2O_{68}{}^{9-}$ anions and with cobalt(II) to form $(H_2OCo)_3W_{18}P_2O_{68}{}^{12-}$. Thermolysis of $Na_8HW_9PO_{34}$ at 140–150 °C causes a solid-state isomerization; reactions of the resulting isomer with $RMCl_3$ and with cobalt(II) follow a different course than those involving unthermolyzed $Na_8HW_9PO_{34}$. The ^{31}P chemical shift anisotropy establishes that unthermolyzed $Na_8HW_4PO_{34}$ has an A-type structure and that thermolysis produces a B-type isomer.

Introduction

The preparations of the monosubstituted Keggin anions $RMW_{11}PO_{39}{}^{4-}$ (RM = PhSn, $CpFe(CO)_2Sn$, CpTi) and the disubstituted Keggin anions $(RM)_2W_{10}PO_{38}{}^{5-}$ (RM = PhSn, $CpFe(CO)_2Sn$) have been reported previously.[1-5] Continuing with this theme, we have attempted to prepare Keggin anions that are trisubstituted with organometallic groups by starting with the reported[6] trivacant lacunary anion $W_9PO_{34}{}^{9-}$. The preparations of two distinctly different classes of trisubstituted Keggin anions from $W_9PO_{34}{}^{9-}$ have already been described. Trisubstituted anions with a normal Keggin structure have been prepared from W_9P and early transition metals by Massart ($Mo_3W_9PO_{40}{}^{3-}$)[6] and by Domaille ($V_3W_9PO_{40}{}^{6-}$),[7] while Finke[8] and Tourne[9] have reported that $W_9PO_{34}{}^{9-}$ reacts with divalent group 8 metals and with zinc(II) to form species that have structures[10] based on two fused trisubstituted Keggin anions, such as $(H_2O)_2Co_4W_{18}P_2O_{68}{}^{10-}$.

Results and Discussion

$(RMOH_2)_3W_{18}P_2O_{68}{}^{9-}$ Anions. Reactions of $Na_8HW_9PO_{34}$, prepared as described in the literature[6] and *vacuum dried at room temperature*, with $RMCl_3$ (RM = PhSn, $CpFe(CO)_2Sn$, CpTi) do not give substituted Keggin anions. Instead, a series of anions with a general formula $(RMOH_2)_3W_{18}P_2O_{68}{}^{9-}$ is formed. The infrared spectra (Figure 1) of potassium salts of these anions are similar in the 1200–600 cm^{-1} region, suggesting that they are grossly isostructural. The ^{31}P NMR spectra in water contain one major line. Although $^2J_{Sn-P}$ coupling satellites are easily seen in the ^{31}P NMR spectra of $PhSnW_{11}PO_{39}{}^{4-}$ and $(PhSn)_2W_{10}PO_{38}{}^{5-}$,[2] no such coupling is observed in the spectrum of $(PhSnOH_2)_3W_{18}P_2O_{68}{}^{9-}$. The ^{183}W NMR spectra of $(PhSnOH_2)_3W_{18}P_2O_{68}{}^{9-}$ (lithium salt in water) and the corresponding $CpFe(CO)_2Sn$ derivative (tetrahexylammonium salt in slightly aqueous acetone) have been measured and consist of two lines in a 1:2 ratio. Both lines (−138.6, −190.0 ppm) in the spectrum of the phenyltin derivative exhibit tungsten–tungsten coupling satellites of 16 Hz, implying that the two sets of tungsten-centered octahedra are corner coupled, as in an A-type W_9P structure.[11,12] The more intense ^{183}W line (−190.0 ppm) has additional satellites (J = 40 Hz) assigned to overlapped $^2J_{^{117}Sn-W}$ and $^2J_{^{119}Sn-W}$ coupling. Line widths in the ^{183}W NMR spectrum of the $CpFe(CO)_2Sn$ derivative are too great to observe similar couplings.

All of our data are consistent with a structure in which two A-type W_9P units are connected through a belt of three RM units as in Figure 2. We have no evidence as to whether the W_9P units are α, as shown in Figure 2, or β. Weakley has determined[13] the structure of $W_{21}P_2O_{73}H_6{}^{4-}$, which is a useful precedent for our proposed structure for two reasons. First, it contains two A,α-W_9P units connected through a belt of three tungsten-centered polyhedra; secondly, two of the tungsten atoms in the belt are connected to terminal oxygen atoms that are *inside* the cavity and that may be protonated. This strongly suggests

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† This paper is dedicated to the memory of Earl Muetterties in recognition of his many contributions to inorganic and organometallic chemistry.

‡ Contribution No. 3522.

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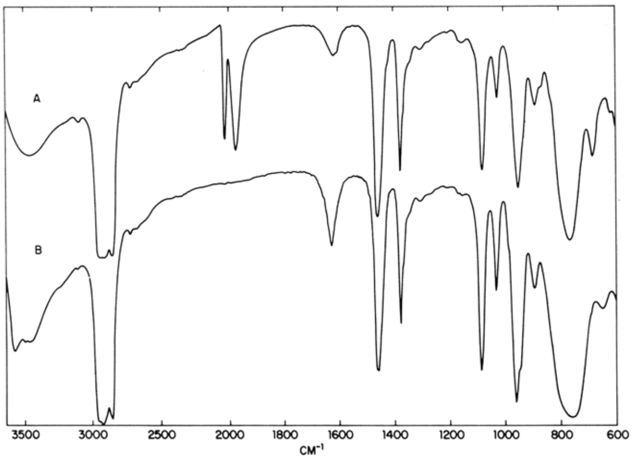

Figure 1. Infrared spectra (mineral oil mulls) of (a) $K_9[CpFe(CO)_2SnOH_2]_3W_{18}P_2O_{68}$ and (b) $K_9(CpTiOH_2)_3W_{18}P_2O_{68}$.

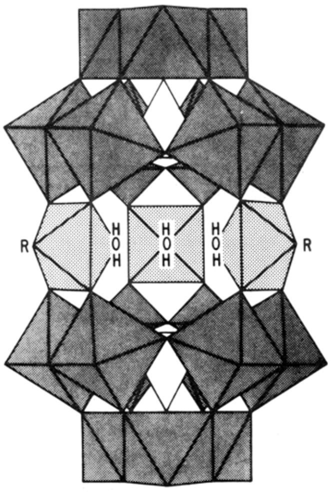

Figure 2. Proposed structure of $(RMOH_2)_3W_{18}P_2O_{68}{}^{9-}$ anions.

there would be room for at least two of the inner constitutional water molecules shown in Figure 2 and possibly for all three. There is evidence that $(PhSn)_3W_{18}P_2$ does contain ionizable protons, consistent with the presence of constitutional water molecules. Salts isolated at pH 5–7 differ from those isolated at pH 1 in cation content (eleven univalent cations vs. nine), in the phosphorus–oxygen stretching region of the infrared spectra, and in their ^{31}P NMR spectra. At pH 1, the ^{31}P NMR spectrum consists of one line, at −10.9 ppm (10-Hz half-width); at pH 6.5, the line is shifted to −11.6 ppm and broadened (53-Hz half-width), consistent with exchange of protons between oxygen sites in partially deprotonated water ligands. These changes are reversible. In addition, titration of the conjugate acid obtained by passing the K_{11} salt through an acidic ion-exchange column gives a neutralization curve that suggests protons of differing degrees of acidity are present. At pH 7, the observed neutral equivalent is 534 compared to 535 calculated for $K_{11}(PhSnOH)_2(PhSnOH_2)W_{18}P_2O_{68}{\cdot}20H_2O$.

It was mentioned above that the ^{183}W NMR spectrum of the tetrahexylammonium salt of $(CpFeCO)_2Sn)_3W_{18}P_2$ in slightly aqueous (100 μL of water/4 mL of acetone) acetone consists of two lines (−109.2 and −169.7 ppm) in a 1:2 ratio. In anhydrous acetone, the latter is split into two overlapping lines of similar height at −170.6 and −171.6 ppm. Similarly, the ^{31}P NMR line, which is a singlet at −10.80 ppm in moist acetone, is split into two lines, at −11.25 and −11.39 ppm in anhydrous acetone. This behavior is also consistent with the presence of constitutional water molecules that contain exchangeable protons.

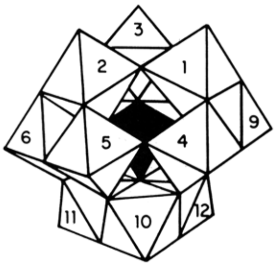

Figure 3. Numbering system for Keggin anions.

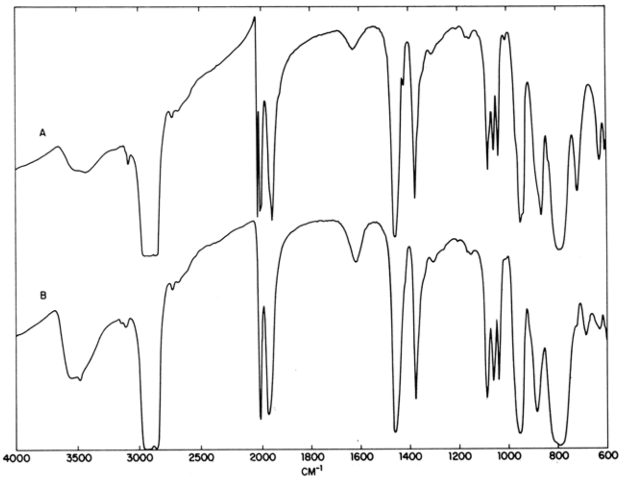

Figure 4. Infrared spectra (mineral oil mulls) of (a) Cs_5-1,5-$[CpFe(CO)_2Sn]_2W_{10}PO_{38}$ (the 20 cm⁻¹ splitting of the high-frequency carbonyl absorption in Figure 4a is a solid-state phenomenon; it is not seen in solution spectra) and (b) $Cs_3H_2[1,4\text{-}CpFe(CO)_2Sn]_2W_{10}PO_{38}$.

The $(PhSn)_3W_{18}P_2$ framework is stable from at least pH 1–7. In fact, 1,5-$(PhSn)_2W_{10}PO_{38}{}^{5-}$ (Figure 3)[14] containing a small amount of another unidentified isomer[15] is converted to $(PhSn)_3W_{18}P_2$ during several hours reflux at pH 7 in aqueous solution. In sharp contrast, $[CpFe(CO)_2Sn]_3W_{18}P_2$ not only is not formed *from* 1,5-$[CpFe(CO)_2Sn]_2W_{10}PO_{38}{}^{5-}$ at pH 7 but also is rapidly converted *to* a new isomer of $[CpFe(CO)_2Sn]_2W_{10}PO_{38}{}^{5-}$ at this pH. This difference between $(PhSn)_3W_{18}P_2$ and $[CpFe(CO)_2Sn]_3W_{18}P_2$ reflects a substituent effect not commonly seen in heteropolyanion chemistry.

The new isomer (believed to be the 1,4 isomer for reasons discussed below) of $[CpFe(CO)_2Sn]_2W_{10}PO_{38}{}^{5-}$ is metastable; it is transformed to the 1,5 isomer we reported previously[5] by additional heating in aqueous solution at pH 7. These transformations are summarized in eq 1 and 2.

$$(PhSn)_2W_{10}P^{5-} \xrightarrow{\text{pH } 7} (PhSn)_3W_{18}P_2{}^{11-} \underset{}{\overset{H^+}{\rightleftharpoons}} (PhSn)_3W_{18}P_2{}^{9-} \quad (1)$$

The 1,4 isomer of $[CpFe(CO)_2Sn]_2PO_{38}{}^{5-}$ (Cs_3H_2 salt) has an infrared spectrum virtually identical with that of the 1,5 (Cs_5 salt) isomer from 4000 to 750 cm⁻¹,[5] but the two

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[14] The numbering system shown in Figure 3 is that proposed by IUPAC. In a previous publication,[5] we used a different numbering scheme; the isomer now numbered 1,5 was then numbered 1,4.

[15] In ref 1, the preparation of $(PhSn)_2W_{10}PO_{38}{}^{5-}$ is reported to give a mixture containing at least four isomers as determined by ^{31}P NMR spectroscopy. More recent preparations of $(PhSn)_2W_{10}PO_{38}{}^{5-}$ have given products containing only two isomers of $(PhSn)_2W_{10}PO_{38}{}^{5-}$ in significant amount. These have ^{31}P NMR lines (lithium salt in water) in a 3:1 intensity ratio at −7.34 ($^2J_{P\text{-}Sn}$ = 20 Hz) and −8.62 ppm ($^2J_{P\text{-}Sn}$ = 17.8 Hz). The ^{183}W NMR spectrum displays five equivalent lines, demonstrating that the major isomer is 1,5-substituted, as reported earlier[5] for $Ti_2W_{10}PO_{40}{}^{7-}$ and $[CpFe(CO)_2Sn]_2W_{10}PO_{38}{}^{5-}$.

$$[CpFe(CO)_2Sn]_3W_{18}P_2{}^{9-} \xrightarrow{pH\ 7} 1,4\text{-}[CpFe(CO)_2Sn]_2W_{10}P^{5-} \xrightarrow{pH\ 7} 1,5\text{-}[CpFe(CO)_2Sn]_2W_{10}P^{5-} \quad (2)$$

can be easily distinguished in the 750–600 cm^{-1} region (Figure 4) and by ^{31}P and ^{183}W NMR spectroscopy. In water, the ^{31}P NMR spectrum of the lithium salt of this new isomer consists of one line (−11.7 ppm), considerably shifted from the −9.68 ppm line found for the 1,5 isomer. The ^{183}W NMR spectrum (Figure 5) comprises six lines of relative intensities 2:2:2:2:1:1. This is consistent with either a 1,2 or a 1,4 configuration.[14] As seen in Figure 5, five of the resonances are clustered between −120 and −146 ppm and the overlapping broad lines do not permit structural inferences from W–W coupling satellites. The remaining line of intensity 1 is at −297 ppm, far removed from the other five lines. It is reasonable that this line represents a tungsten in close proximity to the substitution sites. Both the 1,2 and 1,4 isomers include one unique tungsten far removed from the substitution sites which is bonded through oxygen only to tungsten atoms, while the other unique tungsten in each structure is bonded through oxygen to two tin and two tungsten atoms. We assume the −297 ppm line represents the latter. This line exhibits $^2J_{W-W}$ coupling satellites with J = 26 Hz, which implies assignment to a tungsten atom corner bonded to other tungsten-centered octahedra.[11,12] This is consistent with a 1,4 structure for the new isomer, not a 1,2. This 1,4 isomer tends to form protonated salts; salts of both 1,4-$CpFe(CO)_2W_{10}PO_{38}H^{4-}$ and 1,4-$[CpFe(CO)_2Sn]_2W_{10}PO_{38}H_2{}^{3-}$ have been isolated. This is in sharp contrast to the 1,5 isomer, which has been isolated only as non-protonated salts. The increased basicity of the 1,4 isomer is ascribed to the presence of an Sn–O–Sn group, which is not present in the 1,5 isomer. The oxygen in this group should be more basic than one in a W–O–W or W–O–Sn group and would provide a protonation site.

$Na_8HW_9PO_{34}$ and $(H_2O_2Co)_3W_{18}P_2O_{68}{}^{12-}$. As mentioned above, the $Na_8HW_9PO_{34}$ used for the studies described so far was prepared by the common literature procedure[6] and dried under vacuum at room temperature. This W_9P anion has been assigned[6] a B,β structure, but the evidence for this is not compelling. In fact, a W_9Si anion that was originally also assigned[16] a B,β structure has recently been shown to have an A,β structure[17] and Pope has recently discussed the probability that a B,β-W_9X cannot exist.[18] In Finke's paper[8a] describing the reaction of W_9P with cobalt(II) to form B-$(H_2O)_2Co_4W_{18}P_2O_{68}{}^{10-}$, he notes that the reaction gives a different, unidentified, product unless the W_9P is first dried at 140 °C. This point seemed worth pursuing because we used unheated W_9P in our work and obtained compounds that we believe contain A-type W_9P units.[8b]

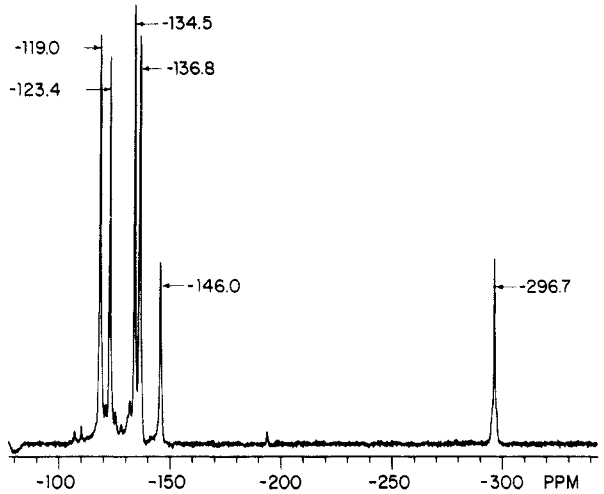

Figure 5. ^{183}W NMR spectrum of $Li_3H_2[1,4\text{-}CpFe(CO)_2Sn]_2W_{10}PO_{38}$.

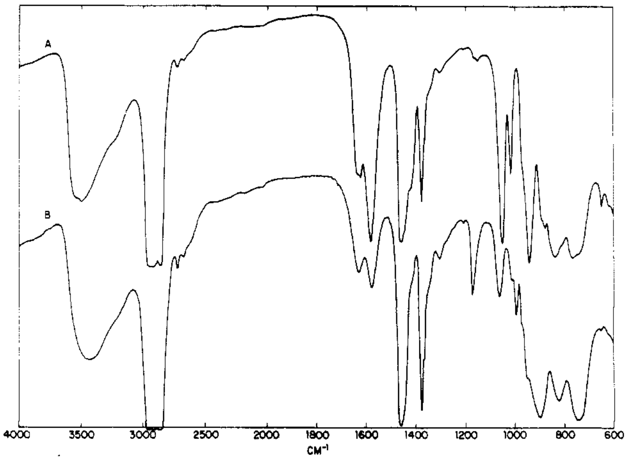

Figure 6. Infrared spectra (mineral oil mulls) of (a) $Na_8HW_9PO_{34}\cdot xH_2O$ and (b) Δ-$Na_8HW_9PO_{34}\cdot xH_2O$.

Accordingly, we thermolyzed W_9P at 140–150 °C for several hours and examined the starting material and product by infrared, ^{31}P magic-angle spinning (MAS), and ^{31}P nonspinning solid-state NMR spectroscopy. All types of spectra changed markedly. We believe the changes in the infrared spectrum and in the ^{31}P chemical shift and chemical shift anisotropy are too great to be explained by an $\alpha \rightarrow \beta$ isomerization or the reverse. They can, however, be rationalized as resulting from an A-type to a B-type isomerization. The infrared spectra of W_9P and Δ-W_9P (temporary designation for the thermolysis product) are shown in Figure 6. Numerous changes are apparent. Perhaps the most significant is the development of an absorption band at 1171 cm^{-1} upon thermolysis. Lyhamn[19] has assigned phosphorus–oxygen stretching bands above 1100 cm^{-1} in molybdophosphates to P=O or P—OH while stating that phosphorus–oxygen (bridge) vibrations are generally in the 1100–1000 cm^{-1} range. The infrared spectrum of Δ-W_9P is therefore more consistent with a B-type structure than with an A-type structure. Correspondingly, the lack of a P–O band above 1050 cm^{-1} in the infrared spectrum of unthermolyzed W_9P argues against it having a B-type structure. We have observed a band at 1131 cm^{-1} in the infrared spectrum of $Na_{12}W_{15}P_2O_{56}$, which contains a B-type anion.[20]

Solid-state ^{31}P NMR spectroscopy is an even more definitive approach to distinguishing between A- and B-type sites in phosphotungstates than is infrared spectroscopy. A B-type site has much lower local symmetry about the phosphorus than does an A-type site. While both sites exhibit axial (local C_{3v}) symmetry, the B-type site has a much larger chemical shift anisotropy (CSA). This was verified by measurement of the ^{31}P MAS and nonspinning spectra of $Na_{12}W_{15}P_2O_{56}$. As seen in Figures 7 and 8, the expected two major lines are observed, and the line assigned to the B-type phosphorus (−0.1 ppm) has

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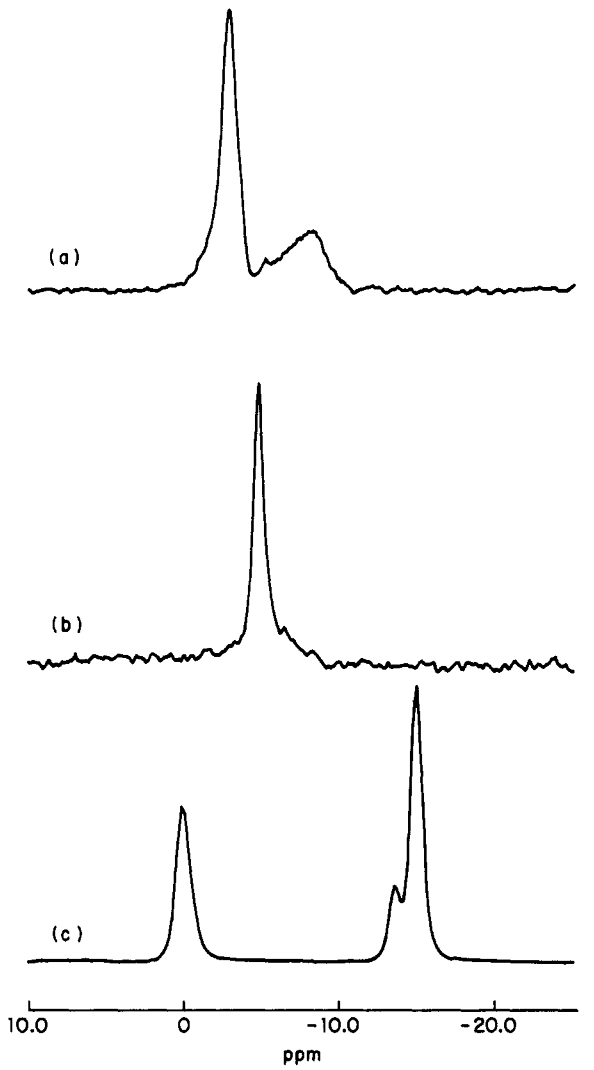

Figure 7. ^{31}P MAS NMR spectra of (a) Δ-W_9P, (b) W_9P, and (c) $W_{15}P_2$. The centerband (isotropic chemical shift) region is shown; those sites with large CSA also have intense spinning sidebands. Intensities reported in the text include integration of the centerband and spinning sidebands of each resonance.

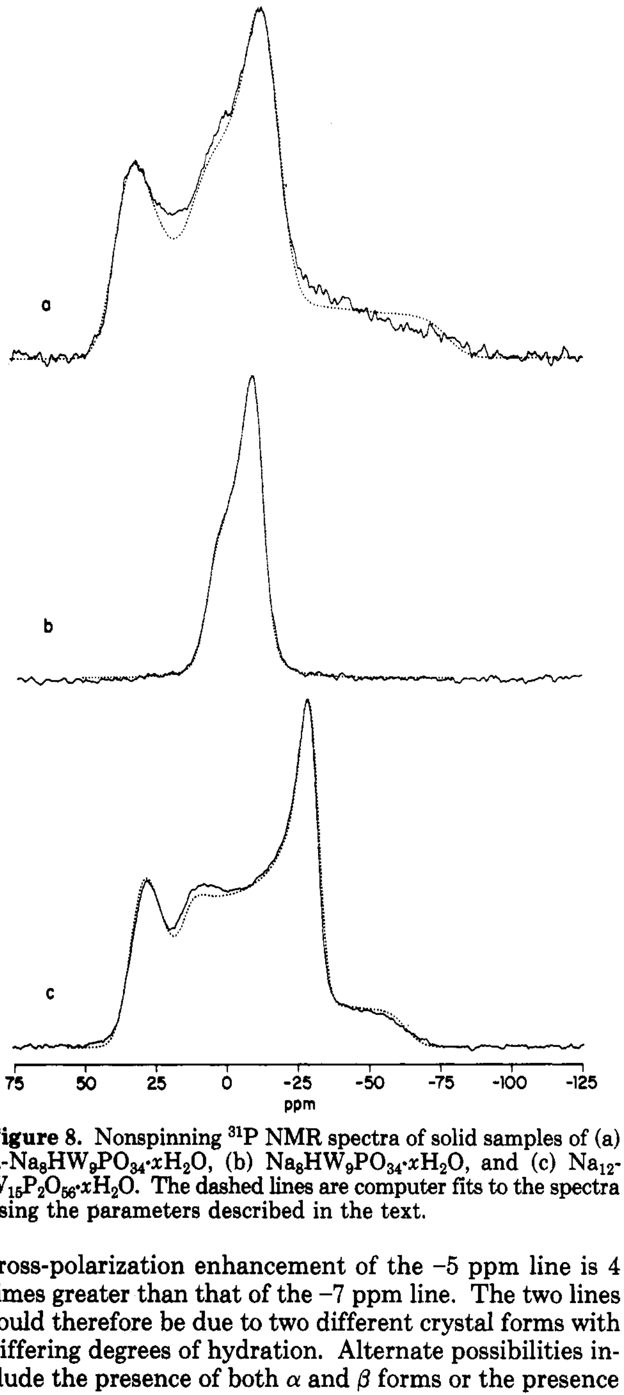

Figure 8. Nonspinning ^{31}P NMR spectra of solid samples of (a) Δ-$Na_8HW_9PO_{34}\cdot xH_2O$, (b) $Na_8HW_9PO_{34}\cdot xH_2O$, and (c) $Na_{12}W_{15}P_2O_{56}\cdot xH_2O$. The dashed lines are computer fits to the spectra using the parameters described in the text.

a much larger CSA (−94.5 ppm) than the CSA (+46 ppm) of the line at −15.2 ppm that is assigned to the other phosphorus. The sign and magnitude of the CSA for the B-type phosphorus atom can be compared with published[21] values for solid phosphates. They are consistent with values expected for phosphates with three bridging oxygens (here P–O–W) and one terminal oxygen.

The ^{31}P MAS and nonspinning spectra of W_9P and Δ-W_9P are also shown in Figures 7 and 8. The MAS spectrum of W_9P exhibits two lines, both with a CSA of +18.5 ppm, at −5 and −7 ppm. These small CSA values are consistent with the A-type structure deduced above from the infrared spectrum of W_9P. We are not sure why there are two lines. In the spectrum shown in Figure 7b, the −7 ppm line is apparent only as a shoulder. However, in the MAS spectra of some other samples of W_9P, the area of the −7 ppm line is up to twice that of the −5 ppm line. The nonspinning spectrum shown in Figure 8b was determined on the same sample used for Figure 7b. The cross-polarization enhancement of the −5 ppm line is 4 times greater than that of the −7 ppm line. The two lines could therefore be due to two different crystal forms with differing degrees of hydration. Alternate possibilities include the presence of both α and β forms or the presence of a gross impurity. We have not detected any reactivity difference between samples of W_9P containing different ratios of the −5 and −7 ppm lines.

As shown in the figures, the ^{31}P MAS and nonspinning spectra of Δ-W_9P also show two lines. These are at −3 and −8 ppm and have CSA's of −116 and +27.5 ppm, respectively; neither cross-polarizes readily. The −116 ppm CSA for the major component of Δ-W_9P establishes that it has a B-type structure; the failure to cross-polarize readily suggests it has a P═O group rather than a P—OH group. Both P═O and P—OH groups are consistent with the infrared spectrum as discussed above. The smaller line, at −8 ppm, is more difficult to assign. Its small CSA is consistent with an A-type structure, and it *may* represent the −7 ppm line in W_9P slightly shifted by thermolytic dehydration. The presence of such an impurity in Δ-W_9P cannot be ruled out by infrared spectroscopy.

Reaction of unheated W_9P with cobalt nitrate in water gives $(H_2OCo)_3W_{18}P_2O_{68}{}^{12-}$. This was isolated as a blue potassium salt and characterized by elemental analysis,

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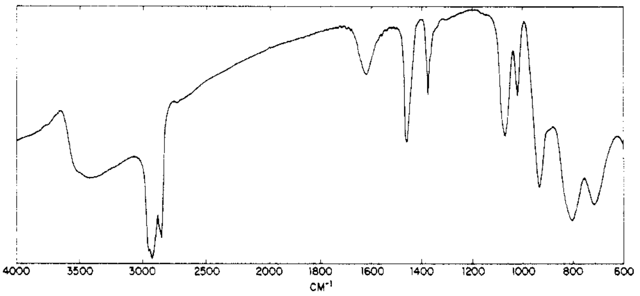
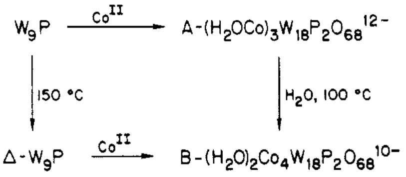


Figure 9. Infrared spectrum (mineral oil mull) of $K_{12}(H_2OCo)_3W_{18}P_2O_{68}$.

Scheme I



by its visible spectrum, which is discussed below, and by its infrared spectrum (Figure 9), which resembles those of the A-type $K_9(RMSnOH_2)_3W_{18}P_2O_{68}$ series (Figure 1). This new cobalt complex can be recrystallized without change if done rapidly below 65 °C. In aqueous solution above this temperature, it is quickly converted to $(H_2O)_2Co_4W_{18}P_2O_{68}^{10-}$. Scheme I has therefore been demonstrated, combining our work with that of Finke.[8]

We have also examined the reactions of Δ-W_9P with $PhSnCl_3$ and $CpFe(CO)_2SnCl_3$. Mixtures of products have been obtained. The only identified products were the mono- and disubstituted Keggin anions $RSnW_{11}PO_{39}^{4-}$ and $(RSn)_2W_{10}PO_{38}^{5-}$.[2,3,5]

Summarizing our conclusions from the above: unheated W_9P has an A-type structure (either α or β), while Δ-W_9P has a B-type structure. Further, A-W_9P reacts with $RMCl_3$ species (defined above) and with cobalt to give anions containing two A-type W_9P groups connected by a belt of three metal-centered polyhedra, while B-W_9P reacts with the same substrates to give Keggin structures. As we noted earlier, $(H_2O)_2Co_4W_{18}P_2O_{68}^{10-}$ consists of two fused Keggin structures.

These conclusions are consistent with insertion reactions of B-$W_{15}P_2O_{56}^{12-}$ that has a lacunary site resembling that of B,α-W_9P and is spectroscopically related to Δ-W_9P as described above. B-$W_{15}P_2O_{56}^{12-}$ reacts with phenyltin trichloride[2] and with cobalt[20] to form $(PhSn)_2W_{16}P_2O_{60}^{3-}$ and $(H_2O)_2Co_4W_{30}P_4O_{112}^{16-}$, respectively, reaction products which are analogous to those obtained from Δ-W_9P and the same substrates. We therefore agree with Finke that a B-type trivacant heteropolytungstate is required to form the $(H_2O)_2M_4W_{18}P_2$ anions and believe that the literature preparation of W_9P initially gives an A-type anion which isomerizes to B,α-W_9P during the 140 °C drying step.[8]

In considering the structure of $(H_2OCo)_3W_{18}P_2O_{68}^{12-}$ more closely, we are faced with the same two problems discussed above for the $(RMOH_2)_3W_{18}P_2O_{68}^{9-}$ series. These are whether the W_9P units are α or β and whether there are inner constitutional water molecules. We have no evidence bearing on the α or β question. Although we are postulating inner constitutional water molecules for the $(RMOH_2)_3W_{18}P_2O_{68}^{9-}$ series, it is quite possible that the cobalt complex is different. We therefore determined the visible spectrum of $K_{12}(H_2OCo)_3W_{18}P_2O_{68}$; it has maxima at 616 ($\epsilon$ 76), 536 (ϵ 64), and 494 (ϵ 70) nm. The relatively low extinction coefficients might suggest the cobalt is octahedral; i.e., the complex has inner water molecules as in Figure 2 (with R also equal to H_2O). Indeed, the visible spectrum of $(H_2OCo)_2OW(W_9AsO_{33})_2^{10-}$, which contains B-type W_9As^{III} units, is quite similar (λ_{max} 629 (ϵ 92), 529 (ϵ 36), 500 (ϵ 40) nm), and this was initially interpreted[22] as implying a distorted octahedral environment for the cobalt molecules. The visible spectra of $(H_2OCo)_2OW(W_9PO_{34})_2^{10-}$, $(H_2OCo)(OW)_2(W_9AsO_{33})_2^{8-}$, and $(H_2OCo)_3(W_9AsO_{33})_2^{12-}$ are reported to be similar to that of $(H_2OCo)_2OW(W_9As)_2$.[23,24] However, a crystal structure has been done on a salt of $(H_2OCo)_3(W_9AsO_{33})_2^{12-}$ and the cobalt has been shown to be square pyramidal.[25] In a recent article the cobalt in $(H_2OCo)(OW)_2(W_9AsO_{33})_2^{2-}$ is also considered to be square pyramidal.[24] All of these previously reported anions have B-type W_9 units and therefore have a smaller cavity than does our A-type $(H_2OCo)_3W_{18}P_2$ anion. Nevertheless, we feel that the similarity of the visible spectrum of our anion to that of $(H_2OCo)_3(W_9As)_2$ makes it likely that $(H_2OCo)_3W_{18}P_2O_{68}^{12-}$ also has square-pyramidal cobalt. The spectrum of $(H_2O)_2Co_4W_{18}P_2$, which does have octahedral cobalt, is quite different (λ_{max} 570, 510 (sh), 495 (sh) nm).[8]

Experimental Section

NMR Spectra. ^{31}P and ^{183}W solution NMR spectra were obtained with either Nicolet NT-360WB or NT-300WB spectrometers.

^{183}W NMR spectra (15 MHz) were obtained at 30 °C in a 20 mm diameter sideways-spinning solenoidal probe ($\pi/2$ pulse 50–80 μs). Chemical shifts are referenced to external 2 M Na_2WO_4 in D_2O.

^{31}P solution NMR spectra (141.6 or 121.8 MHz) were recorded in 10- or 12-mm tubes with a concentric capillary filled with D_2O for field/frequency lock. Chemical shifts are externally referenced to 85% H_3PO_4.

Solid-state ^{31}P NMR spectra were obtained at 121.4 MHz on a Bruker CXP-300 spectrometer, both with magic-angle spinning at 4 kHz, and without spinning. For ^{31}P, the Bruker ^{13}C MAS probe was modified by replacing the coil with $3^1/_2$ turns of 14 ga Au-plated Cu wire, forming a solenoidal coil 11 mm i.d. × 8 mm. Quantitative spectra were obtained by using 30–90° pulses with a 10-s recycle delay, depending on the ^{31}P T_1 of the sample. Proton decoupling ($\gamma(H_2)/2\pi$ = 40 kHz) was employed. Proton cross-polarization was not used to obtain quantitative spectra but yields nonquantitative spectra more quickly (5-ms cross-polarization and 2-s recycle). Chemical shifts are referenced to external 85% H_3PO_4 with an estimated precision of ±0.2 ppm, with positive chemical shifts to low field; chemical shift anisotropy (CSA) is defined as $\delta_{\parallel} - \delta_{\perp}$.

Preparations. $[CpFe(CO)_2SnOH_2]_3W_{18}P_2O_{68}^{9-}$. $Na_8HW_9PO_{34}$ hydrate (26.0 g, ca. 10 mmol)[6] was added to a solution of sodium acetate (30 g) in water (300 mL). The pH was readjusted to 5.2 with acetic acid and a solution of $CpFe(CO)_2SnCl_3$[26] (12 g, 29 mmol) in tetrahydrofuran (40 mL) was added with stirring. Stirring was continued for 15 min; the solution was then filtered. The filtrate was treated with potassium chloride (20 g) to precipitate 3.5 g of crude $K_9[CpFe(CO)_2SnOH_2]_3W_{18}P_2O_{68}$. The filter cake from the first filtration was slurried in water (350 mL) for 30 min and filtered and the filtrate treated with potassium chloride (5 g). Additional $K_9[CpFe(CO)_2SnOH_2]_3W_{18}P_2O_{68}$ (14 g) precipitated for a total crude yield of 49%. Recrystallization of seven grams from water (60 mL) gave 2.3 g of the pure salt as a yellow crystalline solid. Anal. Calcd for $K_9[C_5H_5Fe(CO)_2SnOH_2]_3W_{18}P_2O_{68}{\cdot}20H_2O$: K, 5.76; C, 4.13; H, 1.01; Fe, 2.74; Sn, 5.83; W, 54.1; P, 1.01; H_2O, 5.9. Found: K, 5.98; C, 4.11; H,

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1.01; Fe, 2.74; Sn, 5.98; W, 53.9% P, 1.01; H_2O, 6.2 (TGA, 250 °C).

Two grams of the potassium salt was dissolved in water (200 mL). The addition of trimethylamine hydrochloride precipitated a mixed salt that was washed three times with water before analysis. Anal. Calcd for $[(CH_3)_3NH]_7K_2[C_5H_5Fe(CO)_2SnOH_2]_3W_{18}P_2O_{68}$: C, 8.55; H, 1.55; N, 1.66; K, 1.33; Fe, 2.84; Sn, 6.04; P, 1.05; W, 56.1. Found: C, 8.19; H, 1.50; N, 1.69; K, 1.02; Fe, 2.72; Sn, 6.17; P, 1.22; W, 56.4.

The potassium salt (9.0 g) was dissolved in water (600 mL) containing 12 drops of 12 M hydrochloric acid. This solution was added to a stirred emulsion of tetrahexylammonium bromide (8.0 g) in water (1200 mL). The salt that precipitated had an infrared spectrum consistent with a salt of $[CpFe(CO)_2SnOH_2]_3W_{18}P_2O_{68}^{9-}$ and was used for ^{183}W NMR studies.

$[PhSnOH_2]_3W_{18}P_2O_{68}^{9-}$. Phenyltin trichloride was added dropwise with stirring to a slurry of $Na_8HW_9PO_{34}$ hydrate (90 g, ca. 35 mmol) until the pH fell to 5.5. The mixture was stirred an additional 10 min and then filtered. Potassium chloride (30 g) was added to the filtrate, and stirring was continued another 30 minutes; filtration gave 30.6 g (32%) of hydrated $K_{11}(PhSnOH)_2(PhSnOH_2)W_{18}P_2O_6$ that was recrystallized from water.

One gram of this recrystallized salt was then recrystallized from water containing potassium acetate (pH of solution was 6.2) to obtain 0.51 g of $K_{11}(PhSnOH)_2(PhSnOH_2)W_{18}P_2O_{68}\cdot20H_2O$. Anal. Calcd for $K_{11}(PhSnOH)_2(PhSnOH_2)W_{18}P_2O_{68}\cdot20H_2O$: K, 7.30; C, 3.67; H, 1.01; P, 1.05; Sn, 6.05; W, 56.19; H_2O, 6.1; N equiv, 535. Found: K, 7.05; C, 3.84; H, 0.96; P, 0.94; Sn, 5.79; W, 55.90; H_2O, 6.0 (TGA, 300 °C); N equiv, 534.

The neutral equivalent (N equiv) was determined by passage of the salt through an acid ion-exchange column and titration of the effluent.

One gram of the initial recrystallized potassium salt was recrystallized from water (5 mL) containing 6 drops of 12 M HCl/100 mL of solution to obtain $K_9(PhSnOH_2)_3W_{18}P_2O_{68}\cdot20H_2O$. Anal. Calcd for $K_9Ph(SnOH_2)_3W_{18}P_2O_{68}\cdot20H_2O$: K, 6.05; C, 3.72; H, 1.06; P, 1.07; Sn, 6.13; W, 56.93. Found: K, 5.75; C, 3.70; H, 1.01; P, 1.03; Sn, 6.49; W, 56.70.

Two grams of the initial potassium salt was dissolved in water (10 mL). The solution was heated to boil and brought to pH 1 with 12 M HCl. Excess cesium chloride was added, and the solution was allowed to cool. The solid that separated was recrystallized from water to obtain 1.1 g of $Cs_8K(PhSnOH_2)_3W_{18}P_2O_{68}\cdot9H_2O$. Anal. Calcd for $Cs_8K(C_6H_5SnOH_2)_3W_{18}P_2O_{68}\cdot9H_2O$: Cs, 16.7; K, 0.61; C, 3.40; H, 0.62; Sn, 5.59; W, 52.0; P, 0.97; O, 20.1. Found: Cs, 16.6; K, 0.65; C, 2.84; H, 0.70; Sn, 5.51; W, 51.8; P, 0.98; O, 19.7.

The infrared spectra of the K_9 and K_{11} salts differ significantly only in the P–O stretching region. The K_9 salt has three well-resolved P–O absorptions, at 1084, 1057, and 1030 cm^{-1}; the K_{11} salt has two distinct P–O absorptions, at 1087 and 1029 cm^{-1}, with a shoulder on the former at 1065 cm^{-1}. The ^{31}P NMR spectrum is discussed in the text. A lithium salt, used for the ^{183}W measurements described above, was prepared from the K_9 salt using a lithium ion-exchange resin.

Five grams of $[(CH_3)_3NH]_5(PhSn)_2W_{10}PO_{38}$ was added to water (30 mL) that contained potassium acetate (12 g) and acetic acid (pH 7). The mixture was refluxed for 2 h and filtered hot. The filter cake was extracted with boiling water (50 mL). The solid that separated from the extract on cooling was dissolved in water; tetramethylammonium chloride was added and the resulting precipitate was recrystallized from water to obtain 1.1 g of $[(CH_3)_4N]_9K_2(PhSnOH)_2(PhSnOH_2)W_{18}P_2O_{68}\cdot3H_2O$. Anal. Calcd for $[(CH_3)_4N]_9K_2(C_6H_5SnOH)_2(C_6H_5SnOH_2)W_{18}P_2O_{68}\cdot3H_2O$: C, 11.00; H, 2.21; N, 2.14; K, 1.33; Sn, 6.04; W, 56.1; O, 20.09; H_2O, 1.53. Found: C, 10.55; H, 2.16; N, 2.22; K, 1.10; Sn, 6.13; W, 54.8; O, 20.10; H_2O (KF), 1.43.

The ^1H NMR spectrum had an alkyl to aryl proton ratio of 7:1 (calculated 7.2:1); the aryl multiplet had the same characteristics as those in the spectra of the salts prepared above. The infrared spectrum also agreed with that of the $(PhSn)_3W_{18}P_2$ salt prepared above at pH 7.

$(CpTiOH_2)_3W_{18}P_2O_{68}$. A solution of $CpTiCl_3$ (6.0 g, 27 mmol) in tetrahydrofuran (60 mL) was added to $Na_8HW_9PO_{34}\cdot xH_2O$ (26 g, ca. 10 mmol) in water (300 mL) which had previously been adjusted to pH 5.2 with sodium acetate (30 g) and acetic acid. The mixture was stirred 15 min and then filtered. Potassium chloride (15 g) was added to the yellow filtrate to precipitate 2.9 g (6%) of crude $K_7Na_2(CpTiOH_2)_3W_{18}P_2O_{68}$. This was combined with 5.9 g of similar product from other preparations and recrystallized from water (75 mL) containing three drops of 12 M hydrochloric acid. The recovery of yellow crystalline product was only 0.15 g. Anal. Calcd for $K_7Na_2(C_5H_5TiOH_2)_3W_{18}P_2O_{68}\cdot15H_2O$; K, 5.03; Na, 0.84; C, 3.31; H, 0.94; P, 1.14; Ti, 2.64; W, 60.8; H_2O, 5.0. Found: K, 5.05; Na, 0.66; C, 3.76; H, 0.73; P, 1.09; Ti, 2.84; W, 59.5; H_2O, 4.8 (TGA, 300 °C).

The infrared spectrum is essentially identical with that of $K_9(CpFe(CO)_2SnOH_2)_3W_{18}P_2O_{68}$ from 1200 to 600 cm^{-1}. The low yield and very low recovery from recrystallization are apparently due to a hydrolytic degradation reaction. The yellow color is lost if aqueous solutions are boiled more than a few minutes; colorless salts can be obtained from these solutions. These have not been analyzed but their infrared spectra suggest they may be salts of a Cp cleavage product such as $[(H_2O)_2Ti]_3W_{18}P_2O_{68}^{6-}$.

1,4-$[CpFe(CO)_2Sn]_2W_{10}PO_{38}^{5-}$. Cesium chloride (10 g) was added to a solution of $K_9(CpFe(CO)_2SnOH_2)_3W_{18}P_2O_{68}$ (14.6 g, 2.5 mmol) in water (500 mL) at 70 °C. The mixture was cooled to ambient temperature and filtered. The filter cake was heated in water (200 mL) at boil; the pH was brought to 6.4 with sodium acetate; a solid persisted for about 1 min at boil and then suddenly dissolved to leave a cloudy solution. this was immediately filtered and allowed to cool slowly. Crystalline yellow $Cs_3[CpFe(CO)_2Sn]_2W_{10}PO_{38}H_2\cdot5H_2O$ (6.4 g, 72%) separated. Three grams of this was dissolved in water (100 mL) at 70 °C. The pH was 5.8 and was raised to 7.5 by the slow addition of aqueous cesium hyroxide at 70 °C. The warm solution was filtered and chilled in an ice bath to recover 2.1 g (70% recovery) of Cs_3-1,4-$[CpFe(CO)_2Sn]_2W_{10}PO_{38}H_2\cdot5H_2O$. The infrared spectra of the crude and of the purified material were the same. The infrared and NMR spectra were discussed in the text. Anal. Calcd for $Cs_3[C_5H_5Fe(CO)_2Sn]_2W_{10}PO_{38}H_2\cdot5H_2O$: Cs, 11.20; C, 4.72; H, 0.62; Fe, 3.14; P, 0.87; Sn, 6.67; W, 51.65; O, 21.1; H_2O, 2.5. Found: Cs, 11.59; C, 4.51; H, 0.54; Fe, 3.17; P, 0.88; Sn, 7.10; W, 50.74; O, 21.0; H_2O, 2.6 (TGA, 250 °C).

The lithium salt used for measurement of the ^{183}W spectrum was prepared from the above salt by ion exchange.

A solution of the Cs_3H_2 salt (3.0 g) in water (200 mL) at 45 °C was passed through 25 mL of strongly acidic ion-exchange resin. The effluent was adjusted to pH 7.7 with tetramethylammonium hydroxide and then concentrated to 100 mL. Five grams of tetramethylammonium chloride was added and the mixture was centrifuged to obtain 1.6 g of $[(CH_3)_4N]_4$-1,4-$[CpFe(CO)_2Sn]_2W_{10}PO_{38}H$. Anal. Calcd for $[(CH_3)_4N]_4(C_5H_5Fe(CO)_2Sn]_2W_{10}PO_{38}H$: C, 10.70; H, 1.77; N, 1.66; Fe, 3.31; P, 0.92; Sn, 7.05; W, 54.61. Found: C, 10.57; H, 2.11; N, 1.47; Fe, 3.64; P, 1.05; Sn, 6.47; W, 54.25.

A weighed sample of the Cs_3H_2 salt was dissolved in water and passed through an acidic ion-exchange resin. Titration of the effluent with standard base gave a smooth titration curve with an inflection point at pH 5.8 and an indicated neutral equivalent of 909. The calculated value for the Cs_3H_2 pentahydrate salt as a tetrabasic acid is 890.

A solution of Cs_3-1,4-$[CpFe(CO)_2Sn]_2W_{10}PO_{38}H_2\cdot5H_2O$ was brought to boiling. Sodium acetate was added to raise the pH to 6.4, and boiling was continued for another 2 min. Cooling and addition of cesium chloride precipitated Cs_5-1,5-$[CpFe(CO)_2Sn]_2W_{10}PO_{38}$ identified by infrared analysis.[5]

$(H_2OCo)_3W_{18}P_2O_{68}^{12-}$. A slurry of $Na_6HW_9PO_{34}$ hydrate (15 g, ca. 5.8 mmol) in water (100 mL) was added to cobalt(II) nitrate dihydrate (3.0 g, 13.6 mmol) in water (10 mL). The mixture was stirred 2 min and filtered. Potassium chloride (15 g) was added to the filtrate that was then stirred 5 min and refiltered to obtain 6.5 g (41%) of blue $K_{12}[(H_2O)_2Co]_3W_{18}P_2O_{68}$. This was recrystallized from water with heating to 60 °C. Anal. Calcd for $K_{12}(H_2OCo)_3W_{18}P_2O_{68}\cdot10H_2O$: K, 8.70; Co, 3.28; W, 61.4; P, 1.15; O, 24.9; H_2O, 3.3. Found: K, 8.59; Co, 3.29; W, 61.0; P, 1.15; O, 24.6; H_2O (TGA, 300 °C) 3.8.

Recrystallization of one gram of this product from 6 mL of water at the boil gave 0.4 g of red $K_{10}(H_2O)_2Co_4W_{18}P_2O_{68}$, identified by infrared analysis.[27]

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(27) We thank R. G. Finke and M. Droege for sending us an infrared spectrum of authentic $K_{10}(H_2O)_2Co_4W_{18}P_2O_{68}$.

Δ-$Na_8HW_9PO_{34}$. Fifty grams of $Na_8W_9PO_{34}$ hydrate was heated at 140–150 °C (340 torr) for 2 h and then for 1 h at 1 torr to obtain Δ-$Na_8HW_9PO_{34}$ (46 g) with the infrared spectrum shown in Figure 6b and the ^{31}P MAS described in the text. This product reacted with cobalt(II) nitrate to form $(H_2O)_2Co_4W_{18}P_2O_{68}{}^{10-}$ as described by Finke.[8] The conversion of W_9P to Δ-W_9P is somewat erratic; the conditions described above give the most consistent results. In some thermolyses, particularly if the entire thermolysis was conducted at 1 torr, a product with distinctly different infrared and solid-state ^{31}P MAS NMR spectra was obtained. This product has not yet been identified.

Reaction of Δ-W_9P with $PhSnCl_3$. Phenyltin trichloride was added dropwise with stirring to a fresh solution of Δ-W_9P (10 g) in water (75 mL) until the pH dropped to 5.5. The mixture was filtered. Trimethylamine hydrochloride (5 g) was added to the filtrate, precipitating 6.7 g of a white solid. Infrared analysis suggested this was a mixture containing $[(CH_3)_3NH]_5(PhSn)_2W_{10}PO_{38}$ and $[(CH_3)_3NH]_4PhSnW_{11}PO_{39}$.[2] This was confirmed by comparison of the ^{31}P NMR spectrum in dimethyl sulfoxide with the spectra of the authentic salts in the same solvent. Two of the four major lines, at −7.33 ($^2J_{P-Sn}$ = 26 Hz) and −8.60 ppm ($^2J_{P-Sn}$ = 24 Hz) are identical with the lines found (−7.33 ($^2J_{P-Sn}$ = 24 Hz), −8.69 ppm, ($^2J_{P-Sn}$ = 24 Hz)) in dimethyl sulfoxide for the trimethylammonium salts of the two isomers of $(PhSn)_2W_{10}PO_{38}{}^{5-}$ described in footnote 15.[28] A third major line in the spectrum is at −8.15 ppm ($^2J_{P-Sn}$ = 20 Hz) and may represent a third isomer of $(PhSn)_2W_{10}PO_{38}{}^{5-}$. The fourth major line is at −11.26 ppm ($^2J_{P-Sn}$ = 22 Hz), which agrees with the values found for $[(CH_3)_3NH]_4PhSnW_{11}PO_{39}$ in dimethyl sulfoxide.

Reaction of Δ-W_9P with $CpFe(CO)_2SnCl_3$. A solution of $CpFe(CO)_2SnCl_3$ (5 g) in tetrahydrofuran (20 mL) was added to 10 g of Δ-W_9P in water (150 mL) rapidly with stirring. Stirring was continued for 15 min; the solution was filtered. Ten grams of $(CH_3)_3NHCl$ was added to the filtrate to precipitate 6.7 g of a yellow solid. The infrared spectrum and the ^{31}P NMR spectrum showed this to be a mixture of $CpFe(CO)_2SnW_{11}PO_{39}{}^{4-}$ and 1,5-$[CpFe(CO)_2Sn]_2W_{10}PO_{38}{}^{5-}$.[3,5]

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[28] It is noteworthy that, although the chemical shifts of the lithium salts in water are the same as those of the trimethylammonium salts in dimethyl sulfoxide, the phosphorus–tin coupling constants are different. This has been confirmed by several different measurements of the spectra of authentic salts.

Alkyl, Aryl, Acyl, Formyl, and Hydride Derivatives of Phosphido-Bridged WRe Complexes. Crystal and Molecular Structure of $(CO)_5\overline{W(\mu\text{-}PPh_2)Re}(CO)_4$[†]

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The new heterobimetallic phosphido-bridged complex $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_5$, **2**, has been prepared by reaction of $Li[W(CO)_5PPh_2]$ with $Re(CO)_5Br$. This complex loses CO upon workup to yield $(CO)_5\overline{W(\mu\text{-}PPh_2)Re}(CO)_4$, **3**. These new complexes have been characterized spectroscopically, and $(CO)_5\overline{W(\mu\text{-}PPh_2)Re}(CO)_4$ has been characterized by a complete single-crystal X-ray diffraction study. The latter crystallizes in the space group $P\bar{1}$ with a = 8.609 (1) Å, b = 9.292 (2) Å, c = 18.376 (3) Å, α = 75.37 (1)°, β = 77.50 (1)°, γ = 63.38 (1)°, V = 2525 (2) Å^3, and Z = 2. The structure refined to R = 0.0386 and R_w = 0.0434 for the 3204 reflections with $I \geq 2\sigma(I)$. The μ-PPh_2 ligand bridges the W and Re atoms with W further coordinated by five CO's and Re by four. The W–Re bond length of 3.111 (1) Å together with the geometries about each metal imply a single donor–acceptor bond between these two atoms. Complex **3** reacts with CH_3CN and $PMePh_2$ to displace the metal–metal bond to give $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_4(CH_3CN)$ and $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_4PMePh_2$, **4**. Hydride, alkyl, and aryl complexes result from reaction of **3** with $Li[BHEt_3]$, CH_3Li, and PhLi, respectively, with these ligands attached to Re. Reaction of **4** with $Li[BHEt_3]$ and CH_3Li yields the formyl complex $Li[(CO)_5W(\mu\text{-}PPh_2)Re(CO)_3(PMePh_2)(CHO)]$ and the acetyl complex $Li[(CO)_5W(\mu\text{-}PPh_2)Re(CO)_3(PMePh_2)\{C(O)CH_3\}]$, respectively.

One of the consequences of assembling diverse metal centers into heterobinuclear and polynuclear complexes is that the resultant metal–metal bonds are usually not purely covalent but can have significant donor–acceptor character.[1,2] On an orbital basis this simply means that the metal-localized orbitals that overlap to form the metal–metal bonding and antibonding orbitals are of different initial energies. Hence, the bonding MO will be closer in energy to one of the initial metal orbitals, and thus the electron density in that MO will be more localized on one metal than the other (Scheme I). A similar situation arises for the usual donor–acceptor mode of ligand–metal binding with electron density localized on the ligand. For heterometallic complexes, an important question concerns the strength of these donor–acceptor bonds and the particular chemistry that may result as a consequence of their presence.

[†] In memory of Earl L. Muetterties, a brilliant and dedicated chemist.

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