

## Bridgehead–Bridgehead Communication in Untransannulated ZP(ECH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N Systems

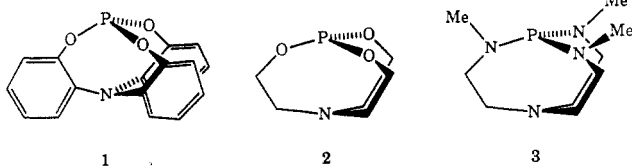
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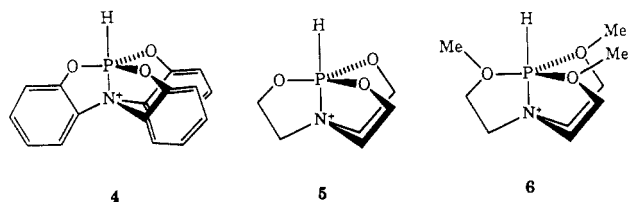
Trigonal-bipyramidal phosphatranes such as ZP(ECH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N<sup>+</sup> (Z = H<sup>+</sup>; E = O, NMe) feature a formal N<sub>ax</sub>→P bond (~2.0 Å) whereas in prophosphatranes such as ZP(ECH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N (Z = S, BH<sub>3</sub>; E = O, NMe) this N→P distance is closer to the sum of the van der Waals radii (3.35 Å). Here we present structural, chemical, and spectroscopic evidence that N→P interactions in prophosphatranes are probably of increasing importance in causing this distance to shrink in the crystallographically determined structures of *trans*-Cl<sub>2</sub>Pt[P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]<sub>2</sub> (3.33 Å), SP(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N (3.250 Å), and S<sub>2</sub>CP(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N (3.008 Å). Chemical equilibrium and NMR (e.g., δ(<sup>31</sup>P), J(PB), J(PSe)) and IR (ν(BH)) spectroscopic evidence presented is in accord with the Lewis basicity orders P(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N > P(OMe)<sub>3</sub> > P(OCH<sub>2</sub>)<sub>3</sub>CMe and P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N > P(NMe<sub>2</sub>)<sub>3</sub> > P(NMeCH<sub>2</sub>)<sub>3</sub>CMe toward Lewis acids such as BH<sub>3</sub> and Se. The superior basicity of the prophosphatranes is suggested to arise from bridgehead–bridgehead N→P enhancement of the electron density of phosphorus.

### Introduction

Prophosphatranes **1**,<sup>1</sup> **2**,<sup>2–4</sup> and **3**<sup>5,6</sup> are proving to be interesting probes of the steric and electronic influences governing the tendencies of this class of compounds to transannulate to the



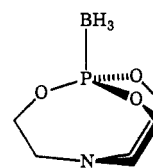
corresponding phosphatrane structures such as **4–6** in the presence



of electrophiles. Spectroscopic criteria for transannulation have included substantial upfield <sup>31</sup>P chemical shifts relative to the prophosphatrane precursors, and in the case of **5** and **6**, spin–spin couplings of the phosphorus to the N<sub>ax</sub>(CH<sub>2</sub>)<sub>3</sub> protons and carbons, which are not observed in the precursors.<sup>2,5</sup> The structures of **5**<sup>7</sup> and **6**,<sup>5</sup> which have been confirmed by X-ray crystallography, reveal P–N<sub>ax</sub> bond lengths of 1.986 and 1.967 Å, respectively.

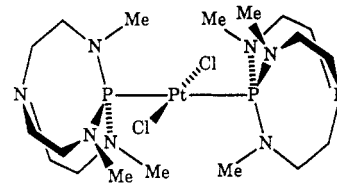
Somewhat more curious is the behavior exhibited by prophosphatranes such as **7–9** toward neutral as well as cationic electrophiles (Scheme 1). Although the vast majority of these phosphatranes are stable only in solution, several compounds of types **7f** and **8c**, for example, could be isolated.<sup>9</sup> Moreover, the structure of **8c** (R = Et) has been verified by X-ray crystallographic means.<sup>10</sup>

The question we address in the present work is, can evidence be adduced for the presence of partial N<sub>ax</sub>→P bonding in prophosphatranes? One of the best indications of such an interaction is structural metrics. However to date, data for only three X-ray crystallographically determined structures of prophosphatranes have been reported, namely, those for **1**,<sup>1</sup> **8**,<sup>12</sup> and **10**.<sup>13a</sup> In these structures, it can be noted that the P–N<sub>ax</sub> distances are rather

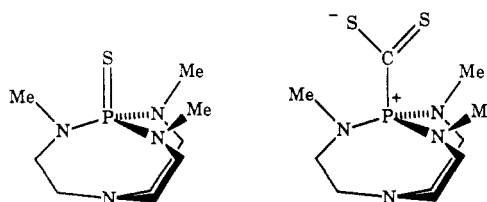


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similar to one another (3.14, 3.098 and 3.132 Å, respectively) but shorter by about 6.3, 7.5, and 6.6%, respectively, than the sum of the van der Waals radii (3.35 Å).<sup>14</sup> Here we report the structures of **11–13**, wherein the shortening of this distance over



11



12

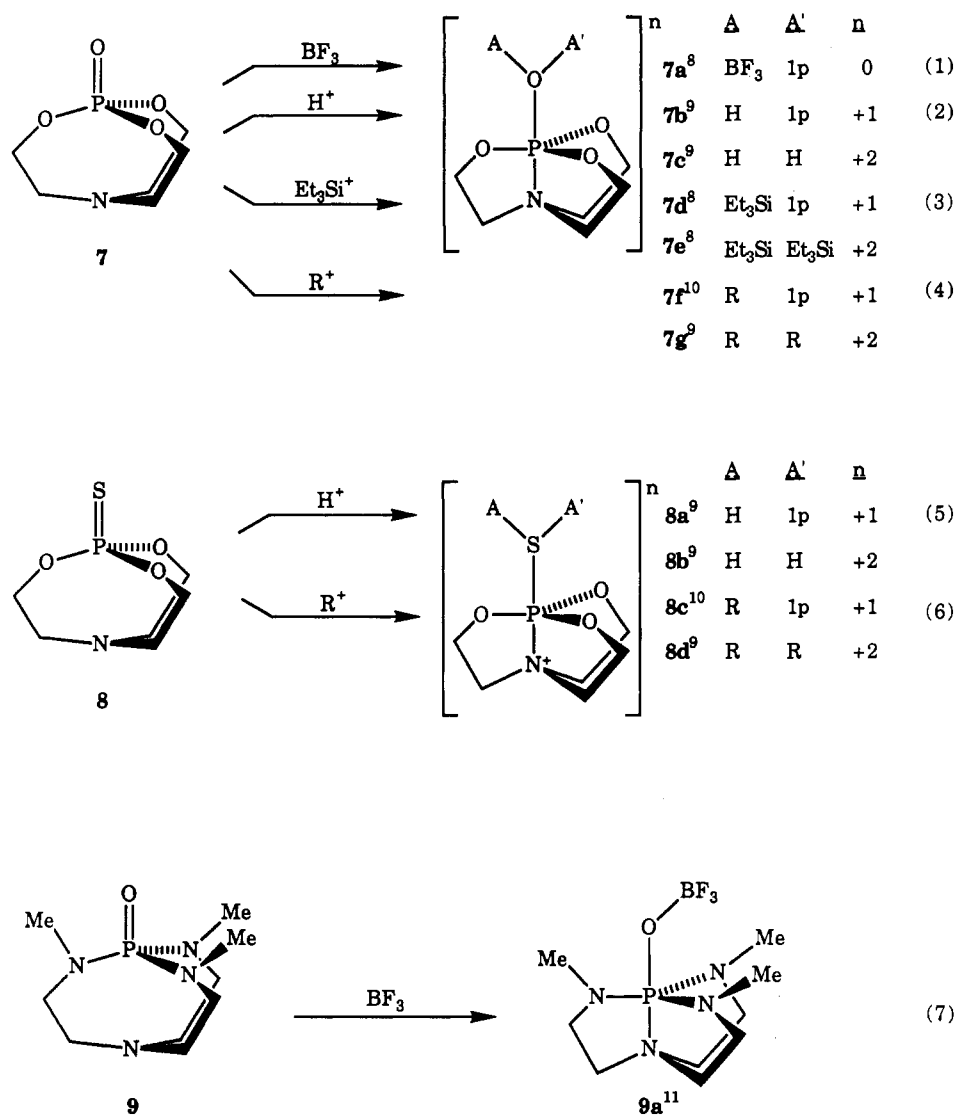
13

the sum of the van der Waals radii spans a substantially larger

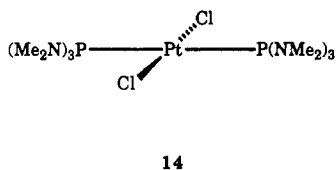
- (1) Müller, E.; Bürgi, H.-B. *Helv. Chem. Acta* **1987**, *70*, 1063.
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- (14) Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441.

Scheme 1



range. Also reported is the structure of an acyclic analogue of **11**, namely **14**, in which the conformations of the NC<sub>2</sub> groups are rather different from those in **11**.



### Experimental Section

Yellow **11**,<sup>6</sup> colorless **12**,<sup>6</sup> dark red **13**,<sup>6</sup> and yellow **14**<sup>13b</sup> were recrystallized from benzene, CH<sub>2</sub>Cl<sub>2</sub>/*n*-C<sub>6</sub>H<sub>14</sub>, MeCN, and benzene, respectively.

**Crystal Structure Analyses of 11 and 12.** Crystals were indexed by using an automatic indexing routine<sup>15</sup> and the results confirmed via axial pictures. Crystal data and additional details of data collection and refinement are given in Table I. Data were corrected for Lorentz and polarization effects and for absorption.<sup>16</sup> For **12**, the observed systematic absences (*h*0*l*, *l* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1) uniquely indicated space group *P*2<sub>1</sub>/*c*; no systematic absences were observed for **11**. For **11**, an examination of the Patterson map indicated the centrosymmetric space group and the platinum atom was placed at the origin; for **12**, the position

of the sulfur and phosphorus atoms were obtained by analyzing the Patterson function using the program ALCAMPS<sup>17</sup> with a S-P vector. In both structures, the positions of the remaining atoms were obtained by subsequent structure factor and electron density calculations. Hydrogen atoms were added in calculated positions and not refined for **11**; for **12**, the hydrogen positions were located from an electron density difference map and their positions refined with the thermal parameters constrained to the isotropic equivalents of the corresponding carbons. A block-matrix/full-matrix refinement program was used<sup>18</sup> that minimized  $\sum w(|F_o| - |F_c|)^2$ . The scattering factors used were those of ref 19, modified for the real and imaginary parts of anomalous dispersion. Positional parameters for **11** and **12** are given in Tables II and III, respectively.

**Crystal Structure Analyses of 13 and 14.** The cell constants for **13** and **14** were determined from lists of reflections found by an automated search routine. Pertinent data collection and refinement information is given in Table I. Lorentz and polarization corrections were applied as well as absorption corrections based on  $\psi$ -scans. Data reduction was performed by using the CAD4-SDP programs.<sup>20</sup>

The space group *P*2<sub>1</sub>/*n* was uniquely defined by the observed systematic absences for both **13** and **14**. For **13**, the positions of all 17 non-

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(20) Enraf-Nonius Structure Determination Package; Enraf-Nonius: Delft, The Netherlands.

**Table I.** Crystal and Refinement Data for 11–14

	11	12	13	14
formula	PtCl <sub>2</sub> (PN <sub>4</sub> C <sub>9</sub> H <sub>21</sub> ) <sub>2</sub> ·C <sub>6</sub> H <sub>6</sub>	C <sub>9</sub> H <sub>21</sub> N <sub>4</sub> PS	PS <sub>2</sub> N <sub>4</sub> C <sub>10</sub> H <sub>21</sub>	PtCl <sub>2</sub> P <sub>2</sub> N <sub>6</sub> C <sub>12</sub> H <sub>36</sub>
fw	698.53	248.33	292.41	592.40
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å	8.425 (3)	13.578 (4)	7.9102 (9)	7.898 (4)
<i>b</i> , Å	8.609 (4)	14.223 (3)	13.730 (1)	12.382 (2)
<i>c</i> , Å	11.217 (4)	13.832 (6)	13.036 (2)	11.127 (2)
$\alpha$ , deg	78.58 (7)			
$\beta$ , deg	75.46 (4)	10.81 (3)	91.856 (5)	99.11 (3)
$\gamma$ , deg	80.67 (8)			
<i>V</i> , Å <sup>3</sup>	766	2497 (2)	1415.1 (2)	1074 (2)
<i>Z</i>	1	8	4	2
<i>d</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.47	1.32	1.37	1.83
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	49.24	3.52	4.59	70.03
temp, K	298	298	295	295
radiation <sup>a</sup> ( $\lambda$ , Å)	Mo K $\alpha$ (0.71034)	Mo K $\alpha$ (0.71069)	Mo K $\alpha$ (0.71073)	Mo K $\alpha$ (0.71073)
data colln instrum	Datex	Syntex P2 <sub>1</sub>	Enraf-Nonius CAD4	Enraf-Nonius CAD4
data calcn range (2 $\theta$ ), deg	4–50	4–50	4–50	4–55
scan method		$\omega$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
octants measd	<i>hkl</i> , $\bar{h}\bar{k}\bar{l}$ , $h\bar{k}\bar{l}$ , $h\bar{k}\bar{l}$	<i>hkl</i> , $h\bar{k}\bar{l}$	<i>hkl</i> , $\bar{h}\bar{k}\bar{l}$ , $h\bar{k}\bar{l}$ , $h\bar{k}\bar{l}$	<i>hkl</i> , $\bar{h}\bar{k}\bar{l}$ , $h\bar{k}\bar{l}$ , $h\bar{k}\bar{l}$
no. reflns colld	3054	4726	4966	5018
no. indep reflns, $F_o^2 > 3\sigma(F_o^2)$ :	2495	2833	2049	1946
ratio of $T_{min}/T_{max}$ ( $\psi$ scans)	0.374	0.949	0.978	0.625
<i>R</i> <sub>F</sub>	0.052	0.041	0.0334	0.0195
<i>R</i> <sub>wF</sub> = $1/\sigma^2(F)$	0.074	0.039	0.0525	0.0298

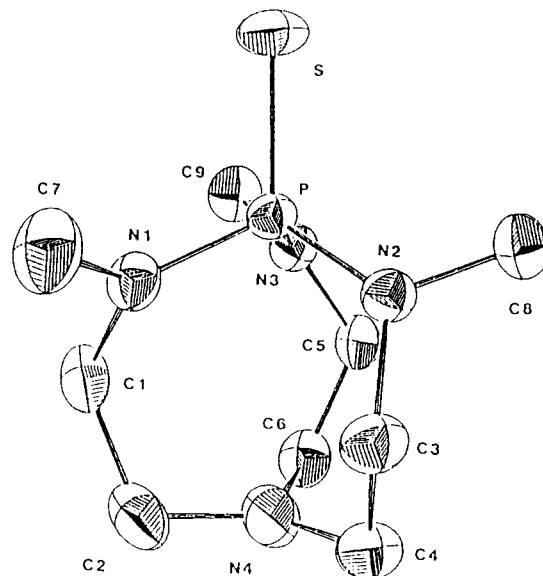
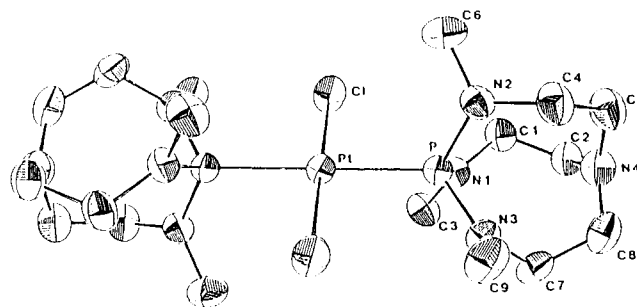
<sup>a</sup> Graphite monochromator.**Table II.** Final Atomic Positional Parameters ( $\times 10^4$ ) for PtCl<sub>2</sub>(PN<sub>4</sub>C<sub>9</sub>H<sub>21</sub>)<sub>2</sub>·C<sub>6</sub>H<sub>6</sub> (11)<sup>a</sup>

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> <sup>b</sup> , Å <sup>2</sup>
Pt	0	0	0	42.9
Cl	-736 (5)	1940 (4)	1266 (3)	70.4
P	-1407 (4)	1734 (3)	-1399 (3)	42.9
N(1)	-824 (11)	3534 (10)	-1577 (9)	46.6
N(2)	-3462 (12)	1917 (11)	-947 (10)	49.9
N(3)	-1063 (13)	1396 (11)	-2880 (9)	51.9
N(4)	-3201 (14)	4612 (12)	-3263 (11)	62.6
C(1)	-1965 (16)	4992 (13)	-1545 (13)	57.3
C(2)	-2431 (16)	5668 (14)	-2791 (13)	58.0
C(3)	911 (15)	3686 (16)	-1740 (14)	64.8
C(4)	-4559 (16)	2316 (16)	-1854 (14)	65.8
C(5)	-4724 (17)	4066 (16)	-2508 (14)	67.6
C(6)	-4299 (17)	1817 (18)	385 (14)	66.6
C(7)	-726 (17)	2674 (16)	-3956 (12)	58.9
C(8)	-2259 (19)	3748 (16)	-4237 (13)	68.7
C(9)	-1455 (20)	-53 (16)	-3180 (13)	79.4
C(10)	-6378 (19)	10286 (22)	-4085 (15)	81.2
C(11)	-5608 (21)	8765 (19)	-4154 (15)	79.0
C(12)	-4258 (22)	8490 (18)	-5072 (17)	85.6

<sup>a</sup>In this and succeeding tables, numbers in parentheses indicate standard deviations in the least significant figures. Positional parameters are in fractional unit cell coordinates. <sup>b</sup> $U_{eq} = (10^3/3) \sum U_{ij} \bar{a}_i \bar{a}_j$ , where the temperature factors are defined as  $\exp(-2\pi^2 \sum h_i h_j a_i^* a_j^* U_{ij})$ .

hydrogen atoms were taken from a direct-methods *E* map.<sup>21</sup> For 14, the volume of the unit cell suggested that the complex was centrosymmetric, so a Pt atom was placed at the origin, and the scale factor and isotropic temperature factor were allowed to refine in three cycles of least-squares refinement. The remaining atoms were found in a subsequent difference Fourier map.

Hydrogen atoms were added in idealized positions for 13 and not refined. The positions of the hydrogen atoms for 14 were observed in a difference map; for refinement, the methyl groups were refined as rigid groups (C–H distance fixed at 1.08 Å, H–C–H angle fixed at 109.5°). A common isotropic thermal parameter was refined for the hydrogen atoms. Refinement of 13 was carried out with the CAD4-SDP programs. The SHELX-76 package was used for the refinement of 14.<sup>22</sup> Scattering factors used were those of ref 19. Positional parameters for 13 and 14

**Figure 1.** ORTEP drawing of *trans*-Cl<sub>2</sub>Pt[P(MeNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]<sub>2</sub> (11) with ellipsoids at the 50% probability level.**Figure 2.** ORTEP drawing of S=P(MeNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N (12) with ellipsoids at the 50% probability level.

are listed in Tables IV and V, respectively.

## Discussion

**Structural Considerations.** From the structures of 11–13 shown in Figures 1–3, respectively, and the summarized structural data in Table VI it is seen that the axial nitrogens are quite planar with

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 (22) Sheldrick, G. M. In *Computing in Crystallography*; Schenk, H., Oltorf-Hazekamp, R., Van Koningsveld, H., Bassi, G. C., Eds.; Delft University: Delft, The Netherlands, 1978.

**Table III.** Final Atomic Positional Parameters ( $\times 10^4$ ) for  $S=P(NMeCH_2CH_2)_3N$  (**12**)

atom	x	y	z	$U_{eq}^a$
S(1)	1476.7 (6)	3443.0 (7)	960.1 (7)	48.2 (3)
P(1)	496.6 (6)	2893.6 (6)	1554.8 (6)	28.5 (2)
N(1)	722 (2)	1760 (2)	1803 (2)	35.1 (9)
N(2)	-740 (2)	3007 (2)	775 (2)	31.8 (8)
N(3)	577 (2)	3389 (2)	2657 (2)	33.9 (9)
C(1)	618 (3)	1300 (3)	2707 (3)	41 (1)
C(2)	-502 (3)	1122 (3)	2646 (3)	46 (1)
C(3)	-1519 (2)	2261 (3)	640 (2)	38 (1)
C(4)	-1937 (3)	2159 (3)	1518 (3)	42 (1)
C(5)	-362 (3)	3557 (2)	2934 (3)	35 (1)
C(6)	-813 (3)	2696 (3)	3270 (3)	40 (1)
N(4)	-1145 (2)	1957 (2)	2507 (2)	43 (1)
C(7)	915 (4)	1138 (3)	1050 (3)	53 (2)
C(8)	-1137 (3)	3909 (3)	293 (3)	43 (1)
C(9)	1586 (3)	3520 (3)	3474 (3)	47 (1)
S(1')	-6827.0 (7)	-477.8 (7)	3251.5 (8)	54.0 (4)
P(1')	-5797.2 (6)	167.0 (6)	2795.4 (6)	30.9 (3)
N(1')	-6256 (2)	338 (2)	1526 (2)	41 (1)
N(2')	-4699 (2)	-442 (2)	3070 (2)	35.5 (9)
N(3')	-5486 (2)	1212 (2)	3331 (2)	35.5 (9)
C(1')	-6055 (3)	1191 (3)	1057 (3)	46 (1)
C(2')	-4944 (3)	1268 (3)	1035 (3)	52 (2)
C(3')	-4109 (3)	-503 (3)	2368 (3)	41 (1)
C(4')	-3496 (3)	377 (3)	2331 (3)	51 (2)
C(5')	-4410 (3)	1589 (3)	3671 (3)	44 (1)
C(6')	-4067 (3)	1923 (3)	2796 (3)	50 (1)
N(4')	-4135 (2)	1214 (2)	2037 (2)	47 (1)
C(7')	-6786 (4)	-429 (3)	850 (3)	57 (2)
C(8')	-4195 (4)	-838 (3)	4095 (3)	55 (2)
C(9')	-6310 (3)	1850 (3)	3368 (4)	49 (1)

<sup>a</sup> $U_{eq} = (10^3/3\epsilon U_{ij} \bar{a}_i^* \bar{a}_j^* a_i a_j)$ , where the temperature factors are defined as  $\exp(-2\pi^2 \sum h_i h_j a_i^* a_j^* U_{ij})$ .

**Table IV.** Final Atomic Positional Parameters for  $S_2CP(MeNCH_2CH_2)_3N$  (**13**)<sup>a</sup>

atom	x	y	z	$B, \text{\AA}^2$
P	0.08996 (7)	0.30786 (4)	0.17947 (4)	2.18 (1)
S(1)	0.35171 (8)	0.44741 (5)	0.10476 (5)	4.10 (1)
S(2)	0.37247 (9)	0.37353 (5)	0.31942 (5)	4.03 (1)
N(1)	-0.0104 (2)	0.3063 (1)	0.2867 (1)	2.91 (4)
N(2)	-0.0341 (2)	0.3540 (1)	0.0892 (1)	2.67 (3)
N(3)	0.1517 (2)	0.1993 (1)	0.1461 (1)	2.68 (3)
N(4)	-0.2187 (3)	0.1808 (2)	0.1567 (2)	3.58 (4)
C(1)	0.2824 (3)	0.3824 (1)	0.2017 (2)	2.68 (4)
C(2)	-0.0543 (4)	0.3962 (2)	0.3398 (2)	4.62 (6)
C(3)	-0.0844 (3)	0.2157 (2)	0.3256 (2)	3.67 (5)
C(4)	-0.2468 (3)	0.1878 (2)	0.2656 (2)	3.87 (5)
C(5)	0.0164 (4)	0.3623 (2)	-0.0187 (2)	3.73 (5)
C(6)	-0.2199 (3)	0.3525 (2)	0.0997 (2)	3.47 (5)
C(7)	-0.2943 (3)	0.2509 (2)	0.0870 (2)	3.70 (5)
C(8)	0.2882 (3)	0.1462 (2)	0.2014 (2)	3.92 (5)
C(9)	0.0478 (3)	0.1395 (2)	0.0746 (2)	3.31 (5)
C(10)	-0.1156 (3)	0.1029 (2)	0.1197 (2)	3.51 (5)

<sup>a</sup> $B$  values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

C-N<sub>ax</sub>-C angles of approximately 120°. It is tempting to infer from Figure 3 that the axial nitrogen in **13** is slightly above the plane of the adjacent carbons. However, this distance (0.0026 (20) Å) is not significant, considering the relatively large size of the esd value. Interesting in going from **11** to **13** are the values of the P-N<sub>ax</sub> distances, the progression in these distances, and the trend in the N-P-N angles (E-P-E angles in Table VI).

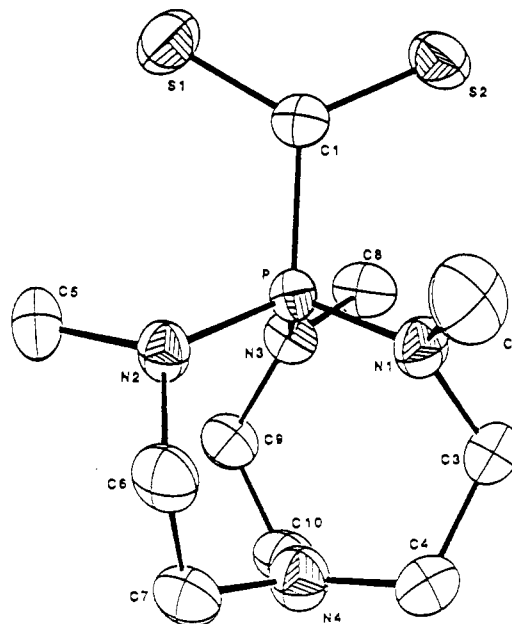
First, two of the P-N<sub>ax</sub> distances in **11-13** are shorter than the sum of the van der Waals radii, namely, in **12** (3.250 Å) and in **13** (3.008 Å). This suggests that perhaps some interaction may be occurring between the phosphorus and axial nitrogen in these compounds.

Second, the P-N<sub>ax</sub> distances progress from being close to the sum of the van der Waals radii (3.35 Å)<sup>14</sup> in **11** to being 3% shorter

**Table V.** Final Atomic Positional Parameters for  $trans\text{-Cl}_2Pt[P(NMe_2)_3]_2$  (**14**)<sup>a</sup>

atom	x	y	z	$B, \text{\AA}^2$
Pt	0.0000	0.0000	0.0000	1.946 (5)
Cl	-0.1147 (1)	0.15645 (7)	0.06729 (8)	3.52 (2)
P	-0.10435 (9)	0.04907 (6)	-0.20031 (6)	1.89 (1)
N(1)	-0.0558 (4)	-0.0247 (2)	-0.3174 (3)	2.38 (5)
N(2)	-0.0294 (4)	0.1701 (2)	-0.2298 (2)	2.86 (6)
N(3)	-0.3166 (3)	0.0448 (3)	-0.2305 (2)	2.86 (6)
C(1)	0.1187 (6)	-0.0190 (4)	-0.3424 (5)	3.45 (9)
C(2)	-0.1361 (5)	-0.1305 (3)	-0.3469 (3)	3.58 (9)
C(3)	0.1154 (5)	0.2199 (3)	-0.1535 (4)	4.30 (9)
C(4)	-0.0778 (7)	0.2256 (3)	-0.3464 (3)	4.5 (1)
C(5)	-0.4230 (5)	0.0416 (4)	-0.1350 (4)	3.63 (8)
C(6)	-0.4156 (5)	0.0618 (4)	-0.3508 (3)	4.3 (1)

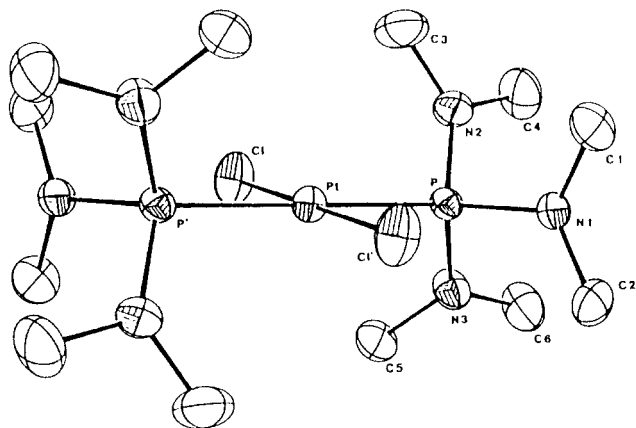
<sup>a</sup> $B$  values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

**Figure 3.** ORTEP drawing of  $S_2CP(MeNCH_2CH_2)_3N$  (**13**) with ellipsoids drawn at the 50% probability level.

than this sum in **12** and 10% shorter in **13**. While the latter shortening may not seem significant at first glance, it should be recalled that the transannular P-N<sub>ax</sub> bond (which is fully achieved in **6**, **8**, **8c**, and **10**; see Table VI) is only ca. 40% shorter than the sum of the van der Waals radii. In contrast, the average length of the three identical P-N bonds in **11** (1.67 Å), **12** (1.65 Å), and **13** (1.633 Å) and the average P-N<sub>eq</sub> length in **6** (1.65 Å) are ca. 50% shorter than the van der Waals radii sum. The greater length of the P-N<sub>ax</sub> bonds in fully formed phosphatranes compared with their P-N<sub>eq</sub> distances can be attributed to their approximately 0.5 bond order expected from a three-center-four-electron MO wherein two of the electrons reside in a nonbonding linear MO.<sup>2</sup> The shortening of the P-N<sub>eq</sub> distances over the sum of the covalent radii (1.84 Å) is quite normal for P-N σ bonds.<sup>23</sup>

Third, there is a distinct increase in the N-P-N bond angles from **12** to **13** (EPE angle in Table VI). It is this angle increase that is largely responsible for the decrease in the P-N<sub>ax</sub> distance, since the C-N<sub>ax</sub>-C angles are hardly affected and the degrees of twist around the P-N<sub>ax</sub> axis in these molecules (which would tend to compress the cage along this axis) are the same within experimental error. The opening of the N-P-N angles in **13** relative to **12** is obviously not steric in nature because the CS<sub>2</sub> moiety is decidedly larger than the sulfur substituent. More reasonable is

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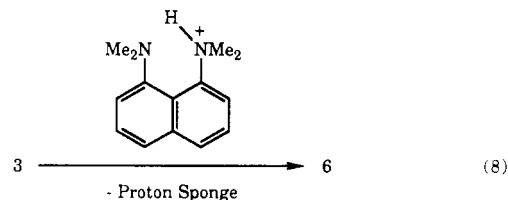
**Figure 4.** ORTEP drawing of *trans*-Cl<sub>2</sub>Pt[P(NMe<sub>2</sub>)<sub>3</sub>]<sub>2</sub> (**14**) with ellipsoids at the 50% probability level.

the supposition that electron donation from the phosphorus to CS<sub>2</sub> in **13** creates a zwitterion, which is stabilized by resonance as shown in the sketch of one of these forms above. To the extent that the P–C bond in **13** is perhaps more polar than the P–S bond in **12**, greater p character would be expected to reside in the P–C bond, thus opening the N–P–N angle in **13**. Indeed, this angle in the latter compound is widened slightly beyond the tetrahedral angle to 110.27°. This observation is also consistent with the notion that some P–N<sub>ax</sub> interaction is occurring. It may be noted here that even in the phosphatranes **5**, **6**, and **8c** (wherein transannulation has occurred) these angles are not quite 120°, since the N<sub>ax</sub>–P–N<sub>eq</sub> angles (which are a more sensitive measure of the angle widening at phosphorus) are not 90° but range between 85 and 87°.<sup>5,7,10</sup> Relevant to the question of bridgehead–bridgehead interactions in phosphatranes is the conclusion from CNDO/2 calculations<sup>24</sup> that the energy of the phosphatrane structure shown for **7** is very close to that for a transannulated polar phosphatrane structure. Although the average NPN angle in **11** (105°) is virtually the same as in the acyclic analogue **14** (104.5°), the conformation of the P(NC<sub>2</sub>)<sub>3</sub> moieties are different (compare Figures 1 and 4). In **11**, the average bond angles around the nitrogens attached to phosphorus are about 120°, the corresponding P–N bond lengths are the same within experimental error, and the NC<sub>2</sub> moieties have roughly C<sub>3</sub> symmetry around the P–Pt–P axis (Figure 1). In **14**, one of the nitrogens on each phosphorus ligand is somewhat more pyramidal than the other two, the average of the bond angles around N(1) being 117.3° compared with 119.6 and 119.7° around N(2) and N(3), respectively. The P–N(1) bond length in each ligand of this complex is slightly longer (1.684 vs 1.66 Å for PN(2) and 1.657 Å for PN(3)) and the PC(1)C(2) plane is rotated approximately 90° around the PN(1) bond relative to the PC(3)C(4) and PC(5)C(6) planes. Moreover, the N(1) lone pair is nearly anti with respect to the Pt–P bond. This type of approximate C<sub>2</sub> symmetry with a longer P–N bond associated with the more pyramidal nitrogen has been observed previously, for example, in Ag[P(NMe<sub>2</sub>)<sub>3</sub>]<sub>2</sub>BPh<sub>4</sub><sup>25</sup> and in *trans*-(OC)<sub>3</sub>Fe[P(NMe<sub>2</sub>)<sub>3</sub>]<sub>2</sub>.<sup>26</sup>

It should be recognized that there are steric reasons why the geometry around a bridgehead nitrogen is maintained at near planarity in bicyclo[3.3.3]undecane systems (wherein transannular interactions are absent). Thus, for example, there are steric repulsions stemming from van der Waals interactions among the methylene protons in HC(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N and in its hydrochloride salt,<sup>27</sup> which are also expected to influence the geometry of the N<sub>ax</sub> atom in phosphatranes.<sup>12</sup> Because of the presence of oxygen atoms in **1** and **2**, no similar effect on the phosphorus

geometry in these molecules is expected. To what extent phosphorus flattening is engendered in **3** by the Me groups is not presently known. In any case, such interactions would be strongly mitigated by the presence of phosphorus substituents as in **11**–**13**. The aromatic bridging groups in **1** provide a rather different steric and electronic environment in which the bridgehead nitrogen is slightly pyramidal with its lone pair directed away from the phosphorus.

**Chemical Considerations.** Compound **3** was recently demonstrated to possess a basicity at least ca. 7 orders of magnitude greater than that of typical R<sub>3</sub>P species.<sup>5</sup> Thus, for example, protonated "Proton Sponge" (Aldrich) is quantitatively deprotonated by **3** (reaction 8) to form **6** which is very difficult to

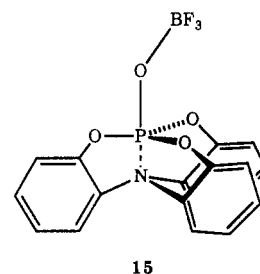


deprotonate. Similarly, **5** (formed from **2**) was found to be difficult to deprotonate.<sup>2</sup> These results suggest that in **2** and **3** the bridgehead nitrogens are within electronic communicating distance of the phosphorus, at least after initial phosphorus protonation has occurred. The same is true for **1** (in which the P–N distance is 6.3% shorter than the sum of the van der Waals radii) since **4** is formed upon protonation.<sup>1</sup> However, strain in the aromatically bridged framework of **4** apparently gives rise to a relatively weak P–N<sub>ax</sub> link (and consequently a weak P–H bond) because attempts to isolate **4** led to decomposition.<sup>1</sup> It is interesting that protonation of the bridgehead tertiary amine is not preferred in **1**–**3**.

When the phosphorus lone pair of **2**, as in **8**, is blocked, preferential protonation of the nitrogen can occur to give SP-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>NH<sup>+</sup> if the reaction is carried out in an aqueous medium.<sup>9</sup> This is in contrast to the transannulated sulfur-protonated products formed under anhydrous conditions in reaction 5.<sup>9</sup> Similarly, the nitrogens in **7** and **8** are methylated to give the corresponding ammonium salts when the reaction mixture is heated.<sup>2</sup> However, under mild conditions, reactions 4 and 6 take place.<sup>9,10</sup>

Equilibration studies have shown that **2** is a stronger base than P(OMe)<sub>3</sub> toward BH<sub>3</sub> in DMSO.<sup>2</sup> While hybridizational and conformational differences at the oxygens between these two phosphite esters cannot be ruled out,<sup>2</sup> it is possible that the bridgehead nitrogen is close enough to the phosphorus in the formally untransannulated **2** to enhance the basicity of the phosphorus, thereby favoring preferential formation of the adduct **10**.

**Spectroscopic Considerations.** As stated earlier, upfield <sup>31</sup>P chemical shifts and measurable <sup>31</sup>PN<sub>ax</sub><sup>13</sup>C and <sup>31</sup>PN<sub>ax</sub>C<sup>1</sup>H spin-spin coupling constants have been primary spectroscopic criteria for postulating transannulation in phosphatranes. Although a remarkably high-field shift of +5.2 ppm was reported for **1**,<sup>1</sup> other investigators<sup>28</sup> independently reported a value of 115 ppm, which is (somewhat surprisingly) virtually the same as that of **2** (115.2 ppm).<sup>2</sup> The upfield <sup>31</sup>P shift displayed by the BF<sub>3</sub> adduct **15**



(24) van Aken, D.; Castelyns, A. M. C. F.; Verkade, J. G.; Buck, H. M. *Recl.: J. R. Neth. Chem. Soc.* **1979**, *98*, 128.  
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Table VI. Selected Distances and Angles in Prophosphatranes and Phosphatranes

	P-N <sub>ax</sub> , Å	C-N <sub>ax</sub> -C,° deg	E-P-E, <sup>a,b</sup> deg	ref
SP(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N (8)	3.132	119.2	108.1	12
H <sub>3</sub> BP(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N (10)	3.098	119.7	107.4	13
EtSP(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N <sup>+</sup> (8c)	2.0	c	~119	10
HP(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N <sup>+</sup> (5)	1.986	113.3	119.8	7
<i>trans</i> -Cl <sub>2</sub> Pt[P(NMeCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N] <sub>2</sub> <sup>d</sup> (11)	3.33	119	105	this work
SP(NMeCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N (12)	3.250	119.6	106.8 <sup>e</sup>	this work
S <sub>2</sub> CP(NMeCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N (13)	3.008	120.0	110.27	this work
HP(NMeCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N <sup>+</sup> (6)	1.967	111	119.6	5

<sup>a</sup> Average value. <sup>b</sup> E = O or N. <sup>c</sup> Not given. <sup>d</sup> The Pt-P bond distance is 2.349 (4) Å in this molecule which is close to that in **14** (2.3312 (7) Å). <sup>e</sup> Average for the two independent molecules in the unit cell.

Table VII. <sup>31</sup>P Chemical Shifts (ppm) of XP(OR)<sub>3</sub> Compounds<sup>a</sup>

x	chem shift				
	XP(OMe) <sub>3</sub>	XP(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N	XP(OCH <sub>2</sub> ) <sub>3</sub> CMe	XP(OCH) <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>	XP(OCH <sub>2</sub> ) <sub>2</sub> CMeO
lone pair	136.9-140 <sup>b,c</sup>	115.2 <sup>h</sup> [2]	91.5 <sup>i</sup>	137.7 <sup>i</sup>	105 <sup>k</sup>
H <sub>3</sub> B	117.1 (103.2) <sup>d</sup>	98.3 (120.3) <sup>h</sup> [10]	97 (96.0) <sup>j</sup>	117 (92.2) <sup>j</sup>	126.8 (63.3) <sup>d</sup>
Se	78.0 (954) <sup>e</sup>	58.0 (972.2) <sup>h</sup>	60.1 (1053.1) <sup>e</sup>		81.4 (1098.0) <sup>e</sup>
S	74 <sup>b,f</sup>	60.9 <sup>h</sup> [8]	57.4 <sup>i</sup>	64.0 <sup>i</sup>	
O	+2.4 to -2.4 <sup>b,g</sup>	-6.6 <sup>h</sup> [7]	-7.9 <sup>j</sup>	-10.4 <sup>i</sup>	16.2 <sup>k</sup>
H <sup>+</sup>	24.4 (826.2) <sup>d</sup>	-20.9 (799.6) <sup>h,l</sup> [5]	32.2 (899.2) <sup>d</sup>	40.5 (880.3) <sup>k</sup>	46.1 (928.8)

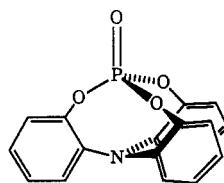
<sup>a</sup> <sup>1</sup>J(PX) couplings in Hz are given in parentheses. <sup>b</sup> Mark, V.; Dungan, C. H.; Crutchfield, M. M.; Van Wazer, J. *Top. Phosphorus chem.* **1967**, 5, 227. <sup>c</sup> -0.5 to -1.2 ppm for P(OEt)<sub>3</sub>. <sup>d</sup> Vande Griend, L. J.; Verkade, J. G.; Pennings, J. F. M.; Buck, H. M. *J. Am. Chem. Soc.* **1977**, 99, 2459. <sup>e</sup> Kroshefsky, R. D.; Weiss, R.; Verkade, J. G. *Inorg. Chem.* **1979**, 18, 469. <sup>f</sup> 71-72 ppm for SP(OEt)<sub>3</sub>. <sup>g</sup> -0.5 to -1.2 ppm for OP(OEt)<sub>3</sub>. <sup>h</sup> Reference 2. <sup>i</sup> Verkade, J. G.; King, R. W. *Inorg. Chem.* **1962**, 1, 948. <sup>j</sup> Verkade, J. G.; King, R. W.; Heitsch, C. W. *Inorg. Chem.* **1964**, 3, 884. <sup>k</sup> Vande Griend, L. J. Ph.D. Thesis, Iowa State University, Ames, IA, 1975. <sup>l</sup> This ion possesses a transannulated structure.

Table VIII. <sup>31</sup>P Chemical Shifts (ppm) of XP(NR<sub>2</sub>)<sub>3</sub> Compounds<sup>a</sup>

X	chem shift				
	XP(NMe <sub>2</sub> ) <sub>3</sub>	XP(MeNCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N	XP(MeNCH <sub>2</sub> ) <sub>3</sub> CMe	XP[(NCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> ] <sup>k</sup>	XP(NCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub>
lone pair	123-121.5 <sup>b</sup>	120.8 <sup>h</sup> [3]	84 <sup>i</sup>	142 or 155	129 <sup>j</sup>
H <sub>3</sub> B	104.4 (104.0) <sup>c,h</sup>	98.8 (142.4) <sup>h</sup>	86.9 (85.8) <sup>h</sup>		127 <sup>j</sup>
Se	82 (854) <sup>d</sup>	72.2 (754) <sup>g</sup>	77.7 (854.5) <sup>d</sup>	146 (890) <sup>i</sup>	133 (851) <sup>j</sup>
S	81.4-81.7 <sup>b,e</sup>	75.9 <sup>g</sup> [12]	73.2 <sup>j</sup>	148 <sup>i</sup>	117 <sup>j</sup>
O	22-25.6 <sup>b,f</sup>	20.3 <sup>g</sup> [9]	19.8 <sup>j</sup>	99 <sup>i</sup>	41 <sup>j</sup>

<sup>a</sup> <sup>1</sup>J(PX) couplings given in parentheses. <sup>b</sup> Mark, V.; Dungan, C. H.; Crutchfield, M. M.; Van Wazer, J. *Top. Phosphorus Chem.* **1967**, 5, 227. <sup>c</sup> 117.5-119.0 ppm for P(NEt<sub>2</sub>)<sub>3</sub>. <sup>d</sup> Kroshefsky, R. D.; Weiss, R.; Verkade, J. G. *Inorg. Chem.* **1979**, 18, 469. <sup>e</sup> 77.8 ppm for SP(NEt<sub>2</sub>)<sub>3</sub>. <sup>f</sup> 23.5 for OP(NEt<sub>2</sub>)<sub>3</sub>. <sup>g</sup> Reference 6. <sup>h</sup> Reference 38. <sup>i</sup> Kroshefsky, R. D.; Verkade, J. G. *Phosphorus Sulfur Relat. Elem.* **1979**, 6, 397. <sup>j</sup> Kroshefsky, R. D.; Verkade, J. G.; Pipal, J. R. *Phosphorus Sulfur Relat. Elem.* **1979**, 6, 377. <sup>k</sup> The (NCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub> moiety is a nine-membered macrocyclic ring. <sup>l</sup> White, D. W.; Karcher, B. A.; Jacobson, R. A.; Verkade, J. G. *J. Am. Chem. Soc.* **1979**, 101, 4921.

(-15.10 ppm) relative to that of the parent phosphate (-12.39 ppm) may be indicative of some N→P interaction.<sup>1</sup> Because of the rigidity of the aromatically bridged cage framework, however, the upfield shift is small compared with those observed in the analogous transformation shown in reactions 1 (11.5 ppm<sup>8</sup>) and 7 (22.5 ppm<sup>11</sup>) for the more flexible alkyl-bridged phosphatranes systems discussed in this paper. Of some relevance here is the observation that **16** displays a phosphoryl <sup>31</sup>P chemical shift of



16

-15.9 ppm<sup>29</sup> which is close to that reported for the parent phosphate (-12.39 ppm<sup>1</sup>) of adduct **15**. If these shieldings arose from interaction of the bridgehead atoms, it would be surprising that these shifts would be so similar for analogues having two different trivalent group 15 bridgehead atoms.

The nmr data assembled in Tables VII and VIII allow some interesting inferences to be drawn. The 45 ppm upfield shift in

Table VII from HP(OMe)<sub>3</sub><sup>+</sup> to the phosphatranane cation **5** is barely twice as large as the shifts from P(OMe)<sub>3</sub> to **2** or H<sub>3</sub>BP(OMe)<sub>3</sub> to **10**. Although such shifts are consistent with N→P interactions in the prophosphatranes, there are also mostly upfield shifts from XP(OMe)<sub>3</sub> to XP(OCH<sub>2</sub>)<sub>3</sub>CMe and to the adamantane-like XP(OCH)<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub> systems in Table VII. That these shieldings are primarily due to a P(OC)<sub>3</sub> conformational change from C<sub>s</sub> to C<sub>3v</sub>, rather than from an increase in strain, is suggested by the mainly downfield shifts from XP(OCH<sub>2</sub>)<sub>3</sub>CMe and XP(OCH)<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub> to the highly strained XP(OCH<sub>2</sub>)<sub>2</sub>CMeO analogue.

In Table VIII are again seen upfield <sup>31</sup>P shifts from the acyclic XP(NMe<sub>2</sub>)<sub>3</sub> systems to the prophosphatranes XP(MeNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N and also to the XP(MeNCH<sub>2</sub>)<sub>3</sub>CMe analogues. Insofar as the conformations of the XP(NMe<sub>2</sub>)<sub>3</sub> and XP(NCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub> species are nearly the same, the deshielding of the <sup>31</sup>P nucleus in the latter can be ascribed to strain at the nitrogen in the aziridinyl rings. In the XP(OCH<sub>2</sub>)<sub>2</sub>CMeO systems (Table VII), this deshielding effect could arise not only from the observed narrowing of the oxygen angles but also from the small OPO angles.<sup>32</sup>

Some NMR spin-spin coupling constants can be used to differentiate prophosphatranes from phosphatranes. <sup>1</sup>J(PH) in trigonal-bipyramidal **5** is 779.6 Hz,<sup>2</sup> which, as expected on the

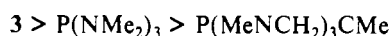
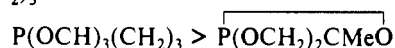
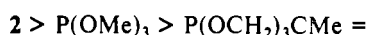
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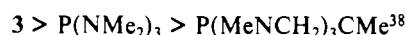
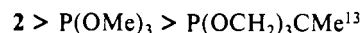
basis of its low *s* character, is considerably lower than that in tetrahedral  $\text{HP}(\text{OMe})_3^+$  (826.2 Hz).<sup>33</sup> The difference of 46.6 Hz is substantially larger than the 26-Hz difference between **4** (849 Hz<sup>1</sup>) and  $\text{HP}(\text{OPh})_3^+$  (875 Hz<sup>31</sup>) suggesting a weaker N→P interaction in this unstable species, even though the <sup>31</sup>P chemical shift (-14.11 ppm<sup>1</sup>) is representative of a phosphatranes. The greater electron richness of the phosphorus in **6** (<sup>1</sup>*J*(PH) = 491 Hz<sup>5</sup>)<sup>34</sup> compared with **5** (<sup>1</sup>*J*(PH) = 779.6 Hz<sup>2</sup>) could account for its relatively low coupling value. This reasoning is also consistent with the lower <sup>1</sup>*J*(PSe) coupling in the prophosphatranes  $\text{SeP}(\text{MeNCH}_2\text{CH}_2)_3\text{N}$  (754 Hz, Table VIII) compared with that in  $\text{SeP}(\text{OCH}_2\text{CH}_2)_3\text{N}$  (973.2 Hz, Table VII). The reduction in these values compared with those for  $\text{SeP}(\text{NMe}_2)_3$  (784 Hz, Table VIII) and  $\text{SeP}(\text{OMe})_3$  (954 Hz, Table VII) respectively, could also be taken to imply the presence of some degree of  $\text{N}_{\text{ax}} \rightarrow \text{P}$  interaction, since lower *s* character in the Se–P bond and a lower positive charge on phosphorus would be expected. <sup>1</sup>*J*(BP) couplings have also been used to order the basicities of series of similar phosphorus ligands.<sup>35</sup> Here, basicity increases are accompanied by increases in coupling.<sup>36</sup> This criterion also supports the notion of some N→P interaction in the borinophosphatranes, since the basicity orders



emerge from Tables VII and VIII, respectively.

Detectable coupling of the phosphorus to the  $\text{NCH}_2$  carbon and protons in phosphatranes is always observed. In prophosphatranes, such couplings are undetectably small. An exception to this rule is **10** wherein a small *J*(PNC) coupling of 2 Hz is observed, but no *J*(PNCH<sub>2</sub>) spin–spin interaction is detected.<sup>13</sup> While this PNC coupling is small compared with that in **5** (12 Hz<sup>2</sup>), it is consistent with some degree of N→P interaction in **10**.

As has been noted earlier, the B–H symmetric and asymmetric stretching frequencies in  $\text{BH}_3$  adducts of phosphite esters increase as the Lewis basicity of the phosphite decreases.<sup>37</sup> Such infrared data also support the superior basicity of **2** and **3**:



**Conclusions.** The bulk of the structural,<sup>17</sup> chemical, and spectroscopic evidence strongly indicates that the  $\text{N}_{\text{ax}} \rightarrow \text{P}$  interaction in some prophosphatranes is not negligible. Despite this observation, the terms “phosphatranes” and “prophosphatranes” are in a sense synonymous with the descriptions “transannulated” and “untransannulated”, respectively, if the former noun is taken to imply the presence of an  $\text{N}_{\text{ax}}\text{--P}$  bond and the latter noun may or may not imply the existence of a substantial degree of bridgehead–bridgehead interaction.

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**Supplementary Material Available:** Tables of hydrogen atom parameters, anisotropic thermal parameters, bond lengths, bond angles, least-squares planes, torsion angles, and general displacement expressions (21 pages); tables of calculated and observed structure factors (40 pages). Ordering information is given on any current masthead page.

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(34) <sup>1</sup>*J*(PH) values for  $\text{HP}(\text{NR}_2)_3^+$  species have not been reported.

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(36) Unlike <sup>1</sup>*J*(PH) or <sup>1</sup>*J*(PSe) couplings, which increase with decreasing basicity, <sup>1</sup>*J*(<sup>31</sup>P<sup>1</sup>B) coupling display the opposite behavior for reasons that are not understood.

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