Chlorobis(triphenylphosphine)(diphenylacetylene)iridium (XXIIIc). To a mixture of the nitrogen complex XXII (500 mg, 0.064 mmole) and diphenylacetylene (200 mg, 0.112 mmole) was added under nitrogen 10 ml of benzene with stirring. After the brown solution had been stirred for 2 hr at 45°, an insoluble precipitate (10 mg) was removed by filtration. Evaporation of the filtrate under vacuum afforded a brown solid which was purified by recrystallization from benzene-methanol, yield 510 mg (85%) of yellow crystals, mp 193–195° dec. *Anal.* Calcd for $C_{50}H_{40}ClP_2Ir$: C, 64.52; H, 4.30; Cl, 2.79; P, 6.67; mol wt, 930. Found: C, 64.30; H, 4.39; Cl, 3.01; P, 6.50; mol wt, 896.

Chlorobis(triphenylphosphine)(ethyl phenylpropiolate)iridium (XXIIId). To a suspension of the nitrogen complex XXII (500 mg, 0.064 mmole) in 5 ml of benzene was added a solution of ethyl phenylpropiolate (150 mg, 0.086 mmole) in 5 ml of benzene under nitrogen at 10°. After the addition was complete the mixture was stirred for 1 hr at room temperature. The solvent was removed under vacuum to give an oily residue. The yellow crystalline product was obtained by crystallization from benzene-methanol, yield 480 mg (81%), mp 192–193° dec. *Anal.* Calcd for $C_{47}H_{40}ClO_2P_2Ir$: C, 60.91; H, 4.32; Cl, 3.89; P, 6.74; mol wt, 926. Found: C, 61.18; H, 4.16; Cl, 4.02; P, 6.48; mol wt, 899.

Chlorobis(triphenylphosphine)(ethyl *p*-nitrophenylpropiolate)iridium (XXIIIe). The purple crystalline complex XXIIIe was prepared in the manner outlined above, yield 570 mg (92%), mp 124–126° dec. *Anal.* Calcd for $C_{47}H_{39}ClNO_2P_2Ir$: C, 58.08; H, 4.02; Cl, 3.71; P, 6.38; mol wt, 971. Found: C, 57.89; H, 4.16; Cl, 3.99; P, 6.15; mol wt, 998.

Phosphorus Trioxide as a Tetradentate Ligand.
II. Borane Complexes

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Contribution from the Central Research Department, Monsanto Company, St. Louis, Missouri 63166. *Received August 8, 1966*

Abstract: When diborane is slowly bubbled through a solution of P_4O_6 in dry chloroform at room temperature, P^{31} nuclear magnetic resonance shows that there is successive coordination of one, two, and three BH_3 groups around the P_4O_6. Crystalline species corresponding to $P_4O_6 \cdot 2BH_3$ and $P_4O_6 \cdot 3BH_3$ have been obtained. In solution, equilibria are reached rapidly between the various $P_4O_6 \cdot xBH_3$ complexes (where $x = 0, 1, 2, 3,$ and 4) so that the distribution of species corresponding to any given BH_3/P_4O_6 mole ratio may be calculated from the set of three equilibrium constants presented herein. A fourth constant relates the partial pressure of diborane to the solution composition.

In paper I[2] and a prior brief communication,[3] it was shown that the P_4O_6 cage molecule acts as a tetradentate nonchelating ligand in the coordination chemistry of transition metals. This finding led to the investigation as to whether phosphorus trioxide would donate lone-pair electrons to Lewis acids. A communication from Japan[4] and one from our laboratory[5] attest to the fact that P_4O_6 reacts with B_2H_6 to give complexes in which BH_3 groups are coordinated around the P_4O_6 molecule. The purpose of this paper is to give a full account of the preparation and properties of the complexes formed between phosphorus trioxide and borane.

Experimental Section

Nmr Measurements. The P^{31}, B^{11}, and H^1 nuclear magnetic resonance (nmr) spectra were obtained at 40.5, 15.1, and 60.0 Mc, respectively, on Varian spectrometers HR-100, HR-60, and A-60. The P^{31} chemical shifts (presented in ref 5) were referenced with respect to P_4O_6, generally as an internal standard, but are reported with respect to 85% H_3PO_4. The H^1 (also see ref 5) and B^{11} chemical shifts are respectively referenced to dissolved tetramethylsilane and to $BF_3 \cdot O(C_2H_5)_2$ contained in a capillary. Upfield shifts are denoted with a positive sign.

Reagents and Reactions. The phosphorus trioxide and nickel carbonyl were the same as previously described,[2] and the diborane was obtained from the Callery Chemical Co., Pittsburgh, Pa. The reaction of P_4O_6 and B_2H_6 was carried out by first passing the diborane through a cold trap at −60° and then slowly bubbling it at a rate of *ca.* 10 ml/min into a 1:2 by volume solution of P_4O_6 in dry chloroform or *n*-hexane maintained at 25°. Samples were removed at regular intervals of time with a syringe through a serum-bottle stopper and transferred into 5-mm precision-bore nmr tubes in a glove bag under dry nitrogen. A number of admixing reactions, such as combining crystalline $P_4O_6 \cdot 2BH_3$ with P_4O_6, were carried out in the nmr tubes, adding dry chloroform when a solvent was needed. All handling operations were performed in a plastic dry bag flushed with dry nitrogen. *Warning:* The $P_4O_6 \cdot xBH_3$ compounds react explosively with water and moist air. Even old samples, minor spillings, etc., can sometimes produce unexpected firecracker-like explosions when present in small quantities.

Preparation of Crystalline $P_4O_6 \cdot 2BH_3$. The crystalline compound $P_4O_6 \cdot 2BH_3$ was prepared by slowly blowing diborane over the surface of pure P_4O_6 (3.04 g) at 25°. Crystals began to form after *ca.* 8 hr, and a solid crystalline mass resulted after 12 hr, at which time the P_4O_6 had been quantitatively transformed into $P_4O_6 \cdot 2BH_3$ (3.40 g). Recrystallization in dry *n*-pentane at Dry Ice temperature gave long transparent needles. The infrared spectrum obtained on a KBr pellet protected from moisture exhibited the characteristic B-H stretching absorption at 2400 cm^{-1}.[6]

Results and Conclusions

Reaction with Diborane. An exothermic reaction takes place when diborane is bubbled through a solution of P_4O_6 in an inert dry solvent without temperature control. The reaction mixture is seen to convert

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

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(3) J. G. Riess and J. R. Van Wazer, *ibid.*, 87, 5506 (1965).

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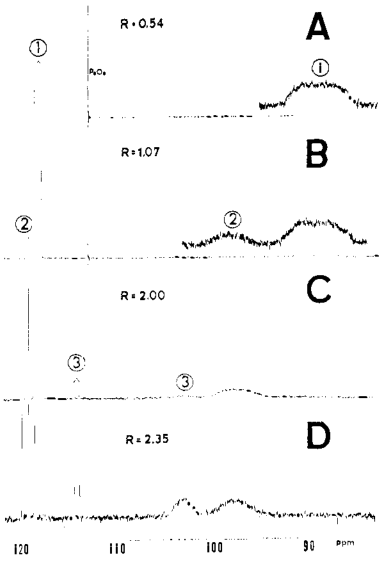

Figure 1. The P^{31} nmr spectra of a series of compositions made by bubbling diborane through a chloroform solution of phosphorus trioxide. The over-all stoichiometry of each composition is given by the value of $R \equiv BH_3/P_4O_6$ mole ratio and the sets of resonances corresponding to individual molecular species are differentiated by the encircled numbers.

rapidly into a transparent yellow gel, probably having a polymeric structure. The reaction takes an alternate path when the diborane is slowly incorporated into a solution maintained at 25°. In this case, the reaction mixture remains liquid and can be analyzed quantitatively by nmr. As the diborane is taken up by the solution of phosphorus trioxide, a given set of nmr peaks is seen to build up and then disappear, while another set is also building up and then disappearing. In other words, the changes observed when going through a time series of nmr spectra are quite similar to those previously seen in the replacement of the carbon monoxide of nickel carbonyl by phosphorus trioxide.[2] Figure 1 shows the successive nmr patterns observed during the course of the reaction between diborane and phosphorus trioxide. There is a continuous gradual change in the nmr patterns corresponding to successive maximization of the peaks labeled ①, then ②, and finally ③, indicating a sequential reaction. Each spectrum contains two groups of peaks, both in the spectral region not far from the P_4O_6 resonance. The group which has a more negative chemical shift than P_4O_6 consists of sharp lines with indirect spin–spin coupling being readily recognizable. This is attributed to triply connected phosphorus not coordinated to boron atoms. The set of peaks lying upfield of P_4O_6 corresponds to the phosphorus atoms bonded to boron. These peaks appear as broad humps due to the complicated system of spin–spin splitting with (1) the uncoordinated phosphorus atoms, (2) the boron atoms, and (3) the protons of the BH_3 groups, as well as to the quadrupole moment of the boron.

Indentification of the spectra corresponding to individual molecules in the mixtures is obtained by observing which peaks exhibit constant area ratios and maximize together. The first set of resonances (Figure 1, A) to appear in addition to the sharp P_4O_6 line consists of a sharp 1:1 doublet accompanied by an upfield hump which has an area which is always equal to one-third of the doublet area. This pattern is consistent with that expected for a compound in which a single BH_3 group is coordinated to one P_4O_6 cage molecule. Although the $P_4O_6 \cdot BH_3$ structure is analogous to the $P_4O_6 \cdot Ni(CO)_3$ molecule,[2,3] its smaller spin–spin coupling constant and the larger difference in shift between the uncoordinated and coordinated phosphorus atoms results in a simple AX_3 type of spectrum instead of the higher order AB_3 type observed for the tricarbonylnickel compound.

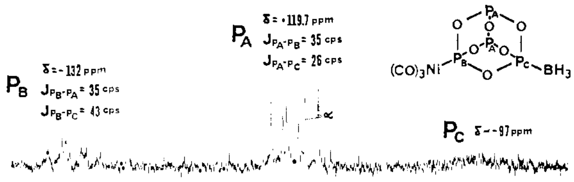

Figure 2. Nmr spectrum recorded during the reaction in chloroform of *ca.* 1 molar equiv of $Ni(CO)_4$ with an equilibrated $P_4O_6 \cdot xBH_3$ mixture containing 88% of the P_4O_6 as $P_4O_6 \cdot BH_3$. The main molecular species seen in this P^{31} spectrum is the molecule shown. The resonances denoted by α correspond to the uncoordinated phosphorus atoms of the $P_4O_6 \cdot BH_3$ starting material. The value given for $J_{P_B-P_C}$ is tentative.

Incorporation of more B_2H_6 results in the development of a 1:2:1 sharp-line triplet, accompanied by an upfield hump exhibiting the same peak area (see Figure 1, B and C). This spectrum is consistent with the coordination of a second BH_3 group to the P_4O_6 core. The next set of peaks to show up (Figure 1, C and D) consists of a 1:3:3:1 quartet plus an upfield hump which exhibits three times the peak area of the quartet. This pattern corresponds to the molecule $P_4O_6 \cdot 3BH_3$. When the diborane is bubbled through the solution of phosphorus trioxide at 1 atm pressure, the coordination process stops (see final plateau in Figure 3) when the mixture consists of *ca.* one-third $P_4O_6 \cdot 3BH_3$ and two-thirds $P_4O_6 \cdot 2BH_3$.

The B^{11} and H^1 spectra are consistent with the interpretation given above for the P^{31} patterns. The B^{11} spectrum exhibits a doubled quartet at +40 ppm due to splitting by the three hydrogens and its coordinated phosphorus ($J_{B-H} = 102$ cps and $J_{B-P} = 47$ cps). The H^1 spectrum is a quartet which is attributed to the $^3/_2$ spin of the boron atom. This is further split into doublets by the phosphorus ($J_{H-P} = 18$ cps and $J_{B-P} = 102$ cps). The chemical shifts of 0.6 ppm in the H^1 spectrum and 40 ppm in the B^{11} spectrum as well as the coupling constants given above should be compared with the constants previously reported[5] from the P^{31} and H^1 spectra.

Additional evidence to prove that the P_4O_6 cage structure remains unaltered in the formation of complexes with the BH_3 group was obtained by treating mixtures having various BH_3/P_4O_6 ratios with nickel carbonyl. Carbon monoxide is displaced during this reaction, in which one first notes in the nmr spectra a decrease of the resonances due to uncoordinated phosphorus with respect to those corresponding to the phosphorus coordinated to boron. Simultaneously with this, a set of new peaks is seen to grow in the spectral region previously attributed[2,3] to the phosphorus coordinated to nickel in the $P_4O_6 \cdot xNi(CO)_3$ complexes. A typical P^{31} spectrum of this type is shown in Figure 2. This spectrum was obtained by addition of *ca.* 1 molar equiv. of $Ni(CO)_4$ to a sample of $P_4O_6 \cdot xBH_3$ complexes containing 88% of the P_4O_6 in the form of the $P_4O_6 \cdot BH_3$ structure. Going from low to high field, there are three groups of nmr peaks corresponding respectively to (1) phosphorus coordinated to nickel, (2) uncoordinated phosphorus, and (3) phosphorus coordinated to boron. The fine structure in this nmr pattern is consistent with the interpretations given here and previously.[2,3,5]

The addition of more nickel carbonyl results in the progressive stripping of the borane groups from the central P_4O_6 moiety, with these groups being replaced by $Ni(CO)_3$ groups. Finally, the symmetrical structure of the well-characterized[2,3] P,P′,P′′,P′′′-tetrakistricarbonylnickel tetraphosphorus hexaoxide, $P_4O_6 \cdot 4Ni(CO)_3$, is obtained, as evidenced by its single-line sharp nmr resonance at −133 ppm. The presence of this compound was unambiguously demonstrated by the exact 32-line spectra obtained during the reaction which it undergoes when additional P_4O_6 is added to its chloroform solution[2] to cause exchange of $Ni(CO)_3$ groups around the P_4O_6 core.

The Crystalline $P_4O_6 \cdot 2BH_3$ Complex. When diborane is incorporated into phosphorus trioxide as the neat liquid, nmr shows that the reaction passes through the initial formation of $P_4O_6 \cdot BH_3$ but stops as the crystalline $P_4O_6 \cdot 2BH_3$ is obtained. This highly reactive material, also recently described by Kodama and Kondo,[4] is stable when stored under dry nitrogen.

An X-ray study involving a zero-level Weissenberg photograph of an oscillating single crystal mounted in a capillary under nitrogen shows that the $P_4O_6 \cdot 2BH_3$ crystals are orthorhombic with $a = 8.023$, $b = 15.500$, and $c = 15.537$ A. Since the sample was found not to be stable under X-ray bombardment, these data were obtained by moving the crystal during the exposure so that a new portion was continuously being bathed in the X-ray beam. Because of this instability, it has not been feasible to carry out a full structure determination by means of single-crystal X-ray diffraction. In the Weissenberg photographs, the systematic absences are $0k0$, $00l$, and $h0l$ for k odd or l odd. These absences are consistent with either of two space groups: $Pmc2_1$ or Pmcm. The distribution of the X-ray intensities suggests a centrosymmetric space group so that Pmcm is the more probable. This space grouping has eight equivalent positions, and the assumption of eight molecules per unit cell leads to a calculated density of 1.702, which is consistent with the density of analogous compounds: [$P_4O_6 \cdot 4Ni(CO)_3$, 1.87;[7] $P_4(NCH_3)_6 \cdot 4BH_3$, 1.36;[8] $P_4(NCH_3)_6 \cdot 4Ni(CO)_3$, 1.70 g/cc[8]]. Thus, the molecule is not required by the space group to have any particular symmetry.

Crystalline $P_4O_6 \cdot 3BH_3$. Upon cooling the concentrated chloroform solutions of mixtures having a BH_3/P_4O_6 ratio of 2.35 (the highest ratio obtainable at a diborane pressure of 1 atm, *vide infra*), well-shaped crystals are observed to form. Although considerable effort was devoted to isolating these crystals, they could never be separated from the mother liquor without decomposing. However, a quantitative analysis performed immediately after dissolution of these crystals in fresh chloroform showed that the crystals are richer in BH_3 than the initial mixture. Thus, a slurry of crystals which after redissolution gave a mixture of 56% $P_4O_6 \cdot 3BH_3$ and 44% $P_4O_6 \cdot 2BH_3$ (*i.e.*, an over-all BH_3/P_4O_6 ratio of 2.56) was obtained from the initial composition consisting of 35.5% $P_4O_6 \cdot 3BH_3$ and 64.5% $P_4O_6 \cdot 2BH_3$ (*i.e.*, over-all $BH_3/P_4O_6 = 2.35$), leaving a supernatant liquid composed of 23.0% $P_4O_6 \cdot 3BH_3$, 75.3% $P_4O_6 \cdot 2BH_3$, and 1.7% $P_4O_6 \cdot BH_3$ (*i.e.*, over-all $BH_3/P_4O_6 = 2.21$). The mixtures having BH_3/P_4O_6 ratios > 2.35 are not stable at 1 atm. Diborane is always observed to be formed by them until the BH_3/P_4O_6 ratio returns to the value of 2.35 under 1 atm pressure.

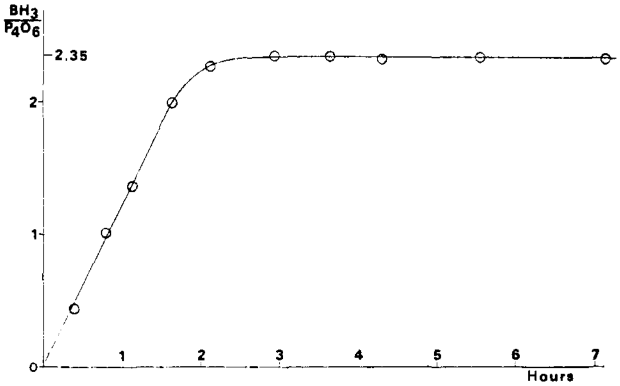

Figure 3. Variation of the over-all solution BH_3/P_4O_6 mole ratio with time as B_2H_6 is bubbled at a constant rate at 1 atm pressure into a chloroform solution of P_4O_6 kept at 25°.

The findings cited above are interpreted to mean that (1) the crystals formed correspond to the $P_4O_6 \cdot 3BH_3$ complex and (2) there is an equilibrium between the $P_4O_6 \cdot xBH_3$ complexes and the gaseous diborane molecule.

Equilibrium Studies. In the work described thus far, it has been observed that the distribution of molecular species did not vary with time in closed tubes unless there was a phase change. In the liquid phase, the distribution was found to change only when the over-all $R \equiv BH_3/P_4O_6$ ratio was modified. Such modification may be achieved as follows: (1) bubbling of gaseous diborane into compositions for which $R < 2.35$, (2) presumed incorporation of B_2H_6 under pressure to raise R above 2.35 (not investigated in these studies), (3) fractional crystallization and redissolution of $P_4O_6 \cdot 3BH_3$, (4) addition of P_4O_6, (5) addition of crystalline $P_4O_6 \cdot 2BH_3$, and (6) admixing of two previously prepared samples. The new distribution of species resulting from any of these operations is promptly reached (<5 min) and depends only on the new BH_3/P_4O_6 over-all ratio. Thus, when the experimental distribution in mole percentage of each species is plotted against the BH_3/P_4O_6 mole ratio, mixtures prepared by any of these procedures are found to fit on the same curves (see Table I herein and the figure of ref 5). Furthermore, the presence of an unreactive solvent has no noticeable effect on the molecular distribution. This proves the existence of a dynamic metastable equilibrium between the various molecular species corresponding to each BH_3/P_4O_6 value.

The equilibria involving the various molecular

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

(8) J. Riess and J. R. Van Wazer, *Bull. Soc. Chim. France*, in press.

species $P_4O_6 \cdot xBH_3$, where $x = 0, 1, 2, 3$, and perhaps 4, may be formally treated as a scrambling of boron groups *vs.* pairs of unshared electrons on the central P_4O_6 moiety which exhibits four exchangeable sites.[9] All of the equilibria between the various complexes can thus be described by a minimum set of three equilibrium constants. Suitable constants may be derived for the chemical equation

$$2P_4O_6 \cdot xBH_3 = P_4O_6 \cdot (x+1)BH_3 + P_4O_6 \cdot (x-1)BH_3 \qquad (1)$$

where $x = 1, 2$, or 3. Two of the constants, $K_1 = [P_4O_6 \cdot 2BH_3][P_4O_6]/[P_4O_6 \cdot BH_3]^2$ and $K_2 = [P_4O_6 \cdot 3BH_3] \cdot [P_4O_6 \cdot BH_3]/[P_4O_6 \cdot 2BH_3]^2$, have been computed[10] from the experimental data collected in Table I. Weighted-average values are $K_1 = (4.0 \pm 0.4) \times 10^{-3}$ and $K_2 = (6.7 \pm 0.6) \times 10^{-3}$. The third equilibrium constant, $K_3 = [P_4O_6 \cdot 4BH_3][P_4O_6 \cdot 2BH_3]/[P_4O_6 \cdot 3BH_3]^2$, cannot be calculated directly since the low concentration of $P_4O_6 \cdot 4BH_3$ in a solution under a 1 atm pressure of B_2H_6 prevented us from detecting it by nmr. However, K_3 could be estimated by choosing the value which, along with the directly determined values of K_1 and K_2, would produce the best fit between the calculated and observed molecular distributions for the higher values of $R = BH_3/P_4O_6$ at equilibrium. This gave $K_3 \approx 4 \times 10^{-3}$. In Table I, the observed distributions of $P_4O_6 \cdot xBH_3$ molecules obtained on 33 different preparations are compared with the distributions (see the numbers given in parentheses) calculated from these values of K_1, K_2, and K_3. It should be noted that the agreement between the experimental data and the phenomenological theory based on three constants (without using activity coefficients other than unity) is gratifyingly good.

There is one further equilibrium constant needed to describe the B_2H_6–P_4O_6 system at metastable equilibrium at 25°, and this is the relationship between the solution composition and the B_2H_6 partial pressure. In Figure 3, a plot is given of the change in the uncoordinated phosphorus atoms of the P_4O_6 molecules with time as presented in terms of the over-all BH_3/P_4O_6 mole ratio of the solution resulting from bubbling diborane into a P_4O_6 solution at a constant slow rate. These data show that, under 1 atm of B_2H_6, the R value levels off at 2.35, as previously noted. According to Table I, this R value corresponds to 63.6 mole % of $P_4O_6 \cdot 2BH_3$ and 35.6 mole % of $P_4O_6 \cdot 3BH_3$. We may then set up the following equilibrium equation.

$$2[P_4O_6 \cdot 3BH_3](l) \rightleftarrows 2[P_4O_6 \cdot 2BH_3](l) + [B_2H_6](g) \qquad (2)$$

For liquid concentrations in mole percentages and gaseous pressures in atmospheres, we have the fourth equilibrium constant needed to define the system fully.

$$K' = [P_4O_6 \cdot 2BH_3]^2[B_2H_6]/[P_4O_6 \cdot 3BH_3]^2 = 3.2 \text{ atm} \qquad (3)$$

Table I. Distribution of Molecular Species for P_4O_6–BH_3 Complexes in Solution at Equilibrium at 25°

No.	$R = BH_3/P_4O_6$	P_4O_6	$P_4O_6 \cdot 1BH_3$	$P_4O_6 \cdot 2BH_3$	$P_4O_6 \cdot 3BH_3$	$P_4O_6 \cdot 4BH_3$
1[a]	0.42	57.9 (58.1)	42.1 (41.8)	0.0 (0.1)	0.0 (0.0)	0.0 (0.0)
2[d]	0.54	46.4 (46.3)	53.6 (53.5)	0.0 (0.2)	0.0 (0.0)	0.0 (0.0)
3[b]	0.79	21.5 (22.0)	79.5 (76.9)	0.0 (1.1)	0.0 (0.0)	0.0 (0.0)
4[a]	0.99	6.5 (6.1)	88.0 (88.7)	5.5 (5.1)	0.0 (0.0)	0.0 (0.0)
5[a]	1.01	5.2 (5.1)	88.7 (88.7)	6.1 (6.1)	0.0 (0.0)	0.0 (0.0)
6[d]	1.07	3.3 (3.0)	86.5 (86.9)	10.2 (10.0)	0.0 (0.0)	0.0 (0.0)
7[c]	1.08	3.4 (2.8)	85.3 (86.4)	11.3 (10.7)	0.0 (0.0)	0.0 (0.0)
8[c]	1.14	1.2 (1.7)	83.8 (82.5)	15.0 (15.7)	0.0 (0.0)	0.0 (0.0)
9[c]	1.21	0.5 (1.1)	77.7 (76.9)	21.8 (21.9)	0.0 (0.0)	0.0 (0.0)
10[b]	1.29	0.6 (0.7)	70.2 (69.8)	29.2 (29.5)	0.0 (0.1)	0.0 (0.0)
11[a]	1.36	0.2 (0.4)	63.9 (63.2)	35.9 (36.2)	0.0 (0.1)	0.0 (0.0)
12[c]	1.44	(0.0) (0.3)	(56.1) (55.7)	(43.9) (43.8)	(0.0) (0.2)	0.0 (0.0)
13[c]	1.58	0.0 (0.1)	42.5 (42.3)	57.5 (57.1)	0.0 (0.5)	0.0 (0.0)
14[d]	1.62	0.0 (0.1)	38.4 (38.4)	61.6 (60.8)	0.0 (0.6)	0.0 (0.0)
15[a]	1.68	0.0 (0.0)	32.1 (32.8)	67.9 (66.3)	0.0 (0.9)	0.0 (0.0)
16[a]	1.98	0.0 (0.0)	8.9 (8.1)	84.1 (85.8)	7.0 (6.1)	0.0 (0.0)
17[e]	2.01 (2.00]	0.0 (0.0)	7.7 (7.0)	83.5 (85.9)	8.7 (7.0)	0.0 (0.0)
18[c]	2.03	(0.0) (0.0)	(7.3) (5.7)	82.2 (85.6)	10.5 (8.7)	0.0 (0.0)
19[c]	2.05	0.0 (0.0)	6.2 (4.9)	83.1 (85.1)	10.8 (9.9)	0.0 (0.0)
20[i]	2.21	0.0 (0.0)	1.7 (1.7)	75.3 (75.6)	23.0 (22.6)	0.0 (0.0)
21[a]	2.22	0.0 (0.0)	2.4 (1.6)	73.6 (74.8)	24.0 (23.5)	0.0 (0.0)
22[a]	2.27	0.0 (0.0)	1.5 (1.2)	69.7 (70.6)	28.8 (28.1)	0.0 (0.0)
23[a]	2.31	0.0 (0.0)	1.7 (1.0)	65.1 (67.1)	33.2 (31.8)	(0.0) (0.1)
24[a]	2.32	0.0 (0.0)	0.8 (0.9)	66.2 (66.3)	33.0 (32.8)	0.0 (0.1)
25[a]	2.35	0.0 (0.0)	1.0 (0.8)	63.4 (63.6)	35.6 (35.6)	0.0 (0.1)
26[a]	2.35	0.0 (0.0)	1.0 (0.8)	63.5 (63.6)	35.5 (35.6)	0.0 (0.1)
27[a]	2.35	0.0 (0.0)	0.0 (0.8)	64.4 (63.6)	35.6 (35.6)	0.0 (0.1)
28[h]	2.35	0.0 (0.0)	0.0 (0.8)	65.0 (63.6)	35.0 (35.6)	0.0 (0.1)
29[a]	2.36	0.0 (0.0)	(0.0) (0.7)	63.8 (62.6)	36.2 (36.6)	0.0 (0.1)
30[a]	2.36	0.0 (0.0)	0.0 (0.7)	63.6 (62.6)	36.4 (36.6)	0.0 (0.1)
31[j]	2.43	0.0 (0.0)	0.0 (0.5)	57.4 (56.2)	42.6 (43.2)	0.0 (0.1)
32[g]	2.43	0.0 (0.0)	0.0 (0.5)	56.7 (56.2)	43.4 (43.2)	0.0 (0.1)
33[f]	2.56	0.0 (0.0)	0.0 (0.2)	44.0 (43.8)	56.0 (55.7)	0.0 (0.3)

[a] By bubbling B_2H_6 through P_4O_6 in a solvent. [b] By bubbling B_2H_6 through P_4O_6 without a solvent. [c] By admixing two samples or addition of P_4O_6 to a previously prepared sample. [d] By admixing P_4O_6 to $P_4O_6 \cdot 2BH_3$ in $CHCl_3$. [e] A chloroform solution of recrystallized $P_4O_6 \cdot 2BH_3$ - the theoretical R value is given in the square brackets. [f] A fresh solution of the crystals obtained by cooling sample #27. [g] and [h] The same solution 2 min and 10 min later at 38° and atmospheric pressure. [i] The supernatant solution of the cooled sample #27. [j] Similar solution of crystals obtained by cooling sample #24.
Values in parentheses were calculated from $K_1 = 4.0 \times 10^{-3}$, $K_2 = 6.7 \times 10^{-3}$, and $K_3 = 4.0 \times 10^{-3}$.

Interpretation of the P[31] Nmr Data. According to a recent quantum-mechanical analysis,[11] the P^{31} chem-

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(9) J. R. Van Wazer and K. Moedritzer, *Angew. Chem. Intern. Ed. Engl.*, 5, 341 (1966); J. R. Van Wazer, *Am. Scientist*, 50, 450 (1962).

(10) L. C. D. Groenweghe, J. R. Van Wazer, and A. W. Dickinson, *Anal. Chem.*, 36, 303 (1964).

ical shift, δ, of compounds based on either triply or quadruply connected phosphorus consists of additive contributions due to the σ and π orbitals, *i.e.*, $\delta = \delta_\sigma + \delta_\pi$. The σ contribution, δ_σ, is a function of the bond angles and electronegativities of the atoms bonded to the phosphorus, while δ_π is simply proportional to the total occupation of the d_π orbitals of the phosphorus. Because of the cage structure of the P_4O_6 moiety, the bond angles are reasonably fixed so that we shall assume that the median value[12] of the OPO bond angles of the uncomplexed phosphorus atoms is 99° and of the complexed atoms is 101.5°. On this basis and the assumption that the Pauling electronegativity of the bridging oxygens is maintained at a constant value of 3.51, we obtain[11] eq 4 and 5 as reasonable approximations of the chemical shift (in ppm, referenced to H_3PO_4) for the phosphorus atoms in a P_4O_6 complex.

For the uncomplexed phosphorus atoms

$$\delta_u = -35 - 400n_\pi - 36\Delta\theta \tag{4}$$

For the complexed phosphorus atoms

$$\delta_c = -201 + 187\chi_M - 21\chi_M^2 - 147n_\pi - (24 - 8\chi_M)\Delta\theta \tag{5}$$

n_π is the total occupation of the d_π orbitals of the phosphorus atom in question, χ_M is the Pauling electronegativity of the Lewis acid complexing agent (in the range $1.6 \leq \chi_M \leq 2.2$), and $\Delta\theta$ is the difference in the OPO bond angle from 99° for the uncoordinated phosphorus and 101.5° for the coordinated phosphorus.

The experimental P^{31} chemical-shift data on the borane and tricarbonylnickel complexes of phosphorus trioxide are summarized in Figure 4. Upon application of eq 4 and 5 to these data on the assumption[13] that the Pauling electronegativity of the boron of the BH_3 group is 2.0 and of the nickel is 1.8 (with no allowance for a contact shift since the nickel is diamagnetic), we see that, in both cases, upon coordination, the total occupation of the d_π orbitals of the phosphorus is raised from *ca.* 0.2 to *ca.* 1.8 electrons/P, with little difference between the effect of nickel and boron. In other words, the *downfield* shift of 10–20 ppm observed upon coordinating a P_4O_6 phosphorus with a nickel atom as compared to the *upfield* shift of about the same magnitude upon coordinating with boron follows from the difference in Pauling electronegativities between these two substituents and the fact that the chemical shifts calculated for zero occupation of the phosphorus d_π orbitals are in the neighborhood of +80 ppm. The observed decrease in chemical shifts (see Figure 4) of the coordinated phosphorus atoms upon successive coordination may be due to small increases (*ca.* 0.03 electron/P) in the occupation of the d_π orbitals of the phosphorus, but this effect may also be totally accounted for by a bond-angle change of 1–2°, as indicated by eq 5. The observed changes in the chemical shifts of the uncoordinated phosphorus atoms upon the coordination of other phosphorus atoms in the P_4O_6 molecule may be entirely accounted for by OPO bond-angle changes of less than 0.2°, according to eq 4.

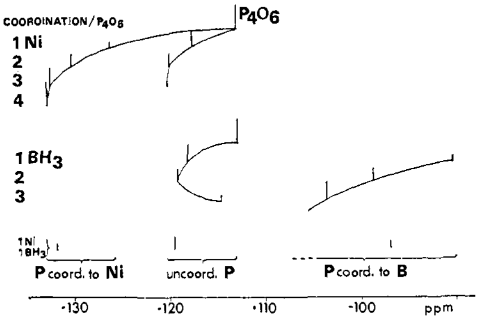
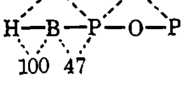


Figure 4. The P^{31} chemical shifts of P_4O_6 and its complexes with tricarbonylnickel and with borane. The heights of the lines denote the relative areas of the complexed and uncomplexed peaks.

Since boron does not have available orbitals for π bonding, the d_π occupation of the phosphorus orbitals calculated from the chemical-shift data must come completely from electrons supplied by the three oxygen atoms. It should be noted that the increase in total occupation of the phosphorus d_π orbitals from *ca.* 0.2 to 1.8 electrons per P upon coordination of oxygen-bonded triply connected phosphorus by either nickel or boron is approximately equal to the increase in d_π occupation observed when the unshared pair is employed to bond with[11,14] either oxygen or sulfur. These findings are in accord with the idea that π bonding is a complicated feedback mechanism for the avoidance of a buildup of positive charge on the phosphorus when it loses its unshared pair of electrons through bond formation with another atom. All other things being equal, such electronic balancing upon conversion of an unshared pair to a bond should be relatively insensitive to the electronegativity of the element with which this bond is formed since the polarity of a bond due to a difference in electronegativity of the bonded atoms represents a small electronic perturbation as compared to the transition from an unshared pair (abortive bond) to an electron-sharing bond.

Typical coupling constants (in cps) for the borane complexes of phosphorus trioxide may be summarized as



The B–P coupling constant is about half as large as the

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(11) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1966). Note: The correct values are $f(3) = 0.0189$ and $f(4) = 0.0067$. These were the values employed in the calculations of this reference.

(12) The OPO bond angles in P_4O_6 have been determined by electron diffraction to be 99 ± 1° and of P_4O_{10} to be 101.5 ± 1°, according to G. C. Hampson and A. J. Stosick, *J. Am. Chem. Soc.*, **60**, 1814 (1938). Also see L. R. Maxwell, S. B. Hendricks, and L. S. Deming, *J. Chem. Phys.*, **5**, 626 (1937). In the P_4O_9 cage structure, the OPO bond angles of the triply connected phosphorus atom were found to be 98°, whereas the OPO bond angles of the three phosphoryl groupings are 103°, according to K. H. Jost, *Acta Cryst.*, **17**, 1593 (1964).

(13) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 93; also see W. Gordy and W. J. O. Thomas, *J. Chem. Phys.*, **24**, 439 (1956).

(14) J. R. Van Wazer, *J. Am. Chem. Soc.*, **78**, 5709 (1956).

B–H, probably because each electron of the pair donated by the phosphorus has only *ca.* $^1/_4$ s character, while the electron donated by the hydrogen is a pure s orbital.[15] The difference between the H–B–P and the P–O–P coupling is not as readily explained in simple terms, even when the relativistic correction is invoked.

Acknowledgment. We wish to thank Dr. Peter J. Wheatley for the X-ray data on the $P_4O_6 \cdot 2BH$ complex as well as for its interpretation.

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(15) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 8.