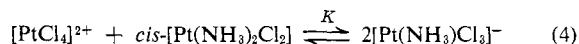


ability of the tributylphosphine ligand is very large compared to that of Cl which is greater than that of piperidine. The configurations of the products of the cleavage reactions also follow the predictions of the *trans* effect.<sup>6a</sup> For the amine complex, a mixture of isomers of Pt(pip)Cl<sub>2</sub> was obtained, but the spectral data indicated the first product was probably *cis*, the expected isomer on the basis of the *trans* effect.

The *trans* effect can also be invoked to explain the symmetrical cleavage of the complexes Pt<sub>2</sub>L<sub>2</sub>X<sub>4</sub>, since in the intermediate it will always be a bond to the platinum which remained the same during the first step which will be labilized most strongly. For the complexes [Pt<sub>2</sub>X<sub>6</sub>]<sup>2-</sup> the situation is less clear. The same group is *trans* to both of the bonds in the intermediate which might be broken, and one might expect a mixture of symmetrical and unsymmetrical cleavage. One explanation of the observed preference for symmetrical cleavage is that a choice of bonds to be cleaved does not exist because the intermediate does not exist. Perhaps the cleavage of the second bridge begins on the other platinum before the ligands on the first platinum atom have finished rearranging from the five-coordinated transition state to their final square-planar or tetragonal configuration.

Another explanation may be found, if one compares

the activation energies for symmetrical and unsymmetrical cleavage by considering the equilibrium between the products of symmetrical and unsymmetrical cleavage. The formation constants for the series of complexes [Pt(NH<sub>3</sub>)<sub>x</sub>Cl<sub>4-x</sub>]<sup>(x-2)+</sup> are known<sup>13</sup> and the equilibrium constant for



is found to be equal to  $5 \times 10^3$ . Since the products of symmetrical cleavage are the more stable products, it may be that the energy barrier for symmetrical cleavage is lower than for unsymmetrical cleavage, in which case the thermodynamically stable products would also be the kinetically observed products.

In summary, although the difference in reactivity is great, the square-planar complexes and the binuclear halogen-bridged complexes of Pt(II) undergo reactions which follow essentially the same mechanism.

**Acknowledgments.** We wish to thank Professor F. Basolo for helpful discussions. This project was partially supported by Atomic Energy Commission Grant AT(11-1)-1087. This is report number COO-1087-94.

(13) "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964, p 284.

## Phosphorus Trioxide as a Tetradentate Ligand.

### I. Transition Metal Complexes

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*Contribution from the Monsanto Company, Central Research Department, St. Louis, Missouri. Received December 20, 1965*

**Abstract:** Phosphorus trioxide, P<sub>4</sub>O<sub>6</sub>, replaces carbon monoxide in metal carbonyl complexes to give a new class of coordination compounds in which P<sub>4</sub>O<sub>6</sub> behaves as a polydentate, nonchelating ligand. When treated with an excess of nickel carbonyl, the symmetrical bird-cage structure of P<sub>4</sub>O<sub>6</sub> successively coordinates from one to four tricarbonyl nickel groups. The symmetrical compound, P<sub>4</sub>O<sub>6</sub>[Ni(CO)<sub>3</sub>]<sub>4</sub>, has been isolated as a crystalline species. When P<sub>4</sub>O<sub>6</sub> is in excess, from one to three of the carbonyls of Ni(CO)<sub>4</sub> may be substituted by different P<sub>4</sub>O<sub>6</sub> groups. When neither reagent is present in large excess, nickel atoms are bridged by P<sub>4</sub>O<sub>6</sub> molecules which, in turn, are bridged by nickel atoms so as to give network structures. As expected from the polyfunctionality of P<sub>4</sub>O<sub>6</sub> and Ni, there are two gel points in the system at Ni/P<sub>4</sub>O<sub>6</sub> mole ratios of *ca.* 0.25 and 4.

As part of a study of the chemistry of phosphorus trioxide,<sup>2</sup> the P<sub>4</sub>O<sub>6</sub> bird-cage molecule was tested as a complexing ligand in coordination chemistry. We were pleased to find that nickel carbonyl and phosphorus trioxide reacted readily, with evolution of carbon monoxide. The results of this study are described below along with some exploratory experiments designed to show the general applicability of the P<sub>4</sub>O<sub>6</sub> molecule as a polydentate ligand which, because of its large tetrahedral structure, is unable to form a chelate with a single atom of a metal.

### Experimental Section

The nickel carbonyl (hereafter called nickel tetracarbonyl) employed in this work was produced by the Mathieson Co.; the phosphorus trioxide, P<sub>4</sub>O<sub>6</sub>, was obtained several years ago from G. Mikulaschek of the University of Munich. The phosphorus trioxide was made according to the standard method<sup>3</sup> and was freed<sup>4</sup> from dissolved white phosphorus by four successive ultraviolet irradiations, each followed by high-vacuum distillation. It was a clear, colorless liquid (sharp mp at 22.6°; lit.<sup>4</sup> 23.8°) exhibiting a single narrow peak at -113 ppm in its P<sup>31</sup> nuclear magnetic resonance (nmr) spectrum. Unless otherwise noted, the reactions reported here were carried out by freezing the P<sub>4</sub>O<sub>6</sub> into a

(1) On leave from the University of Strasbourg, Institut de Chimie, 1964-1966.

(2) J. G. Riess and J. R. Van Wazer, *Inorg. Chem.*, **5**, 178 (1966).

(3) L. Wolf and H. Schmager, *Ber.*, **62B**, 771 (1929).

(4) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, p 282.

thin-walled 5-mm, precision-bore nmr tube, adding a volume of chloroform equal to the total volume of the reagents, and finally floating the nickel tetracarbonyl on top of the chloroform, with weighing at each step. This procedure allowed all ingredients to be measured and the tube to be connected to a standard buret-type gasometer before warming to room temperature (24°) to start the reaction. All handling of reagents was carried out in a plastic drybag flushed with dry nitrogen.

The  $P^{31}$  nmr measurements were carried out at 40.5 Mc on a Varian HR-100 spectrometer. The chemical shifts are reported with respect to 85%  $H_3PO_4$  (positive shifts being upfield), but the reference measurements were made with respect to dissolved  $P_4O_6$ , or, when there was none present in the reaction mixture, to  $P_4O_6$  contained in a capillary.

The thermogravimetric analyses were performed on a DuPont Model 900 differential thermal analyzer with a Model 950 thermogravimetric attachment. Typical runs on a 22-mg  $P_4O_6[Ni(CO)_3]_4$  sample in nitrogen, and on a 24.7-mg sample *in vacuo*, gave respective weight losses of 42 and 43.7% (calculated, 42.3% for total loss of CO). Other analytical data on  $P_4O_6[Ni(CO)_3]_4$  have already been published.<sup>5</sup>

**Preparation of Crystalline  $P_4O_6[Ni(CO)_3]_4$ .**  $P_4O_6$  (1.1 g, 5 mmoles) is mixed with 25 mmoles (4.3 g) of  $Ni(CO)_4$ , without any solvent being employed. In about 10 min at 24°, with evolution of 4 equiv of CO, crystals form and must be washed promptly by pentane to remove excess  $Ni(CO)_4$  in order to prevent rapid decomposition. This is done by repeated crushing of the crystalline powder with Dry Ice cooled dry pentane, followed by filtration, all in a drybag. Further purification is achieved by recrystallization from pentane, using Dry Ice cooling.

## Results and Conclusions

**Reaction with Excess Nickel Tetracarbonyl.** When about 4 moles of nickel tetracarbonyl are combined with 1 mole of  $P_4O_6$ , carbon monoxide evolution is rapid, being essentially complete in *ca.* 20 min at 25°. By rapid scanning of the region of interest (from -135 to -113 ppm) of the  $P^{31}$  nmr spectrum, it is seen that there is a sequence of reactions since successive spectra become more and more complex (with as many as 32 resonances showing up), and then they become more simple until there is only one main peak at -132.9 ppm.

In a single run, it is difficult to get more than one or two spectra during the period of rapid change when the greatest number of resonances appear. However, the over-all picture becomes clear when a number of replicate determinations are made with some variation in timing of the start of individual scans. The over-all aspects are shown in Figure 1a.

In these studies, the first set of  $P^{31}$  resonances (labeled ① in Figure 1a), which appear in addition to the singlet for  $P_4O_6$ , consists of a group of six peaks in the region of -124 to -128 ppm plus a pair of closely lying doublets between -116 and -119 ppm. This pattern is attributable to an  $AB_3$  type of spectrum and is consistent with the coordination of one  $(CO)_3Ni$  group by one phosphorus atom of the  $P_4O_6$  bird-cage molecule. The A of this  $AB_3$  system corresponds to the phosphorus atom which donates an electron pair to a nickel so that its  $P^{31}$  chemical shift undergoes a pronounced downfield displacement from the value corresponding to the uncomplexed  $P_4O_6$ . The  $B_3$  represents the three symmetrically arranged phosphorus atoms of the  $P_4O_6$  molecule, each of which has an unshared pair of electrons. This nmr pattern was exactly simulated by a high-speed computer as shown in Figure 1b. In this calculation, we employed the experimentally measured values of the chemical shifts,  $\delta$ , of the two kinds of phosphorus atoms, as well as the value of the coupling con-

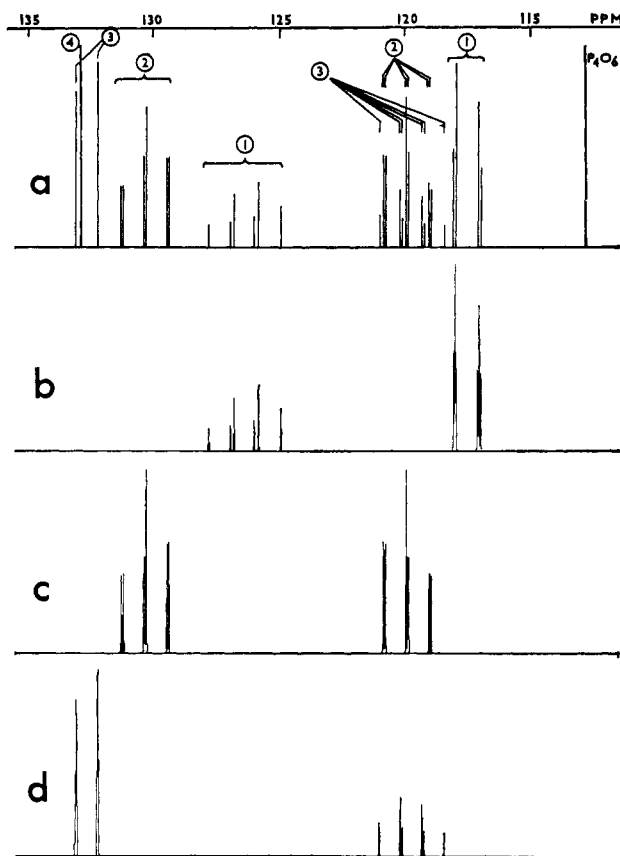


Figure 1.  $P^{31}$  nmr spectra corresponding to the successive coordination of  $P_4O_6$  by  $Ni(CO)_3$  groups in the presence of an excess of  $Ni(CO)_4$ : (a) combined experimental spectra, simplified by omission of the line widths; (b-d) spectra calculated for  $P_4O_6Ni(CO)_3$ ,  $P_4O_6[Ni(CO)_3]_2$ , and  $P_4O_6[Ni(CO)_3]_3$ , respectively.

stant,  $J_{AB}$  between them. These experimental values are presented in Table I. Because of symmetry, the spectrum is completely independent of the coupling constant

Table I.  $P^{31}$  Nmr Data for Complexes Formed from Nickel Carbonyl and Phosphorus Trioxide

| Compound  | $\delta^a$ (ppm)<br>coordinated P<br>(A) | $\delta^a$ (ppm)<br>P with<br>unshared<br>electron<br>pair<br>(B) | $J_{AB}^b$<br>(cps) | Approx<br>area<br>ratio <sup>c</sup> |
|---|--|---|---------------------|--------------------------------------|
| $P_4O_6$  | ...                                      | -113.0  | ...                 | ...                                  |
| $P_4O_6Ni(CO)_3$  | -126.3                                   | -117.6  | 38.8                | 1:3                                  |
| $P_4O_6[Ni(CO)_3]_2$  | -130.3                                   | -120.0  | 36.7                | 1:1                                  |
| $P_4O_6[Ni(CO)_3]_3$  | -132.6                                   | -120.2  | 34.8                | 3:1                                  |
| $P_4O_6[Ni(CO)_3]_4$  | -132.9                                   | ...   | ...                 | ...                                  |
| $P_4O_6[Ni(CO)_3]_3-$<br>[ $Ni(CO)_2(P_4O_6)$ ]<br>( $P_4O_6$ ) <sub>2</sub> $Ni(CO)_2$ | -132.0                                   | -132 ± 1  | 34                  | ...                                  |
| ( $P_4O_6$ ) <sub>2</sub> $Ni(CO)_2$  |  | -117.7  | 40                  |                                      |
| ( $P_4O_6$ ) <sub>3</sub> $Ni(CO)$  |  | -117.9  | 41                  |                                      |

<sup>a</sup> Referenced to 85%  $H_3PO_4$ . <sup>b</sup> Coupling between the coordinated phosphorus and that with an unshared pair of electrons. <sup>c</sup> (Total peak area for coordinated P)/(total area for P with unshared pair).

between the three like phosphorus atoms (the B atoms). The other spectra of Figure 1 are similarly independent of  $J_{BB}$  and/or  $J_{AA}$ .

The next pattern to appear after the ① spectrum of Figure 1a in the course of the reaction consists of the

(5) J. G. Riess and J. R. Van Wazer, *J. Am. Chem. Soc.*, **87**, 5506 (1965).

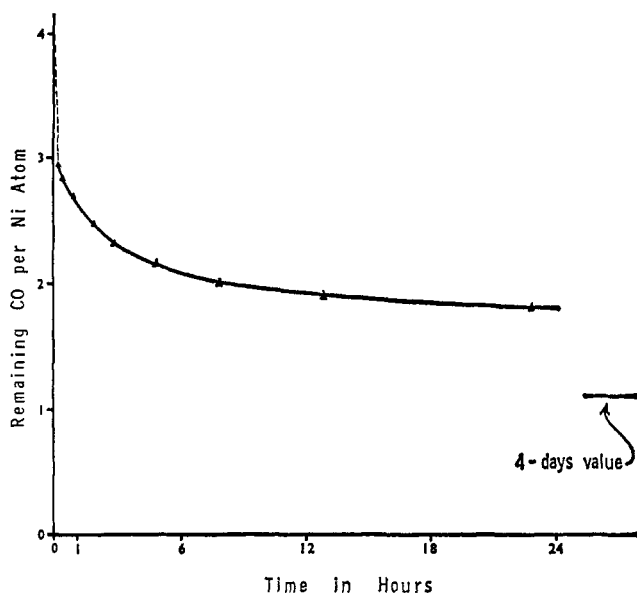


Figure 2. Rate of carbon monoxide evolution at 24° for a Ni/P<sub>4</sub>O<sub>6</sub> mole ratio of 0.25.

resonances labeled ②. This set of nmr lines was attributed to the A<sub>2</sub>B<sub>2</sub> spectrum of the compound resulting from coordination of a second (CO)<sub>3</sub>Ni group on the P<sub>4</sub>O<sub>6</sub>. The third pattern to appear (denoted by ③ in Figure 1a) corresponds to coordination of the third phosphorus atom of the P<sub>4</sub>O<sub>6</sub> molecule to give an A<sub>3</sub>B type of spectrum. The computed spectra of these A<sub>2</sub>B<sub>2</sub> and A<sub>3</sub>B molecules, obtained by using the experimental data of Table I, are shown in Figures 1c and 1d, respectively. The last peak to appear in the course of the reaction, labeled ④ in Figure 1a, is a singlet attributable to coordination of all four phosphorus atoms of the P<sub>4</sub>O<sub>6</sub> molecule by (CO)<sub>3</sub>Ni groups. As can be seen in Table I, the experimentally measured chemical shifts of the series of four molecules obtained by stepwise addition of tricarbonylnickel groups to P<sub>4</sub>O<sub>6</sub> are consistent with the interpretation given here.

When increasingly larger proportions than 4 moles of nickel tetracarbonyl per phosphorus trioxide are employed, the carbon monoxide evolution becomes too rapid to allow nmr measurements to be carried out during the reaction. Under these conditions, one observes only the single nmr peak at -132.9 ppm due to the P<sub>4</sub>O<sub>6</sub> bird-cage in which all four phosphorus atoms are complexed with a tricarbonylnickel group. As described under the Experimental Section, this compound can be prepared in crystalline form by mixing the neat reagents. Dissolution of the pure, recrystallized P<sub>4</sub>O<sub>6</sub>·[Ni(CO)<sub>3</sub>]<sub>4</sub> in chloroform or pentane gives a single sharp P<sup>31</sup> nmr peak having the above shift. Structure proofs in addition to the nmr data are as follows. (1) The X-ray powder pattern is readily attributed<sup>6</sup> to a simple cubic lattice having a unit cell spacing of 8.811 ± 0.003 Å. The measured density of the sample is 1.87 g/cc, as compared to a value of 1.92 calculated from the X-ray data on the assumption of one molecule in each unit cell. As described elsewhere,<sup>7</sup> the Ni-P bond distance is found to be 2.15 Å from a Fourier analysis for the 100 plane. (2) The infrared pattern of the

compound P<sub>4</sub>O<sub>6</sub>·[Ni(CO)<sub>3</sub>]<sub>4</sub> exhibits the carbonyl stretching frequencies at 2035, 2075, and 2095 cm<sup>-1</sup> in chloroform. (3) Furthermore, weight loss on heating at 150° to a constant-weight plateau *in vacuo* corresponds to three carbonyl groups per phosphorus.

The crystalline compound P<sub>4</sub>O<sub>6</sub>·[Ni(CO)<sub>3</sub>]<sub>4</sub> is highly soluble in saturated hydrocarbons, chlorinated hydrocarbons, and ethers; and it is slightly soluble in methanol. It is insoluble in water with which it does not react within several hours. The initially pure white crystals are seen to darken upon storage, with the stability being highly dependent on the purity. The purest samples which we have been able to prepare show only slight yellowing or graying in several months when stored under nitrogen at room temperature (not light sensitive). Studies in a nitrogen atmosphere with a thermobalance showed an initial rapid loss of weight corresponding to evolution of 60–80% of the total carbon monoxide in the temperature range from 60 to 65°, followed by a gradual loss of the remaining CO as the temperature was slowly increased to ca. 250°. When run *in vacuo*, the entire process was speeded up, with the initial loss of CO becoming rapid only slightly above room temperature and the process being completed at ca. 125°. In all cases, the decomposition is accompanied by darkening of the sample, tentatively attributed to the formation of finely divided nickel or nickel phosphide.

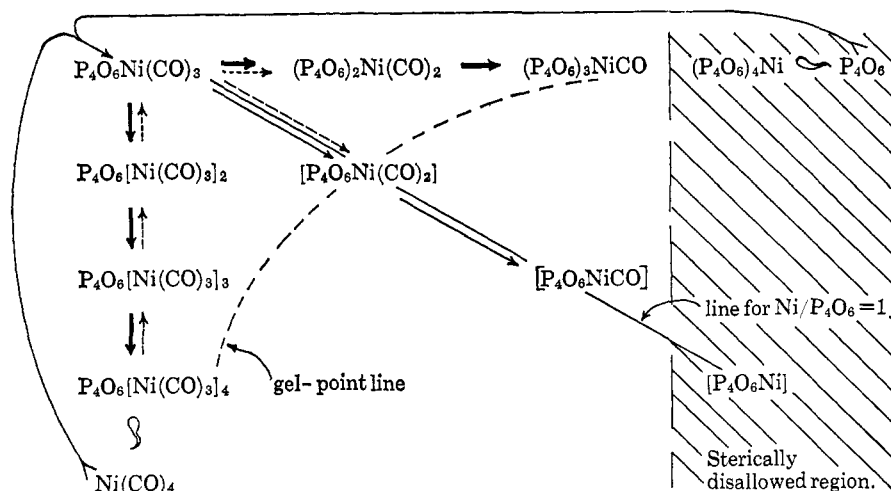
**Reaction with Excess Phosphorus Trioxide.** When more than 4 moles of P<sub>4</sub>O<sub>6</sub> are combined with 1 mole of Ni(CO)<sub>4</sub>, the evolution of the first mole of carbon monoxide is very rapid, the second mole more slowly, and the third mole takes several days, as demonstrated by the curve of Figure 2. Repeated scanning of the region of interest of the P<sup>31</sup> nmr spectrum again shows that there is a sequence of reactions. The first new pattern is that of the compound P<sub>4</sub>O<sub>6</sub>·Ni(CO)<sub>3</sub>, the same compound to appear initially when there is an excess of nickel carbonyl (see Figure 1b). Thereafter, the spectra became increasingly more complicated and there is an early fugitive appearance of the A<sub>2</sub>B<sub>2</sub> spectrum of Figure 1c, corresponding to nonequilibrium maximization of the compound in which two tricarbonylnickel groups are bonded to a single P<sub>4</sub>O<sub>6</sub> molecule. This is due to the fact that the rate of coordination of two tricarbonylnickel groups around one P<sub>4</sub>O<sub>6</sub> molecule is much more rapid than the coordination of two P<sub>4</sub>O<sub>6</sub> molecules around one nickel atom.

As the reaction proceeds, nmr patterns which are quite similar to the AB<sub>3</sub> spectra of the P<sub>4</sub>O<sub>6</sub>·Ni(CO)<sub>3</sub> molecule are seen to appear. These nmr patterns, which are shifted slightly downfield from the P<sub>4</sub>O<sub>6</sub>·Ni(CO)<sub>3</sub> pattern, are attributed to the coordination of more than one P<sub>4</sub>O<sub>6</sub> molecule to one nickel atom. The first such pattern to appear is assigned to (P<sub>4</sub>O<sub>6</sub>)<sub>2</sub>·Ni(CO)<sub>3</sub> and the second to (P<sub>4</sub>O<sub>6</sub>)<sub>3</sub>·Ni(CO)<sub>3</sub>. The chemical shifts and coupling constants for the phosphorus atoms not bonded to nickel in these structures are given in Table I. Spectral overlap and low intensity prevented determination of the constants corresponding to the phosphorus atoms coordinated to the nickel. In summary, the nmr patterns and their variation with time, as also the rate of evolution of carbon monoxide (Figure 2), are consistent with the successive replacement of one to three carbonyl groups on a

(6) H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures," John Wiley and Sons, Inc., New York, N. Y., 1954, pp 336–348.

(7) E. Pierron, P. J. Wheatley, and J. G. Riess, *Acta Cryst.*, in press.

Scheme I



given nickel tetracarbonyl, each by a different  $P_4O_6$  molecule.

Although all four carbon monoxides have been replaced on nickel by such bulky groups as triphenylphosphine,<sup>8</sup> triethyl phosphite,<sup>8</sup> or phosphorus trichloride,<sup>8,9</sup> it may still be possible for a less energetically bound ligand to exhibit steric hindrance even though it is more compact angularly than these substituted phosphines. In other words, it is worth considering whether as many as four  $P_4O_6$  bird-cage molecules can be substituted around a nickel atom, even though this structure, although large, is angularly compact and should not offer much more steric hindrance than the  $PF_3$  ligand. This problem was investigated in an experiment in which the evolved carbon monoxide was bubbled through a column of  $P_4O_6$  to remove any nickel tetracarbonyl that may have been volatilized during its evolution. In this experiment a 10:1 ratio of  $P_4O_6$  to  $Ni(CO)_4$  in an equal volume of  $CHCl_3$  was first cooled and then warmed back to room temperature in order to keep up a gentle evolution of CO. The sample was then held at room temperature for 4 days. Replicate determinations showed 2.8, 2.7, 3.1, and 2.9 CO groups evolved per Ni atom so that it appears steric hindrance does act to prevent the placement of four  $P_4O_6$  groups around a nickel atom under the experimental conditions employed.

**Oligomeric and Polymeric Structures.** Since four tricarbonylnickel groups are easily substituted on a  $P_4O_6$  molecule present in an excess of nickel tetracarbonyl, and since three  $P_4O_6$  molecules can bond to a nickel atom in an excess of phosphorus trioxide, complicated polymeric structures ought to be found when neither reagent is present in excess. Indeed, in the vicinity of equimolar mixtures of the reagents, infinite three-dimensional network polymers, in which nickel atoms bridge between  $P_4O_6$  molecules that in turn bridge between nickel atoms, are to be expected. In accord with this reasoning, two gel points were measured in the  $Ni(CO)_4$  vs.  $P_4O_6$  system, corresponding to  $Ni/P_4O_6$  mole ratios of ca. 0.25 and ca. 4.

The whole family of  $P_4O_6$ -Ni-CO complexes, ranging from the smaller structures based on a single  $P_4O_6$

group or a single nickel atom up through infinite network macromolecules, is best described by the composition diagram (Scheme I) in which several important reaction sequences, discussed below, are shown. The compound  $P_4O_6Ni(CO)_3$  is always the first to appear when phosphorus trioxide is allowed to react with nickel tetracarbonyl, as indicated by the curved arrows to the left and at the top of the diagram. If there is an excess of the nickel carbonyl, the reaction further proceeds down the left-hand column of the diagram, as denoted by the heavy arrows. If there is an excess of the phosphorus trioxide, it proceeds horizontally toward the right of the diagram, again following the heavy arrows.

For a composition characterized by the over-all mole ratio of  $Ni/P = 1$ , the compound  $P_4O_6Ni(CO)_3$  is formed in a matter of minutes. Then it starts to lose carbon monoxide at a much slower rate following the slender arrows along the diagonal of the diagram. This continuing loss of carbon monoxide is accompanied by increasing viscosity, until the liquid becomes so thick that it turns into a foamy mass, which is sufficiently rigid to shatter under stress. For  $Ni/P = 1$ , the gel point should come at a CO/Ni ratio of 2; i.e., at the  $[P_4O_6Ni(CO)_2]$  composition which corresponds to the formula of the infinite straight-chain polymer molecule. At this composition, the rate of evolution of carbon monoxide becomes extremely slow and, at 25°, stops when the CO/Ni ratio is only slightly smaller than 2.

From a number of experiments, it appears that there is an exchange of nickel-bearing groups around the various  $P_4O_6$  molecules and of  $P_4O_6$  for CO around the nickel atoms, but seldom, if ever, is an equilibrium reached in these scrambling reactions. In the general case, any given over-all composition is found to drift continuously downwards in a direction parallel to the diagonal of the diagram, owing to irreversible evolution of carbon monoxide. Furthermore, the rate of evolution of carbon monoxide becomes more and more slow as the amount of crosslinking is believed to increase so that this drifting of the system is kinetically halted when the resulting gel is a hard glass. In Scheme I, a gel-point line is presented. It should be obvious from this discussion that the sequence of compositions corresponding to the gel point in this system is kinetically determined.

(8) L. S. Meriwether and J. R. Leto, *J. Am. Chem. Soc.*, **83**, 3192 (1961).

(9) G. Wilkinson, *ibid.*, **73**, 5501 (1951); R. J. Clark and E. O. Brimm, *Inorg. Chem.*, **4**, 651 (1965).

When the crystalline compound  $P_4O_6[Ni(CO)_3]_4$  is allowed to react with various amounts of  $P_4O_6$  in chloroform, it is found that the initial steps of the reaction consist of the successive stripping of tricarbonylnickel groups from the  $P_4O_6$  molecule until only one is left. This is due to the fact that the rate of exchange of tricarbonylnickel groups between  $P_4O_6$  molecules is considerably faster than the rate of substituting more than one  $P_4O_6$  per nickel atom. This is consistent not only with the nmr data but with the rate of evolution of carbon monoxide from nickel tetracarbonyl. The reaction sequence shown on the composition diagram (Scheme I) by the dashed arrows corresponds to adding *ca.* 7 moles of  $P_4O_6$  per mole of  $P_4O_6[Ni(CO)_3]_4$ . In a matter of a few minutes for this mixture, the tricarbonylnickel groups are stripped from the  $P_4O_6[Ni(CO)_3]_4$  so as to give primarily  $P_4O_6Ni(CO)_3$  and  $P_4O_6$ . The  $P_4O_6Ni(CO)_3$  and its neighboring compound along the top of the diagram then start to lose carbon monoxide at a much slower rate. Thus, the reaction is kinetically controlled, following a path which avoids the region of polymeric structures beyond the gel point, although the most direct path should give network polymers in the intermediate region.

The rigid glasses corresponding to compositions be-

yond the gel point are quite stable. They remain clear and transparent upon being stored for several months (and presumably longer) in dry nitrogen and upon heating for several hours at  $100^\circ$  in dry nitrogen. At  $200^\circ$ , they finally give a Ni mirror on the walls of the tube in which the sample was heated. Unlike the crystalline compound  $P_4O_6[Ni(CO)_3]_4$ , these cross-linked glasses are very reactive with water, giving a black precipitate with rapid evolution of carbon monoxide.  $P^{31}$  nmr of the resulting solution, after filtration through a fine sintered-glass disk, indicates that the phosphorus is not oxidized during this hydrolysis.

**Reaction with Iron Carbonyls.** When  $P_4O_6$  is refluxed with an excess of  $Fe(CO)_5$ , the evolution of the first mole of carbon monoxide per  $P_4O_6$  occurs in about 1 day at  $103^\circ$ . Again the first nmr pattern to appear is of the  $AB_3$  type, corresponding to the molecule  $P_4O_6Fe(CO)_4$ . Continued refluxing leads to evolution of more CO, with the rate decreasing with time. When either  $Fe(CO)_5$  or  $Fe_2(CO)_9$  is reacted with an excess of  $P_4O_6$ , the same  $AB_3$  nmr pattern, ascribed to  $P_4O_6Fe(CO)_4$ , is the first to appear in addition to the line corresponding to unreacted  $P_4O_6$ . The reaction between  $Fe_2(CO)_9$  and excess  $P_4O_6$  is relatively fast with about 1 mole of CO being evolved in 0.5 hr at  $50-60^\circ$ .

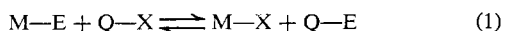
## Transformations of Heterocycles. The Conversion of Silicon and Germanium Imidazolidines into Their Phosphorus(V) Analog in One Step<sup>1</sup>

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*Contribution from the Baker Laboratory, Cornell University, Ithaca, New York.  
Received December 8, 1965*

**Abstract:** The generality of the sequence  $M-E + Q-X \rightleftharpoons Q-E + M-X$  for organometallic transformation reactions, where X is a halide, M and Q are metals or metalloids, and E is RO,  $R_2N$ , etc., has been tested by extending M to include germanium, and Q to include phosphorus(V). Imidazolidines with silicon and germanium replacing carbon in the 2 position are transformed to their phosphorus(V) analog by reaction with phenyldichlorophosphine oxide and release of dimethyldichlorosilane or -germane. The resulting diamide hydrolyzes in two stages through the phenylphosphonic amide of N,N'-dimethylethylenediamine to N,N'-dimethylethylenediamine itself and phenylphosphonic acid.

Recent reports in the literature on the formation of amino derivatives of various elements from the action of halides of these elements on silylamines have made it increasingly apparent that such reactions belong to a general class of organometallic transformations represented by the equation



where M and Q are metals or metalloids, X is a halogen, and E is an organic grouping RO,  $R_2N$ , etc. Such processes are of interest not only because of the chemical relationships they illustrate, but because they can be utilized as new avenues to various chemical systems. The range of these transformations in terms of M, E,

Q, and X is summarized in Table I along with leading references. In this publication we report our results in expanding the scope of such reactions to the  $M = Si$  and Ge cases where  $Q = P(V)$ .

### Discussion of Results

We have examined the reaction between silicon<sup>2</sup> and germanium imidazolidines and phenyldichlorophosphine oxide which produces the novel phosphorus(V) imidazolidine, 2-phenyl-1,3-dimethyldiazaphosphole oxide, with the release of dimethyldichlorosilane or -germane

(1) Work described in part at the Second International Symposium on Organometallic Chemistry, Madison, Wis., Sept 1965.

(2) C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **4**, 116 (1965).