Bicyclic and Tricyclic Phosphatranes. Conditions for Transannular P←N Bonding in a New Class of Phosphorus Cage Compounds

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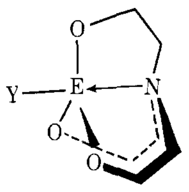
Abstract: The preparation and characterization of nine compounds of the type $YP(OCH_2CH_2)_3N$ are reported. Compound **1** (Y = lone pair) is unstable but forms the stable derivatives **2–9** (Y = O, S, Se, $H^+(BF_4^-)$, $Ph_3C^+(BF_4^-)$, H_3B, $(OC)_5W$, and $(OC)_5Mo$, respectively) upon reaction in situ with appropriate substrates. NMR parameters (^{31}P, ^1H, and ^{13}C) are consistent with a tricyclic structure for **5** and **6** which contains a transannular P←N bond. Such spectra are also consistent with a bicyclic structure for **2–4**, **7**, **8**, and **9** in which phosphorus has a tetrahedral and nitrogen a nearly trigonal planar coordination geometry. Recently obtained crystallographic x-ray data for **3**, **5**, and **7** are confirmatory of these conclusions. Apparently groups such as H^+ and Ph_3C^+, which strongly polarize the phosphorus lone pair, also cause the nitrogen lone pair to engage in transannular P←N bond formation. This bond accounts for the unusual stability of the P-H link in **5** even in strongly basic media. The nitrogen in compounds **2–4**, **8**, and **9** can be quaternized with a methyl group to form the corresponding cations **12–14**, **10**, and **11**, respectively. In these products the H–H steric interactions which favor a planar nitrogen in the reactants are overcome to some extent, causing some puckering of the nitrogen atom toward a tetrahedral configuration.

Atrane structures are generally characterized by the tricyclic model shown below in which a transannular E←N bond is assumed to be present. Where E is Al, polymeric structures are present in solution which have been postulated to be bound by intermolecular N←Al bonding of bicyclic units[10] although association of tricyclic structures via strong intermolecular dipole–dipole interactions cannot be ruled out. Prior to our recent communications on compounds in which E = P and Y = H^+ [11] and S,[12] the only other example of an atrane wherein E is a group V atom was the structurally uncharacterized $Bi(OCH_2CH_2)_3N$ whose preparation was described in an early report.[13a] In bicyclic systems of the type $Q(CH_2CH_2S)_2ECl_x$ (Q = S or O and E = Ge or Sn (x = 2) or E = As or Sb (x = 1)) the Q-E transannular interaction which confers TBP or ψTBP geometry around E appears to be relatively weak with bond orders ranging from 0.2 to 0.7.[13b]



E	Y
B	nothing[1]
Si	H, R, OH, OR, Ar, OAr, X[2]
Sn, Ge	R, OR, Ar[3]
V	O[4]
Sn	nothing[5]
Ti	OAr, SiR$_3$[6]
Fe	nothing[7]
Mo	OH(O)[8]
Zn	Cl[9]

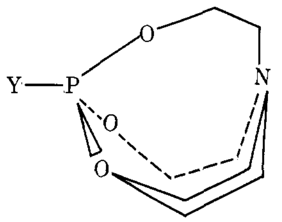
Here we show that atranes **1–14** in which Z is phosphorus (phosphatranes) feature a well-developed transannular P ← N bond when the phosphorus lone pair is strongly polarized by a positively charged Lewis acid (e.g., Y = H^+ or Ph_3C^+) while no P-N interaction is apparent with less polarizing neutral substituents. In the latter case, structural evidence is presented for an extended conformation in which phosphorus is tetrahedral and nitrogen is nearly planar.

$$YP(OCH_2CH_2)_3NZ$$

Z = lone pair (lp),

Y =	lp	O	S	Se	H^+	Ph_3C^+	H_3B	$(OC)_5W$	$(OC)_5Mo$;
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

Z = Me^+, Y =	$(OC)_5W$	$(OC)_5Mo$	O	S	Se
	10	**11**	**12**	**13**	**14**



Experimental Section

Materials. Solvents and reactants unless specifically noted otherwise were all of reagent grade or better. Methylene chloride and chloroform were dried over 4A molecular sieves while acetonitrile was dried by refluxing with and distillation from calcium hydride onto 4A molecular sieves. Aromatic solvents were purified by shaking with concentrated sulfuric acid, neutralized with saturated sodium bicarbonate solution, and dried by distilling off the water azeotrope before collecting over 4A molecular sieves.

Tris(dimethylamino)phosphine (TDP) and the borane adduct of tetrahydrofuran were obtained from Aldrich Chemical Co. The 90% TDP, as supplied, was distilled under vacuum (bp 55–56 °C at 10 mm) and triethanolamine (Fisher) was azeotropically dried with benzene and distilled (bp 172–173 °C at 0.5 mm) before use. Potassium superoxide (KO_2) and the hexacarbonyls of molybdenum and tungsten were used as supplied from Alfa and Pressure Chemical Co., respectively.

Spectral Measurements. All ^1H NMR spectra were obtained in 5–15% solutions using either a Varian A-60 or a Hitachi Perkin-Elmer R20-B spectrometer operating at 60 MHz using tetramethylsilane as internal standard. A Bruker HX-90 spectrometer operating at 22.63 and 36.44 MHz was used to obtain ^{13}C and ^{31}P NMR spectra, respectively. The spectrometer was operated in the FT mode using the block averaging technique to improve the signal to noise ratio. Carbon chemical shifts are reported in parts per million relative to internal tetramethylsilane while phosphorus chemical shifts are reported in parts per million relative to external 85% orthophosphoric acid (downfield and upfield being designated positive and negative, respectively). The carbon spectra were white-noise proton decoupled while the phosphorus spectra were obtained with and without proton decoupling. NMR spectra of **13** and **14** could not be obtained since they decomposed in the only solvents in which they were soluble (Me_2SO and DMF).

A Beckman 4250 spectrometer was used to obtain infrared spectra which were calibrated with polystyrene.

Mass spectra were obtained from an AEI MS-902 high-resolution spectrometer. Exact masses were determined by peak matching with standards.

Preparations. As a general precaution against moisture, a nitrogen atmosphere was maintained insofar as possible throughout the following preparations. Elemental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Triethyloxonium Tetrafluoroborate. This compound was prepared by the literature procedure of Meerwein.[14]

Trimethyloxonium Tetrafluoroborate. This compound was prepared by the procedure of Meerwein.[15]

Triphenylmethyl Tetrafluoroborate. This compound was prepared by the literature method[16] from triphenylcarbinol and fluoroboric acid in acetic anhydride.

18-Crown-6 Ether. The procedure of Gokel and Cram[17] was found preferable to that of Greene[18] for this preparation since the product was more easily purified.

Tetraethylammonium Bromopentacarbonyltungstate. The anion $[(OC)_5WBr]^-$ was prepared by refluxing 88 g (0.25 mol) of $W(CO)_6$ with 42 g (0.20 mol) of Et_4NBr in 300 mL of diglyme.[19]

Acetonitrilopentacarbonyltungsten. The acetonitrile complex of tungsten hexacarbonyl was prepared from the bromide complex above and acetonitrile.[20]

1-Phospha-5-aza-2,8,9-trioxabicyclo[3.3.3]undecane (1). This compound was prepared by the reaction of dilute solutions of triethanolamine and TDP in a three-neck round-bottom flask fitted with two needle-valve pressure equalizing addition funnels and a reflux condenser. The apparatus was flushed continuously with a stream of nitrogen. A solution of 7.5 g (50 mmol) of $N(CH_2CH_2OH)_3$ in 30 mL of $CHCl_3$ diluted to 200 mL with dry toluene and a solution of 9.0 g (55 mmol) of TDP in 200 mL of dry toluene were simultaneously added dropwise over a 2-h period to 250 mL of refluxing toluene in the flask. The presence of dimethylamine in the exit stream of nitrogen indicated that reaction was taking place. The mixture was refluxed for 2 h after the additions were complete. It was found that allowing the reaction to continue for a longer time made separation of the derivative products more difficult and did not significantly increase the yield.

Isolation of **1** has not been successful using a variety of techniques including chromatography (column, thin layer, and high-pressure liquid), sublimation, distillation, and crystallization. Each method resulted in decomposition and/or no substantial increase in purity (see Discussion).

1-Oxo-1-phospha-5-aza-2,8,9-trioxabicyclo[3.3.3]undecane (2). The reaction mixture of **1** was cooled to 45–50 °C after which a fourfold molar excess of finely ground KO_2 (14.2 g, 200 mmol) and a catalytic amount of 18-crown-6 (0.2 g, 0.75 mmol) were added and the mixture was heated carefully to 90–100 °C. As the reaction proceeded, gas was evolved. If heated too rapidly, a foam can overflow the flask. Heating was continued for about 1 h after the gas evolution stopped.

The mixture was then allowed to cool and filtered, and the filtrate was evaporated to dryness on the vacuum line. After the adhesive solid was taken up in a minimum of methylene chloride, dropwise addition of Skelly B resulted in the precipitation of a white solid which upon settling appeared to have a rubbery texture. The mixture was filtered through a layer of Celite on a porous glass frit. This precipitation–filtration process was repeated with the filtrate until the precipitate formed remained as a finely divided solid. After several such cycles the filtrate became too dilute for efficient elimination of impurities and it was evaporated to dryness under vacuum and redissolved in a minimum of methylene chloride before the next addition of Skelly B.

The white powder which resulted from this procedure was recrystallizable from methylene chloride–hexane[21] or chloroform solution cooled to −78 °C and could be sublimed at 120 °C (0.1 mm) (a significant amount of material decomposes during sublimation), mp 208–212 °C dec, *m/e* 193.0504 ± 0.001 (calcd, 193.0489 for $C_6H_{12}NO_4P$), IR $\nu P{=}O$ 1276 cm^{-1} ($CHCl_3$). The overall yield for this product was 3%.

1-Thio-1-phospha-5-aza-2,8,9-trioxabicyclo[3.3.3]undecane (3). The reaction mixture of **1** was cooled to about 50–60 °C and sublimed sulfur (1.8 g, 56 mmol) was added. The mixture was then slowly heated (0.5 h) to reflux and allowed to cool to room temperature. The mixture was filtered to remove any precipitated material (polymer as judged by its general insolubility in a variety of organic solvents). The filtrate was then evaporated to dryness on the vacuum line. Purification was accomplished by the same procedure described for **2.**

The resulting white solid could be recrystallized from methylene chloride–hexane,[21] acetonitrile–ethyl ether,[21] or toluene solution cooled to −78 °C, or sublimed at 120–130 °C (0.1 mm): mp 218–220 °C dec; *m/e* 209.0276 ± 0.0011 (calcd, 209.0276 for $C_6H_{12}NO_3PS$); IR $\nu P{=}S$ 881 and 612 cm^{-1} ($CHCl_3$). The yield of the reaction calculated on the basis of starting materials was 6% for product of >95% purity as judged from NMR spectra. Higher purity material has been obtained after several recrystallizations reducing the yield to less than 1%.

1-Seleno-1-phospha-5-aza-2,8,9-trioxabicyclo[3.3.3]undecane (4). Red selenium[22] (7.9 g, 100 mmol) was added to a cooled reaction mixture of **1** and the mixture heated to 75–80 °C for 2 h. The temperature of the mixture was not allowed to rise above 80 °C since the more reactive red selenium reverts to the gray allotrope above 80 °C.

The isolation procedure was that described for **2** and **3.** Again, the white solid produced was recrystallizable from methylene chloride–hexane[21] solution cooled to −78 °C: mp 208–210 °C dec; *m/e* 256.9648 ± 0.001 (calcd, 256.9720 for $C_6H_{12}NO_3PSe$); IR $\nu P{=}Se$ 580 cm^{-1} ($CHCl_3$). The overall yield was 4%.

1-*H*-1-Phospha-5-aza-2,8,9-trioxatricyclo[3.3.3.0]undecane Fluoroborate (5). This derivative was the product of the reaction of triethyloxonium or trimethyloxonium fluoroborate (60 mmol) with the reaction mixture of **1.** The Meerwein reagent was added dropwise in acetonitrile solution (100 mL) at room temperature. The majority of the white solid which formed was precipitated polymer along with the reaction product. The solid was filtered and extracted with two 25-mL portions of hot acetonitrile. The solvent was removed in vacuo and the residue extracted with 25–30 mL of acetone. The NMR of the remaining solid showed it to be about 80% product.

Further purification was accomplished by the precipitation–filtration procedure described for **2** utilizing a concentrated acetonitrile solution and dropwise addition of ethyl ether to remove polymeric impurities. Eventually the product precipitated and was collected as a white powder which could be recrystallized in 8% overall yield from hot acetonitrile solution: mp 210–212 °C; *m/e* 177.0553 ± 0.0009 (calcd, 177.0555 for $C_6H_{12}NO_3P$ (**1**)). Anal. Calcd: C, 27.31; H, 4.86; N, 5.29; F, 28.80. Found: C, 27.70; H, 4.95; N, 5.29; F, 28.68. IR $\nu P{-}H$ 2240, 2286 cm^{-1} (KBr), conductivity 1:1 electrolyte in Me_2SO.

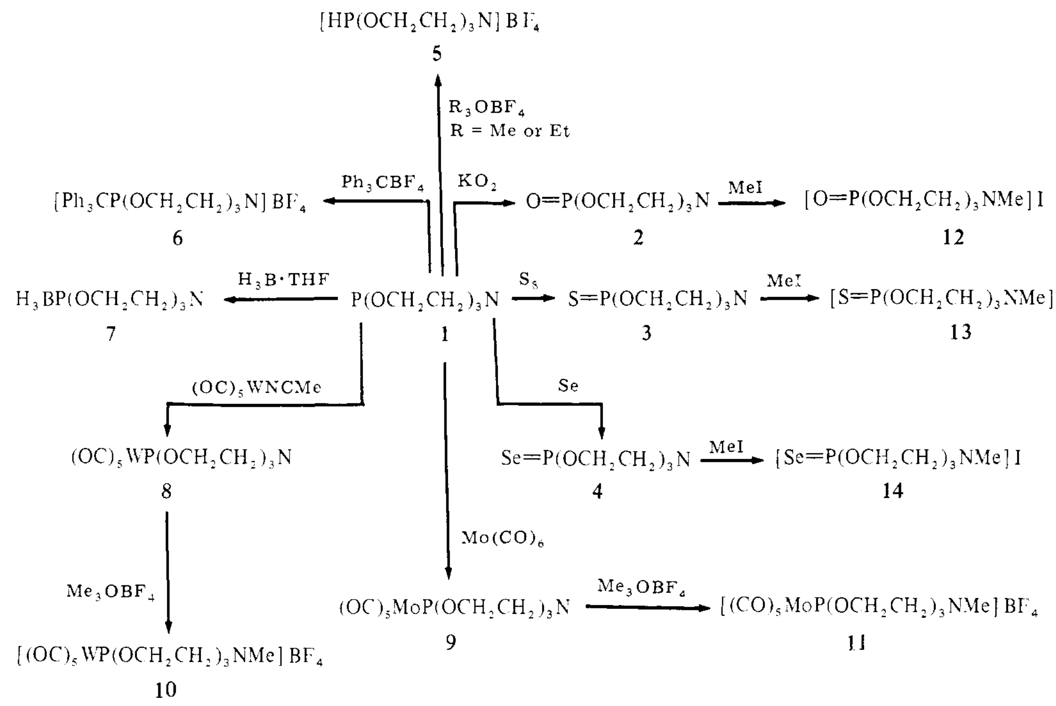
1-Triphenylmethyl-1-phospha-5-aza-2,8,9-trioxatricyclo-[3.3.3.0]undecane Fluoroborate (6). An acetonitrile solution (100 mL) of triphenylmethyl fluoroborate (16 g, 50 mmol) was added dropwise to a reaction mixture of **1** at room temperature. After stirring for 2 h the solvents were removed in vacuo. When the residue was extracted with 100 mL of chloroform, a finely divided solid product remained. This solid was collected by filtration through Celite and extracted into acetonitrile solution.

The crude product in acetonitrile solution was purified by the procedure described for **5** and it was necessary to repeat this process several times, mp 204–206 °C dec, 1:1 electrolyte in acetonitrile. The overall yield was 8%.

1-Borano-1-phospha-5-aza-2,8,9-trioxabicyclo[3.3.3]undecane (7). Two equivalents (100 mL of a 1 M THF solution) of the borane adduct of tetrahydrofuran ($H_3B{\cdot}THF$) was added dropwise to the reaction mixture of **1** at room temperature. After 1 h of stirring the mixture was evaporated to dryness under vacuum and the residue extracted with dry ethyl ether in a Soxhlet extractor for 8 h. Stripping off the ether and sublimation of the residue at 80–100 °C yielded crude **7.** Further purification was accomplished by repeated sublimation: mp 175–178 °C; *m/e* 189.0847 ± 0.001 (calcd, 189.0841 for $C_6H_{15}BNO_3P$); IR νBH 2395, 2351 cm^{-1} (KBr). The yield for this preparation was about 4%.

1-Pentacarbonyltungsten-1-phospha-5-aza-2,8,9-trioxabicyclo-[3.3.3]undecane (8). A toluene solution containing 19 g (52 mmol) of $(OC)_5WNCCH_3$ was added at room temperature to a reaction mixture of **1** which was then heated to 90 °C and held there for 2 h. The yellow solution gradually precipitated a yellow solid and became dark brown in color. The mixture was filtered and the filtrate evaporated to a dark brown tar. The tar was dissolved in 50 mL of chloroform and

Scheme I



absorbed on 50 g of added silica gel by evaporating the mixture to dryness. After grinding the residue to a free-flowing powder it was added to the top of a silica gel column prepared with 350 g of silica gel and a 5:1 ratio of Skelly B/ethyl acetate in a 3 × 120 cm column. The column was eluted with 1 L of 5:1 Skelly B/ethyl acetate, 2 L of 3:1 Skelly B/ethyl acetate, and finally 500 mL of ethyl acetate. The middle fractions (3:1 Skelly B/ethyl acetate) contained **8**. Solvents were stripped from these fractions and the pale yellow residue was recrystallized from ethyl acetate-hexane[21] solution cooled to −78 °C: mp 139-140 °C; *m/e* 498.9683 ± 0.001 (calcd, 498.9783 for $C_{11}H_{12}NO_8PW$); IR νCO 2078, 1956, 1948 cm^{-1} (cyclohexane). Yields of 13% for this species are the best achieved for any derivative of **1**.

1-Pentacarbonylmolybdenum-1-phospha-1-aza-2,8,9-trioxabicyclo[3.3.3]undecane (9). Molybdenum hexacarbonyl (13.2 g, 50.0 mmol) was added to a reaction mixture of **1** and heated until carbon monoxide evolution had ceased (about 2 h). After cooling, the mixture was filtered and evaporated to dryness under vacuum.

As with **8**, the product was isolated by column chromatography on silica gel except that the elutions were carried out with 1 L of 5:1 Skelly B/ethyl acetate, 2.5 L of 3:1 Skelly B/ethyl acetate, and 500 mL of ethyl acetate. The product fractions (3:1 Skelly B/ethyl acetate) were evaporated and the combined residues were recrystallized from ethyl acetate-hexane[21] (1:15) cooled to −78 °C: mp 122-124 °C dec; *m/e* 408.9284 ± 0.001 (calcd, 408.9363 for $C_{11}H_{12}NO_8PMo$); IR νCO 2078, 1956 cm^{-1} (cyclohexane). The yield of this product was 9%.

1-Pentacarbonyltungsten-1-phospha-5-aza-5-methyl-2,8,9-trioxabicyclo[3.3.3]undecane Fluoroborate (10). Trimethyloxonium fluoroborate (0.290 g, 2.00 mmol) and 0.761 g (1.50 mmol) of **8** were placed in a 50-mL round-bottom flask and dissolved in 25 mL of dry acetonitrile. The mixture was stirred at room temperature for 4 h before anhydrous ether was added to the cloud point. The flask was then cooled (−78 °C) whereupon the product crystallized. It was collected by filtration and dried under vacuum: mp 255-258 °C dec; yield 92%; IR νCO 2079, 1959 cm^{-1} (KBr).

1-Pentacarbonylmolybdenum-1-phospha-5-aza-5-methyl-2,8,9-trioxabicyclo[3.3.3]undecane Fluoroborate (11). This compound was prepared from 0.19 g (1.3 mmol) of trimethyloxonium fluoroborate and 0.426 g (1.00 mmol) of **9** by the procedure described for **10**. The molybdenum species appeared to oxidize slightly during the reaction, turning a pale green color. It was necessary to recrystallize the product twice to eliminate the green coloration: mp 165-168 °C dec; yield 83%; IR νCO 2080, 1959 cm^{-1} (KBr).

1-Oxo-1-phospha-5-aza-5-methyl-2,8,9-trioxabicyclo[3.3.3]undecane Iodide (12). Methyl iodide (0.24 g, 1.6 mmol) was added to 0.076 g (0.40 mmol) of **2** in 4 mL of acetonitrile. The mixture was heated to 40 °C for 10 h, by which time a solid had formed in the flask. The white solid was collected by filtration and dried under vacuum (mp 201-202 °C dec). The yield was virtually quantitative.

1-Thio-1-phospha-5-aza-5-methyl-2,8,9-trioxabicyclo[3.3.3]undecane Iodide (13). This compound was prepared by the procedure described for **12** (mp 178-180 °C dec). The yield was virtually quantitative.

1-Seleno-1-phospha-5-aza-5-methyl-2,8,9-trioxabicyclo[3.3.3]undecane Iodide (14). This compound was prepared by the procedure described for **12** (mp 180-182 °C dec). The yield was virtually quantitative.

Discussion

Although phosphatrane **1** apparently forms in reaction 1, the major product is an uncharacterized polymer. The estimated maximum yield of 15% for **1** (based on integration on the ^{31}P spectrum of the reaction) was not improved by longer reaction times, slower additions, or higher dilutions.

$$P(NMe_2)_3 + (HOCH_2CH_2)_3N \xrightarrow[\text{heat}]{\text{toluene}} P(OCH_2CH_2)_3N + HNMe_2 + \text{polymer} \quad (1)$$

Concentration or aging of the reaction mixture of reaction 1 converted **1** to polymer. Polymerization and apparent facile hydrolysis of **1** on silica gel columns prevented its isolation by chromatography. Attempted recrystallization of toluene residues from reaction 1 were unsuccessful and heating these residues under vacuum sublimation conditions produced violent pyrolyses.

The isolation of products **2-14** in Scheme I shows that derivatization of **1** is relatively easy. Surprisingly, however, attempted alkylation of **1** with R_3OBF_4 produced the protonated species **5** rather than $[RP(OCH_2CH_2)_3N]BF_4$ which is ordinarily expected from trialkyl phosphites.[23] Efforts to understand the pathway of this reaction are underway. The oxidation product **2** was isolated only with KO_2 despite many attempts with other oxidizing agents including $(PhCO_2)_2$, *m*-$ClC_6H_4CO_3H$, Me_3NO, $K_2S_2O_8$, singlet O_2 formed photolytically, and N_2O_4.

In the next two sections is discussed the evidence for tricyclic

Table I. ^{31}P NMR Data for Phosphatrane Derivatives

Compd[a]	$\delta^{31}P$[b]	$^3J_{PH}$[c]	Other one-bond couplings
1[d]	115.2	10.0	
2	−6.6	15.8	
3	60.9	16.6	
4	58.0	16.6	$^1J_{PSe} = 973.2$
5[e]	−20.9		$^1J_{PH} = 779.6$
6[f]	5.9	16.1	$^1J_{PC} = 5.9$[g]
7[f]	98.3		$^1J_{PB} = 120.3$
8	119.2	14.4	$^1J_{WP} = 403.6$
9	143.7	14.1	$^1J_{MoP} = 229.0$
10[e]	122.5	14.0	$^1J_{WP} = 416.2$
11[e]	146.4	15.0	$^1J_{MoP} = 235.7$
12[e]	7.2	16.1	
$[Ph_3CP(OCH_2)_3CMe]^+$	51.3		$^1J_{PC} = 5.9$[g]
$[Ph_3CP(OMe)_3]^+$	25.7		$^1J_{PC} = 6.0$[g]

[a] Spectra recorded in $CDCl_3$ unless otherwise noted. Sweep width of 9000 Hz employed. [b] Chemical shifts accurate to ±0.1 ppm. [c] Coupling constants accurate to ±0.5 Hz. Couplings not resolved are blank. [d] Spectrum recorded in benzene. [e] Spectrum recorded in CD_3CN and consisted of a doublet ($^1J_{PH}$) of unresolved multiplets ($^3J_{PH}$ and $^4J_{PH}$). [f] Spectrum recorded in $(CD_3)_2S{=}O$. [g] Obtained from the ^{13}C spectrum.

Table II. ^{13}C NMR Data for Phosphatrane Derivatives

Compd[a]	δCH_2O[b]	$^2J_{PC}$[c]	δCH_2N[b]	$^3J_{PC}$
2	65.9	8.9	49.0	
3	67.7	11.8	50.9	
4	67.6	12.8	50.7	
5[d]	60.0	10.8	48.5	12.8
6[e]	63.2	12.8	48.0	9.8
7[e]	64.9	10.8	49.4	2.0
8	63.3	10.8	49.0	
9[f]	64.1	11.8	50.9[g]	
10[d]	60.2	10.8	62.3[g]	
11[d]	60.2	11.8	62.9[g]	
12[e]	64.3	6.9	63.1[g]	
$N(CH_2CH_2OH)_3$	56.8		54.4	
$MeN(CH_2CH_2OH)_3^+$[h]	54.0		63.2	
$O{=}P(O\text{-}n\text{-}C_4H_9)_3$	66.0	5.9		6.8

[a] Spectra taken in $(CD_3)_3C{=}O$ unless otherwise noted at a sweep width of 8000 Hz. [b] Chemical shifts accurate to ±0.1 ppm. [c] Coupling constants accurate to ±0.5 Hz. Coupling not resolved is shown by a blank. [d] Spectrum recorded in CD_3CN. [e] Spectrum recorded in $(CD_3)_2S{=}O$. [f] Spectrum recorded in CH_2Cl_2 using C_6D_6 as a lock. [g] Nitrogen methyl carbon has coincident chemical shift. [h] Spectrum recorded in CD_3CN/H_2O as the iodide which was prepared by reacting equimolar quantities of MeI and $N(CH_2CH_2OH)_3$ in CH_3CN at 40 °C for 15 min and pumping to dryness. $\delta^{13}CH_3$ 63.1 ppm.

Table III. ^{1}H NMR[a] Data for Phosphatrane Derivatives

Compd	δCH_2O[b]	$^3J_{PH}$[c]	$^3J_{HH}$[c]	δCH_2N[b]
1[d]	3.68 dt	10.5	5.6	2.60 t
2	4.05 dt	16.1	5.8	3.02 t
3	4.10 dt	16.5	6.2	3.01 t
4	4.17 dt	16.5	5.3	3.06 t
5[e,f]	4.16 dt	14.1	6.2	3.43 q
6[e,g]	4.23 dt	16.8	6.0	3.30 td
7[h]	3.96 dt	14.1	5.1	2.97 t
8	3.94 dt	13.8	5.0	2.96 t
9	3.98 dt	13.0	5.6	2.97 t
10[e,i]	4.45 dt	14.0	4.0	3.71 t
11[e,j]	4.38 dt	15.0	5.0	3.80 t
12[h,k]	4.66 dt	16.0	4.0	4.11 t
$N(CH_2CH_2OH)_3$	3.67 t		5.0	2.62 t

[a] Spectra recorded in $CDCl_3$ unless otherwise noted. [b] Chemical shifts accurate to ±0.05 ppm. [c] Coupling constants accurate to ±0.5 Hz. [d] Spectrum recorded in benzene. [e] Spectrum recorded in CD_3CN. [f] $^4J_{PH} = 6.2$, δPH 6.01 d, $^1J_{PH} = 794$. [g] $^4J_{PH} = 3.0$, δC_6H_5 6.79 m. [h] Spectrum recorded in $(CD_3)_2SO$. [i] δCH_3 3.18 s. [j] δCH_3 3.18 s. [k] δCH_3 3.41 s.

phosphatrane structures incorporating a P←N transannular bond and for bicyclic phosphatranes in which this interaction is absent.

Tricyclic Phosphatranes. From the ^{31}P NMR data recorded in Table I the $\delta^{31}P$ value for **5** is seen to be over 40 ppm upfield of the analogues $[HP(OCH_2)_3CMe]^+$ (32.2 ppm)[24] and $[HP(OMe)_3]^+$ (24.4 ppm).[25] Moreover, the $^1J_{PH}$ constant of 779.2 Hz for **5** is substantially smaller than those for the latter cation (899[24] and 826[25] Hz, respectively). The high-field ^{31}P chemical shift is suggestive of five-coordinate phosphorus. The abnormally small $^1J_{PH}$ value is consistent with this idea if the reasonable assumption is made that less phosphorus s character can be expected to contribute to the Fermi contact term from a PH bond on the axis of a trigonal bipyramidal phosphorus compared to tetrahedral phosphorus, and further, that the positive charge contribution to the Fermi term is expected to be less in the P-H coupling of **5** since the bulk of the formal charge is on nitrogen rather than on phosphorus. Confirmatory evidence for these arguments came from the molecular structure determination of the fluoroborate salt of **5** which was communicated recently from our laboratories.[11] Thus the geometry around phosphorus in this salt is very nearly trigonal bipyramidal and the axial P-H (1.35 Å) and P-N (1.986 Å) bonds are well defined.

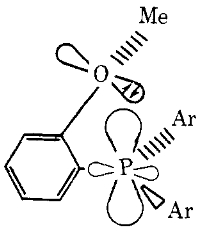
Electron donation in the P←N link in **5** is undoubtedly responsible for stabilizing its P-H bond since protonated forms of all other trialkyl phosphites have thus far been detected only at low temperature in very acidic media.[24-26] According to the ^{31}P NMR spectrum of **5**, in Me_2SO the P-H bond remains intact in the presence of 2 equiv of NaOMe or 4 equiv of 1,8-bis(dimethylamino)naphthalene ("proton sponge"). Deprotonation from a carbon atom in the cation may be indicated by the upfield shift of $\delta^{31}P$ to −10.0 ppm and the increase in $^1J_{PH}$ to 726.9 Hz but the nature of this species is at present not clear. Further evidence for the stability of the tricyclic structure of **5** stems from its ^{31}P spectrum which remains unchanged in $HSO_3F\cdot SbF_5$ in liquid SO_2 ("magic acid") at −50 °C. This result strongly suggests that the nitrogen is not protonated in this strongly acidic medium owing to the strong P←N interaction.

The ^{13}C (Table II) and ^{1}H (Table III) NMR parameters recorded for **5** reveal no unusual chemical shifts compared to the other compounds in this series. Substantial $^3J_{PC}$ and $^4J_{PH}$ couplings observed for this compound compared to those in which the P←N bond is absent (vide infra) are consistent with the presence of this bond since each of the coupling paths is shortened by one bond.

The geometry of this tricyclic cation is undoubtedly in large measure determined by the constraints inherent in the structure and symmetry of the $(OCH_2CH_2)_3N$ moiety. Two other factors which reinforce the particular arrangement of the atoms found in the trigonal bipyramidal coordination sphere of phosphorus in this case are, however, the high apicophilicity of hydrogen and the greater availability of d orbitals in the equatorial plane to accommodate the π-donating oxygens.[27a] That the chelating $(OCH_2CH_2)_3N$ moiety is apparently crucial to the formation of this type of cation is strongly suggested by the failure of a Me_2SO solution of $P(OEt)_3$ and $HCl\cdot N(CH_2CH_2OH)_3$ to show the strong $^1J_{PH}$ coupling in the ^{31}P NMR spectrum expected from the formation of the acyclic $[HP(OEt)_3N(CH_2CH_2OH)_3]^+$ analogue.

Most of the NMR evidence suggests that **6** also contains a P ← N link. While five-coordinated phosphorus is suggested by the ^{31}P chemical shift of **6** which is 45 and 20 ppm upfield of that of $Ph_3CP(OCH_2)_3CMe^+$ and $Ph_3CP(OMe)_3^+$, respectively, $^1J_{PC}$ is very similar in all three compounds (Table I). As in **5**, $^3J_{PC}$ is substantial in **6** (Table II) and $^4J_{PH}$ is resolved (Table III). The high melting point of **6** (204-206 °C) and its superior stability on standing at room temperature compared to $[Ph_3CP(OCH_2)_3CMe]BF_4$ and $[Ph_3CP(OMe)_3]BF_4$, which decompose under these conditions, are also suggestive of a tricyclic structure.

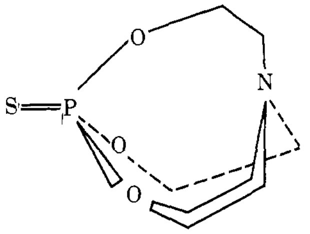
McEwen et al.[27b] have proposed that an oxygen lone pair in a p orbital interacts with an empty phosphorus d orbital to lower the transition state energy of quaternization reactions of *o*-anisyldiarylphosphines. The resulting increase in electron density in the phosphorus d orbitals is believed to be responsible for the marked increase in rate of quaternization with this substrate compared to triarylphosphines lacking ortho oxygens. The stability of five-coordinate phosphorus in **5** is consistent with this rationale although it should be noted that the rings in **5** are larger than that in the transition state depicted above.



Bicyclic Phosphatranes. The chalconides (**2-4**) and pentacarbonyl metal complexes (**8** and **9**) have CH_2N proton shifts which are 0.35-0.4 ppm downfield from those of triethanolamine. Similar shifts of these protons in silatranes (0.1-0.3 ppm) and stannatranes (0.25-0.3 ppm) have been attributed to a reduced electron density on nitrogen arising from the formation of a transannular Si-N or Sn-N bond.[2b,23,28] As we will shortly show, however, the shift in **2-4, 8,** and **9** is not attributable to the presence of a P←N bond. Except for the absence of $^3J_{PC}$ coupling, the ^{13}C NMR spectra (Table II) of **2-4, 8,** and **9** are very similar to those of **5** and **6** which have the tricyclic structure. The ^{31}P chemical shifts in Table I do suggest the presence of four-coordinate phosphorus in **2-4**, however, since their $\delta^{31}P$ values parallel those of $YP(OCH_2)_3CMe$ where Y = O (8.0[29]), S (57.4[29]), and Se (60.5 ppm[30]), respectively. Moreover, $^1J_{PSe}$ for **4** is close to that measured for $SeP(OCH_2)_3CMe$ (1052.0 Hz[30]). Metal-phosphorus couplings in **8** and **9** are also ascribable to four-coordinate phosphorus since $^1J_{PW}$ in **8** compares favorably to $(OC)_5WL$ where L = $P(OMe)_3$ (398) and $P(OCH_2)_3C\text{-}n\text{-}C_5H_{11}$ (393 Hz)[31-33] and $^1J_{PMo}$ in **9** resembles that found for the analogous complex where L = $P(OMe)_3$ (216) and $P(OCH_2)_3CMe$ (226 Hz).[34] The infrared spectra of **2-4** also show no unusual νP=O (1276 cm^{-1}), νP=S (881 and 614 cm^{-1}), or νP=Se (580 cm^{-1}) frequencies according to the ranges set by Thomas.[35]

If phosphorus is indeed four coordinate in **2-4, 8,** and **9**, then the nitrogen might be expected to be tetrahedral also. That the latter is not the case is indicated by the consistently high-field $\delta^{13}C$ value for CH_2N (by ca. 4 ppm) compared to triethanolamine. Further, the reactivity of nitrogen in these compounds toward methylation is greatly reduced in contrast to triethanolamine. Thus **2-4** in the presence of methyl iodide at 40 °C in acetonitrile quaternize to **12-14**, respectively, over a period of 10 h compared to 30 min for triethanolamine. Compounds **8** and **9** take 4 h to methylate to **10** and **11**, respectively, using trimethyloxonium fluoroborate in acetonitrile. Interestingly **2-4** do not methylate under these conditions.

The question regarding the stereochemistry at nitrogen in **2-4, 8,** and **9** is essentially answered by the crystal and molecular structure determination of **3**.[12] The phosphorus coordination geometry is indeed tetrahedral as expected from the ^{31}P NMR shifts, with SPO and OPO angles averaging 110.8 and 108.1°, respectively. The nitrogen, however, is nearly trigonal planar with CNC angles averaging 119.2°. The nitrogen is puckered out of the carbon plane by 0.13 Å and the PN distance is 3.132 Å. Although this distance is 1.3 Å longer than the sum of the single bond covalent radii, it is 0.3 Å shorter than the sum of the van der Waals radii. Further studies are planned to elucidate the consequences of this possible interaction.



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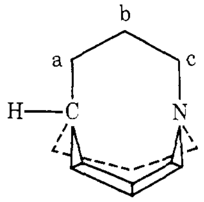
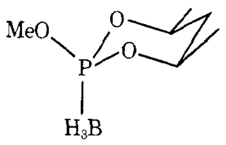


manxine

The planar nitrogen in **3** is probably caused by steric rather than electronic circumstances in the molecule. It has been concluded from chemical and spectroscopic studies of manxine that the nitrogen and methine carbon are substantially flattened to relieve 1,5 hydrogen-hydrogen interactions.[36-38] These interactions involve the hydrogens on carbons a and c and carbon b of different bridging moieties of the cage. The best evidence for this flattening is the structure of manxine hydrochloride,[39] wherein CNC angles are opened to 115.5° and the ring angles (NCC = 117.4° and CCC = 113.9-119.7°) deviate substantially from the tetrahedral value. In **3** the absence of hydrogens on the three oxygens along with the flexibility of oxygen in organophosphorus compounds[40] allows phosphorus to retain normal angles. However, the hydrogen interactions from carbons b and c apparently cause ring strain (NCC = 117.6° and CCO = 116.6°) and consequently flatten the nitrogen bridgehead.

By analogy to **3** the structures of **2, 4, 8,** and **9** probably possess a tetrahedral phosphorus and a nearly trigonal planar nitrogen. The reduced reactivity of nitrogen in these compounds can then be rationalized by invoking the steric hindrance afforded by the methylene hydrogens which blocks approach to the nitrogen lone pair. This argument has also been used to explain the low reactivity of nitrogen in manxine.[36] It is worth noting that although the values for the ^{13}C and ^1H chemical shifts of the CH_2N group of manxine (50.1 and 2.85 ppm,[35] respectively) are close to the values in Tables II and III for compounds **2-4, 8,** and **9,** they also lie near the corresponding values for **5** and **6** which have the tricyclic structure and a tetrahedral nitrogen. Thus caution must be exercised in using these spectral parameters for stereochemical assignments in the systems under discussion.

The spectroscopic and chemical evidence does not permit the assignment of the structure of the BH_3 adduct **7**. The near identity of the ^{31}P chemical shift (Table I) compared to $H_3BP(OCH_2)_3CMe$ (−97 ppm[41]) strongly supports a bicyclic structure while the value of $^1J_{PB}$, however, is larger for **7** by about 20 Hz compared to $H_3BP(OCH_2)_3CMe$ (96.0 Hz[41]) and $H_3BP(OMe)_3$ (97.2 Hz[41]), and it exceeds that of **15** by 12 Hz (108.0 Hz[41]). Although correlations of $^1J_{PB}$ with phosphorus basicity are tenuous,[42] it would be tempting to ascribe



15

the unusually large PB coupling in **7** to a tricyclic geometry.

Equilibration studies summarized in reactions 2 and 3 indeed show that **7** is a stronger adduct than $H_3BP(OMe)_3$ which in turn is stronger than the $H_3BP(OCH_2)_3CMe$ caged adduct.[43] A comparison of the BH stretching frequencies of **7** (2385, 2355 cm^{-1}, Me_2SO) with those of **15** (2390, 2361 cm^{-1}, Me_2SO), $H_3BP(OCH_2)_3CMe$ (2420, 2361 cm^{-1}, Me_2SO), and $H_3BP(OMe)_3$ (2398, 2352 cm^{-1}, CCl_4[41]) shows that **7** is not abnormal in this respect and therefore the infrared data do not demand a P←N bond. Although it would have been interesting to use **15** and its parent phosphite in equilibrium studies with **1** and **7**, respectively, the parent phosphite of **15** readily isomerizes to a less basic phosphite.[44]

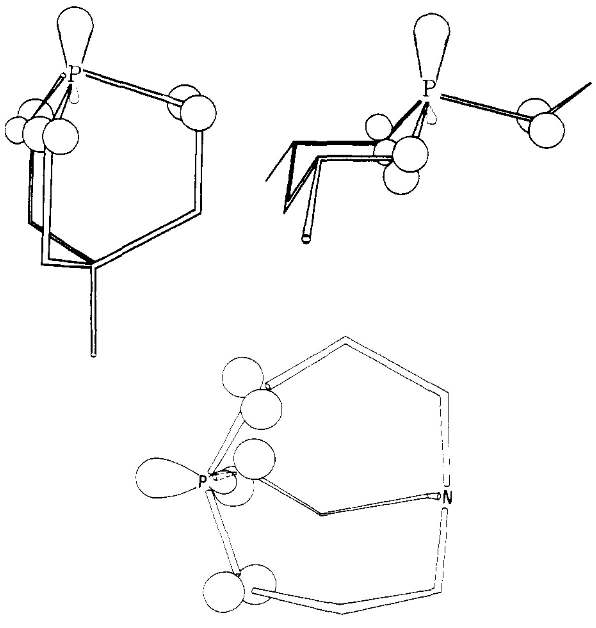
$$7 + \text{base} \xrightarrow{\text{toluene}} \text{no reaction} \qquad (2)$$

$$\text{base} = P(OMe)_3,\ PPh_3,\ NEt_3,\ \text{or}\ C_5H_5N$$

$$1 + H_3BP(OMe)_3 \overset{Me_2SO}{\rightleftarrows} 7 + P(OMe)_3 \qquad (3)$$

The ^1H and ^{13}C NMR data are of no assistance in assigning the structure of **7** since a $^3J_{PC}$ coupling is detected which is small compared to those in **5** and **6**, but in contrast to the latter compounds no $^4J_{PH}$ interaction is resolved in **7**.

The structure of **7** revealed by x-ray means[45] is very similar to that of **3**[35] in that the phosphorus and nitrogen have a tetrahedral and trigonal planar coordination sphere, respectively. While this result is not inconsistent with the NMR data, it would seem to be at variance with the equilibrium experiments implied in reactions 2 and 3 and with the BH stretching frequency data. Thus the weighted average of the asymmetric and symmetric BH modes[43] suggest that the order of basicity is **7** (2375) > **15** (2380) ≥ $P(OMe)_3$ (2383) > $P(OCH_2)_3CMe$ (2400 cm^{-1}). A possible rationale for the unusual basicity of **1** toward BH_3 in **7** compared to other phosphite esters can be found in the orbital interaction effects which are postulated to accompany conformational changes of the alkoxy groups around phosphorus in constrained phosphites.[46] For example, the oxygen 2p orbitals depicted in the structure of $P(OCH_2)_3CR$ are unable to interact with the phosphorus lone pair whereas in the monocyclic phosphite two orbitals are capable of such an interaction. While the average conformation of $P(OMe)_3$ has not been determined, it is likely to resemble that of **1**. In the latter compound there may be a substantial orbital repulsion effect stemming from the sterically controlled conformation of the $(CH_2CH_2)_3N$ moiety. To what extent the resulting enhancement of phosphorus basicity may be augmented by a long-distance N–P interaction in **1** remains to be clarified by continuing investigations. Barring the presence of other substantial influences, the orbital conformation of the parent phosphite of **15** is about the same in its effect on phosphorus basicity as in $P(OMe)_3$ if the infrared criterion for ordering base strengths is reliable.



The only spectroscopic evidence for the structure of **1** is its ^{31}P chemical shift (Table I), which is in the range for pyramidal phosphorus in phosphites such as $P(OMe)_3$ (140), $P(OCH_2)_3CR$ (92), and the adamantane phosphite $P(OCH)_3(CH_2)_3$ (137.7 ppm).[43] In view of the foregoing discussion, it is reasonable to assert that it contains a pyramidal phosphorus and a nearly planar nitrogen. Thus transannular bond formation leading to a tricyclic structure appears to occur only with Lewis acids such as H^+ and Ph_3C^+ which highly polarize the lone pair of **1**. Whereas silatranes are generally tricyclic owing to the presence of a transannular P←N bond, this class of compounds apparently can also exhibit a bicyclic configuration with a tetrahedral silicon and a trigonal planar nitrogen as was recently observed for the structure of *trans*-$[Cl(PMe_2Ph)_2PtSi(OCH_2CH_2)_3N]$ wherein the electron donating character of the $Cl(PMe_2Ph)_2Pt$ moiety is sufficient to prevent P←N bond formation.[47]

The small changes in $\delta^{31}P$ upon methylating **2**, **8**, and **9** to **12**, **10**, and **11**, respectively (Table I), indicate that the tetrahedral phosphorus geometry is preserved. Noteworthy, however, are the small increases in $^1J_{MP}$ in **10** and **11** which are ascribable to an increase in charge and/or s character on phosphorus owing to the inductive and/or steric effects of a quaternizing methyl group. Consonant with such effects are the observed small increases (1–3 cm^{-1}) in the CO frequencies which accompany methylation, but these increases may not be significant in view of the change in medium (see Experimental Section). The presence of quaternized nitrogen in **10–12** is signaled by a downfield shift in the CH_2N protons (Table III) and a downfield shift of the methylene carbon compared to triethanolamine. It is to be expected that the nitrogen is puckered out of the carbon plane to a greater extent in these compounds than in their unmethylated analogues but the degree to which this occurs is as yet undetermined.

Silatranes are highly toxic convulsants in mice[2b] and cages of the type $YP(OCH_2)_3CR$ (Y = lp or chalcogen) have recently been found to function similarly in a variety of animals.[48] Despite the structural similarity of phosphatranes to the aforementioned systems, **3**, **5**, and **6** are only moderately toxic.[48]

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Transition Metal Eight-Coordination. 8. Stereochemical Integrity, Geometrical Isomers, and Isomerization of Mixed Ligand Tungsten(IV) Chelates Containing Picolinic Acid and 8-Quinolinol Derivatives

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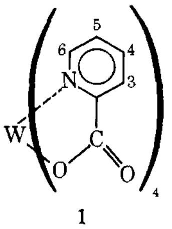
Abstract: The entire series of eight-coordinate tetrakis W(mpic)$_n$(dcq)$_{4-n}$ complexes has been prepared, isolated, and characterized. The proton magnetic resonance (^{1}H NMR) spectrum of W(mpic)$_3$(dcq) has two methyl signals of 2:1 intensity even at 50 °C and provides the first example of "stereochemical integrity" or pseudorigidity on a ^{1}H NMR time frame for an eight-coordinate tetrakis (chelate) complex above room temperature. Another first, the separation of two geometrical isomers (designated α and β) for an eight-coordinate transition-metal complex from solution, has been obtained for W(mpic)$_2$(dcq)$_2$ through liquid and thin layer chromatography, which have been used to separate the entire series. Spectroscopic rate studies indicate the kinetics parameters $E_a = 114$ kJ mol^{-1}, $\Delta H^{\ddagger} = 111$ kJ mol^{-1}, and $\Delta S^{\ddagger} = 35$ J mol^{-1} deg^{-1} for the isomerization of the β isomer toward the ($\beta \rightleftarrows \alpha$) equilibrium, where $K_{eq} \sim 5$ in the temperature range studied. Chemical analysis, magnetic moments, and electronic and ^{1}H NMR spectra together allow consistent stereochemical conclusions. The inertness and the π-acceptor and π-donor site preferences for d^2 dodecahedral complexes allow for the "stereochemical integrity" observations, even with polytopal transformations, which normally produce nonrigidity.

In order to evaluate the stereochemical dynamics of inert d^2 eight-coordinate complexes, we decided to synthesize mixed ligand complexes based on the inert W(pic)$_4$[2] and W(q)$_4$[3] complexes, **1** and **2**, respectively, where the ligands are derivatives of picolinic acid (Hpic) and 8-quinolinol (Hq). Prior to this study, previous reports of eight-coordinate transition-metal tetrakis chelates all indicated fast exchange limit proton magnetic resonance (^{1}H NMR) signals well below room temperature.[4] In fact, Fay and his co-workers[4a] have designated the tetrakis(N,N-dimethyldithiocarbamato)tantalum(V) as stereochemically rigid based on its nonequivalent



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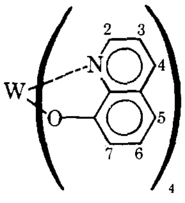

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