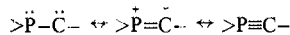
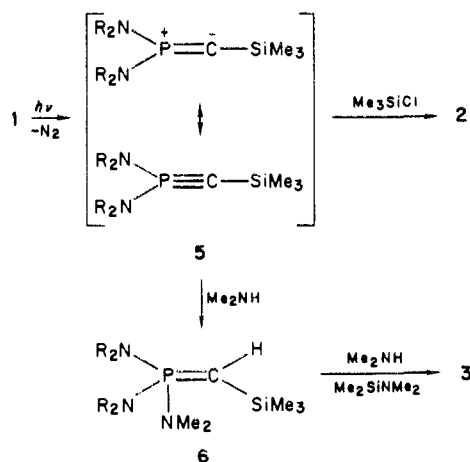


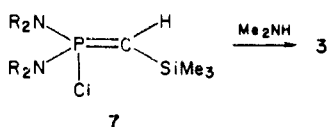
This lack of typical carbene reactivity and the nature of products 2-4 must be explained. The presence of an electron-rich phosphorus atom adjacent to an electron-deficient carbon suggests that delocalization of phosphine nonbonded electron pair would complete the octet of carbon and produce a dipolar species. Moreover, like phosphorus ylides, some back-bonding of the carbon electron with the phosphorus d orbital could also contribute to decrease the charge separation.



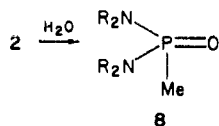
Thus, it is reasonable to postulate that  $\lambda^5$ -phosphorus compounds 2 and 3 result from 1,2-addition of the trapping agents to the phosphorus-carbon multiple bond of a "phosphorus vinyl ylide-phosphaacetylene" intermediate 5.



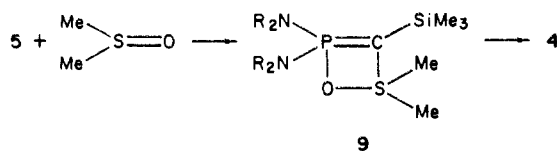
The subsequent cleavage of the carbon-silicon bond in 6 was confirmed by the action of dimethylamine on the phosphorus ylide 7:<sup>16</sup>



In the same way, mild hydrolysis of 2 led to the oxide of methylbis(diisopropylamino)phosphorane 8.<sup>12</sup>



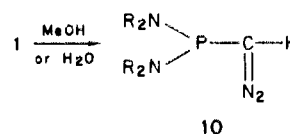
Formation of sulfur ylide 4 can be rationalized by a 2 + 2 cycloaddition leading to a four-membered cyclic phosphorus ylide 9 followed by ring opening.<sup>17</sup>



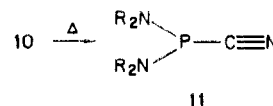
(16) Appel, R.; Schmitz, R. *Chem. Ber.* **1983**, *116*, 3521.

(17) Such a mechanism has already been demonstrated in the case of sulfinylnitrene.<sup>3</sup>

The choice of the trapping agents was limited by the lack of reactivity of 5 with nonpolar reagents and by the great lability of the silicon-carbon bond in the starting material 1. Indeed a stoichiometric amount of water or methanol readily gives rise to the formation of a new diazo product 10 in 90% yield.<sup>12</sup>



In marked contrast with 1, [bis(diisopropylamino)phosphino]diazomethane (10) is thermally unstable and rearranged under attempted distillation to give the unexpected bis(diisopropylamino)phosphinenitrile 11<sup>12</sup> in 30% yield, most probably via an intermolecular reaction.



**Acknowledgment.** Thanks are due to A. Jacquy for technical assistance and to the CNRS for financial support.

**Registry No.** 1, 97135-48-3; 2, 97135-50-7; 3, 97135-51-8; 4, 97135-52-9; 5, 97135-53-0; 6, 97135-54-1; 7, 97135-55-2; 8, 97135-56-3; 9, 97135-57-4; 10, 97135-58-5; 11, 97135-59-6; Me<sub>3</sub>SiC(=N<sub>2</sub>)Li, 84645-45-4; (i-Pr<sub>2</sub>N)<sub>2</sub>PCL, 56183-63-2; Me<sub>3</sub>SiCl, 75-77-4; Me<sub>2</sub>NH, 124-40-3; Me<sub>2</sub>SO, 67-68-5.

## New Chromia Pillared Clay Catalysts

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Pillared clays are members of the smectite family of 2:1 layered silicates in which the gallery cations are robust species capable of preventing the collapse of the interlayer region upon dehydration. These intercalation compounds allow a rational approach to the design of new families of microporous solids because the pores formed between the gallery cations can be systematically regulated by varying the cation size, shape, and spacing. Several types of cations have been used as pillaring agents, including alkylammonium ions,<sup>1-3</sup> metal chelates,<sup>4-6</sup> and polyoxymetal cations.<sup>7-13</sup> Clays pillared by certain polyoxycations are of particular importance, because they can be converted upon dehydration and dehydroxylation to intercalates containing molecular-size oxide aggregates and protons which impart catalytically

(1) Barrer, R. M. "Zeolites and Clay Minerals as Sorbents and Molecular Sieves"; Academic Press: New York, 1978; Chapter 8.

(2) (a) Mortland, M. M.; Clementz, D. M. *Clays Clay Miner.* **1974**, *22*, 223. (b) Mortland, M. M.; Berkheiser, V. *Clays Clay Miner.* **1976**, *24*, 60.

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(10) Vaughan, D. E. W.; Lussier, R. J. Preprints, 5th International Conference on Zeolites, Naples, Italy, June 2-6, **1980**, p 94.

(11) Yamanaka, S.; Brindley, G. W. *Clays Clay Miner.* **1978**, *26*, 21.

(12) Brindley, G. W.; Yamanaka, S. *Am. Mineral.* **1979**, *64*, 830.

(13) Oades, J. M. *Clays Clay Mineral.* **1984**, *32*, 49.

**Table I.** Chromia Pillared Montmorillonites

cmpd	Cr(OH) <sub>3-q</sub> <sup>q+</sup> per unit cell	q	d <sub>001</sub> , Å <sup>a</sup>			surf. area, m <sup>2</sup> /g <sup>b</sup>	mmole adsorbed/g <sup>c</sup>		
			25 °C	350 °C	500 °C		C <sub>6</sub> H <sub>6</sub> (6.2) <sup>d</sup>	1,3,5-Et <sub>3</sub> C <sub>6</sub> H <sub>3</sub> (9.2)	(C <sub>4</sub> F <sub>9</sub> ) <sub>3</sub> N (10.4)
			I	1.24	0.48		26.8	21.0	21.0
II	3.53	0.17	27.6	22.6	21.0	353	1.92	0.57	0.44
III	1.88	0.32	16.8	14.2	13.7	61	0.37	0.03	

<sup>a</sup>Prior to X-ray analysis each product was heated 2 h under Ar at the temperatures indicated. <sup>b</sup>N<sub>2</sub> BET values after dehydration in vacuo at 350 °C for 3 h. <sup>c</sup>The equilibrium vapor pressures (torr) at 25 °C were as follows: C<sub>6</sub>H<sub>6</sub>, 73; 1,35-Et<sub>3</sub>C<sub>6</sub>H<sub>3</sub>, 0.36; (C<sub>4</sub>F<sub>9</sub>)<sub>3</sub>N, 0.39. <sup>d</sup>Values in parenthesis are kinetic diameters in angstrom units.

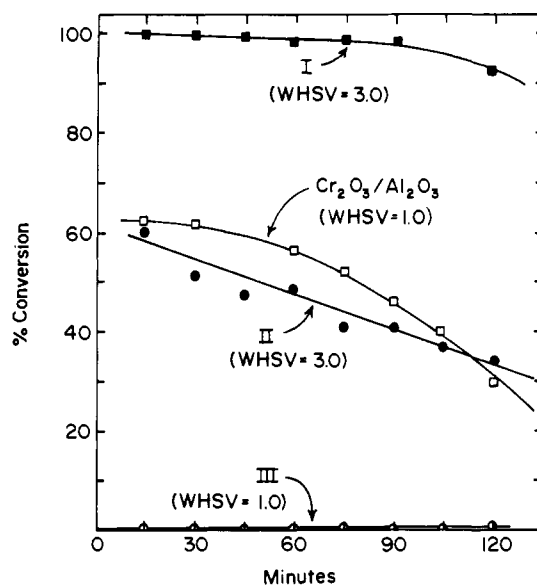
useful Brønsted acidity.<sup>10</sup> Clays intercalated by alumina and zirconia, for instance, are petroleum cracking catalysts with shape selectivities comparable to those of commercial zeolite catalysts.<sup>14-16</sup>

Although several polyoxocation exchange forms of smectite clays have been synthesized, only a few, such as the alumina and zirconia derivatives noted above, exhibit d<sub>001</sub> spacings (~18 Å) and corresponding gallery heights (~8.7 Å) sufficient for facile intracrystal catalysis. Clays pillared by catalytically useful transition metal oxides, such as those of Ni,<sup>11</sup> Cr,<sup>12</sup> and Fe,<sup>13</sup> typically exhibit chlorite-like spacings of ≤14.5 Å when dehydrated above 250 °C. We now wish to report the synthesis of a new family of chromia pillared clays which have basal spacings substantially larger than those of previously reported pillared clays. These novel intercalates also represent the first examples of pillared clays in which the intracrystal pillaring agent itself is the catalytic species, as demonstrated by their activity for the dehydrogenation of cyclohexane to benzene.

Solutions containing cationic polyoxochromium oligomers were prepared by the hydrolysis of 0.10 M chromium nitrate at 95 °C using Na<sub>2</sub>CO<sub>3</sub> as the base. The base to Cr ratio (n) was varied over the range 0.0-2.50 (equiv/mol), and the hydrolysis time was 1-72 h. To the hot solutions was added 1 wt % suspensions of Na<sup>+</sup>montmorillonite, a typical smectite, with an anhydrous unit cell formula of Na<sub>0.60</sub>[Al<sub>3.13</sub>Fe<sub>0.40</sub>Mg<sub>0.48</sub>](Si<sub>7.86</sub>Al<sub>0.14</sub>)O<sub>20</sub>(OH)<sub>4</sub>. The Cr was kept in large excess during the pillaring reaction, typically 60 mol/equiv of clay. After a reaction time of 1.5 h, the products were collected by centrifugation and washed free of excess salt. The intercalates prepared from Cr solutions hydrolyzed at n = 1.50-2.50 exhibited d<sub>001</sub> X-ray spacings of 23.0-27.6 Å under air-dried conditions. In contrast, the products obtained from solutions hydrolyzed at n = 0.0-1.0 exhibited spacings of only 16.0-18.5 Å. Solutions prepared at n > 2.50 were unsatisfactory pillaring reagents due to the formation of a chromium hydroxide precipitate.

Intercalates with d<sub>001</sub> spacings near 27 Å were best prepared at n = 2.0 and a hydrolysis time of 6-36 h. The Cr content was 1.2-4.0 mol/unit cell, depending on the degree of cation oligomerization. Table I summarizes the properties of two representative products I and II with Cr contents of 1.24 and 3.53 mol/cell, respectively. The intercalated Cr is expressed empirically as Cr(OH)<sub>3-q</sub><sup>q+</sup>, where q is the apparent net charge per chromium. Included in the table is a chromia pillared clay (III) prepared by the method of Brindley and Yamanaka,<sup>12</sup> wherein the polyoxochromium oligomers were formed under stoichiometric conditions equivalent to those used for preparation of I and II, except that the hydrolysis temperature was 25 °C (III) rather than 95 °C (I and II).

It is apparent from the data in Table I that larger polyoxocations are formed by hydrolysis of Cr<sup>3+</sup> at 95 °C than at 25 °C. Both I and II exhibit d<sub>001</sub> spacings near 27 Å, whereas III has a spacing of only 16.8 Å. Moreover, when dehydrated under Ar at 500 °C I and II maintain a high spacing of 21.0 Å, but III collapses to a value of 13.7 Å. The differences in basal spacings are accompanied by differences in N<sub>2</sub> surface areas. The values of 433 and



**Figure 1.** Conversions of cyclohexane to benzene at 550 °C over chromia pillared clays I-III and a commercial chromia catalyst supported on alumina (Chemical Dynamics Corp., 19.0 wt % Cr<sub>2</sub>O<sub>3</sub>). The values of WHSV represent the weight hourly space velocities. The cyclohexane contact time (He vector) was 6.0 s. Each sample was pre-reduced for 1 h under a flow of hydrogen at 550 °C before use as a dehydrogenation catalyst.

353 m<sup>2</sup>/g for I and II, as compared to 61 m<sup>2</sup>/g for III, are indicative of an appreciable intracrystal surface area. Also, much of the surface area of I and II is available for the adsorption of organic molecules with kinetic diameters up to 10.4 Å. It is significant that the basal spacings of I and II are similar despite the fact that the Cr content of II is almost twice as large as that of I. We tentatively interpret this result in terms of rod- or disk-shaped chromia aggregates which orient in the galleries with the rod axis or disc diameter parallel to the silicate layers. Under these conditions, differences in the degree of oligomerization would be reflected in the Cr contents and surface areas but not in the basal spacings.<sup>17</sup>

As shown in Figure 1, both I and II are catalyst precursors for the dehydrogenation of cyclohexane to benzene at 550 °C, but III is essentially inactive. Included in the figure is the activity of a commercial chromia catalyst supported on alumina. The substantially greater activity of I relative to II or to Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> is attributed to the greater degree of chromia dispersion in the clay galleries. The differences in activity between our new pillared clays and III are related to the accessibility of Cr in the galleries. For instance, I and II after use as catalysts have d<sub>001</sub> = 20.5 Å and readily adsorb cyclohexane (1.4 and 0.95 mmol/g, respectively), whereas III has d<sub>001</sub> = 10.2 Å and adsorbs little cyclohexane (0.05 mmol/g). The decrease in activity for I and II with reaction time may result in part from pore plugging due to coke formation, because the surface areas are observed to decrease with

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(15) Shabtai, J.; Lazar, R.; Oblad, A. G. *Stud. Surf. Sci. Catal.* **1981**, 1, 828.

(16) Ocelli, M. L. *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, 22, 553.

(17) Since I and II both were prepared in the presence of a large excess of Cr, the extent of Cr saturation of the external surfaces should be similar. Also, the external surface area (~20 m<sup>2</sup>/g) is small relative to the total observed surface area. Therefore, differences in the extent of oligomerization of externally bound Cr cannot account for the difference in Cr content.

increasing catalyst turnovers, even though the 20.5-Å basal spacings are retained.

In summary, our new chromia pillared clays exhibit gallery heights (11.7 Å after dehydration at 500 °C) that are ~3.0 Å larger than those of zirconia and alumina pillared clay catalysts. The scope of their intracrystalline catalytic and sorptive properties, along with structural studies of the intercalated chromia aggregates, are under active investigation and will be the subjects of future reports.

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**Registry No.** Cyclohexane, 110-82-7; chromia, 1308-38-9.

### Dynamic NMR Study of Phenyl Thioformate. Nonaromaticity of the Z Conformation<sup>1</sup>

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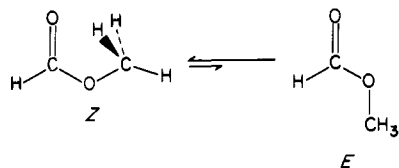
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The interaction in amides, esters, and thiol esters between a lone pair of electrons on the heteroatom and  $\pi^*$  of the carbonyl group stabilizes the planar conformations, and most of these compounds are planar or nearly planar.<sup>2</sup> Esters of carboxylic acids generally have a strong preference for the conformation in which the alkyl group attached to the "ether" oxygen is cis to the carbonyl oxygen.<sup>3,4</sup> The corresponding (*Z*) conformation of secondary amides is also generally of lower energy than the *E* isomer,<sup>5</sup> and this preference is of importance in determining the conformations of proteins.

In compounds such as methyl acetate, steric repulsion in the *E* conformation between the alkyl groups is expected to favor the *Z* conformation. However, the *E* isomer of methyl formate contributes only 0.3% to the conformational mixture at -83 °C in DMF/acetone-*d*<sub>6</sub> solvent,<sup>6</sup> corresponding to a free energy difference of 2.2 kcal/mol, although any steric repulsion between the methyl group and formyl hydrogen in this conformation should be more than offset by repulsion between the methyl group and the larger carbonyl oxygen in the *Z* isomer. Indeed, the free energy difference for *tert*-butyl formate is smaller (0.5 kcal/mol),<sup>6</sup> but the equilibrium still favors the *Z* isomer. Thus, steric repulsion between the two alkyl groups in acetates and higher esters may reinforce the conformational preference that exists in formate esters but cannot entirely account for the conformational preferences in these compounds.

A number of possible explanations for the lower energy of the *Z* conformation of esters have been proposed,<sup>7</sup> three of these are



(1) This work was supported by the National Institutes of Health (Grant S06RR08047).

(2) (a) Formamide: Hirota, E.; Sugisaki, R.; Nielsen, C. J.; Sorensen, G. O. *J. Mol. Spectrosc.* **1974**, *49*, 251. (b) Methyl formate: Curl, R. F., Jr. *J. Chem. Phys.* **1959**, *30*, 1529. (c) Methyl thioformate: Jones, G. I. L.; Lister, D. G.; Owen, N. L. *J. Mol. Spectrosc.* **1976**, *60*, 348.

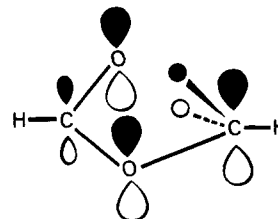
(3) For the esters discussed here, this conformation will be the *Z* isomer. For compounds such as methyl fluoroformate, the conformational designations would be reversed.

(4) For a review, see: Jones, G. I. L.; Owen, N. L. *J. Mol. Struct.* **1973**, *18*, 1.

(5) Stewart, W. E.; Siddall, T. H., III. *Chem. Rev.* **1970**, *70*, 517.

(6) Grindley, T. B. *Tetrahedron Lett.* **1982**, *23*, 1757.

probably important for methyl formate: (1) Dipole-dipole interactions destabilize the *E* conformation, relative to the *Z*, as indicated by the dipole moments of the two conformations of formic acid.<sup>9</sup> (2) Interaction of the "ether" oxygen lone pair with  $\sigma^*$  of the carbonyl group of the *Z* conformation may stabilize this isomer.<sup>8</sup> (3) A cyclic "aromatic" system of six electrons is possible for the *Z* conformation,<sup>10</sup> with the carbonyl group, the "ether" oxygen, and the methyl group<sup>12</sup> each contributing two electrons, as indicated below. A similar stabilizing interaction is not possible for the *E* isomer.



The first two factors should be of lower importance for thiol esters than for esters. The dipole moments for the two conformations of thioformic acid differ by 1.3 D,<sup>13</sup> while the corresponding difference for formic acid is 2.4 D,<sup>9</sup> indicating that dipole-dipole repulsion will be more important in decreasing the population of the *E* conformations of carboxylic acids and esters than for the related sulfur compounds. A CXC bond angle of 90° in RCO(XR') would leave one lone pair of electrons in an s orbital and the other pair in a p orbital. The electrons of the p orbital could not interact with  $\sigma^*$ , and any interaction of the remaining lone pair with  $\sigma^*$  should be of nearly equal importance for either conformation. The smaller CSH bond angle for (*Z*)-thioformic acid (92.7°)<sup>14</sup> than for the COH angle of (*Z*)-formic acid (106.8°)<sup>15</sup> suggests that the n- $\sigma^*$  interaction may be lower for thioformic acid.

The position of equilibrium for a thiol ester in solution should then be influenced mainly by the "aromaticity" of the *Z* isomer.<sup>16</sup>

(7) For a summary, see ref 8.

(8) Larson, J. R.; Epiotis, N. D.; Bernardi, F. *J. Am. Chem. Soc.* **1978**, *100*, 5713.

(9) (*E*)-Formic acid,  $\mu = 3.79$  D; (*Z*)-formic acid,  $\mu = 1.420$  D. Hocking, W. H. *Z. Naturforsch., A* **1976**, *31A*, 1113.

(10) For a discussion of aromaticity in (*Z*)-methyl vinyl ether, see: Bernardi, F.; Epiotis, N. D.; Yates, R. L.; Schlegel, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 2385. The importance of aromaticity or antiaromaticity in other systems has been noted by: Cremer, D.; Binkley, J. S.; Pople, J. A.; Hehre, W. J. *Ibid.* **1974**, *96*, 6900. A nonbonded attraction has been suggested for the *Z* conformations of methyl formate and related compounds<sup>11a</sup> and for (*Z*)-methyl nitrite.<sup>11b</sup> A number of compounds, including esters and amides, have been discussed in detail by: Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R. L.; Bernardi, F. *Top. Curr. Chem.* **1977**, *70*, 1.

(11) (a) Lister, D. G.; Palmieri, P. *J. Mol. Struct.* **1976**, *32*, 355. (b) Cordell, F. R.; Boggs, J. E.; Skancke, A. *Ibid.* **1980**, *64*, 57.

(12) For a description of the  $\pi$ -type orbitals of a methyl group, see: Hoffman, R.; Radom, L.; Pople, J. A.; Schleyer, P. von R.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.*, **1972**, *94*, 6221.

(13) (*E*)-Thioformic acid,  $\mu = 2.87$  D; (*Z*)-thioformic acid,  $\mu = 1.54$  D. Hocking, W. H.; Winnewisser, G. *Z. Naturforsch., A* **1976**, *31A*, 995.

(14) Hocking, W. H.; Winnewisser, G. *Z. Naturforsch., A* **1976**, *31A*, 438.

(15) Bellet, J.; Deldalle, A.; Samson, C.; Steenbeckeliers, G.; Wertheimer, R. *J. Mol. Struct.* **1971**, *9*, 65.

(16) The acidic proton of a thiol acid cannot complete an aromatic sextet in the *Z* conformation, and we have observed both conformations of thioacetic acid using low-temperature NMR.<sup>17</sup> Kalinowski et al.<sup>18</sup> have reported populations of 0.525 and 0.475 for the *E* and *Z* conformations of thioformic acid at -113 °C in CD<sub>2</sub>Cl<sub>2</sub> solution. However, the room-temperature chemical shifts reported by these authors ( $\delta$  7.88 and 2.32) differ markedly from the values of  $\delta$  10.18 and 4.66 obtained by Engler and Gattow<sup>19</sup> for a solution in CDCl<sub>3</sub>. In a preliminary study of thioformic acid, we have found chemical shifts above coalescence of  $\delta$  10.3 and 5.1, indicating that the values of ref 18 are in error by more than 200 Hz. Our preliminary study has qualitatively confirmed that both conformations are appreciably populated at low temperatures. Populations of 0.25 (*E*) and 0.75 (*Z*) at 27 °C were obtained<sup>13</sup> from a microwave study of thioformic acid in the gas phase.

(17) Noe, E. A. *J. Am. Chem. Soc.* **1977**, *99*, 2803, 7400.

(18) Kalinowski, H. O.; Hocking, W. H.; Winnewisser, B. P. *J. Chem. Res., Synop.* **1978**, 260.