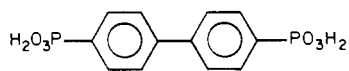


isfactory for the formula  $Zr(O_3POH)(O_3P(CH_2)PO_3)_{1/2}$ , and the X-ray powder pattern exhibited a broadened reflection at 13.6 Å. A single weight loss at ca. 600 °C was observed in the thermogravimetric curve, as expected for the hydrolyzed material. The dried product now has a surface area of 209 m<sup>2</sup>/g, which we suggest is greatly increased due to available void space within the particles. The maximum surface area estimated on the basis of 24 Å<sup>2</sup> being available per OH group<sup>4</sup> is about 430 m<sup>2</sup>/g. We have assumed that the particle size has not changed considerably in the hydrolysis and that nitrogen may freely diffuse to cover all internal surface.

The <sup>31</sup>P MAS NMR spectrum of the hydrolyzed product (Figure 2b) exhibits two peaks of equal intensities with chemical shifts as expected for phosphonate (10.5 ppm) and disordered orthophosphate (-17 ppm). In future experimentation, we hope to demonstrate that such materials can manifest molecular sieving properties, by virtue of specific micropore structure.

It is worthy of note that, when we attempted to prepare such pillared products by anion substitution of  $\gamma$ -zirconium phosphate with the rigid bisphosphonic acid substituted in the *p,p* positions of biphenyl



the product obtained seems to have a bilayered structure (with a pendant free phosphonic acid group on each layer). This assignment is based on X-ray diffraction data (*d* spacing 26.4 Å) and the observation of three <sup>31</sup>P signals in the NMR spectrum, attributable to phosphate and free and sheet-bound phosphonate.

When the exchange reaction was carried out with a more flexible bisphosphonic acid, the desired pillared product was obtained. Thus  $H_2O_3PC_{12}H_{24}PO_3H_2$  yielded a product with a *d* spacing of 20.3 Å while the  $H_2O_3PCH_2(4,4'$ -biphenyl)- $CH_2PO_3H_2$ -exchanged product had a *d* spacing of 15.9 Å. Neither product exhibited a <sup>31</sup>P resonance indicative of free phosphonate. We can only presume that, since the inorganic layers are already formed and are in place, the steric accessibility of two exchange sites to a bisphosphonic acid determines whether the product has a pillared or bilayered structure.

**Registry No.**  $Zr(O_3PO(CH_2)_6OPO_3)$ , 84057-65-8;  $Zr(O_3P(C-H_2)_8PO_3)$ , 84057-66-9.

- (4) This is the area available per site in  $\alpha$ -zirconium phosphate, which is the structure assumed for precipitated phosphonates.<sup>1</sup>  
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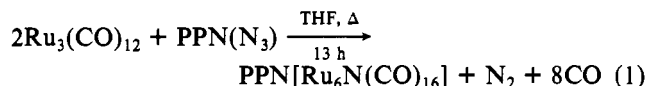
### Formation of a New Nitrido Cluster from a Cluster Coordinated Isocyanate

Sir:

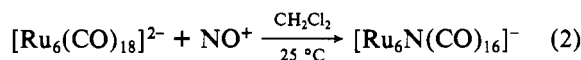
The dissociative chemisorption of small molecules having multiple bonds between the atoms is often the pivotal step in any catalytic scheme utilizing the molecule. This step is proposed to occur with N<sub>2</sub> in the Haber process<sup>1</sup> and with CO

in some mechanisms of the Fisher-Tropsch reaction.<sup>2</sup> These reactions have few analogues in mononuclear metal complexes and only a small number with metal clusters. For instance, the formation of many carbido<sup>3,4</sup> and nitrido clusters<sup>5</sup> results from the dissociation of CO and NO with subsequent (or concomitant) loss of the oxygen as CO<sub>2</sub>, precluding studies of the reverse process. Examples of such scissions in which all the fragments of the molecule remain bound to the complex have been reported for CS<sub>2</sub> to give a coordinated CS and S ligand<sup>6</sup> and ultimately a carbide and two sulfide ligands<sup>7</sup> and for substituted acetylenes to give alkylidyne clusters.<sup>8</sup> Once again, these reactions have not been found to be reversible. We report here the dissociation of a coordinated isocyanate (NCO) into a coordinated nitrogen atom and carbon monoxide and also evidence that an isocyanate can be re-formed under the appropriate conditions.

The reaction of Ru<sub>3</sub>(CO)<sub>12</sub> and PPN(N<sub>3</sub>) has been found to generate isocyanato carbonyl clusters within minutes at room temperature.<sup>9</sup> The initial products are [Ru<sub>3</sub>(NCO)(CO)<sub>11</sub>]<sup>-</sup> and [Ru<sub>3</sub>(NCO)(CO)<sub>10</sub>]<sup>-</sup>, the former having a terminal isocyanate ligand and the latter species containing a bridging NCO. At room temperature in the absence of CO the trinuclear clusters slowly form the tetranuclear species [Ru<sub>4</sub>(NCO)(CO)<sub>13</sub>]<sup>-</sup>. In refluxing tetrahydrofuran (THF) the trimers generate some [Ru<sub>4</sub>(NCO)(CO)<sub>13</sub>]<sup>-</sup> and a new nitrido cluster characterized as [Ru<sub>6</sub>N(CO)<sub>16</sub>]<sup>-</sup>. When the stoichiometry was appropriately adjusted according to eq 1,



maroon, slightly air-sensitive crystals of [Ru<sub>6</sub>N(CO)<sub>16</sub>]<sup>-</sup> were isolated in 92% recrystallized yield. The new cluster has been characterized by elemental analysis,<sup>10</sup> <sup>15</sup>N and <sup>13</sup>C NMR, and infrared spectroscopy, its degradation to a known compound, and its independent synthesis by a precedented method of nitrido cluster preparation (eq 2). Martinengo and co-

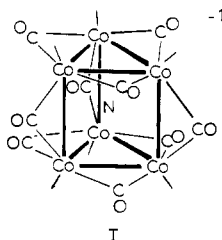


workers<sup>11</sup> used the analogous reaction of NO<sup>+</sup> with M<sub>6</sub>(CO)<sub>15</sub><sup>2-</sup> (M = Co, Rh) to form [M<sub>6</sub>N(CO)<sub>15</sub>]<sup>-</sup>, the first low-valent clusters with an interstitial nitrogen atom.<sup>12</sup> The infrared spectrum of [Ru<sub>6</sub>N(CO)<sub>16</sub>]<sup>-</sup> is quite simple, having one intense peak with a weak shoulder at 2010 and 1965 cm<sup>-1</sup>, respectively, in the terminal carbonyl region and a weak absorbance at 1839 cm<sup>-1</sup> in the bridging CO region. This pattern is commonly observed for octahedral clusters such as [H-Ru<sub>6</sub>(CO)<sub>18</sub>]<sup>-</sup>.<sup>13</sup> The <sup>13</sup>C NMR spectrum even at -87 °C exhibits only one sharp resonance at 207.5 ppm (downfield from Me<sub>4</sub>Si) indicative of rapid CO exchange.

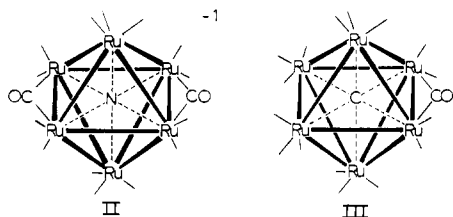
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The  $^{15}\text{N}$  NMR spectrum exhibits a resonance at 559.4 ppm downfield from liquid ammonia. This spectrum was obtained on a cluster that was  $\sim 48\%$  enriched with  $^{15}\text{N}$  resulting from the reaction of 95% enriched  $[\text{N}^{15}\text{N}=\text{N}]^-$  with  $\text{Ru}_3(\text{CO})_{12}$ . It is similar to the shift obtained for  $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$  (618.3 ppm) and several related nitrido clusters and is about 150 ppm downfield from the terminal metal nitrosyl region ( $\sim 400$  ppm).<sup>14</sup> For similar functional groups, the nitrogen chemical shifts often follow the same trends as their carbon analogues.<sup>15</sup> However, unlike the  $^{13}\text{C}$  chemical shifts of metal carbonyls and carbido clusters, in which the pattern consistently is terminal  $\text{CO} < \text{bridging CO} < \text{carbido}$ , the shifts of bridging nitrosyls appear several hundred ppm downfield (at  $\sim 800$  ppm)<sup>14</sup> of the nitrido chemical shifts. Adding to this complexity are the shifts observed for  $[\text{Co}_6\text{N}(\text{CO})_{15}]^-$  and  $[\text{Rh}_6\text{N}(\text{CO})_{15}]^-$  at 196.2 and 107.6 ppm, respectively. These clusters are known to have trigonal-prismatic (I) rather than



octahedral structures, which may in part be responsible for the dramatic upfield shifts.<sup>11</sup> Although we were not able to obtain X-ray-quality single crystals, we propose that the structure of  $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$  contains an octahedral arrangement of ruthenium atoms with a possible distribution of carbonyl ligands shown in II, similar to  $\text{Ru}_6\text{C}(\text{CO})_{17}$  (III).<sup>16</sup>

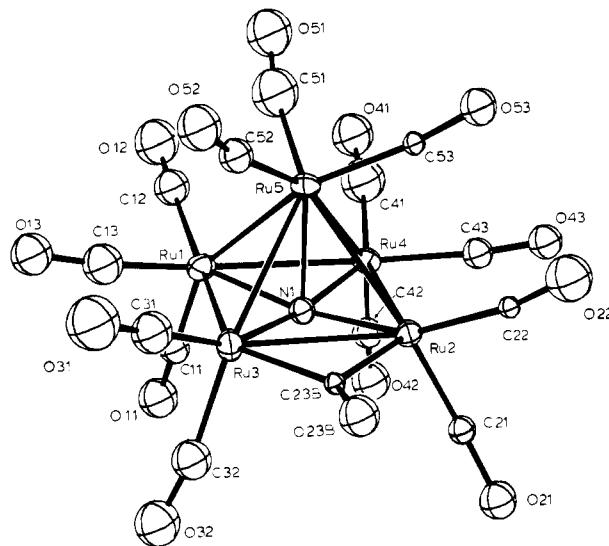


Both of these structures obey the skeletal electron pair bonding arguments for a closo octahedral cluster, whereas  $\text{Co}_6\text{N}(\text{CO})_{15}^-$  and  $\text{Rh}_6\text{N}(\text{CO})_{15}^-$  have four additional electrons, resulting in a structure based on an arachno square antiprism.

Within minutes under 1 atm of carbon monoxide  $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$  quantitatively converts to  $[\text{Ru}_5\text{N}(\text{CO})_{14}]^-$  and  $\text{Ru}_3(\text{CO})_{12}$  (eq 3). The latter is presumably formed by the



trimerization of three  $\text{Ru}(\text{CO})_5$  molecules, which were not individually detected because of the overlapping absorbances of both the hexaruthenium and pentaruthenium clusters. This facile degradation is unusual for interstitial-atom-containing clusters which are commonly more robust than their related clusters without the interstitial atom. For instance, even the closely related carbido cluster  $\text{Ru}_6\text{C}(\text{CO})_{17}$  (III) requires 80 atm of CO at 70 °C for 3 h to convert to  $\text{Ru}_5\text{C}(\text{CO})_{15}$ .<sup>17</sup> The pentaruthenium nitrido cluster,  $[\text{Ru}_5\text{N}(\text{CO})_{14}]^-$ , had previously been formed in low yield by the thermolysis of  $[\text{Ru}_3(\text{CO})_{10}]^-$



**Figure 1.** View of the  $[\text{Ru}_5\text{N}(\text{CO})_{14}]^-$  anion with atomic labeling scheme. Selected distances (Å): Ru1–Ru3, 2.868 (4); Ru3–Ru2, 2.809 (3); Ru2–Ru4, 2.911 (4); Ru4–Ru1, 2.818 (3); Ru5–Ru1, 2.747 (3); Ru5–Ru2, 2.817 (3); Ru5–Ru3, 2.848(3); Ru5–Ru4, 2.751 (4); N1–Ru1, 2.01 (2); N1–Ru2, 2.06 (2); N1–Ru3, 2.07 (2); N1–Ru4, 1.97 (2); N1–Ru5, 2.14 (2). Selected angles (deg): Ru1–N1–Ru2, 167 (1); Ru1–N1–Ru4, 90.1 (8); Ru1–N1–Ru5, 83.0 (7).

$[\text{NO}]^-$ .<sup>18</sup> A single-crystal X-ray crystallographic analysis of  $(\text{BzEt}_3\text{N})[\text{Ru}_5\text{N}(\text{CO})_{14}]^-$ <sup>19</sup> revealed that it has the expected square-pyramidal structure and ligand arrangement (Figure 1), similar to  $[\text{Fe}_4\text{RhC}(\text{CO})_{14}]^{2-}$ .<sup>20</sup> The basal ruthenium to nitride bond distances are slightly shorter than those observed for the related carbido clusters  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ <sup>21</sup> (2.045 (7) Å),  $\text{Ru}_6\text{C}(\text{CO})_{17}$ <sup>16</sup> (2.05 (5) Å),  $\text{Ru}_5\text{C}(\text{CO})_{15}$  (2.04 (2) Å),<sup>17</sup> and  $\text{Ru}_5\text{C}(\text{CO})_{14}(\text{PPh}_3)$  (2.06 (2) Å).<sup>17</sup> However, the apical ruthenium to nitrogen distance is noticeably longer at 2.14 (2) Å. It is interesting to note that the nitrogen atom is actually 0.21 (2) Å below the average plane of the basal ruthenium atoms. In  $\text{HFe}_5\text{N}(\text{CO})_{14}$ <sup>22</sup> the analogous distance is 0.093 Å while the carbide is even closer to the plane in  $\text{Fe}_5\text{C}(\text{CO})_{15}$ .<sup>23</sup> For  $\text{Ru}_5\text{C}(\text{CO})_{15}$  and  $\text{Ru}_5\text{C}(\text{CO})_{14}(\text{PPh}_3)$ , the carbon is located 0.11 and 0.19 Å, respectively, below the basal plane.<sup>17</sup> This somewhat unexpected preference of nitrogen to protrude below this plane may be related to the observation of the ease of removal of the sixth ruthenium atom of  $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$ .

The migration of the CO from the nitrogen to the metal is related to recent work that involves the analogous equilibrium of the ketylidene (CCO) ligand with a carbide and CO.<sup>24–31</sup>

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(19) X-ray diffraction data for  $(\text{BzEt}_3\text{N})[\text{Ru}_5\text{N}(\text{CO})_{14}]^-$ : crystal system triclinic; space group  $P\bar{1}$ ;  $a = 12.123$  (6) Å,  $b = 14.263$  (5) Å,  $c = 10.642$  (3) Å;  $\alpha = 104.74$  (3)°,  $\beta = 93.28$  (3)°,  $\gamma = 80.25$  (4)°;  $V = 1754$  (2) Å<sup>3</sup>;  $Z = 2$ ; absorption coefficient 21.2 cm<sup>-1</sup>; diffractometer Enraf-Nonius CAD4; radiation graphite-monochromatized Mo K $\alpha$ ; scan range 0°  $\leq 2\theta \leq 36$ °; reflections collected 2314 unique, 1437 with  $F_o > 2.0\sigma(F_o)$ ;  $R = 0.068$ ,  $R_w = 0.074$ . Severe decay (80%) of the crystal in the X-ray beam precluded collection of higher angle data and limits the overall quality of the structure.

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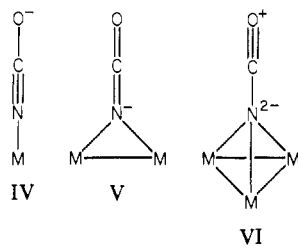
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Shown below is a scheme that illustrates why the decomposition of NCO may be promoted by polynuclear species via the successive weakening of the N-C bond.



Structures IV and V are documented,<sup>32</sup> but examples of NCO bridging more than two metals either as a mono, di, or trihapto ligand are unknown. The reverse reaction of a nitrido cluster to form an isocyanate would not occur under mild conditions but was clearly demonstrated at high CO pressure.  $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$  was dissolved in THF and the solution pressurized to 3000 psig CO at 70 °C for 3 h. The infrared spectrum of the solution observed after the pressure was released revealed absorbances characteristic of a mixture of  $[\text{Ru}_5\text{N}(\text{CO})_{14}]^-$  and  $[\text{Ru}_4(\text{NCO})(\text{CO})_{13}]^-$ . In particular, the sharp peak at 2189  $\text{cm}^{-1}$  confirms the re-formation of a coordinated isocyanate. The details of this unique method of forming carbon-nitrogen bonds and the reactivity of  $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$  are being studied.

**Acknowledgment.** We gratefully acknowledge the National Science Foundation for support of this work (Grant No. CHE8106096). We also thank Professor John Shapley for early communication of this results on the nitrosylation of  $[\text{Ru}_6(\text{CO})_{18}]^{2-}$ .

**Supplementary Material Available:** Lists of atomic coordinates, thermal parameters, observed and calculated structure factors, and distances and angles (12 pages). Ordering information is given on any current masthead page.

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## Trivacant Heteropolytungstate Derivatives. 2. Synthesis, Characterization, and $^{183}\text{W}$ NMR of $\text{P}_4\text{W}_{30}\text{M}_4(\text{H}_2\text{O})_2\text{O}_{112}^{16-}$ (M = Co, Cu, Zn)

Sir:

Recently<sup>1a</sup> we described the high-yield, rational synthesis and full characterization of the M = Co, Cu, Zn disubstituted, tri(tungsten)vacant<sup>2a</sup> heteropolytungstates  $\text{B-P}_2\text{W}_{18}\text{M}_4$ -

$(\text{H}_2\text{O})_2\text{O}_{68}^{10-}$ . As a result of these studies, we concluded that an important implication is that  $\text{B-P}_2\text{W}_{18}\text{M}_4(\text{H}_2\text{O})_2\text{O}_{68}^{10-}$  is not unique but rather is just the first member<sup>1b</sup> of a previously unrecognized class of massive, disubstituted, trivacant heteropolytungstate dimers.

Herein we report the synthesis, characterization, and  $^{31}\text{P}$  and  $^{183}\text{W}$  NMR of  $\text{B-P}_4\text{W}_{30}\text{M}_4(\text{H}_2\text{O})_2\text{O}_{112}^{16-}$  (M = Co, Cu, Zn), thereby providing the second member of this class of heteropolytungstates. The results described below fortify our earlier preliminary conclusion<sup>1a</sup> that a B-type<sup>2b</sup> trivacant heteropolytungstate is a key structural requirement for the formation of this class of heteropolytungstates. The results also support a single structural assignment from among the 16 possible structural isomers and correct the previous misformulation of these complexes<sup>3</sup> as " $\text{P}_2\text{W}_{16}\text{M}_2(\text{H}_2\text{O})_2\text{O}_{60}^{10-}$ ".

The trivacant heteropolytungstate starting material,  $\alpha\text{-Na}_{12}\text{P}_2\text{W}_{15}\text{O}_{56}\cdot x\text{H}_2\text{O}$  (previously thought to be  $\alpha\text{-Na}_{12}\text{P}_2\text{W}_{16}\text{O}_{59}$ ),<sup>3a</sup> was prepared as described in the literature<sup>3b</sup> by base degradation of  $\alpha\text{-K}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ . The Co, Cu, and Zn derivatives of  $\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}^{12-}$  were prepared in 77-88% yields from  $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ,  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ , and  $\text{ZnBr}_2$  in 1 M NaCl or in an acetate buffer.<sup>3d</sup> In the case of the Zn complex, 0.56 g (2.0 equiv) of  $\text{ZnBr}_2$  was dissolved in 50 mL of 1 M NaCl followed by 5.0 g of  $\alpha\text{-Na}_{12}\text{P}_2\text{W}_{15}\text{O}_{56}$  and gentle heating and stirring to obtain a homogeneous solution. Cooling overnight at 5 °C yielded 4.44 g (88%) of white crystalline solid, which was dried at 80 °C under vacuum for  $\leq 0.5$  h but not for longer times or at higher temperatures as it was discovered, after considerable experimentation, that more vigorous drying produces a product with different  $^{31}\text{P}$  and  $^{183}\text{W}$  NMR data<sup>4</sup> (vide infra) via an apparent solid-state isomerization reaction.<sup>5</sup> The white crystalline solid was formulated as the disubstituted dimer  $\text{Na}_{16}[\text{P}_2\text{W}_{15}\text{Zn}_2(\text{H}_2\text{O})\text{O}_{56}]_2 = \text{Na}_{16}\text{P}_4\text{W}_{30}\text{Zn}_4(\text{H}_2\text{O})_2\text{O}_{112}$  on the basis of a  $\pm 0.4\%$  Na, P, W, Zn elemental analysis, molecular weight measurements ( $M_r(\text{calcd})$  for  $\text{P}_4\text{W}_{30}\text{Zn}_4(\text{H}_2\text{O})_2\text{O}_{112}^{16-} = 7728$ ;  $M_r(\text{obsd}) = 7652$ ) obtained by using an ultracentrifuge and the sedimentation equilibrium method,<sup>6</sup> and the  $^{31}\text{P}$  and  $^{183}\text{W}$  NMR data presented below.

In the case of the Co and Cu derivatives, 4.20 g (83%) of a dark green powder ( $\lambda_{\text{max}}(\text{H}_2\text{O}) = 570$  nm) and 3.92 g (77%) of light green-yellow crystals ( $\lambda_{\text{max}}(\text{H}_2\text{O}) = \text{end absorption beginning at } 600 \text{ nm}$ ) were formed, respectively. Significantly, the distinctive<sup>7</sup>  $\lambda_{\text{max}} = 570$  nm of the cobalt derivative of  $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$  is identical with the  $\lambda_{\text{max}} = 570$  nm of the  $\text{PW}_9\text{O}_{34}^{9-}$ -derived dimer,  $[\text{PW}_9\text{Co}_2(\text{H}_2\text{O})\text{O}_{34}]_2^{10-}$ , indicating a very similar ligand field and thus primary coordination

- (2) (a)  $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$  and  $\text{PW}_9\text{O}_{34}^{9-}$  are derived by formally removing a " $\text{W}_3\text{O}_6^{6+}$ " unit from the saturated tungstates  $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$  and  $\text{PW}_{12}\text{O}_{40}^{3-}$ , respectively, and hence are referred to as tri(tungsten)vacant, or just trivacant, heteropolytungstates. (b) For a discussion of  $\alpha$ ,  $\beta$ , and  $\gamma$  isomerism see: Massart, R.; Contant, R.; Fruchart, J. M.; Ciabrini, J. P.; Fournier, M. *Inorg. Chem.* **1977**, *16*, 2916.  
 (3) (a) The  $\alpha\text{-Na}_{12}\text{P}_2\text{W}_{15}\text{O}_{56}\cdot x\text{H}_2\text{O}$  preparation used was that listed under<sup>3b</sup> " $\alpha\text{-Na}_{12}\text{P}_2\text{W}_{16}\text{O}_{59}$ ". In a subsequent paper,<sup>3c</sup> it is noted that "new samples (of " $\alpha\text{-Na}_{12}\text{P}_2\text{W}_{16}\text{O}_{59}$ ") agree with  $\alpha\text{-Na}_{12}\text{P}_2\text{W}_{15}\text{O}_{56}\cdot x\text{H}_2\text{O}$ ". The data presented in the text strongly suggest that this material is primarily, but maybe not completely,  $\alpha\text{-Na}_{12}\text{P}_2\text{W}_{15}\text{O}_{56}\cdot x\text{H}_2\text{O}$ . (b) Contant, R.; Ciabrini, J. P. *J. Chem. Res., Miniprint* **1977**, 2601; *J. Chem. Res., Synop.* **1977**, 222. (c) Contant, R.; Ciabrini, J. P. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1525. (d) Use of an acetate buffer produced identical  $\text{P}_4\text{W}_{30}\text{M}_4(\text{H}_2\text{O})_2\text{O}_{112}^{16-}$  by  $^{31}\text{P}$  and  $^{183}\text{W}$  NMR and elemental analysis (M = Zn<sup>2+</sup>).  
 (4) Major NMR peaks:  $^{31}\text{P}$  in  $\text{D}_2\text{O}$   $\delta = -3.43, -3.90, -4.01, -12.27$ ;  $^{183}\text{W}$  in  $\text{D}_2\text{O}$   $\delta = -122.1, -132.3, -152.6, -157.8, -180.1, -183.4, -186.7, -237.3, -267.4, -272.4, -272.8$ .  
 (5) Finke, R. G.; Droegge, M. W., unpublished results.  
 (6) Chervenka, C. H. "A Manual of Methods for the Analytical Ultracentrifuge"; Spinco Division of Beckman Instruments: Palo Alto, CA, 1969.  
 (7) (a) The following monosubstituted heteropolytungstates appear at shorter wavelengths:  $\text{P}_2\text{W}_{17}\text{Co}(\text{H}_2\text{O})\text{O}_{61}^{10-}$  ( $\lambda_{\text{max}}(\text{H}_2\text{O}) = 540\text{-}550$  nm);<sup>2b</sup>  $\text{PW}_{11}\text{Co}(\text{H}_2\text{O})\text{O}_{39}^{3-}$  ( $\lambda_{\text{max}}(\text{H}_2\text{O}) = 540, 526, 505$  (sh) nm).<sup>7b</sup> (b) Komura, A.; Hayashi, M.; Imanaga, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 87.