

# Communications

## Mixed-Component Layered Tetravalent Metal Phosphonates/Phosphates as Precursors for Microporous Materials

Sir:

One of the more intriguing consequences of the structure of the layered tetravalent metal phosphonates<sup>1</sup> is the possibility of incorporating microporous voids within the interlayer by the use of appropriate mixed-component compounds.<sup>2</sup> Of particular interest in this respect are those phases which would result from co-inclusion of "pillaring" bisphosphonic acids with small groups that could be chemically active (e.g. P-OH). One route to such compounds is simple coprecipitation of the two groups with  $M^{4+}$ ; however, this approach usually results in very poorly crystalline products difficult to characterize. Another is to employ the anion replacement reaction (which starts with  $\gamma$ -zirconium phosphate) first reported by Yamanaka.<sup>3</sup> We will briefly mention the outcome of such a reaction below. A third approach, the subject of this paper, is to prepare a mixed pillared compound of phosphate and phosphonate and, subsequently, to selectively hydrolyze away the phosphate. In the last two cases, the products are limited to mixed-phosphate compounds  $M(O_3POH)_x(O_3P-R-PO_3)_{2-x/2}$  (see Figure 1).

Given that preparations of mixed-component (solid solution) phases are most likely to succeed when the groups are chemically and geometrically similar, the best strategy is to use a phosphate ester having the same effective length as the phosphonate. We chose for this purpose the system  $H_2O_3PO(CH_2)_6OPO_3H_2/H_2O_3P(CH_2)_8PO_3H_2$ . The phosphate ester is afforded by the reaction of 1,6-hexanediol with  $P_2O_5$  (with mild hydrolysis), and the bisphosphonic acid was made by a double Arbuzov reaction of 1,8-dibromooctane and triethyl phosphite, followed by more vigorous hydrolysis. A solution containing equimolar amounts of the two bis acids was then treated with zirconyl chloride (the former were in excess), leading to a precipitate, which was refluxed 2 h, filtered, and washed with water and acetone. After drying at 125 °C, the product weighed 95% of the expected amount for  $Zr(O_3PO(CH_2)_6OPO_3)_{1/2}(O_3P(CH_2)_8PO_3)_{1/2}$ . This material had the correct elemental analysis for the formulation, and its X-ray diffraction pattern showed a prominent  $d$  spacing of 14.1 Å, which is the value expected on the basis of previous experience<sup>2</sup> and CPK molecular models. The measured surface area (one-point nitrogen BET) was 49 m<sup>2</sup>/g, which is typical for these products. The magic angle spinning (MAS) NMR spectrum of the <sup>31</sup>P nuclei (Figure 2) showed two somewhat broadened resonances, of approximately equal intensities, attributable to the phosphate ester and phosphonate functions. Chemical shift dispersion due to a disordered placement of the two groups between the layers is likely the cause for the broadening. In addition, some hydrolysis of the phosphate ester to P-OH groups may also have occurred.

On the basis of the thermogravimetric curve for the product (which showed two distinct dissociation processes at 320 and

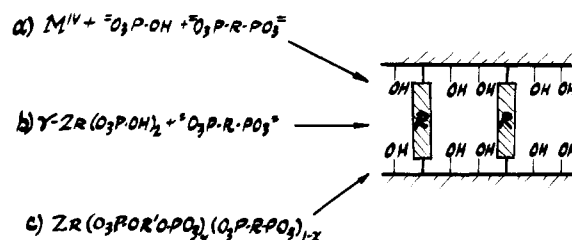


Figure 1. Three pathways toward the preparation of mixed-component phase pillared products having P-OH groups and void space for access and sieving: (a) coprecipitation; (b) anion substitution of the  $\gamma$ -zirconium phosphate phase; (c) selective decomposition of a phosphate ester pillar in the presence of a phosphonate. In all cases -R- denotes the pillaring group.

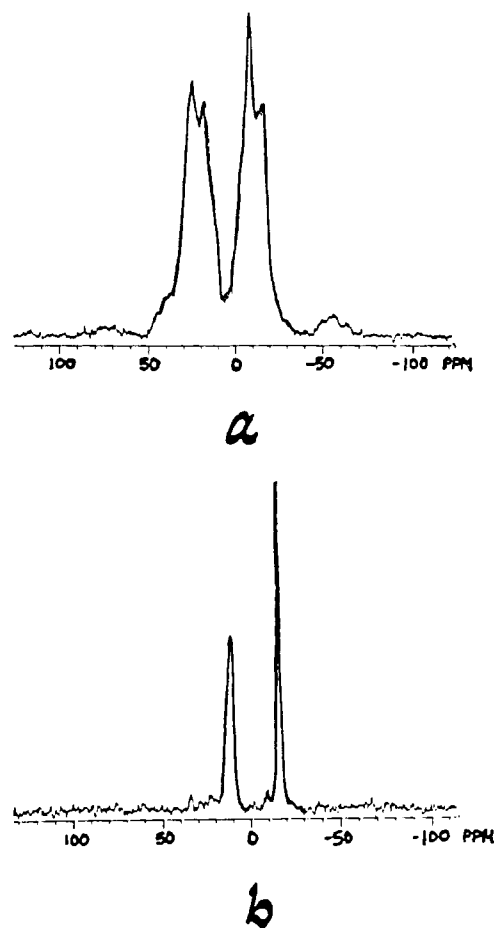


Figure 2. <sup>31</sup>P magic angle NMR spectra of the phosphate ester/phosphonate mixed-phase precursor  $Zr(O_3PO(CH_2)_6OPO_3)_{1/2}(O_3P(CH_2)_8PO_3)_{1/2}$  (a) and the product of exhaustive HBr hydrolysis (b). Triphenylphosphine is the external reference. Relative areas were approximately equal in both cases. Generally, phosphonates occur between 0 and about +30 ppm, while phosphates fall between 0 and -30 ppm.

590 °C, presumably due to ester and phosphonate decomposition, respectively), we hoped that careful thermolysis at 350 °C might accomplish our purpose. However, we did not obtain clean products in any attempts.

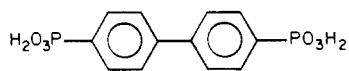
The conditions necessary to effect selective hydrolysis of the phosphate ester were 1 week at reflux with concentrated hydrobromic acid. As before, the elemental analysis was sat-

- Alberti, G.; Costantino, U.; Alluli, S.; Tomassini, N. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1113. Also: Dines, M. B.; DiGiacomo, P. M. *Inorg. Chem.* **1981**, *20*, 92.
- Dines, M. B.; DiGiacomo, P. M.; Callahan, K. P.; Griffith, P. C.; Lane, R. H.; Cooksey, R. E. In "Chemically Modified Surfaces in Catalysis and Electrocatalysis"; Miller, J., Ed.; American Chemical Society: Washington, DC, 1982; ACS Symp. Ser. No. 192, Chapter 13.
- Yamanaka, S.; Hattori, M. *Chem. Lett. Jpn.* **1979**, 1073. Also: Yamanaka, S.; Hattori, M. *Inorg. Chem.* **1981**, *20*, 1929.

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>  
 (5) Deceased Aug 16, 1982.

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Received August 10, 1982

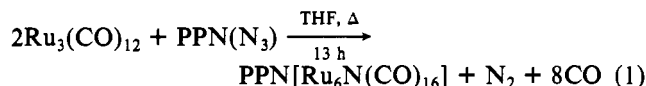
### Formation of a New Nitrido Cluster from a Cluster Coordinated Isocyanate

Sir:

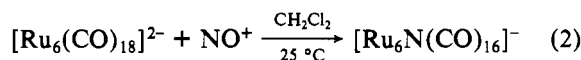
The dissociative chemisorption of small molecules having multiple bonds between the atoms is often the pivotal step in any catalytic scheme utilizing the molecule. This step is proposed to occur with N<sub>2</sub> in the Haber process<sup>1</sup> and with CO

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.

- (2) Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447-474.  
 (3) Tachikawa, M.; Muetterties, E. L. *Prog. Inorg. Chem.* **1981**, *28*, 203-238.  
 (4) Hayward, C.-M. T.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3816-3820.  
 (5) Fjare, D. E.; Gladfelter, W. L. *Inorg. Chem.* **1981**, *20*, 3533-3539.  
 (6) Broadhurst, P. V.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1980**, *194*, C35-C38.  
 (7) Bor, G.; Gervasio, G.; Rossetti, R.; Stanghellini, P. L. *J. Chem. Soc., Chem. Commun.* **1978**, 841.  
 (8) Fritch, J. R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 559-561.  
 (9) Fjare, D. E.; Jensen, J. A.; Gladfelter, W. L. *Inorg. Chem.*, in press.  
 (10) Anal. Calcd for PPN[Ru<sub>6</sub>N(CO)<sub>16</sub>]<sup>-</sup>: C, 38.86; H, 1.88; N, 1.74. Found: C, 38.68; H, 2.00; N, 1.63.  
 (11) Martinengo, S.; Ciani, G.; Sironi, A.; Heaton, B. T.; Mason, J. *J. Am. Chem. Soc.* **1979**, *101*, 7095-7097.  
 (12) John R. Shapley and Chi-Mi Tai Hayward have also found that nitrosylation of [Ru<sub>6</sub>(CO)<sub>18</sub>]<sup>2-</sup> with NO<sup>+</sup> generates [Ru<sub>6</sub>N(CO)<sub>16</sub>]<sup>-</sup>.  
 (13) Eady, C. R.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Dalton Trans.* **1980**, 383-392.

(1) Emmett, P. H. "The Physical Basis for Heterogeneous Catalysis"; Drauglis, E., Jaffe, R. I., Eds.; Plenum Press: New York, 1975; pp 3-34.