Crystal and Molecular Structure of a Caged Polycyclic Tetraoxycarbophosphorane, $(PO_4C)(C_6H_5CN)(CF_3)_2(C_6H_9)$

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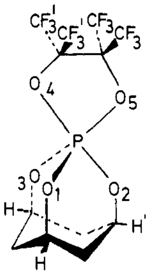
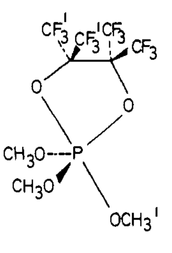
Received June 19, 1974

Abstract: The reaction of 2-benzoylimino-1,1,1,3,3,3-hexafluoropropane with 1-phospha-2,8,9-trioxaadamantane gives a caged carbotetraoxyphosphorane. X-Ray crystallographic analysis shows that the phosphorus is at the center of a *distorted* trigonal bipyramid with the five-membered ring in an apico–equatorial skeletal position, the ring oxygen apical and the ring carbon equatorial. The magnitudes and the directions of the distortions from the ideal D_{3h} skeletal symmetry are nearly identical in this molecule and in its azatetraoxyphosphorane analog. The C_3-skeletal axis is bent (167.8° angle); the diequatorial angle of the adamantanoid cage has contracted (106.6° angle); the apico–equatorial angle of the five-membered ring has also contracted (83.3° angle). The introduction of the adamantanoid cage into a molecule which has four oxygens and a fifth ligand bonded to phosphorus has a different effect on the ^{31}P nmr chemical shift when the fifth ligand is carbon, than when it is nitrogen or oxygen.

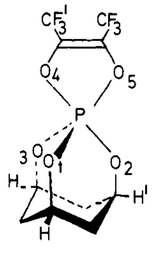
The ligands to the phosphorus in the caged polycyclic pentaoxyphosphorane[2] **1** exchange positions on the skeletal sites by a process of intramolecular bond deformations in solutions of the compound in the temperature range 30 to −165°, according to ^1H, ^{19}F, ^{13}C, and ^{31}P nmr spectroscopy.[3,4] This phenomenon has also been observed, at least in the temperature range 30 to *ca.* −50°, in solutions of the caged unsaturated *pentaoxyphorane,*[5] **3**, and azatetraoxyphosphorane,[6] **5**, as well as in solutions of the monocyclic analogs,[7] **2**, **4** and **6**.



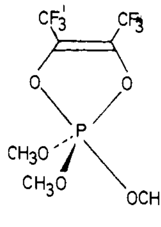
1, $\delta^{31}P$ = +42.4 PPM
vs. H_3PO_4 =O



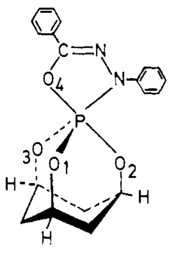
2, $\delta^{31}P$ = +49.7 PPM



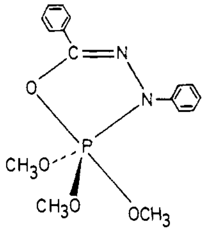
3, $\delta^{31}P$ = +41.7 PPM



4, $\delta^{31}P$ = +46.7 PPM

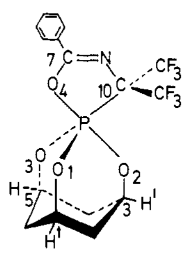


5, $\delta^{31}P$ = +56.8 PPM

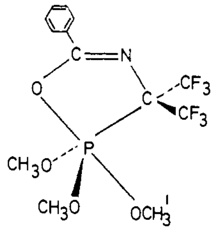


6, $\delta^{31}P$ = +56.7 PPM

X-Ray crystallography[6] shows that in the molecule of the caged azaphosphorane **5** the phosphorus atom is at the center of a *distorted* trigonal bipyramid (TBP[8]). This paper describes the synthesis and the X-ray crystallographic analysis of the caged carbophosphorane **7**. We were concerned with: (a) the effect on the molecular structure caused by the substitution of a carbon ligand for a nitrogen ligand; (b) the effect of this substitution on the permutational isomerization (PI[8]) of the molecules in solution; (c) the influence exerted by the adamantanoid cage on the ^{31}P nmr shift of monocyclic oxyphosphoranes having different types of ligands: **2** → **1**, **4** → **3**, **6** → **5**, and **8** → **7**.



7, $\delta^{31}P$ = +17.9 PPM



8, $\delta^{31}P$ = +34.7 PPM

The monocyclic carbophosphorane **8** was first described by Burger, *et al.*[9]

Experimental Section

Preparation of 2-Benzoylimino-1,1,1,3,3,3-hexafluoropropane (10).[9-11] Hexafluoroacetone was introduced slowly into a stirred suspension of benzamide (60 g) in CH_2Cl_2 (300 ml) containing *p*-toluenesulfonic acid (100 mg), at 40°. The reaction was carried out in a flask fitted with a gas inlet and a condenser cooled by a Dry Ice–acetone mixture. Hexafluoroacetone was bubbled for an additional 3 hr after a clear solution had been obtained (*ca.* 8 hr). The solvent was evaporated (30°, 30 mm), and the residue was recrystallized from hexane to give 2-benzamido-2-hydroxy-1,1,1,3,3,3-hexafluoropropane (**9**, 115 g, 80% yield, mp 65–67°).

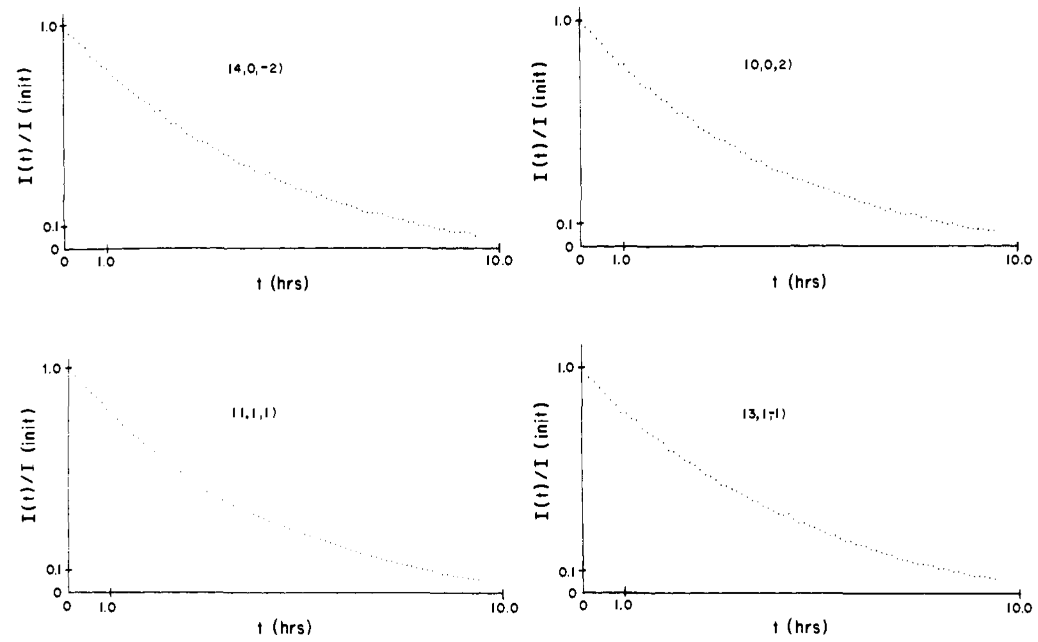


Figure 1. The average curve of the intensity decline for the four check reflections.

The hydroxyamide **9** (14.6 g, 50 mmol) and quinolinium trifluoroacetate (12.3 g, 50 mmol, from quinoline and trifluoroacetic acid) were dissolved in trifluoroacetic anhydride (22 ml). The solution was diluted with ether (40 ml) and was kept 3.5 hr at reflux temperature, and overnight at 20°, with stirring. The clear solution was slowly treated with a solution of quinoline (18 ml) in ether (75 ml), which caused the immediate precipitation of quinolinium trifluoroacetate. The mixture was kept 1 hr at 20°, 1 hr at 0°, and was then filtered. The solution was concentrated to *ca.* 25 ml (at 30° and 30 mm), and was filtered again. The last traces of solvent were removed, and the residue was distilled to give 2-benzoylimino-1,1,1,3,3,3-hexafluoropropane[9,11] (**10**, 10.6 g, 80% yield, bp 43-44° at 0.7 mm). The imine **10** had the following ir bands (in cm^{-1}, in CH_2Cl_2 solution): 1739, 1701, 1597, 1445, 1321, 1241, 1198, 1037, 1018, and 990.

Reaction of 2-Benzoylimino-1,1,1,3,3,3-hexafluoropropane (10) with 1-Phospha-2,8,9-trioxaadamantane[12] (11). A solution of the phosphite[12] (**11**, 1.02 g) in methylene chloride (5 ml) was added dropwise (20 min) to a stirred solution of the imine (10, 1.71 g, 1 mol equiv) in methylene chloride (5 ml), at 20°, under Ar. The solution was stirred 12 hr at 20°, and was evaporated at 30° (30 mm). The residue was dissolved in hot benzene (6 ml), and the solution was diluted with hexane and cooled to −5°. The carbophosphorane 7 (2.2 g, 80% of the theory) separated as crystals which contained 0.5 mol benzene of crystallization, mp *ca.* 129-133°, with decomposition. The benzene of crystallization was readily lost on standing at 20°; therefore, the elemental analysis varied with the treatment of the sample. The best figures for the benzene-free compound were the following.

Anal. Calcd for $C_{16}H_{14}O_4NF_6P$: C, 44.8; H, 3.3. Found: C, 44.7; H, 3.4.

$C_{16}H_{14}O_4NF_6P \cdot 0.5C_6H_6$ requires: C, 48.7; H, 3.7. One sample which was not completely free from benzene analyzed as: C, 46.7; H, 3.8.

The ir spectrum of 7 in KBr disk had the following main bands (in cm^{-1}): 1620, 1580, 1450, 1350, 1310, 1260, 1240, 1220, 1200, 1105, 1070, 940, 920.

The sample of 7 used for X-ray crystallographic analysis was prepared as follows. The sample (0.65 g) was dissolved in hot benzene (3 ml); the hot solution was diluted with hexane (1.5 ml), and cooled to 4°. Crystals of suitable size were obtained in *ca.* 30 min and were kept under the solvent until the X-ray analysis was undertaken.

The analogous reaction of the imine **10** with trimethyl phosphite gave the monocyclic carbophosphorane **8**, mp 87-88° (hexane), δ ^{31}P +34.7 ppm (CH_2Cl_2), τ CH_3O 6.28 ppm, and J_{HCOP} = 13.0 Hz, in agreement with data in the literature.[9]

Crystal Data. Compound 7: $C_{16}H_{14}NO_4PF_6 \cdot 0.5C_6H_6$; monoclinic; $P2_1/c$; a = 17.188 (6), b = 8.904 (4), c = 14.511 (6) Å, β = 114.60 (3) (λ Cu Kα at 21°); Z = 4; μ(Cu Kα) = 11.56 cm^{-1}; d_{calcd} = 1.54 g/cm^{-1}.

Data Collection and Structure Refinement. It was found from preliminary attempts to collect the intensity data for 7 that the crystals showed a rapid loss of intensity during the data collection process. It was assumed that this intensity loss was primarily due to the loss of benzene of crystallization from the crystal surface. Sealing the crystals in capillaries was not effective. Therefore, the crystals were coated with Krylon immediately after being glued onto a glass fiber. For the data collection, three crystals were used. For the first crystal, all of the data out to 2θ = 130° were recorded by the θ-2θ scan technique at a scan rate of 24°/min using Cu Kα (λ 1.5418 Å) radiation. Four check reflections were measured at intervals of ~15 min. The X-ray exposure time for this data collection was 9.5 hr with the elapsed time being ~15 hr. The intensities of the four check reflections fell off to 6% of their original values. Figure 1 shows the intensity decline as a function of time for the four check reflections.

The data collection for crystal 2 was carried out in a manner similar to the first crystal except that the data were collected to 2θ = 90°. The exposure time during the data collection on this crystal was 3.3 hr. For the third crystal the data were collected for the h = 0-2 reflections out to 2θ = 90°; then the shell of data between 2θ = 80 and 2θ = 120° was collected for all values of h. The total exposure time for the third crystal was ~4.8 hr. The data from the three crystals were scaled using the 441 data with $I \geq 4\sigma(I)$ which were common to all three data sets. Before the scaling was done, the data were corrected for decay using curves computed from the check reflections.

The 3443 independent structure amplitudes were derived in the usual way. No absorption or extinction corrections were applied. Normalized structure factors were used in a multiple solution direct methods technique—MULTAN.[13] The first E-map revealed most of the atoms. The rest of the atoms including the centrosymmetric benzene of crystallization were derived from subsequent Fourier maps. The structure was refined by full-matrix least-squares, minimizing $w(\Delta F)$ where $\Delta F = |F_o| - |F_c|$ and $w = 1/\sigma$. For $1.8 < F_o < 14$, $\sigma = 2.1 + 0.14F_o$: $F_o < 14$, $\sigma = 4.2$: $F_o < 1.8$, $w = 0.0$.

The atomic scattering factors for all non-hydrogen atoms were taken from the International Tables;[14] the scattering factors for hydrogen atoms are those of Stewart, Davidson, and Simpson.[14] The hydrogen atoms were placed in calculated locations, and their temperature factors were chosen to be the same as the atoms to which they are bonded. The non-hydrogen atoms were refined an-

Table I. The Final Fractional Coordinates ($\times 10^4$) and Anisotropic Thermal Parameters (and their esd's in parentheses)[a]

(a) Refined Parameters of Heavy Atoms

	x	y	z
P	2105 (2)	303 (3)	4702 (2)
N	2129 (6)	−1426 (12)	3118 (7)
O(1)	2747 (5)	−154 (10)	5782 (6)
O(2)	1226 (5)	220 (12)	4834 (7)
O(3)	2167 (7)	2059 (12)	4635 (8)
O(4)	2933 (5)	237 (11)	4301 (7)
C(1)	2688 (9)	692 (17)	6612 (9)
C(2)	1813 (10)	462 (19)	6638 (11)
C(3)	1128 (10)	1098 (23)	5646 (12)
C(4)	1277 (14)	2755 (26)	5488 (13)
C(5)	2157 (14)	2899 (19)	5518 (13)
C(6)	2810 (12)	2320 (22)	6443 (14)
C(7)	2785 (7)	−618 (14)	3514 (8)
C(8)	1504 (9)	−2691 (15)	4048 (10)
C(9)	709 (8)	−639 (20)	2812 (11)
C(10)	1581 (6)	−1179 (12)	3652 (8)
F(81)	1227 (6)	−3740 (10)	3362 (7)
F(82)	2255 (5)	−3157 (9)	4739 (7)
F(83)	979 (6)	−2732 (10)	4518 (8)
F(91)	78 (4)	−706 (11)	3085 (6)
F(92)	487 (5)	−1442 (13)	1969 (6)
F(93)	790 (5)	770 (13)	2577 (6)
C(1′)	3481 (6)	−607 (9)	3144 (7)
C(2′)	3343 (7)	−1366 (12)	2255 (9)
C(3′)	3956 (8)	−1392 (14)	1864 (9)
C(4′)	4719 (7)	−586 (11)	2404 (9)
C(5′)	4869 (8)	156 (13)	3279 (9)
C(6′)	4231 (7)	178 (11)	3687 (8)
C(1B)	5061 (16)	1374 (17)	399 (13)
C(2B)	5778 (13)	659 (26)	572 (13)
C(3B)	5747 (14)	−786 (27)	185 (14)

	B_{11}	B_{12}	B_{33}	B_{12}	B_{13}	B_{23}
P	3.7 (1)	3.4 (1)	3.0 (1)	−0.0 (1)	1.3 (0)	−0.8 (1)
N	2.6 (4)	7.5 (5)	4.0 (4)	−1.0 (4)	1.1 (3)	−1.7 (4)
O(1)	4.7 (4)	6.3 (5)	3.9 (3)	0.4 (3)	1.8 (3)	−0.6 (3)
O(2)	4.5 (4)	9.0 (6)	5.8 (4)	−1.5 (4)	2.8 (3)	−3.8 (4)
O(3)	12.1 (7)	6.5 (5)	6.6 (5)	2.5 (5)	6.1 (5)	0.5 (4)
O(4)	5.1 (4)	7.3 (5)	7.5 (5)	−2.8 (3)	4.5 (4)	−3.2 (4)
C(1)	7.0 (8)	6.6 (8)	4.7 (5)	−0.9 (6)	2.8 (5)	−3.4 (5)
C(2)	8.5 (9)	8.1 (9)	6.4 (7)	−1.0 (7)	5.3 (7)	−1.3 (7)
C(3)	5.3 (8)	13.0 (12)	5.6 (8)	−1.1 (8)	3.2 (6)	−5.1 (8)
C(4)	10.2 (12)	9.5 (13)	8.0 (10)	4.8 (10)	2.2 (9)	−1.5 (9)
C(5)	11.0 (12)	5.7 (9)	7.5 (9)	2.7 (8)	3.3 (9)	0.2 (7)
C(6)	9.4 (10)	8.2 (11)	6.9 (11)	−2.8 (9)	3.6 (9)	−5.9 (9)
C(7)	3.7 (4)	3.7 (6)	3.5 (4)	−0.0 (4)	2.1 (4)	−0.3 (4)
C(8)	5.0 (6)	5.8 (6)	4.1 (5)	−1.1 (5)	1.4 (5)	−1.2 (5)
C(9)	3.3 (5)	8.5 (9)	5.0 (6)	−0.2 (6)	1.6 (5)	0.9 (7)
C(10)	2.8 (4)	3.5 (4)	3.9 (4)	−1.1 (3)	9.5 (3)	−1.3 (3)
F(81)	8.4 (4)	7.4 (4)	8.3 (4)	−4.5 (4)	3.8 (4)	−3.6 (4)
F(82)	7.0 (4)	4.0 (3)	8.6 (5)	0.1 (3)	0.6 (3)	0.7 (3)
F(83)	11.1 (6)	6.7 (5)	12.4 (7)	1.0 (4)	9.0 (6)	2.3 (4)
F(91)	2.9 (3)	11.2 (6)	6.5 (4)	0.5 (3)	1.8 (2)	0.6 (4)
F(92)	5.0 (4)	16.5 (8)	4.6 (3)	−0.3 (4)	0.1 (3)	−3.1 (4)
F(93)	4.9 (4)	12.2 (7)	6.4 (4)	1.2 (4)	1.0 (3)	4.3 (4)
C(1′)	4.4 (4)	0.5 (3)	3.3 (3)	0.1 (3)	1.4 (3)	0.8 (3)
C(2′)	3.8 (5)	4.3 (5)	4.7 (5)	0.1 (4)	2.6 (4)	0.4 (4)
C(3′)	5.9 (6)	5.1 (5)	4.6 (5)	1.6 (5)	2.8 (5)	0.4 (4)
C(4′)	5.4 (6)	8.5 (5)	4.9 (5)	−0.0 (5)	3.0 (5)	1.4 (4)
C(5′)	3.4 (6)	6.4 (5)	7.2 (5)	−1.0 (5)	1.2 (4)	1.0 (4)
C(6′)	2.8 (5)	5.1 (4)	5.9 (5)	−0.7 (4)	1.1 (4)	1.2 (4)
C(1B)	13.1 (12)	3.4 (7)	6.0 (8)	−0.9 (8)	4.0 (9)	−1.3 (6)
C(2B)	9.4 (11)	7.7 (12)	7.5 (9)	−1.4 (9)	3.4 (8)	−0.4 (9)
C(3B)	10.7 (13)	8.3 (13)	7.4 (9)	1.4 (10)	5.1 (9)	1.6 (9)

(b) Calculated Parameters for Hydrogen Atoms

	x	y	z	B
H(3)	0.052	0.095	0.562	7.0
H(2a)	0.179	0.099	0.726	7.0
H(2b)	0.170	−0.068	0.671	7.0
H(1)	0.316	0.030	0.729	6.0
H(6a)	0.287	0.297	0.707	7.5
H(6b)	0.341	0.247	0.640	7.5
H(5)	0.227	0.406	0.548	8.0

Table I (*Continued*)

	x	y	z	B
H(4a)	0.083	0.310	0.481	8.5
H(4b)	0.121	0.337	0.606	8.5
H(2′)	0.276	−0.193	0.189	4.0
H(3′)	0.386	−0.196	0.120	3.5
H(4′)	0.518	−0.056	0.213	6.2
H(5′)	0.544	0.070	0.365	2.9
H(6′)	0.433	0.073	0.434	3.3
H(1B)	0.513	0.243	0.074	6.9
H(2B)	0.637	0.109	0.095	8.0
H(3B)	0.630	−0.144	0.039	7.9

[a] Anisotropic temperature factors are of the form $\exp[-{}^1/_4(B_{11}h^2a^{*2} + \ldots + 2B_{12}hka^*b^* \ldots)]$ and B values are given in Å.

isotropically; the hydrogen atoms were not refined. The final values of

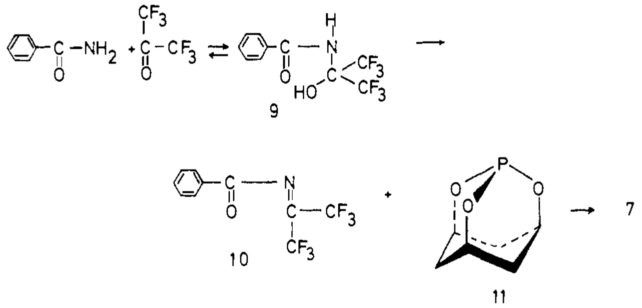
$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

and

$$R_2 = [(\Sigma w||F_o| - |F_c||^2)/\Sigma w|F_o|^2]^{1/2}$$

are 0.118 and 0.129, respectively for the 2014 reflections with nonzero weights. The positional and thermal parameters, including the calculated hydrogen positions are given in Table I. The thermal parameters should be most affected by the rapid deterioration of the crystals. Atom C(1′) shows the worst effect. The observed and calculated structure factors are given in Table II.[15]

Nmr Data for 7. The spectrum of a 1.65 *M* CH_2Cl_2 solution of the carbophosphorane, 7, at ambient temperature had one multiplet ^{31}P nmr signal at δ ^{31}P +17.9 ppm *vs.* H_3PO_4 = 0 (at 40.5 MHz). The addition of 2 mol equiv of the acidic alcohol $(CF_3)_2CHOH$ to the CH_2Cl_2 solution had no appreciable effect on the ^{31}P shift (δ ^{31}P +18.1 ppm). The ^{19}F nmr spectrum of a CH_2Cl_2 solution of 7 had one doublet, J_{FCCP} = 4 Hz, at δ ^{19}F −13.5 ppm *vs.* CF_3COOH = 0 (at 94.1 MHz). The ^1H nmr spectrum of a $CDCl_3$ solution of 7 had one doublet, J_{HCOP} = 23.0 Hz, with fine structure, at τ 5.13 ppm *vs.* TMS = 10 (at 60 MHz), and an AB quartet centered at τ 7.73 ppm. *The ^1H nmr spectra did not change appreciably from 30° to ca. −50°.*



Discussion of Results

Molecular Structure of 7. The interatomic distances[16] and bond angles, and their standard deviations, are summarized in Table III. The least-square planes are given in Table IV. The structure will be discussed with reference to Figure 2, which shows the vibrational thermal elipsoids for the atoms. Figure 2 includes the planar benzene of solvation.

The phosphorus atom is situated at the center of a *distorted* TBP,[8] with the five-membered ring in an apico-equatorial skeletal position, and the carbon equatorial. The deviations from the ideal skeletal TBP symmetry are as shown in Table V (*cf.* formula 7 and Figure 2). The magnitudes of the first three bond angles (Table V) disclose not only the deviations from ideal TBP symmetry but also the deviations from regularity in the adamantanoid cage, as follows: O(1)-P-O(3) = 106.6°, P-O(3)-C(5) = 115°, O(2)-P-O(1) = 100.2°, P-O(1)-C(1) = 116°, O(2)-P-O(3) = 98.3°, P-O(2)-C(3) = 120°. These effects probably represent a compromise between the tendency of five-coordinate phosphorus to acquire skeletal TBP symmetry,[4,7] and the tendency toward regularity on the part of the adamantanoid cage. The net result should be a relatively energetic molecule, 7, which in solution should undergo a relatively rapid PI according to a mechanism discussed in a later section.[3,4,6]

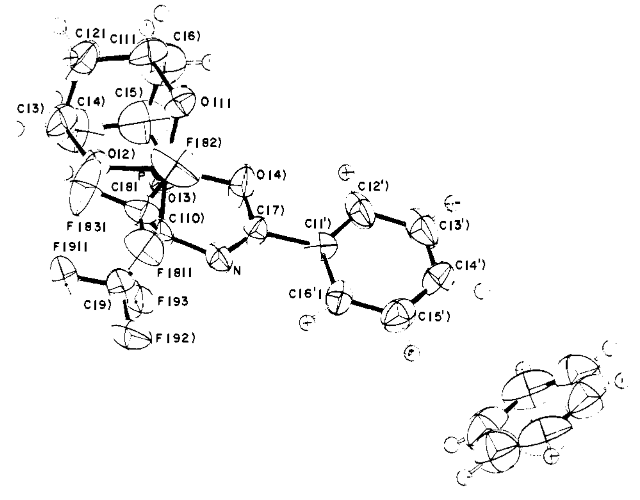


Figure 2. A drawing of one molecule with the benzene of crystallization showing the thermal ellipsoid.

The angle O(4)-P-O(2) corresponds to the threefold axis of the ideal D_{3h} point group, and it is clear that this axis is "bent" in the caged-phosphorane (note the deviations −12.3, −6.7, and −4.8°). One can speak of a slight tilt of ligands O(4) and C(10) toward O(2). The contraction of the angle O(4)-P-O(3) and the expansion of the angle C(10)-P-O(3) are also noteworthy.

The five-membered ring in 7 is a distorted pentagon, with angles ranging from O(4)-P-C(10) = 83.3° to O(4)-C(7)-N = 123°. The cyclohexane ring, on the other hand, has the classic chair conformation with torsion angles of −58.5, 55.6, 59.3, −56.3, 56.4, and −57.3°.

For comparison purposes, the bond angles of the distorted TBP phosphorus in the azaphosphorane,[6] 5, are included in Table III. The values are very close to those in the carbophosphorane 7. This point is emphasized in Figure 3a. The main difference between the two molecules is that the phenyl substituent on C(7) is nearly coplanar with the five-membered ring in the carbophosphorane 7 (angle of 8.5°), but not in the azaphosphorane 5 (angle of 19.8°); *cf.* Figure 3b. This difference is understandable if the contribution of resonance structure **7a** is more significant than that of **5a** to their respective hybrids, due to a greater stabilization of the formal negative charge on nitrogen by the electron-withdrawing CF_3 groups (*vis-a-vis,* the anilino group). The

Table III. Bond Distances (Å) and Angles (deg) in the Polycyclic Carbotetraoxyphosphorane, Compound 7[a]

(a) In Trigonal Bipyramid (Corresponding Values for the Polycyclic Azatetraoxyphosphorane, Compound **5**, Are Included)

Bond angles (deg)	7	**5**	Bond distances (Å)	7	**5**
O(4)–P–O(2)	167.7	169.8	P–O(4)	1.749	1.754
O(4)–P–C(10)[b]	83.3	83.8	P–O(2)	1.602	1.627
O(4)–P–O(1)	89.6	87.0	P–O(1)	1.549	1.601
O(4)–P–O(3)	85.9	89.4	P–O(3)	1.573	1.590
O(2)–P–C(10)[b]	85.2	86.4	P–C(10)[b]	1.949	1.671
O(2)–P–O(1)	100.2	97.1			
O(2)–P–O(3)	98.3	98.4			
O(1)–P–C(10)[b]	121.7	129.5			
O(1)–P–O(3)	106.6	106.3			
C(10)[b]–P–O(3)	130.1	123.1			

(b) In Phenyl Group

A	B	C	∠ABC (deg)	*D*(A–B) (Å)	*D*(BC) (Å)
C(1′)	C(2′)	C(3′)	121	1.39	1.39
C(2′)	C(3′)	C(4′)	117	1.39	1.41
C(3′)	C(4′)	C(5′)	123	1.41	1.36
C(4′)	C(5′)	C(6′)	121	1.36	1.55
C(5′)	C(6′)	C(1′)	116	1.45	1.39
C(6′)	C(1′)	C(2′)	122	1.39	1.39

(c) In Five-Membered Ring

Bond angles (deg)				Bond distances (Å)		
C(10)	P	O(4)	83.3	C(10)	N	1.44
P	C(10)	N	109.3	C(10)	C(9)	1.55
P	C(10)	C(9)	112.4	C(10)	C(8)	1.50
P	C(10)	C(8)	112.1	N	C(7)	1.26
N	C(10)	C(8)	105	C(7)	O(4)	1.31
N	C(10)	C(9)	106	C(7)	C(1′)	1.50
C(10)	N	C(7)	109			
N	C(7)	O(4)	123			
N	C(7)	C(1′)	122			
C(1′)	C(7)	O(4)	114			
P	O(4)	C(7)	115			
C(7)	C(1′)	C(6′)	119			
C(7)	C(1′)	C(2′)	118			

(d) In CF_3 Groups

Bond angles (deg)				Bond distances (Å)		
C(10)	C(8)	F(81)	117	C(10)	C(8)	1.50
C(10)	C(8)	F(82)	111	C(8)	F(81)	1.30
C(10)	C(8)	F(83)	115	C(8)	F(82)	1.33
F(81)	C(8)	F(82)	106	C(8)	F(83)	1.34
F(82)	C(8)	F(83)	105	C(10)	C(9)	1.55
F(81)	C(8)	F(83)	105	C(9)	F(91)	1.30
C(10)	C(9)	F(91)	114	C(9)	F(92)	1.33
C(10)	C(9)	F(92)	111	C(9)	F(93)	1.32
C(10)	C(9)	F(93)	109			
F(91)	C(9)	F(92)	107			
F(92)	C(9)	F(93)	107			
F(91)	C(9)	F(93)	108			

(e) In Adamantanoid Ring

Bond angles (deg)				Bond distances(Å)		
P	O(1)	C(1)	116	C(1)	O(1)	1.46
P	O(3)	C(5)	115	O(3)	C(5)	1.49
P	O(2)	C(3)	120	O(2)	C(3)	1.48
O(1)	C(1)	C(2)	111	C(1)	C(2)	1.53
O(1)	C(1)	C(6)	108	C(2)	C(3)	1.54
C(2)	C(1)	C(6)	110	C(3)	C(4)	1.53
C(1)	C(2)	C(3)	108	C(4)	C(5)	1.50
O(2)	C(3)	C(2)	105	C(5)	C(6)	1.44
O(2)	C(3)	C(4)	108	C(6)	C(1)	1.50
C(2)	C(3)	C(4)	113			
C(3)	C(4)	C(5)	108			
O(3)	C(5)	C(4)	108			
O(3)	C(5)	C(6)	110			
C(4)	C(5)	C(6)	112			
C(1)	C(6)	C(5)	113			

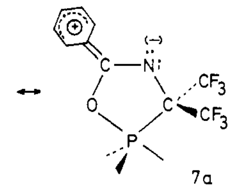
(f) In Benzene of Crystallization

A	B	C	∠(ABC) (deg)	*D*(AB) (Å)	*D*(BC) (Å)
C(1B)	C(2B)	C(3B)	119	1.31	1.40
C(2B)	C(3B)	C(1B)[c]	117	1.39	1.40
C(2B)	C(1B)	C(3B)[c]	124	1.31	1.39

[a] The esd's for phosphorus bond distances are 0.006 Å, and for bond angles 0.5°; for attached phenyl distances 0.012 Å, and for bond angles 1°; for benzene of crystallization, bond distances 0.03 Å, and bond angles 1.6°; for trifluoromethyl groups, bond distances 0.02 Å, bond angles 1.1°; cyclohexane bond distances 0.02 Å, bond angles 1.2°. [b] In compound **5** this is a nitrogen atom. [c] These are related by inversion center.

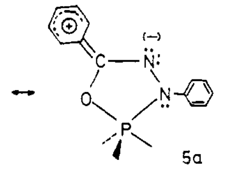
C(7)-phenyl substituent in **7** is planar within experimental error.

7



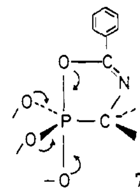
7a

5

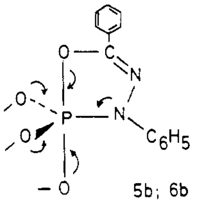


5a

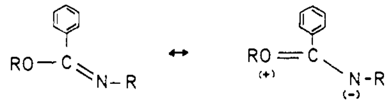
The bond distances in the carbophosphorane **7** follow the trend observed in other oxyphosphoranes which adopt the skeletal TBP symmetry with a certain degree of distortion.[6,18-20] The apical bond, P-O(2) is somewhat longer than the corresponding equatorial bonds,[21,22] P-O(1) and P-O(3). The apical P-O(4) bond is significantly longer than the apical P-O(2) bond. This effect has also been observed in the azaphosphorane[6] **5** and is in the direction to be expected if there is relatively less pπ-dπ back-bonding to the phosphorus from the apical five-membered endocyclic oxygen than from the apical six-membered endocyclic oxygen; *i.e.*, if there is a "steric inhibition of pπ-dπ back-bonding" (see **7b** and **5b**). The result would be a lower bond order and hence a longer bond distance P-O(4) > P-O(2). The usual resonance structures written for imido esters probably play an insignificant role in the phosphoranes **5, 6, 7**, and **8**.



7b; 8b



5b; 6b



The relationship, apical 5-endocyclic P-O > apical exocyclic P-O bond distances has been noted in phosphoranes derived from 1,3,2-dioxaphospholenes.[18] The C═C stretching vibration of these compounds[7,23] gives rise to an ir band at a remarkably high frequency, *ca.* 1740-1720 cm^{-1}, indicating a relatively high bond order for this group. This effect is again in agreement with the steric inhibition of pπ-

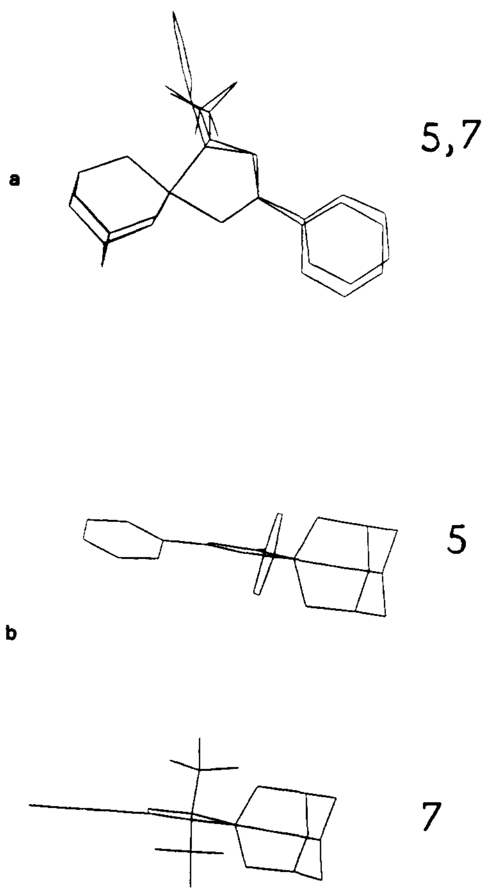
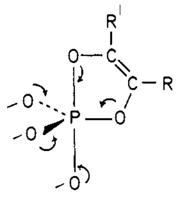
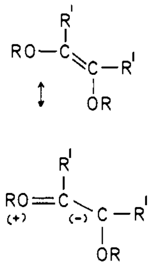


Figure 3. (a) A superposition of structures of compound 7 and compound 5. (b) A comparison of 7 and 5 emphasizing the noncoplanarity of the phenyl group with the five-membered ring in 5.

dπ back-bonding suggested above (*cf.* **3b, 4b**). The usual resonance structures written for enol ethers probably contribute little to the phosphorane hybrid in these compounds.



3b; 4b



The contents of the unit cell are shown in Figure 4. The shortest intermolecular contact involves two trifluoromethyl groups: $CF_3(8)\cdots CF_3(8)$. The benzene rings pack in the "herringbone" arrangement.

^{31}P Chemical Shifts. The displacement, $\Delta\delta$ ^{31}P, of the ^{31}P chemical shift caused by the introduction of the adamantanoid cage into the azaphosphorane, **6** → **5**, is negligible.[6] On the other hand, a significantly large displacement of the shift, Δ −17 ppm, toward lower magnetic field is observed when the cage is introduced into the carbophosphorane, **8** → **7**. A relatively small low-field displacement of the ^{31}P shift is observed[3,5] in the pentaoxyphosphoranes, **2** → **1** and **4** → **3**.

Table IV. Least-Squares Planes

(a) Five-Membered Ring
Equation of Plane
$-0.203x + 0.744y - 0.636z + 3.92 = 0$

Atom	Deviation (Å)
P	+0.02
O(4)	−0.03
C(10)	−0.01
N	+0.00
C(7)	+0.02

(b) Equational Plane of Trigonal Bipyramid
Equation of Plane
$0.972x - 0.027y - 0.233z + 0.607 = 0$

Atom	Deviation (Å)
P	−0.089
O(1)	+0.029
O(3)	+0.032
C(10)	+0.029

(c) Phenyl Ring
Equation of Plane
$-0.204x + 0.823y - 0.529z + 3.47 = 0$

Atom	Deviation (Å)
C(1′)	0.000
C(2′)	+0.003
C(3′)	−0.006
C(4′)	+0.007
C(5′)	−0.005
C(6′)	+0.001

(d) Benzene of Crystallization
Equation of Plane
$-0.402x - 0.394y + 0.826z + 3.46 = 0$

Atom	Deviation (Å)
C(1B)	+0.007
C(2B)	−0.007
C(3B)	+0.007
C(1B)	−0.007
C(2B)	+0.007
C(3B)	−0.007

[a] x, y, and z are in orthogonal coordinates with deviations of the individual atoms from the planes given in Å.

It is recognized that the interpretation of ^{31}P nmr shifts[24] in terms of structure is hazardous. Nevertheless, the relatively large difference in the shift displacement, caused by the adamantanoid cage in two compounds as similar in molecular structure as the carbo- and azaphosphoranes **7** and **5**, is striking. (It is assumed that the monocyclic phosphoranes **8** and **6** also have comparable structures.) A possible explanation is as follows. The introduction of the adamantanoid cage probably results, in all cases, in a slight decrease in pπ–dπ back-bonding from the three oxygen ligands. This slight steric inhibition of pπ–dπ back-bonding causes a decrease in the extent of the shielding of the P nucleus by electrons and results in a displacement of the shift toward lower magnetic field. However, this effect is partly or totally off-set by the pπ–dπ back-bonding from the remaining ligands, *i.e.*, the two oxygens of **1** and **3** and the oxygen and the nitrogen in **5**. Evidently, the carbon in **7** is incapable of contributing to the P shielding in this manner,

Table V. Deviations from Ideal Skeletal TBP Symmetry

Bond angle	Deviation from skeletal D_{3h} symmetry	Bond angle	Deviation from skeletal D_{3h} symmetry
O(1)-P-O(3)	−13.4° (from 120°)	C(10)-P-O(4)	−6.7° (from 90°)
O(2)-P-O(1)	+10.2° (from 90°)	C(10)-P-O(2)	−4.8° (from 90°)
O(2)-P-O(3)	+8.3° (from 90°)	O(4)-P-O(3)	−4.1° (from 90°)
O(4)-P-O(2)	−12.3° (from 180°)	C(10)-P-O(3)	+10.1° (from 120°)

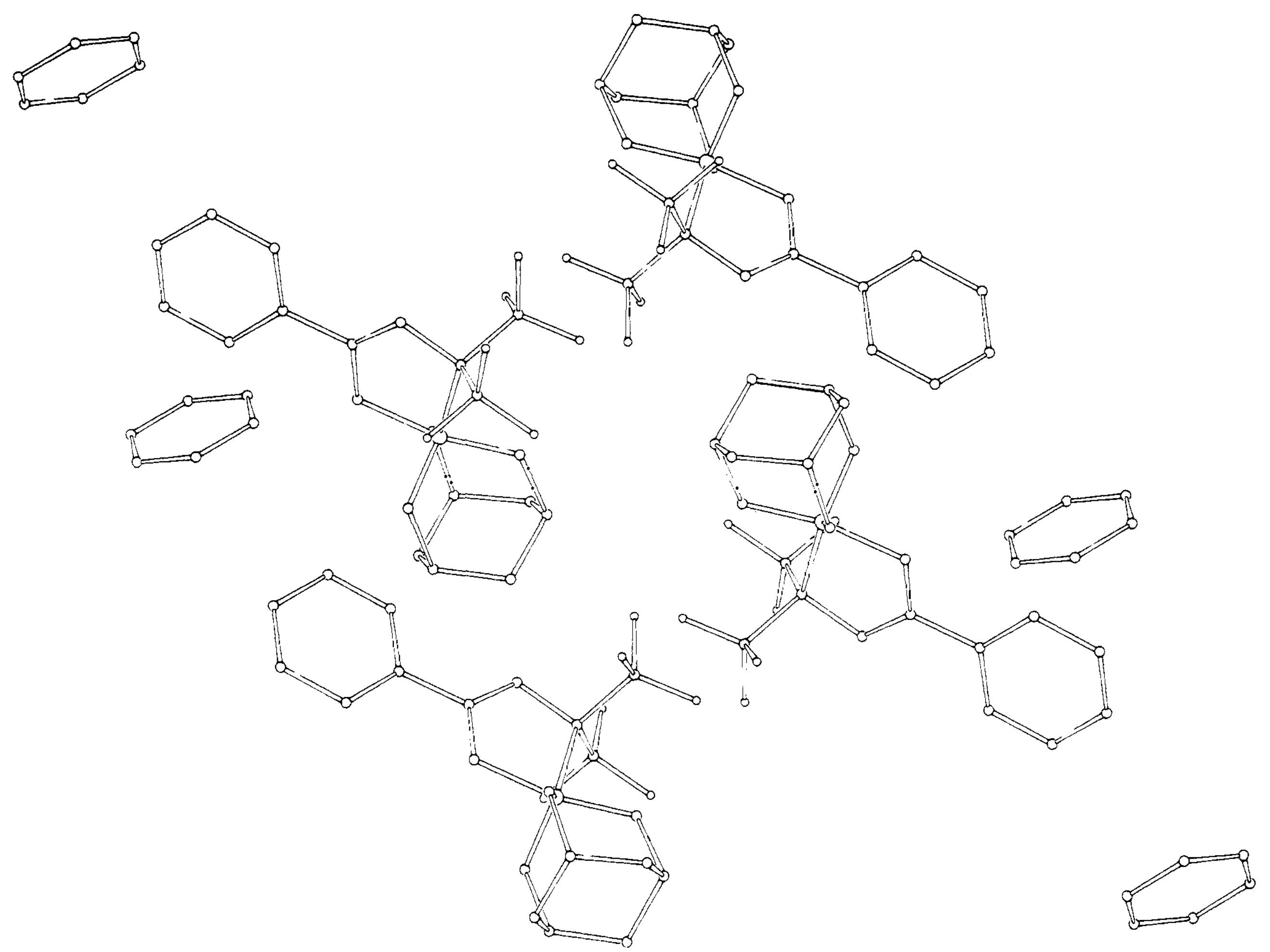


Figure 4. A view of the unit cell contents of compound 7.

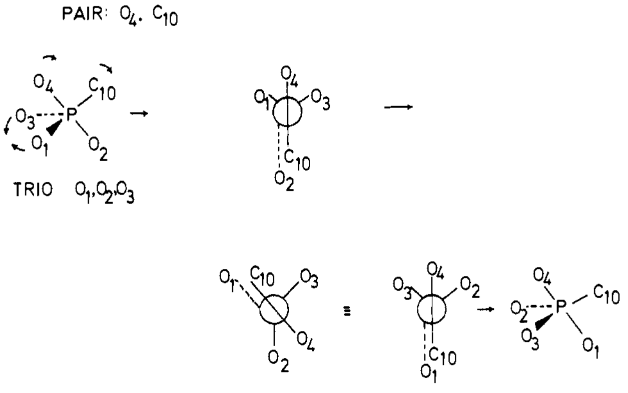
and the net effect is a marked decrease in the positive value of the shift in 7.

Dynamic Stereochemistry of Caged Polycyclic Oxyphosphoranes. The variable temperature ^1H nmr spectra of the carbophosphorane 7 parallel those of the other caged compounds,[3-6] **1**, **3**, and **5**, in the range 30 to *ca.* −50°. It should be emphasized that the methine protons of 7 show a relatively large coupling with the phosphorus, J_{HCOP} = 23.0 Hz, and that the fluorine nuclei are also coupled with the phosphorus, J_{FCCP} = 4 Hz (the two CF_3 groups are, as expected, magnetically equivalent). These observations, and the fact that an acidic alcohol such as hexafluoroisopropanol does not affect the ^{31}P nmr shift[3-7] of 7, support the hypothesis that PI in 7 occurs by a regular process,[4] *i.e.*, by intramolecular bond deformations.

The reasons why the regular PI of 7 cannot take place by the Berry pseudorotation mechanism[25] have already been given.[3,6] The TR mechanism explains the experimental facts satisfactorily. The motions of the ligands in this mechanism have been described in detail elsewhere.[4] Scheme I shows how the $(TR)^2$ mechanism[4,8] achieves the positional exchange of the methine protons among the skeletal position, without the need to move the apicophilic[4] oxygen to an equatorial position and the carbon to an apical position.

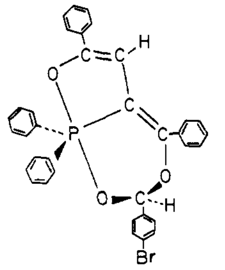
In the caged oxyphosphoranes **1**, **3**, **5**, and **7**, the "ground state" is relatively energetic since the establishment of the distorted TBP arrangement of the P valencies involves a certain amount of distortion of the adamantanoid cage, which requires some energy. The 'transition state" is relatively low because the TR barrier configuration, where the adamantanoid moiety has C_{3v} local symmetry, is established without much interference from that moiety or from any other structural feature. The result is a relatively low energy barrier and a relatively rapid PI at least to −50° (and to −165° in the case of **1**).

Scheme I

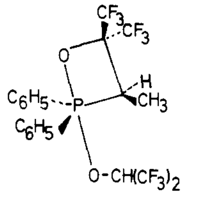


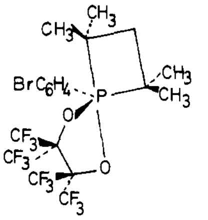
The molecular structures of 5 and 7 in the crystal are in line with these speculations concerning their behavior in solution.

A Note on Regular and Distorted Skeletal TBP Symmetry in Oxyphosphoranes. The strong tendency of the P atom of certain oxyphosphoranes to acquire, or to approach, skeletal TBP symmetry is disclosed by X-ray crystallography of several molecules of this type.[7,18-20] For example, the P atom is at the center of a nearly perfect TBP even in a seemingly strained molecule such as **12**.[19] The four-membered tricarbodioxaphosphorane[20] **13** clearly approaches skeletal TBP symmetry, although now the degree of distortion from the ideal D_{3h} point group is significant. A much greater deviation from regular skeletal TBP symmetry is found in another four-membered tricarbodioxaphosphorane[26] **14**; Trippett, *et al.*,[26] have placed this molecule, **14**, in the category of "square pyramidal phosphorus." Schmutzler, *et al.*,[27] have also emphasized the "square pyramidal" geometry of the P atom in some oxyphosphoranes.

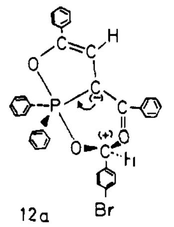


12, $\delta^{31}P$ = +50.2 PPM





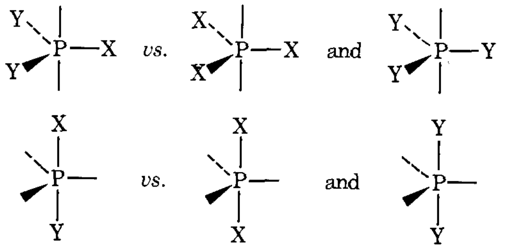
13 $\delta^{31}P$ = +32.1 PPM 14



12a

The deviations from regular TBP symmetry in the two caged tetraoxyphosphoranes, **5** and **7**, and in the four-membered dioxyphosphorane **13** have been analyzed in terms of a trend toward TR configurations and not toward square pyramidal configurations.[6,20] It is possible that the far greater deviations from regular TBP symmetry in Trippett's compound,[26] **14**, could also be fruitfully considered along the same lines. However, what is clear at this time is that without further quantitative data, the classification of the distortions from ideal skeletal D_{3h} symmetry in terms of "square pyramidal phosphorus" or of a "30°-TR configuration" in a *highly distorted* structure such as that found for **14**, is purely subjective.

The most striking difference between the two phosphetanes, **13** and **14**, is the relative placements of the two oxygen ligands and of the three carbon ligands. It has been found[4,28] that, among phosphoranes, an overall weakening of the bond system occurs when either the equatorial ligand subset or the apical ligand subset contains two different types of substituents. The binding energy contribution from the P 3d orbitals in the "heterosystem" is generally lower than the mean value for the two "homosystems." This effect has been called *stabilization by ligand subset symmetry.*[28]



The ligand subset symmetry effect[4,28] may account for the differences in the skeletal geometries[29] of the two phosphetanes, **13** and **14**; in the former, **13**, both ligand subsets have symmetry in this sense, but, in the latter, **14**, neither one of the subsets has symmetry. The bicyclic phosphorane[17] **12** exhibits double ligand subset symmetry.[4,29] This compound has an unusually large positive ^{31}P nmr shift for a tricarbodioxaphosphorane,[7] which may be due to a relatively effective shielding of the P nucleus by the type of electron delocalization pictured in resonance structure **12a** (enol ether resonance).

Acknowledgments. We wish to thank Larry Andrews for his helpful discussions on data reduction. The research was supported by U.S. Public Health Service Grants No. CA-04769, CA-10925, CA-06927, and RR-05539, by the National Science Foundation Grants GP-23018 and AG370 by the Atomic Energy Commission, and by an appropriation from the Commonwealth of Pennsylvania.

Supplementary Material Available. Table II will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journal Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-75-38.

References and Notes

(1) (a) The Institute for Cancer Research, Philadelphia, Pa. (b) Send correspondence to this author at the Institute for Cancer Research. (c) Brookhaven National Laboratory. (d) State University of New York at Stony Brook. (3) Technische Universität, München. (f) Deceased.

(2) Formulas **1-8** are based on the ideal trigonal bipyramidal skeleton; the deviations from it, where known (**5** and **7**), will be discussed below. The numbering of the ligands are those used in the X-ray analyses of **5** and **7**.

(3) F. Ramirez, I. Ugi, F. Lin, S. Pfohl, P. Hoffmann, and D. Marquarding, *Tetrahedron*, in press.

(4) (a) P. Gillespie, P. Hoffmann, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **10**, 687 (1971); (b) F. Ramirez and I. Ugi, *Advan. Phys. Org. Chem.*, **9**, 25 (1971).

(5) F. Ramirez, J. Marecek, I. Ugi, and D. Marquarding, *Phosphorus*, **3**, 91 (1973).

(6) W. C. Hamilton, J. S. Ricci, Jr., F. Ramirez, L. Kramer, and P. Stern, *J. Amer. Chem. Soc.*, **95**, 6335 (1973).

(7) (a) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968); (b) *Bull. Soc. Chim. Fr.*, 3491 (1970).

(8) The following abbreviations will be employed in this paper: TBP = trigonal bipyramid or trigonal bipyramidal; PI = permutational isomerization, *i.e.*, the exchange of ligands among the TBP skeletal sites (The PI phenomenon may generate a new stereoisomer or simply the same molecule with the ligands in different skeletal positions, depending on the type of molecule and the kind of mechanism involved.); TR = turnstile rotation mechanism of regular PI; $(TR)^2$ = double turnstile rotation.

(9) K. Burger, J. Fehn, and E. Moll, *Chem. Ber.*, **104**, 1826 (1971).

(10) We experienced considerable difficulties in the synthesis of this particular imino derivative **10** by the general procedures suggested in the literature (see ref 9 and 11). The method described here proceeds *via* the hydroxyamide, **9**, and probably also *via* the trifluoroacetoxyamide as intermediates.

(11) (a) F. J. Bourne, C. E. M. Tatlow, and J. C. Tatlow, *J. Chem. Soc.*, 1367 (1950); (b) P. E. Newallis and E. I. Rumanowski, *J. Org. Chem.*, **29**, 3114 (1964); (c) Yu.V. Zeifman, N. P. Gambaryan, and I. L. Knunyants, *Izv. Akad. Nank SSSR, Ser. Khim.*, **11**, 2046 (1965); W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965).

(12) (a) J. G. Verkade and R. W. King, *Inorg. Chem.*, **1**, 948 (1962); (b) J. G. Verkade, R. W. King, and C. W. Heitsch, *ibid.*, **3**, 884 (1964); (c) J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King, *ibid.*, **4**, 83 (1965).

(13) P. Main, M. M. Woolfson, and G. Germain, MULTAN A computer program for the automatic solution of Crystal Structures (1971).

(14) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, 1962; R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(15) See paragraph at end of paper regarding supplementary material.

(16) The pure single bond values are P–O, 1.76 Å and P–C, 1.82 Å; D. W.

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(17) In compounds **5** and **7**, angle O(4)–P–O(1) of one molecule can be compared with angle O(4)–P–O(3) of the other and *vice versa*. Ditto for O(1)–P–C(10)* and C(10)*–P–O(3).

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Some 1:1 Base-Catalyzed Addition Reactions of Compounds Containing Two or More Phosphorus-Hydrogen Bonds to Various Vinylphosphorus Derivatives

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Abstract: Some 1:1 base-catalyzed additions of primary phosphines to vinylphosphorus compounds are discussed. Treatment of the primary phosphines RPH_2 (R = phenyl, *n*-hexyl, and neopentyl) with $CH_2{=}CHP(O)(OCHMe_2)_2$ in a 1:1 mole ratio in the presence of potassium *tert*-butoxide followed by $LiAlH_4$ reduction of the intermediate gives the corresponding secondary-primary diphosphines $RP(H)CH_2CH_2PH_2$. A similar reaction sequence with methylphosphine gives only the new tertiary-diprimary triphosphine $CH_3P(CH_2CH_2PH_2)_2$. Base-catalyzed 1:1 addition of $C_6H_5PH_2$ to $CH_2{=}CHP(S)(CH_3)_2$ gives crystalline $C_6H_5P(H)CH_2CH_2P(S)(CH_3)_2$ which undergoes desulfurization with $LiAlH_4$ in boiling dioxane to give $C_6H_5P(H)CH_2CH_2P(CH_3)_2$. Attempts to carry out a base-catalyzed 1:1 addition of $C_6H_5PH_2$ to $CH_2{=}CHP(C_6H_5)_2$ give mainly the known 1:2 adduct $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$, although a low yield of the corresponding 1:1 adduct $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$ can be isolated under optimum conditions. A much more efficient conversion of $C_6H_5PH_2$ to $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$ uses the base-catalyzed 1:1 addition of $C_6H_5PH_2$ to $CH_2{=}CHP(S)(C_6H_5)_2$ followed by $LiAlH_4$ desulfurization in boiling dioxane. Base-catalyzed 1:1 additions of $(C_6H_5)_2PCH_2CH_2PH_2$ and $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$ to $CH_2{=}CHP(O)(OCHMe_2)_2$ give the tertiary-secondary-primary triphosphines $(C_6H_5)_2PCH_2CH_2P(H)CH_2CH_2PH_2$ and $C_6H_5P(H)CH_2CH_2P(C_6H_5)CH_2CH_2PH_2$, respectively, after $LiAlH_4$ reduction. Base-catalyzed addition of $(CH_3)_2PH$ to $CH_2{=}CHP(O)(OCHMe_2)_2$ followed by $LiAlH_4$ reduction gives the new tertiary-primary diphosphine $(CH_3)_2PCH_2CH_2PH_2$, which undergoes a base-catalyzed 1:1 addition to $CH_2{=}CHP(O)(OCHMe_2)_2$ to give the tertiary-secondary-primary triphosphine $(CH_3)_2PCH_2CH_2P(H)CH_2CH_2PH_2$. A similar base-catalyzed 1:1 addition occurs at the secondary rather than a primary phosphorus atom in the secondary-primary diphosphine $C_6H_5P(H)CH_2CH_2PH_2$. For example, the base-catalyzed 1:1 addition of $C_6H_5P(H)CH_2CH_2PH_2$ to $CH_2{=}CHP(S)(CH_3)_2$ followed by desulfurization with $LiAlH_4$ in boiling dioxane gives $C_6H_5P(CH_2CH_2PH_2)[CH_2CH_2P(CH_3)_2]$. The infrared, proton and ^{31}P nmr, and mass spectra of new organophosphorus compounds arising from this work are discussed as well as some general aspects of the mechanism of their formation.

Previous papers from this laboratory have discussed the preparation of organophosphorus compounds containing PCH_2CH_2P units by the base-catalyzed additions of phosphorus-hydrogen bonds to vinylphosphines,[2,3] vinylphosphonates,[4-6] and vinylphosphine sulfides.[7] This paper describes a more detailed study of base-catalyzed additions of phosphorus-hydrogen compounds containing two or more phosphorus-hydrogen bonds to vinylphosphorus compounds. We sought methods where a single phosphorus-hydrogen bond in a compound containing two or more phosphorus-hydrogen bonds could be made to react selectively with a vinyl-phosphorus derivative under base-catalyzed conditions with retention of the remaining phosphorus-hydrogen bonds. Development of such methods significantly increases the range of organophosphorus compounds containing two or more phosphorus atoms that can be prepared by base-catalyzed additions of phosphorus-hydrogen bonds to vinylphosphorus compounds. The only related reactions reported in the literature[8] involve the treatment of primary phosphines RPH_2 with vinylphosphines $CH_2{=}CHPR'_2$ to give the tertiary-secondary diphosphines $RPHCH_2CH_2PR'_2$, but these reactions all occur under free-radical rather than base-catalyzed conditions and cannot be controlled to form the 1:1 adducts $RPHCH_2CH_2PR'_2$ without forming appreciable quantities of the 1:2 adducts $RP(CH_2CH_2PR'_2)_2$.

Experimental Section

Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Ga., and by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points were taken in capillaries and are uncorrected. For air-sensitive compounds, the melting point capillaries were loaded in a nitrogen-filled glove bag, and the open end was sealed with stopcock grease. Infrared spectra of the liquid