

1991

# Synthesis, characterization, and reactivity of unusually basic prophosphatranes

Mary Anne Hardy Laramay  
*Iowa State University*

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**Synthesis, characterization, and reactivity of unusually basic  
prophosphatranes**

**Laramay, Mary Anne Hardy, Ph.D.**

**Iowa State University, 1991**

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Ann Arbor, MI 48106



**Synthesis, characterization, and reactivity of  
unusually basic prophosphatranes**

by

**Mary Anne Hardy Laramay**

**A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of the  
Requirements for the Degree of  
DOCTOR OF PHILOSOPHY**

**Department: Chemistry  
Major: Inorganic Chemistry**

**Approved:**

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**For the Major Department**

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**For the Graduate College**

**Iowa State University  
Ames, Iowa**

1991

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DEDICATION

**This manuscript is dedicated to my parents, Jim and Nancy Hardy. Without the tenacity, optimism, and creativity they taught and encouraged in me, this work would not have been possible.**

## GENERAL INTRODUCTION

The prophosphatranes upon which this thesis focusses,  $P(NMeCH_2CH_2)_3N$ ,  $P(NHCH_2CH_2)_3N$ , and  $P(NBnCH_2CH_2)_3N$  have been found to be at least  $10^7$  times more basic than any known phosphine derivative.

The unusually high basicities observed for the prophosphatranes has been postulated to be due to the formation (upon protonation of the pro-azaphosphatranes) of three chelate rings and a 3-center-4-electron molecular orbital system between the axial nitrogen, the phosphorus and the proton on the phosphorus in the conjugate-acid phosphatranes.

The basicities of these species were compared to each other by spectroscopic means and by competitive deprotonation experiments, as discussed in Parts I and II. The unexpected basicity order, in which the hydrogen analogue was found to be more basic than the methyl analogue which in turn was more basic than the benzyl analogue, could not be explained sufficiently either by steric or inductive arguments, however the observed trend may be explained by an extra stability that may occur due to an anomalously high electron delocalization in the hydrogen analogue.

An attempt to determine how much stability in the phosphatranes is gained from the chelate rings as apposed to from the H-P-N<sub>ax</sub> bond gave another unexpected result. In  $(Me_2N)_2P(NMeCH_2CH_2)NMe_2$ , there is only the possibility of forming one chelate ring upon the formation of a 3-center-4-electron molecular orbital system with a Lewis acid such as a proton. However, if such a transannular interaction occurred in this compound, it did not offer enough stability in the conjugate acid to prevent the evolution of  $HNMe_2$ , giving the phosphonium cation,  $(Me_2N)(:)\overline{P}NMeCH_2CH_2N^+Me_2$ , strongly indicating that chelate rings contribute substantially to the unusual stability of phosphatrane cations.

The unusually high basicity of  $P(NMeCH_2CH_2)_3N$  may also be associated with its

unexpected redox behavior with mercuric ions. This prophosphatane reduces mercury(II) to give the dioxaphosphetane dimer,  $[\text{HMe}_2\text{NCH}_2\text{CH}_2\text{N}(\overline{\text{CH}_2\text{CH}_2\text{MeN}})_2\text{PO}]_2(\text{OTf})_4$  and  $\text{Hg}_2^{2+}$ , whereas the less basic  $\text{P}(\text{NMe}_2)_3$  will only coordinate to the mercuric cations. It was also found that upon hydrolysis,  $\text{Cl}_2\text{Hg}[\text{P}(\text{NMeCH}_2\text{CH}_2)_3\text{N}]_2$  gives  $\text{HP}(\overline{\text{NMeCH}_2\text{CH}_2})_3\text{N}^+$ ,  $\text{Hg}^0$ , and a peroxide, whereas  $\text{Cl}_2\text{Hg}[\text{P}(\text{NMe}_2)_3]_2$  is stable under the same conditions.

As yet another unexpected result, during the preparation of 1,1,2,2-tetraethylcarboxylatocyclobutane, a starting material for  $\text{P}(\text{OCH}_2)_2\text{CCH}_2\text{CH}_2\text{CCH}_2\text{OCH}_2\text{OH}$ , another bicyclic phosphorus(III) species, the heretofore unknown tetraester, tricyclo[4.2.1.1<sup>2,5</sup>]-1,2,5,6-tetraethylcarboxylatodecane-9,10-dione, was also discovered.

The above results are presented in this manuscript along with the synthetic and spectroscopic data and crystallographic determinations for  $\text{HP}(\overline{\text{NHCH}_2\text{CH}_2})_3\text{N}^+\text{Cl}^-$ ,  $(\text{Me}_2\text{N})(\text{:})\overline{\text{PNMeCH}_2\text{CH}_2\text{NMe}_2}(\text{BF}_4)$ ,  $\text{Cl}_2\text{Hg}[\text{P}(\text{NMeCH}_2\text{CH}_2)_3\text{N}]_2$ ,  $[\text{HMe}_2\text{NCH}_2\text{CH}_2\text{N}(\overline{\text{CH}_2\text{CH}_2\text{MeN}})_2\text{PO}]_2(\text{OTf})_4$ ,  $\text{Br}(\text{CO})_4[\text{P}(\text{NMeCH}_2\text{CH}_2)_3\text{N}]$ , and tricyclo[4.2.1.1<sup>2,5</sup>]-1,2,5,6-tetraethylcarboxylatodecane-9,10-dione.

## EXPLANATION OF THESIS FORMAT

This thesis is written so that each section can be regarded as a separate article in publishable form. The numbering of the compounds, figures, schemes, tables, and references are independent in each section.

The manuscript presented in Part I is a published communication: Laramay, M. A. H.; Verkade, J. G. *J. Amer. Chem. Soc.* **1990**, *112*, 9421. The manuscript presented in Part II is a more detailed description of the work discussed in Part I and contains additional experimental results: Laramay, M. A. H.; Verkade, J. G., *Zeitschr. anorg. allg. Chem.*, invited by the editor, submitted. The manuscript in Part III is written as a communication: Laramay, M. A. H.; Verkade, J. G., *J. Amer. Chem. Soc.*, in progress. The manuscript presented in Part IV is a detailed description of the metal chemistry of  $\text{P}(\text{NMeCH}_2\text{CH}_2)_3\text{N}$ : Laramay, M. A. H.; Ringrose, S. L.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.*, in progress. The new chemistry presented therein was performed by the first author, and S. Ringrose, from R. A. Jacobson's research group, determined the crystal structure for the compound numbered **11** in the text. The crystal structures for compounds **15** and **12** and **8** in the text were determined by Dr. Lee Daniels and by Dr. Victor Young, respectively, from the Iowa State Molecular Structure Laboratories. The manuscript presented in Part V is designed to be published as a note: Laramay, M. A. H.; Verkade, J. G., *J. Amer. Chem. Soc.*, in progress.

Some of the work presented was based on preliminary results obtained by previous researchers working in our group, namely, Dr. Harry Schmidt and Dr. Cees Lensink.

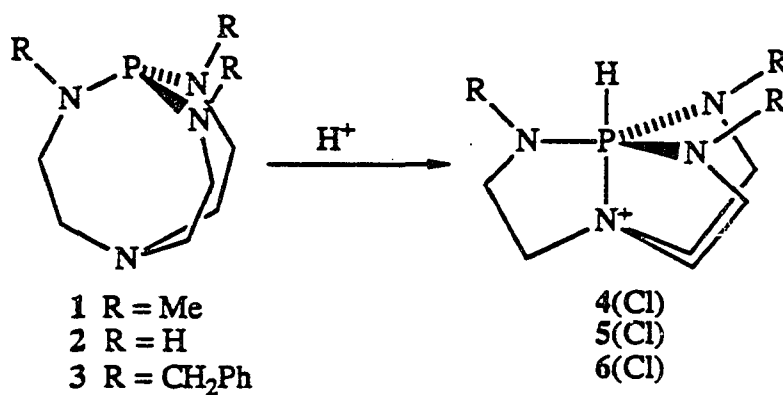
PART I: THE "ANOMALOUS" BASICITY OF  $P(NHCH_2CH_2)_3N$  RELATIVE TO  
 $P(NMeCH_2CH_2)_3N$  AND  $P(NBnCH_2CH_2)_3N$ : A CHEMICAL  
CONSEQUENCE OF ORBITAL CHARGE BALANCE?

## ABSTRACT

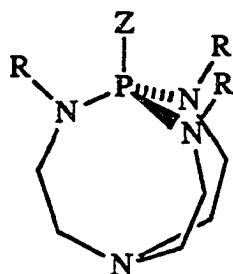
Competitive deprotonation of the precursor tricyclic acids to the corresponding bicyclic phosphine bases  $\text{P}(\text{NHCH}_2\text{CH}_2)_3\text{N}$  (2),  $\text{P}(\text{NMeCH}_2\text{CH}_2)_3\text{N}$  (1), and  $\text{P}(\text{NBnCH}_2\text{CH}_2)_3\text{N}$  (3), respectively, reveal the unexpected basicity order  $3 < 1 < 2$ . This order is corroborated by the observed trends in the B-H stretching and  $^{31}\text{P}$ - $^{11}\text{B}$  spin-spin coupling frequencies of the  $\text{BH}_3$  adducts of 1 - 3, the  $^1\text{J}(^{31}\text{P}-^{77}\text{Se})$  values of the selenium adducts of 1-3, and the  $^1\text{J}(^{31}\text{P}-^1\text{H})$  values of  $\overline{\text{HP}(\text{NMeCH}_2\text{CH}_2)_3\text{N}^+}$ ,  $\overline{\text{HP}(\text{NHCH}_2\text{CH}_2)_3\text{N}^+}$ , and  $\overline{\text{HP}(\text{NBnCH}_2\text{CH}_2)_3\text{N}^+}$ , 4 - 6, respectively. The unexpected stability (and weak acidity) of 5 is attributed to comparatively strong electron delocalization along its 3-center H-P- $\text{N}_{\text{ax}}$  MO system which is suggested to be signaled by its unusually shielded  $^{31}\text{P}$  chemical shift (-42.9 ppm) compared with 6 (-11.0 ppm) and 4 (-10.1 ppm).

## COMMUNICATION

The prophosphatrane **1** was recently shown to be ca.  $10^7$  times more basic in solution toward  $H^+$  than any known phosphine derivative, giving the unusually robust phosphatrane cation **4**.<sup>1</sup> Here we report that although analogue **3** is less basic than



**1** as expected on inductive grounds, such reasoning fails to explain our observation that the parent analogue **2** is more basic than either **1** or **3**. As in the synthesis of **1**, for which **4(Cl)** is the precursor,<sup>1</sup> **5(Cl)** and **6(Cl)** are the sources of **2** and **3**, respectively, and they are made in an analogous manner. Although like **1**, **3** can be isolated and purified, prophosphatrane **2** has resisted isolation owing to facile polymerization. However, the previously characterized prophosphatrane derivative **7**<sup>2</sup> and the analogously synthesized **8** and **9**<sup>3</sup> reported here are sufficiently stable in solution for spectroscopic measurements. Moreover, **10**,<sup>2</sup> **11**<sup>2</sup> and **12**<sup>4</sup> have been isolated and characterized, and **11** has been structured by X-ray



- 7 R = Me, Z = Se  
 8 R = H, Z = Se  
 9 R = CH<sub>2</sub>Ph, Z = Se  
 10 R = Me, Z = O  
 11 R = Me, Z = S  
 12 R = H, Z = O

means.<sup>2</sup>

From <sup>31</sup>P NMR peak integrations of separate DMSO solutions of **4**, **5** and **4**, **6** treated with a stoichiometric deficit of KO-*t*-Bu, it was demonstrated that **6** is more acidic than **4**, and that **4** is more acidic than **5**, which provides the basicity order 3<1<2 for the corresponding conjugate bases. Assuming a pK<sub>a</sub> of 28.6 for HO-*t*-Bu in DMSO,<sup>5</sup> a pK<sub>a</sub> of 29.6 is calculated for **5** and an upper limit of 26.8 is estimated for **4** and **6** in DMSO.<sup>6</sup> There is ample evidence in the literature that for bases of similar structure, rising solution and gas phase basicity for similar phosphorus-containing bases can be linearly correlated with decreasing <sup>1</sup>J(<sup>31</sup>P-<sup>77</sup>Se) values of their selenium adducts<sup>7,8</sup> and with decreasing <sup>1</sup>J(<sup>31</sup>P-<sup>1</sup>H) couplings of their protonated forms.<sup>8,9</sup> Such coupling trends are also found for the selenium adducts of prophosphatranes **3**, **1** and **2** (**12** (774 Hz), **8** (754 Hz), **10** (590 Hz), respectively) and for their corresponding protonated forms (**6** (506 Hz), **4** (491 Hz), **5** (453 Hz)).

A comparison of the crystallographic parameters for cation **4**<sup>1</sup> with those of **5**<sup>10</sup> (see Figure 1) does not provide a satisfactory rationale for the basicity order 1<2. In fact, the P-N<sub>ax</sub> bond in **4** is unexpectedly slightly shorter (1.976(8)Å) than in **5** (2.0778(4)Å) and the N<sub>eq</sub>-P-N<sub>ax</sub> angle in **4** (85.9(4)°, 86.5(2)°) is larger than in **5** (84.01(3)°), giving rise to a slightly more distorted TBP for **5**. The other metrics are all within experimental error for the two structures. While steric effects of the carbon



substituents in **4** and **6** might be expected to enhance their acidity relative to **5**, it is puzzling that the trigonal bipyramidal geometry of **5** is more axially distorted than that of **4** with an accompanying longer P–N<sub>ax</sub> bond. Van der Waals contacts between the exocyclic substituents of the planar equatorial nitrogens and the hydrogen or selenium substituents on phosphorus also do not offer a rationale for the trends in the  $^1J_{\text{PH}}$  and  $^1J_{\text{PSe}}$  values, assuming that the solid state structures of **4** and **5** reflect their solution structures. The greater stability and hence weaker acidity of cation **5** compared with **4** and **6** may stem from a dominant electronic stabilization effect associated with greater delocalization and hence greater charge balance in the phosphorus orbitals involved in the three-center four-electron H–P–N<sub>ax</sub> bond for which a rationale is now proposed. It is reasonable to assume that the contributions of the excitation energy and of the orbital radial extensions to the dominating Ramsey paramagnetic shielding term of a large atom such as phosphorus is relatively constant among the analogous cations **4**–**6**. Since the anomalously high  $^{31}\text{P}$  NMR shielding value in **5** (–42.9 ppm) compared with **6** (–11.0 ppm) and **4** (–10.1 ppm) obviously can not be rationalized upon inductive grounds, the only major factors remaining in the model are the orbital charge imbalance terms in the paramagnetic shielding equation which then must be small for **5** compared with **4** and **6**, thus leading to pronounced  $^{31}\text{P}$  shielding associated with greater orbital charge balance<sup>11</sup> in **5**. Decreased orbital charge imbalance signalling a greater basicity of **2** can also account for the upfield shift of **2** (89.3 ppm) relative to those of **1** and **3** (120.81 and 128.3 ppm, respectively).

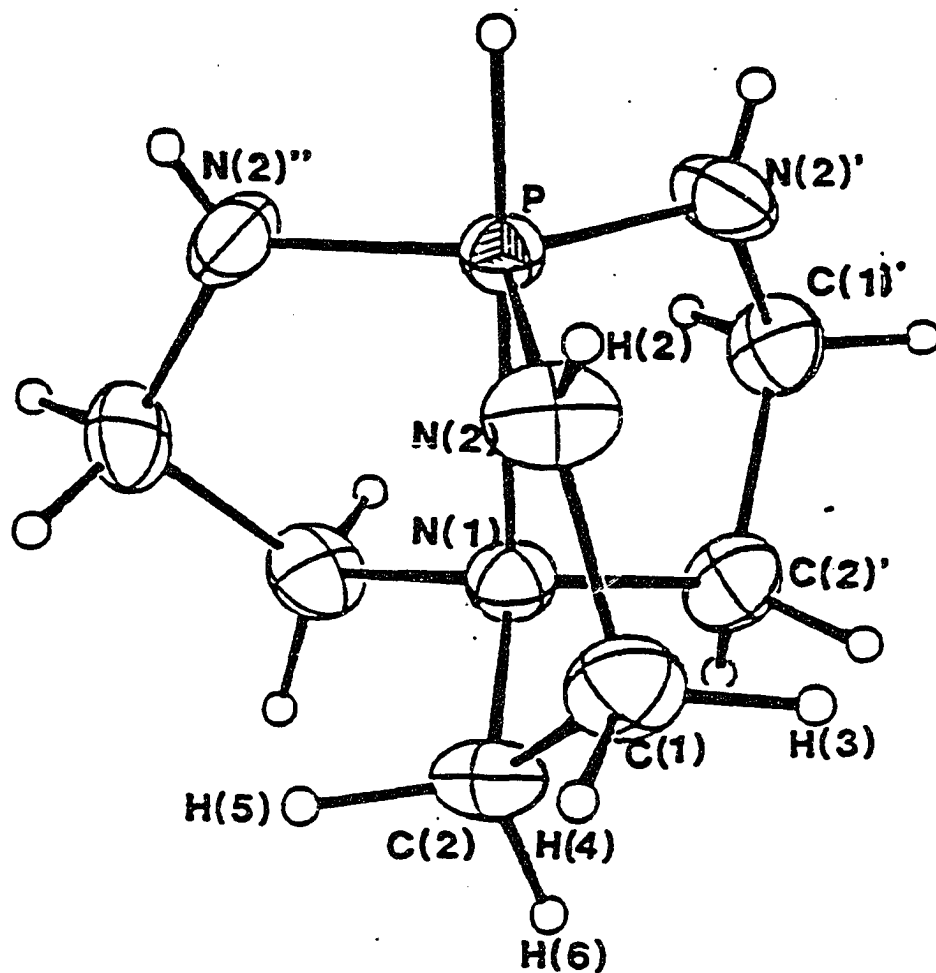


Figure 1. ORTEP drawing of cation 5, with ellipsoids drawn at the 50% probability level: hydrogen atoms are drawn as arbitrarily sized spheres for clarity

**Supplementary Material.** Tables of  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR, high resolution mass spectral data; X-ray crystallographic data; positional parameters; bond distances and angles; general displacement parameters and structure factors (12 pages).

**Acknowledgments.** The authors are grateful to the Petroleum Research Foundation, administered by the American Chemical Society, for a grant supporting this work. They also thank Dr. Lee Daniels of the Iowa State Molecular Structure Laboratory for the crystal and molecular structure of  $5(\text{Cl})$ , Dr. W. Menge for his synthetic route to  $(\text{HBzNCH}_2\text{CH}_2)_3\text{N}$ , and the W.R. Grace Company for a research sample of tren.

## REFERENCES

1. Lensink, C.; Xi, S.-K.; Daniels, L. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 3478.
2. Xi, S. K.; Schmidt, H.; Lensink, C.; Kim, S.; Wintergrass, D.; Daniels, L. M.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1990**, *29*, 2214 and references therein.
3. Compound **8** was generated from **5** (OTf) (0.30 g, 0.92 mmol in 2.5 mL ice-cooled THF) by adding n-BuLi (0.95 mL, 0.98 M in hexanes, 0.92 mmol) and after stirring for 10 min adding 0.073 g (1.0 mmol) of red selenium. After stirring for an additional 10 minutes, the mixture was used for spectroscopic measurement. Because **5**(Cl) is insoluble in THF, **5**(OTf) was prepared from a 10 mL CH<sub>2</sub>Cl<sub>2</sub> solution of HOSO<sub>2</sub>CF<sub>3</sub> (3.88 g, 15.5 mmol) which was added to an ice-cooled 35 mL CH<sub>2</sub>Cl<sub>2</sub> solution of (HMeNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N (2.26 g, 15.5 mmol) and 2.52 g (15.5 mmol) of P(NMe<sub>2</sub>)<sub>3</sub>. After allowing the reaction mixture to warm to room temperature and stirring for 15 min., the solvent was removed under vacuum and the residue washed with hexanes giving spectroscopically pure **5**(OTf). Adduct **9** was synthesized from 0.31 g (0.70 mmol) of **3** in 3 mL of toluene and 0.054 g (0.69 mmol) of red selenium. The precipitated selenide was dissolved in THF for spectroscopic measurements.
4. Compound **12** was prepared from a solution of **2** in MeCN made by adding **5** (OTf) (0.303 g, 0.934 mmol in 10 mL MeCN) to a 15 mL suspension of KO-*t*-Bu (0.105 g, 0.937 mmol in 15 mL MeCN) followed by bubbling in O<sub>2</sub> for 4 hr. Volatilization in vacuo followed by extraction with MeCN (25 mL) gave upon

evaporation of the solvent a nearly quantitative yield of **12**.

5. Arnett, E. M.; Small, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 808.
6. Cations **4** and **6** by  $^{31}\text{P}$  NMR spectroscopy appear to be completely deprotonated by  $\text{KO}-t\text{-Bu}$  in DMSO. In the pKa calculations it was assumed that **4** and **6** could be present up to 5% concentration without detection by  $^{31}\text{P}$  NMR spectroscopy.
7. Kroshefsky, R. D.; Weiss, R.; Verkade, J. G. *Inorg. Chem.* **1979**, *18*, 469.
8. Verkade, J. G.; Mosbo, J. A. "One Bond Couplings to Other Non-Metals and to Metals" in "Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis", J.G. Verkade and L.D. Quin, Editors; VCH Publishers: New York, Chapter 13.
9. Hodges, R. V.; Houle, F. A.; Beauchamp, J. L.; Montag, R. A.; Verkade, J. G. *J. Am. Chem. Soc.* **1980**, *102*, 932.
10. Crystal data: cubic space group  $\text{P}2_13$  (No. 198),  $a = 9.9443(2) \text{ \AA}$ ,  $V = 983.39(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $d_{\text{calc}} = 1.423 \text{ g/cm}^3$ ,  $\mu(\text{MoK}\alpha) = 5.034 \text{ cm}^{-1}$ ; 705 unique reflections for  $4 < 2\theta < 50^\circ$ ; 616 observed ( $F_o^2 > 3\sigma(F_o^2)$ ) at  $-25 \text{ }^\circ\text{C}$ . Refinement of 56 parameters converged with agreement factors of:  $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o| = 0.0204$  and  $R_w = \text{sqrt}[\Sigma w(F_o - F_c)^2 / \Sigma w(F_o^2)] = 0.0254$ . The refinement was carried out on a Digital Equipment Corp. MicroVAX II computer using the CAD4-SDP programs. Details of the crystallographic procedures appear in the Supplementary Material.
11. Wrackmeyer, B. *Ann. Rep. NMR Spectroscopy* **1985**, *16*, 73.

## APPENDIX

**Data Collection.** A colorless, tetrahedral-shaped crystal of the title compound was mounted on the end of a glass fiber in a random orientation. The crystal was then moved to the diffractometer and cooled to  $-25 \pm 1$  °C. The cell constants were determined from a list of 25 reflections found by an automated search routine. The  $m\bar{3}$  symmetry of the cubic cell was confirmed by photography. Pertinent data collection and reduction information are given in Table 1.

A total of 2592 reflections were collected in the  $hkl$ ,  $h\bar{k}l$ , and  $hk\bar{l}$  octants. Equivalent data were merged, leaving 705 data ( 616 with  $F_o^2 \geq 3\sigma(F_o^2)$ ), which included 241 Friedel pairs ( 219 pairs with both members observed). The agreement factors for the averaging of 2237 observed reflections was 1.6% ( based on  $F_{obs}$ ). Lorentz and polarization corrections were applied. No decay was detected, and psi-scans of several reflections indicated that an absorption correction was not necessary.

**Structure Solution and Refinement.** Systematic absences indicated that the space group was one of  $P23$  ( no. 195),  $P2_13$  ( no. 198), or  $Pm\bar{3}$  ( no. 200). If the structure was as expected, the molecule was required to reside on a three-fold axis to give  $Z = 4$ ; space group  $Pm\bar{3}$  was therefore initially eliminated from consideration. Direct methods solutions<sup>1</sup> in both of the remaining possible space groups gave a sensible solution only in space group  $P2_13$ ; the successful refinement of the structure verified this choice. All of the non-hydrogen atoms were taken from the direct methods E-map. Following anisotropic refinement of the 6 unique atoms, a difference Fourier map revealed the positions of all the expected hydrogen atoms. The hydrogen atoms were added to the refinement with isotropic thermal parameters, but the

temperature factor for the hydrogen atom bound to the equatorial nitrogen atom persisted in refining to a negative value. Therefore the temperature factors for the 5 hydrogen atoms bound to N(2), C(1), and C(2) were refined as a single common variable. The temperature factor for the hydrogen bound to the P was allowed to refine freely. A plot of  $I_C/I_O$  vs.  $I_C$  indicated a secondary extinction effect, so an extinction coefficient was included in the refinement which then converged to a value of  $5(1) \times 10^{-7}$  (in absolute units).

The final refinement cycles involved 56 parameters fitted to 616 observed data. A set of 219 Friedel pairs were treated as unique reflections, since anomalous dispersion effects would make averaging undesirable. The residuals (for the enantiomorph chosen, I) were:  $R = 0.0204$ ;  $R_w = 0.0254$ ; quality-of-fit indicator, 0.982.<sup>2</sup> The largest positive peak in the final difference electron density map had a height of  $0.29(5) \text{ e}/\text{\AA}^3$ .

The absolute configuration was determined by an application of Hamilton's significance test<sup>3</sup> to the weighted  $R$ -values from independent refinements of both enantiomorphs. For enantiomer II the refinement led to the following residuals:  $R = 0.0219$ ;  $R_w = 0.0276$ ; quality-of-fit indicator, 1.067. The ratio of the two residuals,  $R_w(\text{II})/R_w(\text{I}) = 1.087$ , is larger than the relevant 0.01% significant point, and so enantiomer I is established at the 99.99% confidence level.

X-ray data collection and the structure solution were carried out at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. MicroVAX II computer using the CAD4-SPD programs.<sup>4</sup>

#### References.

1. SHELXS-86, G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Göttingen. F. R. G.

2. Neutral-atom scattering factors and anomalous scattering corrections were taken from *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.
3. Hamilton, W. C. *Acta Crystallogr.* 1965, 18, 502.
4. Enraf-Nonius Structure Determination Package; Enraf-Noniu: Delft, Holland.



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Table 1. X-ray crystallographic data for  $\overline{\text{HP}(\text{NHCH}_2\text{CH}_2)_3\text{N}^+\text{Cl}^-}$ , 5

Crystal data	
Formula	$[\text{PN}_4\text{C}_6\text{H}_{16}]\text{Cl}$
Formula weight	210.65
Space group	$\text{P2}_13$ (No. 198)
$a$ , Å	9.9443(2)
$V$ , Å <sup>3</sup>	983.39(2)
$Z$	4
$d_{\text{calc}}$ g/cm <sup>3</sup>	1.423
Crystal size, mm	0.38 x 0.38 x 0.38
$\mu(\text{MoK}\alpha)$ , cm <sup>-1</sup>	5.034
Data collection instrument	Enraf-Nonius CAD4
Radiation	$\text{MoK}\alpha$ ( $\lambda = 0.71073$ Å)
Orientation reflections, number, range	25, 17.8 - 33.9
Temperature, °C	$-25 \pm 1$
Scan method	$\theta - 2\theta$
Data collection range, $2\theta$ , deg	4-50
No. unique data, total:	705
with $F_o^2 > 3\sigma(F_o^2)$ :	616

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$^c \text{Quality-of-fit} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

Table 1, continued. X-ray crystallographic data  $\overline{\text{HP}(\text{NHCH}_2\text{CH}_2)_3\text{N}^+\text{Cl}^-}$ , 5

Crystal data	
Number of parameters refined	56
R <sup>a</sup>	0.0204
R <sub>w</sub> <sup>b</sup>	0.0254
Quality-of-fit indicator <sup>c</sup>	0.982
Largest shift/esd, final cycle	0.01
Largest peak, e/Å <sup>3</sup>	0.29(5)

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b R_w = [ \sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2 ]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$^c \text{Quality-of-fit} = [ \sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}}) ]^{1/2}$$

Table 2. Positional parameters and their estimated standard deviations for  
 $\overline{\text{HP}(\text{NHCH}_2\text{CH}_2)_3\text{N}^+\text{Cl}^-}$ , 5

Atom	x	y	z	B(Å <sup>2</sup> )
Cl	0.87502(4)	0.87502	0.87502	2.287(3)
P	0.52059(4)	0.52059	0.52059	1.739(3)
N(1)	0.6412(1)	0.6412	0.6412	2.02(1)
N(2)	0.5241(2)	0.6498(1)	0.4177(1)	2.71(3)
C(1)	0.6155(2)	0.7609(2)	0.4348(2)	2.73(3)
C(2)	0.6310(2)	0.7791(2)	0.5844(2)	2.62(3)
H(1)	0.446(2)	0.446	0.446	0.5(6) <sup>a</sup>
H(2)	0.499(2)	0.638(2)	0.356(2)	0.7(2) <sup>a</sup>
H(3)	0.702(2)	0.743(2)	0.392(2)	0.7 <sup>a</sup>
H(4)	0.585(2)	0.841(2)	0.399(2)	0.7 <sup>a</sup>
H(5)	0.547(2)	0.824(2)	0.624(2)	0.7 <sup>a</sup>
H(6)	0.702(2)	0.827(2)	0.609(2)	0.7 <sup>a</sup>

<sup>a</sup>Atoms refined isotropically.

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

Table 3. Bond distances (Å) for  $\overline{\text{HP}(\text{NHCH}_2\text{CH}_2)_3\text{N}^+\text{Cl}^-}$ , 5

Atom 1	Atom 2	Distance
P	N(1)	2.0778(4)
P	N(2)	1.644(1)
P	H(1)	1.29(1)
N(1)	C(2)	1.486(2)
N(2)	C(1)	1.440(2)
N(2)	H(2)	0.67(2)
C(1)	C(2)	1.506(3)
C(1)	H(3)	0.97(2)
C(1)	H(4)	0.93(2)
C(2)	H(5)	1.02(2)
C(2)	H(6)	0.89(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 4. Torsion angles (deg) for  $\overline{\text{HP}(\text{NHCH}_2\text{CH}_2)_3\text{N}^+\text{Cl}^-}$ , 5

Atom 1	Atom 2	Atom 3	Atom 4	Angle
N(2)	P	N(1)	C(2)"	-105.97 (0.06)
N(2)	P	N(1)	C(2)	14.03 (0.10)
N(2)	P	N(1)	C(2)'	134.03 (0.07)
N(1)	P	N(2)	C(1)	12.01 (0.13)
N(2)'	P	N(2)	C(1)	91.76 (0.14)
N(2)"	P	N(2)	C(1)	-67.74 (0.14)
P	N(1)	C(2)"	C(1)"	-33.40 (0.01)
C(2)	N(1)	C(2)"	C(1)"	-148.76 (0.07)
C(2)'	N(1)	C(2)"	C(1)"	81.96 (0.03)
P	N(2)	C(1)	C(2)	-34.61 (0.19)
N(2)	C(1)	C(2)	N(1)	41.48 (0.17)

Table 5. Spectral data for new compounds

Compound	Data
1	$^{31}\text{P}$ (DMSO) $\delta$ 120.8 (s).
2	$^{31}\text{P}$ (DMSO) $\delta$ 89.3 (s).
3	$^{31}\text{P}$ ( $\text{C}_6\text{D}_6$ ) $\delta$ 128.3 (s); $^1\text{H}$ ( $\text{CDCl}_3$ ) $\delta$ 4.04 (d, $^3\text{J}_{\text{PH}} = 12.1$ Hz) $\delta$ 7.30 (m, $\text{C}_6\text{H}_5$ ) $\delta$ 2.71 (m, $\text{CH}_2\text{CH}_2$ ); $^{13}\text{C}$ ( $\text{C}_6\text{D}_6$ ) $\delta$ 40.6 (d, $^2\text{J}_{\text{PC}} = 15.2$ Hz, $\text{CH}_2\text{Ph}$ ) $\delta$ 128.0, 128.3, 129.4, 138.1 (all s, $\text{C}_6\text{H}_5$ ) $\delta$ 54.7 (br, $\text{PNCH}_2\text{CH}_2$ ) $\delta$ 50.4 (s, $\text{PNCH}_2\text{CH}_2$ ); HRMS (m/e) calculated 444.24429, found 444.24374.
5	$^{31}\text{P}$ (MeOD) $\delta$ -42.9 (d, $^1\text{J}_{\text{PH}} = 453$ Hz; $^1\text{H}$ (MeOD) $\delta$ 5.64 (d, $^1\text{J}_{\text{PH}} = 453$ Hz) $\delta$ 5.07 (d, $^2\text{J}_{\text{PH}} = 28.3$ Hz, NH) $\delta$ 2.95 (m, $\text{CH}_2\text{CH}_2$ ); $^{13}\text{C}$ (MeOD) $\delta$ 50.6 (d, $^2\text{J}_{\text{PC}} = 11.1$ Hz, $\text{N}_{\text{eq}}\text{CH}_2$ ) $\delta$ 34.2 (s, $\text{N}_{\text{ax}}\text{CH}_2$ ).
6	$^{31}\text{P}$ ( $\text{CDCl}_3$ ) $\delta$ -11.0 (d, $^1\text{J}_{\text{PH}} = 503$ Hz); $^{13}\text{C}$ ( $\text{CDCl}_3$ ) $\delta$ 39.9 (d, $^2\text{J}_{\text{PC}} = 4.1$ Hz, $\text{CH}_2\text{Ph}$ ) $\delta$ 127.9, 128.3, 129.2, 137.7 (all s, $\text{C}_6\text{H}_5$ ) $\delta$ 47.8 (d, $^2\text{J}_{\text{PC}} = 5.2$ Hz, $\text{N}_{\text{eq}}\text{CH}_2$ ) $\delta$ 52.1 (s, $\text{N}_{\text{ax}}\text{CH}_2$ ); $^1\text{H}$ ( $\text{CDCl}_3$ ) $\delta$ 5.81 (d, $^1\text{J}_{\text{PH}} = 503$ Hz,) $\delta$ 4.15 (d, $^3\text{J}_{\text{PH}} = 17.1$ Hz, $\text{CH}_2\text{Ph}$ ) $\delta$ 3.65 (m, $\text{PN}_{\text{eq}}\text{CH}_2$ ), $\delta$ 3.11 (m, $\text{PN}_{\text{ax}}\text{CH}_2$ ).
8	$^{31}\text{P}$ (DMSO) $\delta$ 46.0 ( $^1\text{J}_{\text{PSe}} = 590$ Hz).
9	$^{31}\text{P}$ (DMSO) $\delta$ 84.1 ( $^1\text{J}_{\text{PSe}} = 774$ Hz).

Table 5, continued. Spectral data for new compounds

Compound	Data
12	$^{31}\text{P}$ (MeCN) $\delta$ 21.3; $^1\text{H}$ ( $\text{d}_6$ -DMSO) $\delta$ 3.28 (br, NH) $\delta$ 2.80 (dt, $^3J_{\text{PH}} = 16.4$ Hz, $^3J_{\text{HH}} = 5.4$ Hz, $\text{PNCH}_2$ ) $\delta$ 2.54 (t, $^3J_{\text{HH}} = 5.4$ Hz); $^{13}\text{C}$ ( $\text{d}_6$ -DMSO) $\delta$ 42.8 (s, $\text{PNCH}_2\text{CH}_2$ ) $\delta$ 53.6 (s, $\text{PNCH}_2\text{CH}_2$ ); HRMS (m/e) calculated 190.09835, found 190.09796.



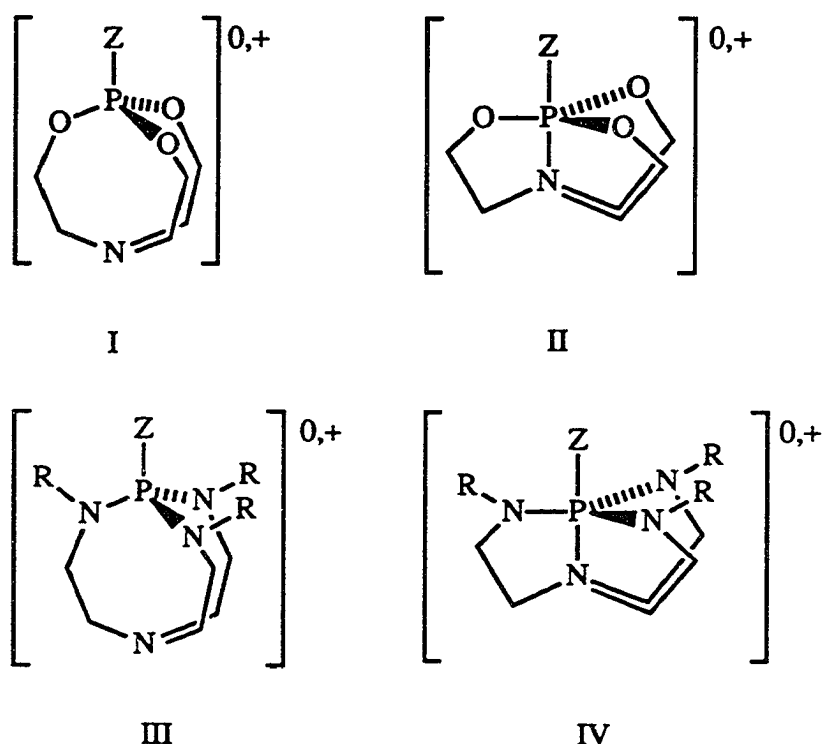
**PART II: UNUSUALLY LEWIS BASIC PRO-AZAPHOSPHATRANES.**

## ABSTRACT

The title compounds of the type  $P(RNCH_2CH_2)_3N$  (**1**, R = H; **2**, R = Me; **3**, R =  $CH_2Ph$ ) display the unexpected basicity trend  $1 > 2 > 3$  with respect to protonation which forms the azaphosphatranes  $HP(\overline{RNCH_2CH_2})_3N^+$  (**4**, R = H; **5**, R = Me; **6**, R =  $CH_2Ph$ ). The unusual basicity trend of  $1 > 2 > 3$  is also supported by the trend in  $^1J_{PSe}$  values obtained for  $SeP(RNCH_2CH_2)_3N$  (**8**, R = H; **9**, R =  $CH_2Ph$ ; **10**, R = Me). Deprotonation of **4** is shown to produce a variety of deprotonated derivatives which were trapped by alkylation with MeI. A favored rationale for the unusual weakness of **4** as a protonic acid ( $pK_a$  in DMSO, 29.6) is an unusual stability of the axial three-center four-electron bond signalled by the unusually high field  $^{31}P$  chemical shift of this cation (-42 ppm).

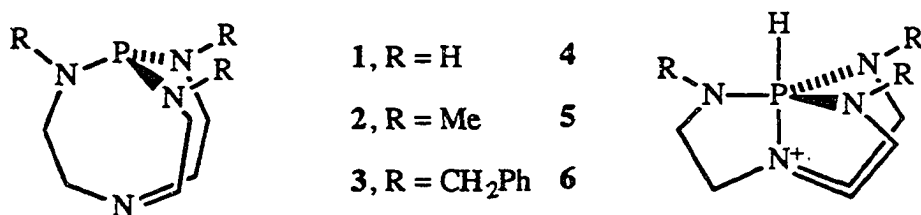
## INTRODUCTION

Some time ago we described the synthesis of two new related classes of polycyclic phosphorus compounds known as prophosphatranes (I) and phosphatranes (II).<sup>1-8</sup> In more recent years we extended these classes to include the analogous

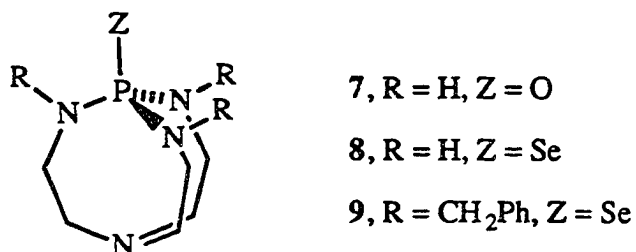


pro-azaphosphatranes (III) and azaphosphatranes (IV).<sup>9-14</sup> The phosphatranes and azaphosphatranes are isoelectronic and isostructural analogues of silatranes<sup>15</sup> and azasilatranes.<sup>9,16-22</sup> The prophosphatranes have no known prosilatrane counterpart. Very recently, however, we reported the first example of a "quasi" pro-azasilatrane in which steric interactions of the apical and equatorial substituents almost completely severed the  $\text{Si-N}_{ax}$  transannular bond.<sup>17</sup>

Of interest in systems of type I-IV is the relationships of the substituent Z or Z<sup>+</sup> to the stabilization of structure I relative to II and that of III relative to IV. While the former relationship has already been described,<sup>4</sup> the latter one is still not well developed. For proazaphosphatranes and azaphosphatranes an additional variable of interest is the possibility of utilizing different R groups such as R = H, Me and CH<sub>2</sub>Ph.<sup>14</sup> In this paper we address ourselves to a consideration of the anomalous basicity of pro-azaphosphatranes 1-3 and some unusual properties of their protonated products, namely the azaphosphatranes 4-6.



Here we also describe in more detail and also extend what we have communicated in preliminary form<sup>14</sup> concerning the syntheses of 1, 3, 4 and 6; NMR spectroscopic studies of these compounds; protonation reactions of 1-3; deprotonation experiments on 4-6; and the structural features of 4(Cl).



## EXPERIMENTAL

All reactions were carried out under dry argon. The solvents were dried and distilled under nitrogen using standard methods.<sup>23</sup> Commercial phosphorus trichloride, trifluoromethane sulfonic acid, and tetrahydrofuran borane adduct were used without purification. Tris(dimethyl)aminophosphine and triethylamine were purified by trap-to-trap distillation at 0.5 mm Hg. Tris(1-aminoethyl)amine was distilled from lithium aluminum hydride at 55 °C, 0.05 mm Hg. Potassium *t*-butoxide was sublimed at 175 °C, 0.05 mm Hg, and red selenium was prepared using standard procedures.<sup>24</sup> Proton and carbon-13 spectra were obtained on a Nicolet NT300 instrument. Phosphorus-31 NMR spectra were recorded on a Bruker WM200 instrument using C<sub>6</sub>H<sub>6</sub> as an external lock solvent and P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> as an external standard.

$[\overline{\text{HP}(\text{NHCH}_2\text{CH}_2)_3\text{N}}]\text{Cl}$ , 4(Cl). A solution containing 1.215 g (8.853 mmol) of PCl<sub>3</sub> in 5.0 mL of CH<sub>2</sub>Cl<sub>2</sub> was added all at once to a solution containing 2.889 g (17.70 mmol) of P(NMe<sub>2</sub>)<sub>3</sub> in 25 mL of CH<sub>2</sub>Cl<sub>2</sub>. This solution was then cooled to 5 °C and 3.882 g (26.55 mmol) of tren in 25 mL of CH<sub>2</sub>Cl<sub>2</sub> was added over a period of 15 minutes. The resulting precipitate was separated by filtration and washed with 25 mL of CH<sub>2</sub>Cl<sub>2</sub> (5.581 g, quantitative yield). The precipitate was spectroscopically pure according to the <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra (Table 1). Crystals suitable for X-ray diffraction were grown from a concentrated MeOH solution.

$[\overline{\text{HP}(\text{NHCH}_2\text{CH}_2)_3\text{N}}]\text{OSO}_2\text{CF}_3$ , 4(OTf). A solution containing 3.88 g (15.5 mmol) of triflic acid in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to a solution containing 2.26 g (15.5 mmol) of tren and 2.52 g (15.5 mmol) of P(NMe<sub>2</sub>)<sub>3</sub> in 35 mL of CH<sub>2</sub>Cl<sub>2</sub> cooled in an ice bath. The resulting solution was stirred at room temperature for 15 minutes. The volatiles were removed *in vacuo* and the residue was washed with hexanes. The resulting white

solid product was spectroscopically pure and was used without further purification (4.96 g, 99% yield). The NMR spectroscopic data for this compound were identical to those of 5(Cl) (see Table 1).

**[HP(N(CH<sub>2</sub>Ph)CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]Cl, 6(Cl).** A solution containing 0.233 g (1.70 mmol) of PCl<sub>3</sub> in 5 mL CH<sub>2</sub>Cl<sub>2</sub> was added all at once to a solution containing 0.555 g (3.41 mmol) of P(NMe<sub>2</sub>)<sub>3</sub> in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. To this solution was slowly added a solution containing 2.12 g (5.11 mmol) of tris (N-benzyl-2-aminoethyl)amine<sup>25</sup> in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture was stirred at room temperature for one hour. The volatiles were then removed and the white solid residue was washed with hexanes giving 2.40 g (98% yield) of spectroscopically pure 6(Cl) (Table 1).

**P[N(CH<sub>2</sub>Ph)CH<sub>2</sub>CH<sub>2</sub>]<sub>3</sub>N, 3.** To a solution containing 0.572 g (5.11 mmol) of KO-*t*-Bu in 20 mL of THF was added a solution containing 2.21 g (4.64 mmol) of 6(Cl) in 20 mL of THF. After stirring the reaction mixture at room temperature for one hour, the volatiles were removed *in vacuo*. The residue was extracted with several 100 mL portions of hexanes for 3 hours. The extracts were collected and the hexanes removed *in vacuo* to give an oily residue which was spectroscopically pure 3 (<sup>31</sup>P NMR (Et<sub>2</sub>O) δ 128.3 (s); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 7.30 (15H, m, C<sub>6</sub>H<sub>5</sub>), δ 4.04 (6H, d, <sup>3</sup>J<sub>PH</sub> = 12.1 Hz), δ 2.71 (12H, br, NCH<sub>2</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 40.6 (d, PhCH<sub>2</sub>, <sup>2</sup>J<sub>PH</sub> = 15.2 Hz), δ 50.2 (s, N<sub>eq</sub> CH<sub>2</sub>), δ 54.7 (s, N<sub>ax</sub> CH<sub>2</sub>), δ 128.0 (s, C<sub>6</sub>H<sub>5</sub>), δ 128.3 (s, C<sub>6</sub>H<sub>5</sub>), δ 129.4 (s, C<sub>6</sub>H<sub>5</sub>), δ 138.1 (s, C<sub>6</sub>H<sub>5</sub>); HRMS: *m/e* (measured) 444.24374, *m/e* (calculated) 444.24429 for C<sub>27</sub>H<sub>33</sub>N<sub>4</sub>P).

**O=P(NHCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N, 7.** A solution containing 0.303 g (0.934 mmol) of 4(OTf) in 10 mL of CH<sub>3</sub>CN was added to 0.105 g (0.937 mmol) of KO-*t*-Bu suspended in 15 mL of CH<sub>3</sub>CN. Molecular oxygen was bubbled through this mixture for 16 hours. The CH<sub>3</sub>CN and the resulting HO-*t*-Bu were removed *in vacuo* and the residues were extracted with 25 mL of CH<sub>3</sub>CN. The solvent was collected and the CH<sub>3</sub>CN was evaporated giving a

yellowish solid which was recrystallized from CH<sub>3</sub>OH to give 0.08 g of **7** in 48% yield (<sup>31</sup>P (CH<sub>3</sub>CN) δ 21.3; <sup>1</sup>H (MeOD) δ 2.54 (6H, t, N<sub>ax</sub>CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 5.4 Hz), δ 2.80 (6H, dt, N<sub>eq</sub> CH<sub>2</sub>, <sup>3</sup>J<sub>PH</sub> = 16.4 Hz, <sup>3</sup>J<sub>HH</sub> = 5.4 Hz), δ 3.28 (3H, br, NH); <sup>13</sup>C (MeOD) δ 42.8 (s, N<sub>ax</sub> CH<sub>2</sub>), δ 53.6 (d, <sup>2</sup>J<sub>PC</sub> = 2.01 Hz, N<sub>eq</sub> CH<sub>2</sub>); HRMS m/e (found) 190.09796, m/e (calculated) 190.09835 for C<sub>6</sub>H<sub>15</sub>N<sub>4</sub>PO).

**Se=P[NHCH<sub>2</sub>CH<sub>2</sub>]<sub>3</sub>N, 8.** A solution containing 0.30 g (0.92 mmol) of **4**(OTf) in 2.5 mL of THF was cooled in an ice bath. To this solution was added 0.95 mL of a 0.98 M solution of *n*-BuLi in hexanes (0.92 mmol). After the reaction mixture had stirred for 10 minutes, 0.073 g (0.92 mmol) of red selenium was added. The mixture was stirred for another 10 minutes and then transferred to an NMR tube for <sup>31</sup>P NMR spectroscopic characterization (see text).

**Se=P[N(CH<sub>2</sub>Ph)CH<sub>2</sub>CH<sub>2</sub>]<sub>3</sub>N, 9.** To a solution containing 0.31 g (0.70 mmol) of **3** in 3 mL of toluene was added 0.054 g (0.69 mmol) of red selenium. The mixture was stirred until the selenium had dissolved. A colorless precipitate formed which was dissolved by the addition of DMSO. The solution was transferred to an NMR tube for spectroscopic measurements (see text).

**Reaction of 4(Cl) with KO-*t*-Bu.** A suspension of 1.00 g (4.74 mmol) of **4**(Cl) in 25 mL of CH<sub>3</sub>CN, DMSO or THF was added over a period of 5 minutes to a suspension of 0.584 g (5.21 mmol) of KO-*t*-Bu in 25 mL of CH<sub>3</sub>CN, DMSO or THF, respectively. The reaction mixture was stirred for 1.2 hours after which the volatiles were removed *in vacuo*. Attempts to dissolve the residue from the CH<sub>3</sub>CN and DMSO reactions in hexanes, CH<sub>2</sub>Cl<sub>2</sub>, pyridine, CH<sub>3</sub>CN or DMSO gave no signals in the <sup>31</sup>P NMR spectra of the supernatants. Some of the residue (1.0 g) from the THF reaction dissolved in DMSO. The <sup>31</sup>P NMR spectrum of this solution displayed a peak at δ -42.6 ppm (<sup>1</sup>J<sub>PH</sub> = 450 Hz).

**Reaction of 4(OTf) with KO-*t*-Bu.** A solution of 1.00 g (3.09 mmol) of 4(OTf) in 25 mL of CH<sub>3</sub>CN, DMSO or THF was added over a period of 5 minutes to a suspension of 0.380 g (3.40 mmol) of KO-*t*-Bu in 25 mL of CH<sub>3</sub>CN, DMSO or THF, respectively. The reaction mixture was stirred at room temperature for 1.2 hours after which the volatiles were removed *in vacuo*. Attempts to dissolve the residue in hexanes, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, pyridine or DMSO gave no signals in the <sup>31</sup>P NMR spectra of the supernatants.

**Reaction of 4(Cl) with LiX.** A suspension of 1.00 g (4.74 mmol) of 4(Cl) in 30 mL of THF was cooled to -78 °C. To this suspension was added either 0.242 g (4.75 mmol) of LiNMe<sub>2</sub> in 10 mL of THF or 4.85 mL of 0.98 M solution of *n*-BuLi in hexanes (4.76 mmol). The reaction mixture was then warmed to room temperature and stirred for 48 hours. The volatiles were removed *in vacuo* and the residue extracted with DMSO (<sup>31</sup>P NMR (DMSO) δ -42.8, <sup>1</sup>J<sub>H-P</sub> = 450 Hz).

**Reaction of 4(OTf) with LiX.** To a suspension of 1.00 g (3.09 mmol) of 4(OTf) in 30 mL of THF cooled to -78 °C was added either 0.158 g (3.10 mmol) of LiNMe<sub>2</sub> in 10 mL of THF or 3.2 mL of a 0.98 M solution of *n*-BuLi in hexanes (3.1 mmol). The reaction mixture was allowed to warm to room temperature and then stirred for 48 hours. The volatiles were removed *in vacuo*. Attempts to dissolve the residue in hexanes, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, pyridine or DMSO gave no signals in the <sup>31</sup>P NMR spectra of the extracts.

**Reactions of tren with P(NMe<sub>2</sub>)<sub>3</sub>.** Attempts to synthesize **1** by the title route were carried out under a variety of conditions. In all cases 1.50 g (10.3 mmol) of tren and 1.67 g (10.3 mmol) of P(NMe<sub>2</sub>)<sub>3</sub> were combined in a flask equipped with an argon flow. The mixture was stirred at room temperature or heated both with and without solvents. Stirring the mixture neat, in toluene or acetonitrile at room temperature for 14 days produced no detectable evolution of HNMe<sub>2</sub>. The only <sup>31</sup>P NMR peak detected (δ 123) corresponded to that of unreacted P(NMe<sub>2</sub>)<sub>3</sub> as was shown by adding this substance to the NMR tube.



Heating the neat reactant mixture for 48 hours, or refluxing it in toluene or acetonitrile for 14 days did produce  $\text{HNMe}_2$ . The neat reaction mixture produced a black oil which was extracted with hexanes followed by pyridine,  $\text{CH}_2\text{Cl}_2$ , MeCN and DMSO. Only the hexanes extract gave a  $^{31}\text{P}$  NMR peak corresponding to  $\text{P}(\text{NMe}_2)_3$ , while the others showed no detectable  $^{31}\text{P}$  NMR resonances. The toluene and acetonitrile reaction mixtures precipitated white solids which were insoluble in hexanes,  $\text{CH}_2\text{Cl}_2$ , MeCN,  $\text{C}_5\text{H}_5\text{N}$  and DMSO. Only a  $^{31}\text{P}$  NMR peak in the hexanes extract corresponding to  $\text{P}(\text{NMe}_2)_3$  could be detected.

**Attempted reaction of 4(Cl) with "Proton Sponge".** Loaded in an NMR tube were 0.0551 g (0.243 mmol) of 4(Cl) and 0.537 g (0.251 mmol) of "Proton Sponge" (1,8-bis-dimethylamino naphthalene). The solid mixture was dissolved in 3 mL of DMSO giving a  $^{31}\text{P}$  NMR peak at  $\delta$  -42.9 (d,  $^1J_{\text{HP}} = 450$  Hz).

**Reaction of 4(Cl) and 5(Cl) with KO-*t*-Bu.** To a solution containing 0.0261 g (0.104 mmol) of 4(Cl) and 0.0429 g (0.202 mmol) of 5(Cl) in 2.5 mL of DMSO was added 0.016 g (0.142 mmol) of KO-*t*-Bu. The  $^{31}\text{P}$  NMR spectrum was taken one hour later (see text).

**Reaction of 6(Cl) and 5(Cl) with KO-*t*-Bu.** To a solution containing 0.041 g (0.163 mmol) of 6(Cl) and 0.027 g (0.056 mmol) of 5(Cl) in 2.5 mL of DMSO was added 0.010 g (0.090 mmol) of KO-*t*-Bu. The  $^{31}\text{P}$  NMR spectrum was taken one hour later (see text).

**Methylation of 4(OTf).** To a solution containing 1.00 g (3.09 mmol) of 4(OTf) in 2.5 mL of  $\text{CH}_3\text{CN}$  was added 1.26 g (12.4 mmol) of KO-*t*-Bu followed by 1.76 g (12.4 mmol) of MeI, while cooling in an ice bath. After one hour the  $^{31}\text{P}$  NMR spectrum was recorded (see text).

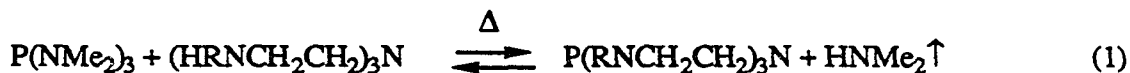
**Deuteration of 4(OTf).** To a solution containing 1.00 g (3.09 mmol) of 4(OTf) in 2.5 mL of  $\text{CH}_3\text{CN}$  was added 0.69 (6.2 mmol) of KO-*t*-Bu followed by 0.701 (6.2 mmol) of

DO<sub>2</sub>CCF<sub>3</sub> while cooling in an ice bath. After one hour the following <sup>31</sup>P NMR spectrum was recorded: δ -45.9 (d, <sup>1</sup>J<sub>HP</sub> = 450 Hz), δ -45.7 ppm (t, <sup>1</sup>J<sub>DP</sub> = 71 Hz).

**Reaction of 4(Cl) with increments of KO-*t*-Bu.** To a solution containing 0.1513 g (0.721 mmol) of 4(Cl) in 3 mL of DMSO was added 0.0801 g (0.721 mmol) of KO-*t*-Bu. The <sup>31</sup>P NMR spectrum was recorded after 15 minutes (see text). To the above reaction solution was added 0.0401 g (0.360 mmol) of KO-*t*-Bu and the <sup>31</sup>P NMR spectrum was taken 15 minutes thereafter (see text). To this reaction solution was added 0.0401 g (0.360 mmol) of KO-*t*-Bu. The <sup>31</sup>P NMR spectrum was taken 15 min. later (see text).

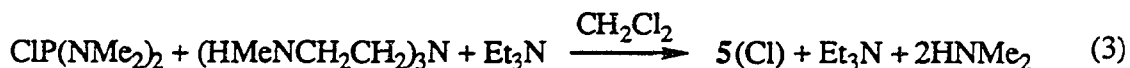
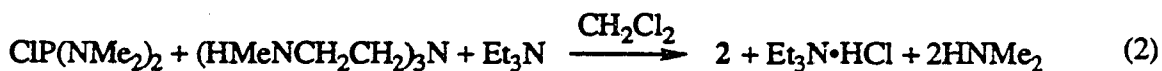
## RESULTS AND DISCUSSION

**Syntheses.** It would appear reasonable to suppose that pro-azaphosphatranes 1-3 could be made by transamination as shown in reaction 1. Previously, we showed that this

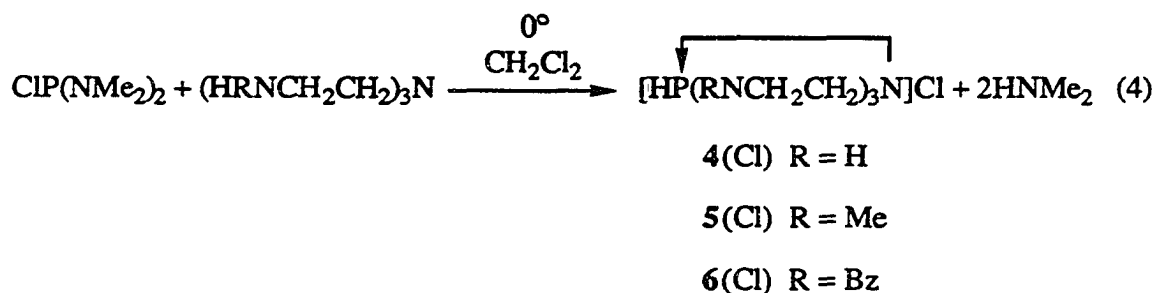


approach works well for  $\text{P(MeNCH}_2)_3\text{CMe}$ .<sup>26</sup> For **2**, however, this method is slow (taking weeks) and the yields are mediocre (~ 20-50%).<sup>10</sup> When reaction 1 is applied to the synthesis of **1**, we find no evidence of a reaction of tren and  $\text{P(NMe}_2)_3$  at room temperature in the absence of solvent, or in toluene or MeCN. At 110 °C, the reaction mixture in the absence of solvent decomposes to an insoluble tar-like material, extracts of which in a range of solvents contained only some unreacted  $\text{P(NMe}_2)_3$  in the first extraction solvent (hexane). The refluxed toluene and MeCN reaction mixtures precipitated a white solid that was largely insoluble in a variety of organic solvents. The reaction mixtures that were heated did produce some  $\text{HNMe}_2$  in all cases.

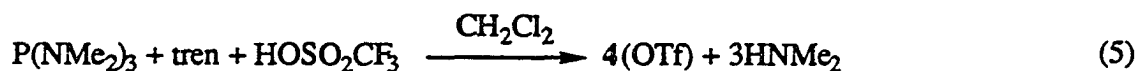
To improve the yield of **2**, reaction 2 incorporating a more reactive phosphorus reagent was attempted.<sup>10</sup> Surprisingly, **5(Cl)** was quickly formed in virtually quantitative



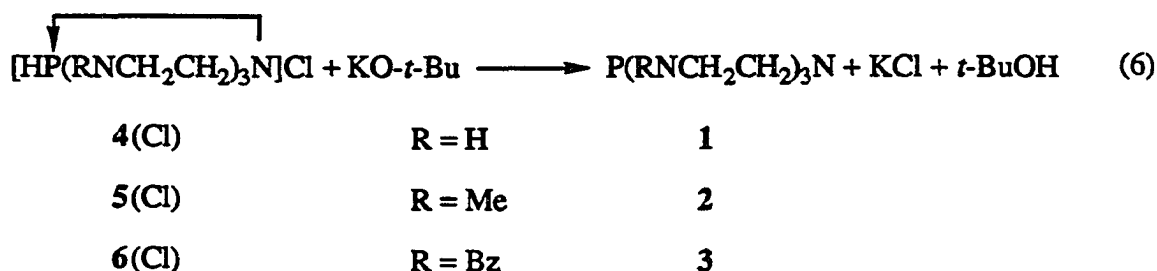
yield, reaction 3. This result indicated that **2** is apparently capable of deprotonating amine hydrochlorides. Indeed, the preferred synthesis of azaphosphatranes **4-6** is shown in reaction 4. In contrast to **5(Cl)** and **6(Cl)**, **4(Cl)** is not soluble in  $\text{CH}_2\text{Cl}_2$  and precipitates from solution in virtually quantitative yield. Compounds **5(Cl)** and **6(Cl)** are easily precipitated in high yields by adding hexane to the reaction mixture in reaction 4.



The relative insolubility of **4(Cl)** in solvents other than MeOH and DMSO made it desirable to change the chloride anion to triflate. This was easily accomplished according to reaction 5. The salt **4(OTf)** is highly soluble in THF,  $\text{CH}_2\text{Cl}_2$  and MeCN, as well as in MeOH and DMSO.



Still faced with the necessity to synthesize pro-azaphosphatranes **1** and **3**, we adopted the approach embodied in reaction 6 in which the corresponding azaphosphatrane conjugate acid is deprotonated with a very strong base.<sup>10</sup> The solvents for the reactions

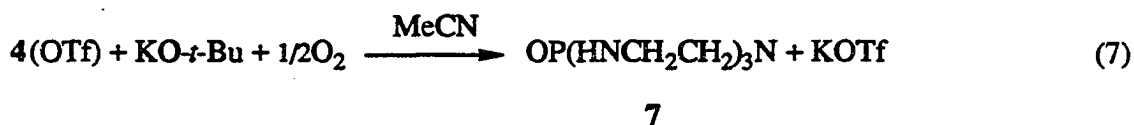


involving **5(Cl)** and **6(Cl)** are MeCN and THF, respectively. Because **4(Cl)** is insoluble in THF and thereby inhibits the reaction with KO-*t*-Bu, MeCN is employed; a solvent in which **4(Cl)** is slightly soluble.

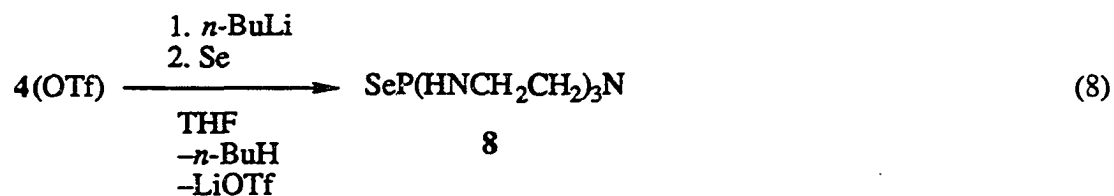
While **2** and **3** can be obtained as solids from reaction 6, we have been unsuccessful in isolating **1** despite numerous attempts under a variety of conditions. Room-temperature reactions of **4(OTf)** with KO-*t*-Bu in MeCN, DMSO or THF and of **4(Cl)** with KO-*t*-Bu in MeCN and DMSO all produced a  $^{31}\text{P}$  NMR chemical shift at 89 ppm indicative of the presence of **1** in solution (in addition to unreacted **4**:  $\delta$  -40 ppm,  $^1J_{\text{HP}} = 450$  Hz). However, when the residue left upon evaporation was extracted with a variety of solvents (including hexanes,  $\text{CH}_2\text{Cl}_2$ , MeCN, pyridine and DMSO) the only solubilized material was unreacted **4(Cl)** or **4(OTf)**. This was also true of reactions of these salts in THF with *n*-BuLi and LiNMe<sub>2</sub> at -78 °C. Apparently **1** easily polymerizes; a phenomenon reported earlier for prophosphatane I (Z = lone pair).<sup>4</sup>

To demonstrate that **1** was indeed generated *in situ* in the above reactions, we attempted to derivatize it in the reaction mixture. By adding two equivalents of KO-*t*-Bu to **4(Cl)** in DMSO, we observed that the  $^{31}\text{P}$  NMR chemical shift at 89 ppm appeared and that no peak for unreacted **4(Cl)** was present. Bubbling oxygen through the solution for one hour caused a new  $^{31}\text{P}$  NMR peak at 21.3 ppm to grow at the expense of the 89 ppm peak. For ease of preparation, this reaction was repeated using **4(OTf)** in the presence of

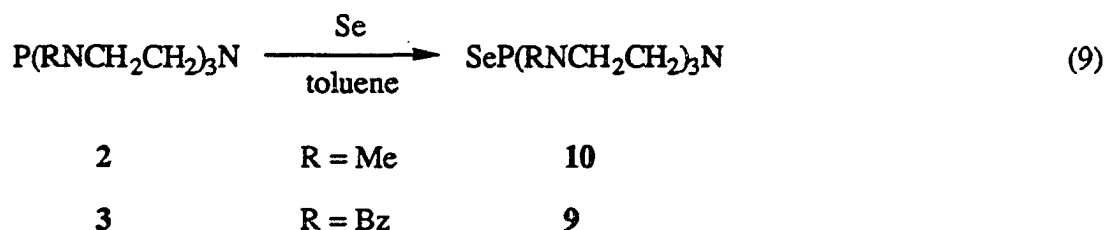
one equivalent of KO-*t*-Bu in MeCN as a solvent and bubbling O<sub>2</sub> through the solution for 16 hours. From this reaction, **7** was isolated in reasonable yield (48%) and characterized.



The selenide derivative of **1** (namely, **8**) was made by generating **1** *in situ* according to reaction 8 and then adding red selenium:



The selenides of **2** and **3** were generated from the corresponding isolated proazaphosphatranes.



**Spectroscopic Characteristics of 4(Cl), 5(Cl) and 6(Cl).** Collected in Table 1 are <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR data for **4(Cl)**, **5(Cl)** and **6(Cl)** for comparison. There is a surprisingly

Table 1.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR Chemical shifts for 4(Cl), 5(Cl) and 6(Cl).<sup>a,b</sup>

	$[\text{}^1\text{H} \text{---} \text{}^{31}\text{P} \text{---} \text{RN} \text{---} \text{}^{13}\text{C} \text{---} \text{}^1\text{H}_2 \text{---} \text{}^{13}\text{C} \text{---} \text{}^1\text{H}_2)_3\text{N}]\text{Cl}$						
4(Cl)	5.64d (453) <sup>d</sup>	-42.9 (453) <sup>d</sup>	<sup>c</sup>	50.6d (11.1) <sup>e</sup>	2.95m	34.2s	2.95m
5(Cl)	5.02 <sup>d</sup> (491) <sup>d</sup>	-10.1 (491) <sup>d</sup>	<sup>f</sup>	47.3 <sup>d</sup> (7.3) <sup>e</sup>	3.58m	41.3d (6.1) <sup>h</sup>	3.03m
6(Cl)	5.81d (506) <sup>d</sup>	-11.0 (506) <sup>d</sup>	<sup>g</sup>	52.1s	3.65m	47.8d (5.2) <sup>h</sup>	3.11m

<sup>a</sup>Data for 4(Cl) and 5(Cl) taken in dimethylsulfoxide.

<sup>b</sup>Data for 5(Cl) (in chloroform) taken from reference 2.

<sup>c</sup> R = H;  $^1\text{H}$   $\delta$  5.07d,  $^2\text{J}_{\text{PH}} = 28.3$  Hz.

<sup>d</sup> $^1\text{J}_{\text{PH}}$  in Hz.

<sup>e</sup> $^2\text{J}_{\text{PC}}$  in Hz.

<sup>f</sup>R = Me;  $^1\text{H}$   $\delta$  2.61d,  $^3\text{J}_{\text{PH}} = 17.4$  Hz;  $^{13}\text{C}$   $\delta$  34.4d,  $^2\text{J}_{\text{PC}} = 17.1$  Hz.

<sup>g</sup>R =  $\text{CH}_2\text{Ph}$ ;  $^1\text{H}$   $\delta$  4.15d,  $^3\text{J}_{\text{PH}} = 17.1$  Hz,  $\delta$  7.34,  $\text{C}_6\text{H}_5$ ;  $^{13}\text{C}$   $\delta$  39.9d,  $\text{CH}_2$ ,  $^2\text{J}_{\text{PC}} = 4.1$  Hz,  
 $\delta$  127.9s, 128.3s, 129.2s, 137.7s,  $\text{C}_6\text{H}_5$ .

<sup>h</sup> $^1\text{J}_{\text{PC}}$  in Hz.

large upfield  $^{31}\text{P}$  chemical shift of 4(Cl) compared with 5(Cl) and 6(Cl). The upfield trend of this shift in the order 5(Cl) < 6(Cl) << 4(Cl) does not follow a simple electron inductive effect of the equatorial nitrogen substituents  $\text{H} < \text{CH}_2\text{Ph} < \text{Me}$  which would have given rise to an upfield shift order of 4(Cl) < 6(Cl) < 5(Cl). The observed order of  $^{31}\text{P}$  shifts may appear to follow a build-up of positive charge on the phosphorus in the expected order  $\text{Me} < \text{CH}_2\text{Ph} < \text{H}$ . Earlier we reported a similar effect in a series of increasingly positively charged isoelectronic isostructural metal complexes of bicyclic phosphorus esters.<sup>27</sup> As we will see later, this effect may be more properly attributable to a decrease in orbital imbalance, rather than augmenting positive charge.

Interestingly, the  $^1\text{J}_{\text{PH}}$  values in Table 1 do not follow the  $^{31}\text{P}$  chemical shift order. Because the Fermi contact term for one-bond coupling depends on the nuclear charge of the adjacent nuclei,<sup>28</sup> it would appear that the positive charge on the phosphorus is *decreasing* in the order 6(Cl) > 5(Cl) >> 4(Cl); a strange notion indeed since it supposes that the net effect of the hydrogen on the equatorial nitrogen in 4(Cl) results in a more negative phosphorus than does the Me or  $\text{CH}_2\text{Ph}$  substituent in 5(Cl) or 6(Cl), respectively. Although hybridizational effects also influence one-bond couplings,<sup>28</sup> the structures of 4(Cl) and 5(Cl) are so similar (see later) that variations in hybridization are likely to be negligibly small. It should be mentioned here that the  $^{31}\text{P}$  chemical shifts for 4(Cl) and 5(Cl) in the solid state are within experimental error of their values in solution, thus ruling out significant structural changes from the solution to the solid state for these compounds.

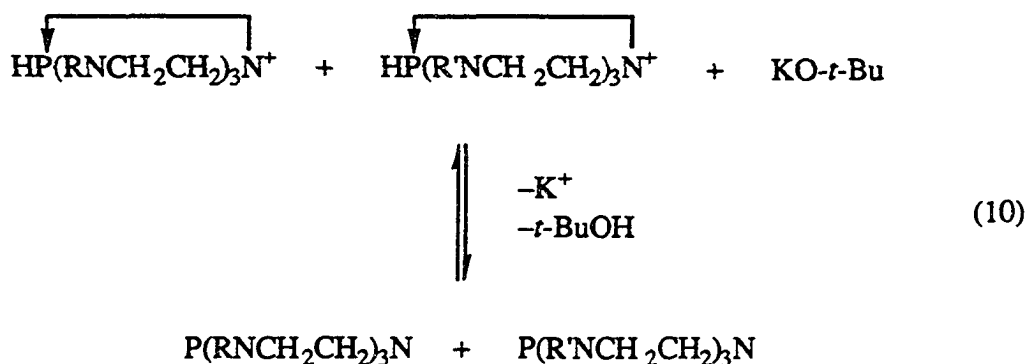
If negative charge on the phosphorus indeed increases in the order 6(Cl) < 5(Cl) < 4(Cl) as is suggested by decreasing  $^1\text{J}_{\text{PH}}$  values in the same order, it might be expected that the  $^1\text{J}_{\text{PSe}}$  couplings in the pro-azaphosphatranes selenide analogues would parallel this trend. Thus decreasing  $^1\text{J}_{\text{PSe}}$  coupling in selenophosphates has been observed to correlate



with increasing basicity of the corresponding trivalent phosphorus esters.<sup>28,29</sup> In accord with our expectation,  $^1J_{\text{PSe}}$  decreases in the order **9** (774 Hz) > **10** (754 Hz) > **8** (590 Hz).<sup>14</sup>

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **4(Cl)**, **5(Cl)** and **6(Cl)** possess several interesting but puzzling features. Both sets of  $\text{CH}_2$  protons in the bridges move upfield in the order **6(Cl)** < **5(Cl)** < **4(Cl)**. However, only one of the bridging carbons parallels this trend in the  $^{13}\text{C}$  spectrum (i.e.,  $\text{N}_{\text{ax}}\text{-C}$ ). The upfield trends in the  $^1\text{H}$  NMR shift of the  $\text{H-P}$  proton and the  $\text{N}_{\text{eq}}\text{-C}$  carbon are in both cases **6(Cl)** < **4(Cl)** < **5(Cl)**. In this order, **6(Cl)** and **4(Cl)** seem to be reversed on inductive grounds and **4(Cl)** and **5(Cl)** appear to be reversed if the negative charge of phosphorus increases in the order **6(Cl)** < **5(Cl)** < **4(Cl)**.

**Competitive deprotonation of 4(Cl), 5(Cl) and 6(Cl).** To ascertain the relative basicities of the pro-azaphosphatranes **1**, **2** and **3**, the relative acidities of their respective conjugate acids **4(Cl)**, **5(Cl)** and **6(Cl)** were measured with respect to  $\text{KO-}t\text{-Bu}$  in DMSO. By using a stoichiometric deficit of base, the areas of the  $^{31}\text{P}$  NMR peaks of a pair of azaphosphatranes and their respective pro-azaphosphatranes could be measured:



From the data collected in Table 2, it is clear that the order of acidities of the azaphosphatrane cations is  $6 > 5 > 4$ , implying the basicity order  $3 < 2 < 1$  for the corresponding pro-azaphosphatrane conjugate bases. In this table, the pairs of

Table 2. Data for deprotonation of azaphosphatrane pairs 4(Cl), 5(Cl) and 5(Cl), 6(Cl) in DMSO

Azaphosphatrane pair	Initial ratio <sup>a</sup>	Azaphosphatrane to pro-azaphosphatrane ratio <sup>b</sup>
4(Cl):5(Cl)	1:2	4(Cl):1 = 4.54
		5(Cl):2 = 2.30
5(Cl):6(Cl)	3:1	5(Cl):2 = 4.00
		6(Cl):3 = < 0.1

<sup>a</sup>In equivalents.

<sup>b</sup>From <sup>31</sup>P NMR peak areas.

azaphosphatranes in each experiment contained a higher proportion of the less acidic compound in order to provide an adequate concentration of the corresponding pro-azaphosphatrane for <sup>31</sup>P NMR peak area measurement. From the equilibrium data it is possible to calculate a pK<sub>a</sub> of 29.6 for 4(Cl) in DMSO and an estimate of 26.8 as an upper limit for the pK<sub>a</sub> values of 5(Cl) and 6(Cl).<sup>14</sup> Because attempts to isolate **1** were frustrated by the formation of polymer, reaching equilibrium **10** in the reverse manner was precluded. That polymeric **1** did not form in our experiments was shown by acidifying the basic solution and regenerating only the signal due to cation **4**.

In the next section we present evidence that determining the basicity of **1** by measuring the acidity of cation **4** with respect to P-H proton less to form **1** does not tell the whole story.

**Cation 4 as a tetraprotonic acid.** In arriving at the ratio of **4(Cl)** to **1** in the last column of Table 2, it was assumed that the  $^{31}\text{P}$  NMR peak observed at -40.5 ppm could be assigned to **4(Cl)**, even though it seemed slightly shifted downfield from its -42.0 to -42.9 ppm values observed in DMSO. From Table 3 it is clear, however, that successive addition of base causes a dramatic downfield shift of over 30 ppm of the azaphosphatrane peak as the resonance of the pro-azaphosphatrane **1** rises. That the azaphosphatrane cage

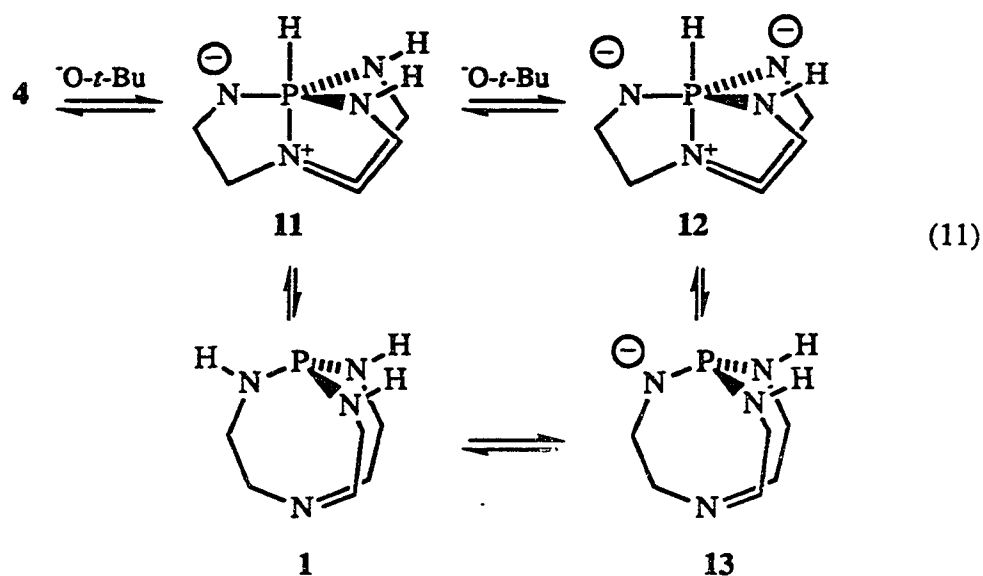
Table 3.  $^{31}\text{P}$  NMR Chemical shifts data for **4(Cl)** in the presence of KO-*t*-Bu in DMSO

Equivalents of KO- <i>t</i> -Bu	$\delta^{31}\text{P}$ (ppm)	Ratio of azaphosphatrane to pro-azaphosphatrane <sup>a</sup>
0	-42	—
0.5	-39.5	1.3
0.8	-38.0	1.1
1.0	-31.6	0.57
1.2	-29.0	0.31
1.5	-12.0	0.21
1.6	-11.6	0.18
1.8	-11.5	0.13
2.0	<sup>b</sup>	0

<sup>a</sup>From integration of the upfield peak and the peak at 89 ppm.

<sup>b</sup>Not observed.

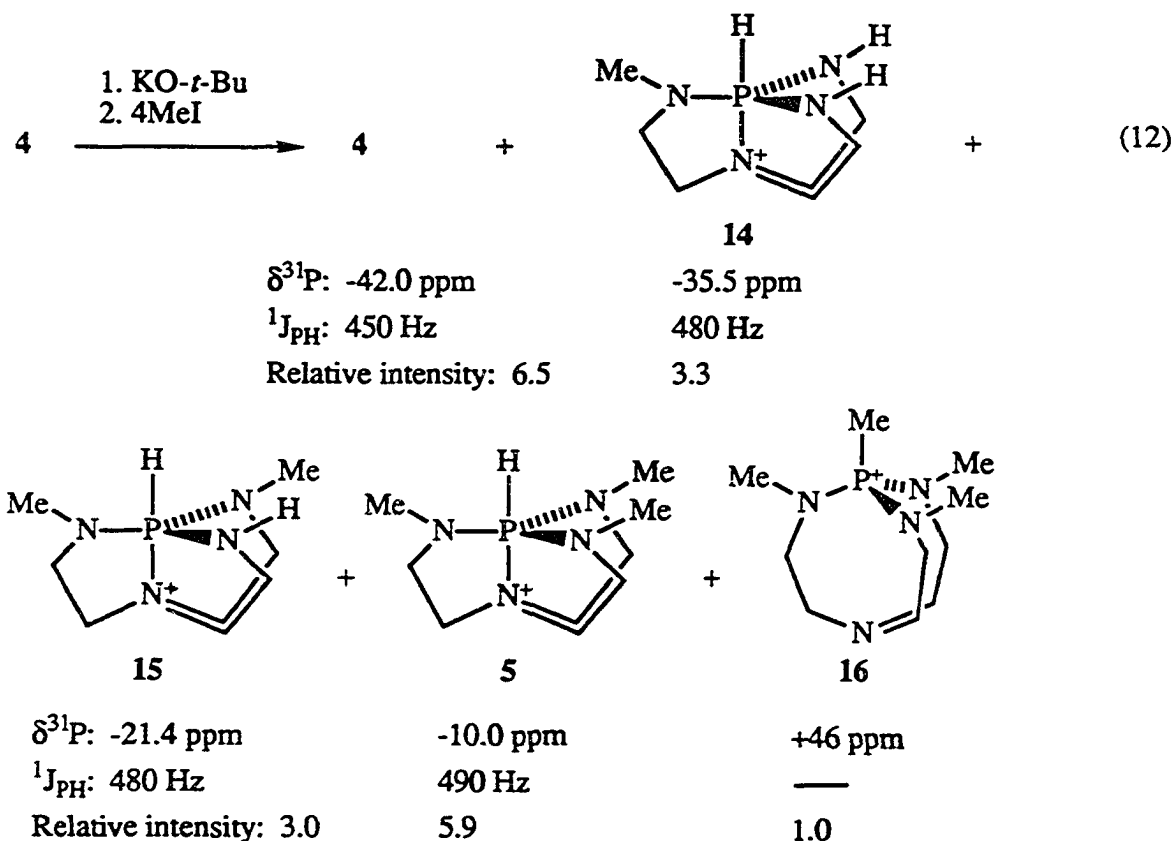
structure is maintained over this range is indicated by the upfield shift and the maintenance of a constant  $^1J_{\text{PH}}$  coupling until the peak disappears. It would appear from these data that relatively facile deprotonation occurs at the equatorial nitrogen until two equivalents of base are consumed, suggesting an equilibrium such as:



Here it must be assumed that the peak at 89 ppm for **1** is not as sensitive to deprotonation of this species and may also represent **13** (or further deprotonated analogues thereof). Indeed, **4**(Cl) in the presence of six equivalents of KO-*t*-Bu shows no appreciable movement in the peak at 89 ppm. Noteworthy is the apparent rapidity on the NMR time scale of the equilibria involving azaphosphatrane structures and the relative slowness of the equilibria involving azaphosphatrane and pro-azaphosphatrane skeletons. It may also be noted that **4** in the presence of deuterio-trifluoroacetic acid (DOTFA) does not appear to exchange the P-H proton (as shown by  $^{31}\text{P}$  NMR spectroscopy). However, a solution

of cation **4** and KO-*t*-Bu in MeCN to which DOTFA is added reveals two  $^{31}\text{P}$  NMR peaks; a doublet at -42.9 ppm ( $^1J_{\text{PH}} = 450$  Hz) and a triplet at -42.9 ppm ( $^1J_{\text{PD}} = 71$  Hz). The latter observation attests to the existence of pro-azaphosphatrane species in solution.

Interestingly, when four equivalents of KO-*t*-Bu were added to a solution of **4**(Cl) in DMSO, followed by four equivalents of MeI, the  $^{31}\text{P}$  NMR peaks shown in reaction 12



were observed. The assignments for **4**, **14**, **5**<sup>10</sup> and **16**<sup>30</sup> were made by adding authentic samples to the NMR solution. The assignments for **14** and **15** were inferred from the relative chemical shifts of the unsubstituted cation **4** and that of fully equatorially methyl substituted cation **5**.

The results *in toto* strongly indicate that deprotonation of the P–H proton of cation **4** may in part be difficult because initial deprotonation occurs at an equatorial nitrogen, thereby strengthening the P–H bond. Moreover, further deprotonation would be made more difficult owing to the buildup of negative charge on the ion. Forcing such a negative charge augmentation would eventually weaken the P–N<sub>ax</sub> transannular bond, therefore giving rise to pro-azaphosphatrane species. This tentative conclusion does not negate the conclusion reached earlier in this paper based on  $^1\text{J}_{\text{PSe}}$  data for the selenophosphates **8-10**, that the basicity order for the pro-azaphosphatranes is  $3 < 2 < 1$ . Nor does it negate our earlier conclusion based on  $^1\text{J}_{\text{PH}}$  couplings that the corresponding acidity order of the corresponding conjugate acids is  $6 > 5 > 4$ . In further support of the anomalously high basicity of **1** and the low acidity of **4**, is the observation that the equilibrium implied in the azaphosphatrane:pro-azaphosphatrane ratio of 4.54 in Table 2 involves mainly **4** and **1**, and very little **11**. Thus the  $^{31}\text{P}$  chemical shift assigned to azaphosphatrane in this experiment (-40.5 ppm) is very close to that of the fully protonated cation **4** (-42.9 ppm). Assuming from Table 3 that **11** would have a  $\delta^{31}\text{P}$  value of about -32 ppm, the mole fraction  $\alpha_A$  of **4** present would be *ca.* 80%.<sup>31</sup> Because basicity is an equilibrium phenomenon, we can say that the equilibrium implied in Table 2 is primarily between **4** and **1**, the species directly comparable with their analogues **5**, **6** and **2**, **3**, respectively, wherein deprotonation beyond the P–H proton is not significant.

**Concluding Remarks.** At this point we do not have a clear rationale for the anomalously high basicity of **1** and the unusually low acidity of cation **4**. While we cannot entirely rule out initial N<sub>eq</sub>–H deprotonation of **4** as an inhibiting factor for the departure of the P–H proton, we have the anomalously low  $^1\text{J}_{\text{PH}}$  and  $^1\text{J}_{\text{PSe}}$  couplings in **4** and **8**, respectively, which also favor the unusual acidity and basicity orders put forth here. It is also conceivable that the hydrocarbon substituents on the equatorial nitrogens of cations **5** and

6 sterically assist P-H proton departure in contrast to the relatively smaller proton substituents in cation 4. Indeed, molecular mechanics calculations based on the X-ray crystal structural parameters of 4(Cl) and 5(Cl) do indicate the presence of steric interactions in the case of 5.<sup>32</sup> The difference in the van der Waals repulsions between the P-H and N-H protons of 4(Cl), and the P-H proton and methyl groups of 5(Cl) is calculated to be a maximum of *ca.* 5 kcal/mole. Apparently, however, these repulsions are insufficient to alter the P-H stretching frequency which is observed to be at 2205 cm<sup>-1</sup> (DMSO) for both compounds. A particularly puzzling feature of the solid state structures is that the P-N<sub>ax</sub> bond length in cation 4 is slightly *longer* (2.0778(4) Å<sup>14</sup>) than in 5 (1.976(8) Å<sup>10</sup>) and the N<sub>eq</sub>-P-N<sub>ax</sub> angle in 4 is smaller (84.01(3)°) than in 5 (85.9(4)°, 86.5(2)°), giving rise to a somewhat even more distorted trigonal bipyramid for 4 than for 5. Noteworthy in this regard is that the solid state <sup>31</sup>P NMR chemical shifts for 4(Cl) and 5(Cl) are within experimental error of their respective solution values.

If steric and inductive electronic effects do not dominate the behavior of 4, there may be an overriding electronic stabilization of the axial three-center four-electron bond which operates more strongly in cation 4 than in 5 or 6. This possibility is signalled by the unusually high field <sup>31</sup>P NMR chemical shift of cation 4 compared with those of 5 and 6 (Table 1). High field NMR shifts of hypercoordinate nuclei have been associated with decreasing imbalance in the orbitals of the NMR-active atom used in bonding.<sup>33</sup> Such a relatively low orbital imbalance may lead to better electron delocalization along the three-center bond, thereby stabilizing the P-H bond as well as the P-N<sub>ax</sub> link.

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## REFERENCES

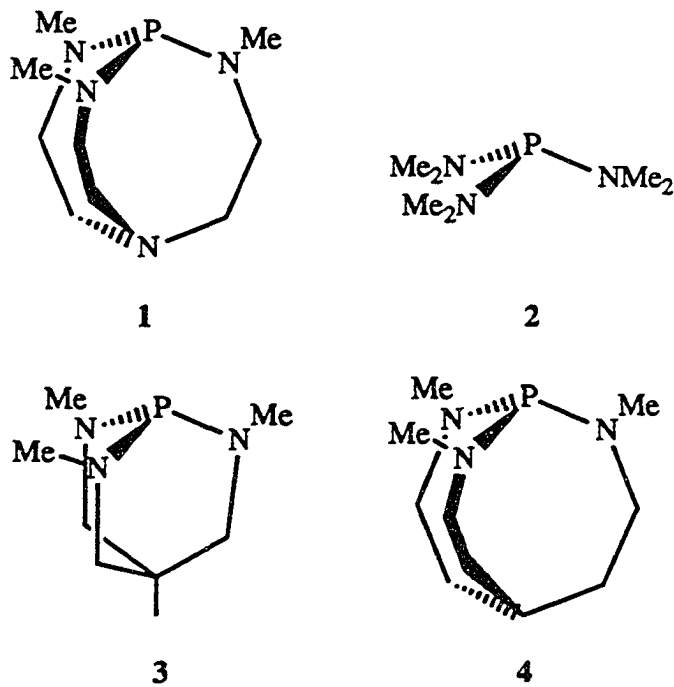
1. Clardy, J. C.; Milbrath, D. S.; Springer, J. P.; Verkade, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 623.
2. Milbrath, D. S.; Clardy, J. C.; Verkade, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 631.
3. Clardy, J. C.; Milbrath, D. S.; Verkade, J. G. *Inorg. Chem.* **1977**, *16*, 2135.
4. Milbrath, D. S.; Verkade, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 6607.
5. van Aken, D.; Castelyns, A. M. C. F.; Verkade, J. G.; Buck, H. M. *Recueil, Journal of the Royal Netherlands Chemical Society* **1979**, *98*, 12.
6. Carpenter, L. E.; Verkade, J. G. *J. Am. Chem. Soc.* **1985**, *107*, 7084.
7. Carpenter, L. E.; van Aken, D.; Buck, H. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1986**, *108*, 4918.
8. Carpenter, L. E.; Verkade, J. G. *J. Org. Chem.* **1986**, *51*, 4287.
9. Gudat, D.; Lensink, C.; Schmidt, H.; Xi, S.-K.; Verkade, J. G. *Phosphorus, Sulfur and Silicon* **1989**, *41*, 21.
10. Lensink, C.; Xi, S.-K.; Daniels, L. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 3478.
11. Schmidt, H.; Lensink, C.; Xi, S.-K.; Verkade, J. G. *Zeitschr. anorg. allg. Chem.* **1989**, *578*, 75.
12. Schmidt, H.; Xi, S.-K.; Lensink, C.; Verkade, J. G. *Phosphorus, Sulfur and Silicon* **1990**, *49/50*, 163.
13. Xi, S. K.; Schmidt, H.; Lensink, C.; Kim, S.; Wintergrass, D.; Daniels, L. M.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1990**, *29*, 2214.
14. Laramay, M. A. H.; Verkade, J. G. *J. Am. Chem. Soc.* **1990**, *112*, 9421.



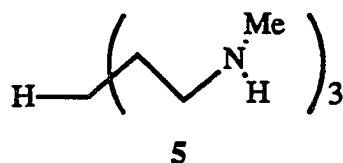
15. See for example, Voronkov, M. G.; Dyakov, V. M.; Kirpichenko, S. V. *J. Organomet. Chem.* **1982**, *233*, 1 and references therein.
16. Lukevics, E.; Zelchan, G. I.; Solomennikova, I. I.; Liepin'sh, E. E.; Yankovska, I. S.; Mazheika, I. B. *J. Gen. Chem. USSR (Engl. Transl.)* **1977**, *47*, 98.
17. Gudat, D.; Daniels, L. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 8520.
18. Gudat, D.; Verkade, J. G. *Organometallics* **1989**, *8*, 2772.
19. Gudat, D.; Daniels, L. M.; Verkade, J. G. *Organometallics* **1990**, *9*, 1464.
20. Woning, J.; Daniels, L. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1990**, *112*, 4601.
21. Gudat, D.; Verkade, J. G. *Organometallics* **1990**, *9*, 2172.
22. Woning, J.; Verkade, J. G. *J. Am. Chem. Soc.* **1991**, *113*, 944.
23. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals, Third Edition*, Pergamon Press: New York, NY 1988.
24. Campbell, T. W.; McCullough, J. D. *J. Am. Chem. Soc.* **1945**, *67*, 1965.
25. Menge, W.; Verkade, J. G., manuscript in progress.
26. Laube, B. L.; Bertrand, R. D.; Casedy, G. A.; Compton, R. D.; Verkade, J. G. *Inorg. Chem.* **1967**, *6*, 173.
27. Coskran, K. J.; Bertrand, R. D.; Verkade, J. G. *J. Am. Chem. Soc.* **1967**, *89*, 4535.
28. Verkade, J. G.; Mosbo, J. A. in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: New York, 1986.
29. Kroshefsky, R. D.; Weiss, R.; Verkade, J. G. *Inorg. Chem.* **1979**, *18*, 469.
30. Lensink, C.; Schmidt, H.; Verkade, J. G., to be published.
31. Here  $\delta$  (obsd) =  $\alpha_A(\delta_A) + (1-\alpha_A)(\delta_B)$ .
32. Jacobson, R. A., private communication.
33. Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73.

## APPENDIX

It has been previously determined that the basicity of the pro-azaphosphatane, **1**, is considerably higher than both the acyclic **2**, and the bicyclic **3**.<sup>1</sup> This was determined spectroscopically by comparing the  $^1J_{\text{BP}}$  and the  $^1J_{\text{SeP}}$  of the borane adducts and the selenides of **1-3**, respectively. The  $^1J_{\text{BP}}$  increased and the  $^1J_{\text{SeP}}$  decreased, respectively, in going from the borane and selenium derivatives of **3** to **2** to **1**, giving the basicity trend of  $1 > 2 > 3$ .<sup>1</sup> In order to determine what effect the ring strain in **3** may have on its basicity, the preparation of the extended bicyclic species, **4**, was attempted. This necessitated the preparation of the tri-amine precursor, **5**. If

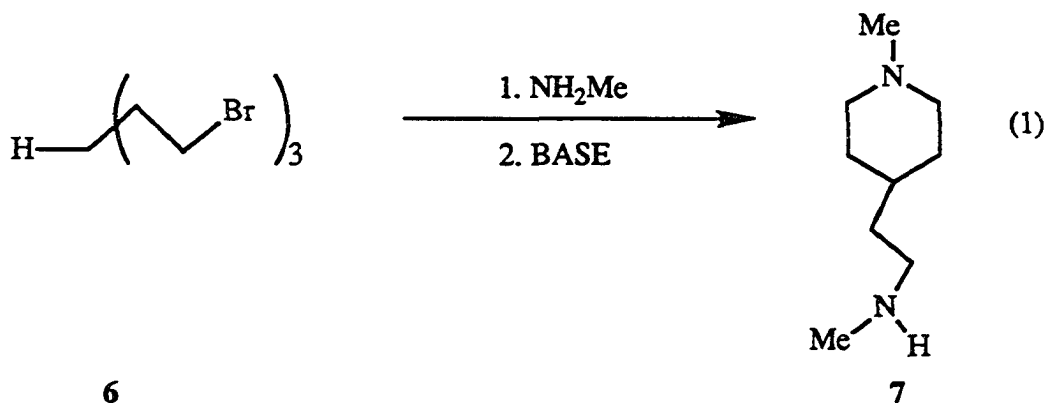


this compound could have been prepared, it was hoped that **4** could have been prepared through a transamination reaction similar to that invoked in the synthesis of

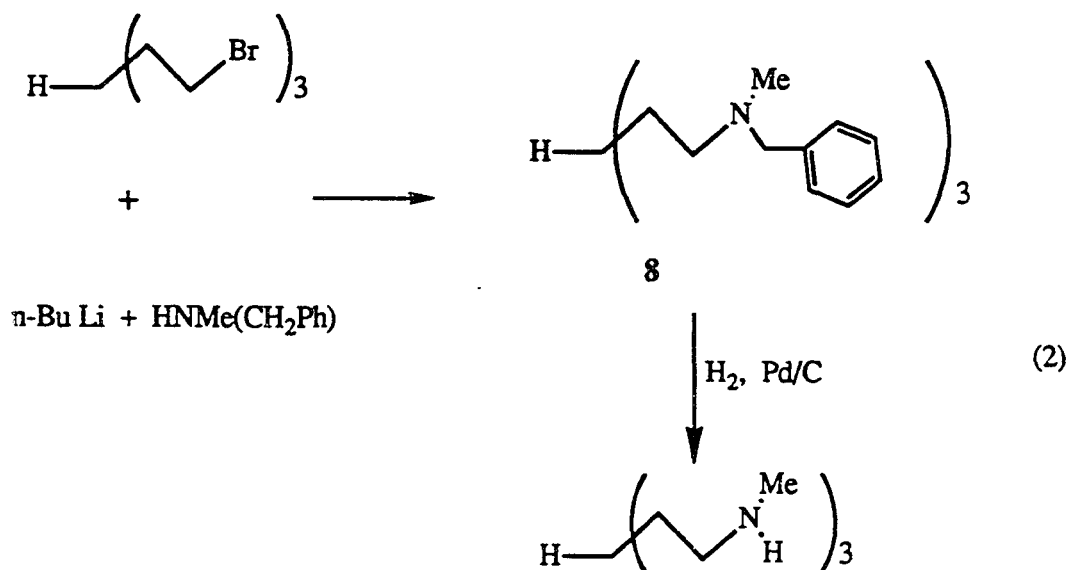


## 3.2

The first attempts were modelled after the previously reported preparation of 3,<sup>2</sup> in which the bromide precursor, 6, was heated in a high temperature bomb with HNMe<sub>2</sub>. The reaction temperatures chosen ranged from 22°C to 180°C and the reaction times were from 6 hours to 24 hours. In the case in which the temperature was not raised above room temperature, the bromide was retrieved (87%) along with unidentified decomposition products. In all the other cases, approximately 55% of the material decomposed, while the rest cyclized to give diamine 7, reaction 1. The tosyl derivative instead of the bromide was also used,<sup>3</sup> leading to the same result as shown in reaction 1.



An attempt to prepare **8** from the bromide and  $\text{LiNMe}(\text{CH}_2\text{Ph})^4$  gave a mixture of inseparable products by either recrystallization or chromatography. The  $^1\text{H}$  NMR spectrum of the chromatographed product did not fit the expected pattern. Had the isolation of **8** been realized, it might have been hydrogenated in the presence of  $\text{Pd/C}$  to hopefully give **5**,<sup>5</sup> reaction 2.



The synthesis of **5** through a cyano- derivative was also attempted. In starting with the benzyl sulfonate precursor of **3**<sup>3</sup> and  $\text{NaCN}$  using conditions more mild than previously reported,<sup>6</sup> cyclization products similar to those previously reported<sup>6</sup> were formed. If the tri-cyano derivative, **9**, would have been formed, it would have been treated with  $\text{Me}_3\text{O}^+\text{BF}_4^-$  then  $\text{NaBH}_4$  to hopefully give the methyl analogue of **5**, reaction 3.<sup>7</sup>



ups were dried and distilled under nitrogen using standard methods.<sup>9</sup> Precursors **6**,<sup>10</sup> **10**,<sup>11</sup> and  $\text{MeC}(\text{CH}_2\text{OSO}_2\text{Ph})_3$ <sup>3</sup> were prepared using standard methods. Methyl amine was condensed into an evacuated flask using  $\text{N}_2(\text{l})$  cooling, then directly condensed into the intended reaction vessel, again using  $\text{N}_2(\text{l})$  cooling. Commercial sodium cyanide, benzyl methyl amine, diethyl azodicarboxylate, and triphenylphosphine were used without further purification. Proton NMR spectra were recorded on a Nicolet NT300 instrument.

**Reactions of  $\text{HC}(\text{CH}_2\text{CH}_2\text{Br})_3$  with  $\text{H}_2\text{NMe}$ , reaction 1.** Attempts to synthesize **5** by the title route were carried out under a variety of conditions. In all cases, a 1 to 3.2 molar ratio of **6** to  $\text{H}_2\text{NMe}$  was used, with initial weights of the bromide ranging from 8.30 g ( 24.6 mmole) to 15.0 g ( 44.5 mmole). The bromide was first loaded into the high pressure bomb. Then the vessel was sealed, the pressure inside was reduced to 0.5 torr, the bomb was cooled in  $\text{N}_2(\text{l})$ , and the amine was condensed into the reaction vessel using the intake valve. The pressure was increased to 760 torr by the addition of argon. The vessel was heated to the desired temperatures for the times indicated: 180 °C for 16 hours, 180 °C for 6 hours, 100 °C for 16 hours, 22 °C for 24 hours. The pressure was released and the volatiles were removed *in vacuo*. The residue was refluxed with 3 equivalents of KOH ( with respect to the initial amount of **6** used) in toluene for 8 hours. The resulting solution was removed from the KOH by filtration and dried over  $\text{MgSO}_4$ . The toluene was removed and the resulting residue from the reactions that were heated above 22 °C was distilled at 55 °C, 0.5 torr ( the reaction that was held at 22 °C showed only starting material in the  $^1\text{H}$  NMR spectrum of the crude residues after work up). The spectroscopic data of the distillates are as follows:  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$  1.25 (1H, m,  $-\text{CH}_2-$ ),

$\delta$  1.40 (2H, br dt,  $^3J_{\text{HH}} = 6.6$  Hz,  $^3J_{\text{HH}} = 6.6$  Hz,  $\text{CH}_2\text{CH}$ , arm),  $\delta$  1.64 (2H, br d,  $^3J_{\text{HH}} = 8.1$  Hz,  $\text{CH}_2\text{CH}$ , ring),  $\delta$  1.86 (1H, br t,  $^3J_{\text{HH}} = 11.1$  Hz,  $\text{HN}$ ),  $\delta$  2.21 (3H, s,  $\text{NCH}_3$ , ring),  $\delta$  2.39 (3H, s,  $\text{NCH}_3$ , arm)  $\delta$  2.56 (2H, t,  $^3J_{\text{HH}} = 7.35$  Hz,  $\text{NCH}_2$ , arm),  $\delta$  2.78 (2H, br d,  $^3J_{\text{HH}} = 9.9$  Hz,  $\text{NCH}_2$ , ring); ms (m/e) 156.2 amu; calculated for  $\text{C}_9\text{H}_{20}\text{N}_2$  156.3 amu.

**Reaction of  $\text{HC}(\text{CH}_2\text{CH}_2\text{Br})_3$  with  $\text{LiNMe}(\text{CH}_2\text{Ph})$ , reaction 2.** A solution containing  $n\text{Bu-Li}$  (2.3 M in hexane, 30.2 mL, 69.6 mmole of  $n\text{Bu-Li}$ ) was added dropwise to a solution containing 8.44 g (69.6 mmole) of  $(\text{PhCH}_2)\text{MeNH}$  in 100 mL of THF, cooled in a  $-78$  °C bath. The mixture was slowly warmed to room temperature then stirred for 1 hour. The mixture was then cooled back down to  $-78$  °C and a solution containing 5.87 g (17.4 mmole) of  $\text{HC}(\text{CH}_2\text{CH}_2\text{Br})_3$  in 20 mL of THF was added dropwise. The mixture was warmed to room temperature and stirred for 16 hours. The  $\text{LiBr}$  was removed via filtration and the volatiles removed *in vacuo*. The residue (an oil) was chromatographed using 1:1 EtOAc/Hexanes. The  $^1\text{H}$ NMR spectrum gave the following:  $\delta$  0.89 (1H, m),  $\delta$  1.31 (2H, m),  $\delta$  2.17 (2H, d,  $^3J_{\text{HH}} = 9.9$  Hz),  $\delta$  2.34 (3H, s),  $\delta$  2.91 (2H, d,  $^3J_{\text{HH}} = 9.9$  Hz),  $\delta$  3.51 (2H, s),  $\delta$  7.23 (5H, m).

**Reaction of  $\text{MeC}(\text{CH}_2\text{OSO}_2\text{Ph})_3$  with  $\text{NaCN}$ , reaction 3.** A suspension containing 33.21 g (61.50 mmole) of  $\text{MeC}(\text{CH}_2\text{OSO}_2\text{Ph})_3$  and 49.00 g (276.8 mmole) of  $\text{NaCN}$  was stirred at room temperature for 3 days in 250 mL of  $\text{CH}_3\text{CN}$ . The  $^1\text{H}$  NMR of an aliquot of the reaction mixture showed only a very small amount of pure  $\text{MeC}(\text{CH}_2\text{OSO}_2\text{Ph})_3$ . The mixture was then heated to  $50$  °C for 2 hours. The  $^1\text{H}$ NMR spectrum of the reaction mixture showed a mixture of starting material and  $\text{NCCHCH}_2\text{C}(\text{CH}_2\text{CN})\text{HCH}_3$ .<sup>6</sup>

**Reaction of HC(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub> with HNMe<sub>2</sub> and PPh<sub>3</sub>/**

**EtO<sub>2</sub>CNNCO<sub>2</sub>Et, reaction 4.** Into a solution containing 15.9 g (91.2 mmole) of EtO<sub>2</sub>CNNCO<sub>2</sub>Et and 3.00 g (20.3 mmole) of HC(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub> in 200 mL of THF frozen in N<sub>2</sub>(l) was condensed 2.83 g (91.2 mmole) of HNMe<sub>2</sub>. The mixture was then melted by warming the flask to -78 °C. A solution containing 23.9 g (91.2 mmole) of PPh<sub>3</sub> in 100 mL of THF was added dropwise to the reaction mixture, followed by stirring for 4 hours at -78 °C, then at room temperature for 5 days. The volatiles were removed *in vacuo* and the residue was extracted with Et<sub>2</sub>O. After the removal of the Et<sub>2</sub>O *in vacuo*, the extracts were distilled at 90 °C, 0.7 torr. The <sup>1</sup>H NMR spectrum showed: δ 1.26 (t), δ 4.19 (q)(DEAD); δ 1.51(m), δ 3.69 (t), 2.03 (m), δ 4.6 (br) (HC(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub>); δ 1.15 (2H, t, CH<sub>2</sub>CH), 2.76(3H, s, Me), δ 3.37 (2H, t, CH<sub>2</sub>N).

**References.**

1. Xi, S. K.; Schmidt, H.; Kim, S.; Wintergrass, D.; Daniels, L. M.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1990**, *29*, 2214.
2. Laube, B. L.; Bertrand, R. D.; Casedy, G. A.; Compton, R. D.; Verkade, J. G. *Inorg. Chem.* **1967**, *6*, 173.
3. Geue, R. J.; Searle, G. H. *Aust. J. Chem.* **1983**, *36*, 927.
4. House, H. O.; Wickman, P. P.; Muller, H. C. *J. Amer. Chem. Soc.* **1962**, *84*, 3139.
5. Yagi, H.; Thakker, D. R.; Lehr, R. E.; Jerina, D. M. *J. Org. Chem.* **1979**, *44*, 3442.
6. Quast, H.; Berneth, C. P. *Chem. Ber.* **1983**, *116*, 1345.
7. Borch, R. F. *J. Chem. Soc., Chem. Comm.* **1968**, 442.



8. Mitsunobu, R. *Synthesis* **1981**, 1.
9. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals, Third Edition*, Pergamon Press: New York, NY 1988.
10. Doering, W. von E.; Levy, L. K. *J. Amer. Chem. Soc.* **1955**, *77*, 509.
11. Wetzell, R. B.; Kenyon, G. L. *J. Amer. Chem. Soc.* **1974**, *96*, 1589.

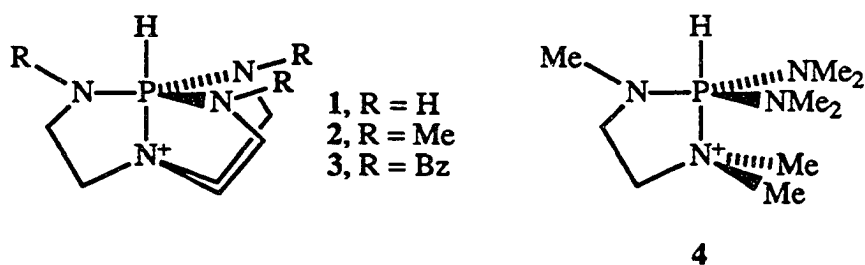
**PART III: CHELATION EFFECTS IN THE STABILIZATION OF PROTONATED  
PHOSPHORUS(III)**

## ABSTRACT

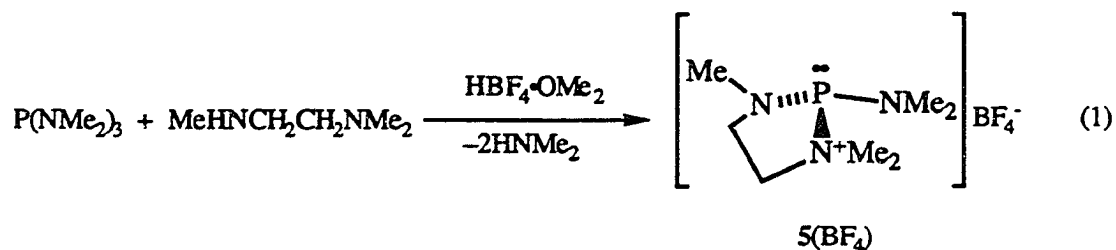
The reaction of  $\text{P}(\text{NMe}_2)_3$  with  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NHMe}$  in the presence of  $\text{HBF}_4 \cdot \text{OMe}_2$  rapidly produces the stabilized phosphonium compound  $\text{Me}_2\text{N}(\cdot)\overline{\text{PNMeCH}_2\text{CH}_2\text{NMe}_2}(\text{BF}_4)$  (**5**( $\text{BF}_4$ )) with the elimination of  $\text{HNMe}_2$ . Arguments are brought forward for postulating  $(\text{Me}_2\text{N})_2(\text{H})\overline{\text{PNMeCH}_2\text{CH}_2\text{N}^+\text{Me}_2}$  as a kinetically favored intermediate, which stems from  $(\text{Me}_2\text{N})_2(\cdot)\overline{\text{PNMeCH}_2\text{CH}_2\text{NMe}_2}$ , a reactive conformation of this precursor phosphine in equilibrium with its acyclic conformer. An attempt to form **5** by methylating  $\text{Me}_2\text{N}(\cdot)\overline{\text{PNMeCH}_2\text{CH}_2\text{NMe}_2}$  resulted in quantitative formation of the isomer of cation **5**, namely,  $\text{Me}_2\text{N}(\text{Me})\overline{\text{P}^+\text{NMeCH}_2\text{CH}_2\text{NMe}_2}$  (**15**). Attempts to thermally interconvert these isomers failed.

## COMMUNICATION

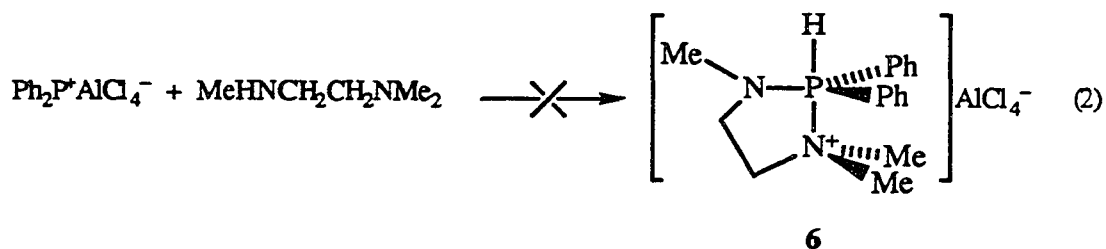
Phosphatrane cations such as 1-3 are remarkably stable, possessing  $pK_a$  values in DMSO between 26.8 and 29.6.<sup>1-3</sup> In order to gain some insight into the influence of chelation on the stability of these species, it was of interest to determine whether cation 4 could be synthesized.



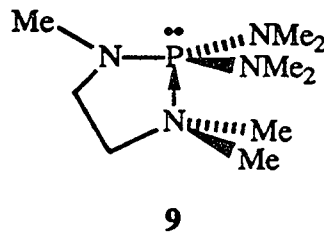
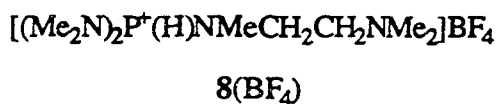
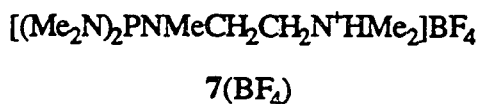
Employing reaction 1, the analogue of which we have used to synthesize 2 using  $(\text{HMeNCH}_2\text{CH}_2)_3\text{N}$ ,<sup>2</sup> we find no evidence for 4.<sup>4</sup> Instead,  $5(\text{BF}_4)$  is formed in approximately 70% isolated yield whether the  $\text{HBF}_4 \cdot \text{OMe}_2$  is present during the room temperature reaction of the phosphine and amine or is added at room temperature after heating the reaction mixture. We also saw no evidence for  $6(\text{AlCl}_4)$  in reaction 2;<sup>5</sup> only for  $[(\text{Ph})_2\text{PNMeCH}_2\text{CH}_2\text{NHMe}_2]\text{AlCl}_4$ .



It is conceivable that despite three-center four-electron delocalization along the  $N_{ax}$ -P-H axis, cations **4** and **6** are sterically unstable owing to steric strain induced by the eclipsing of two of the phosphorus substituents with two of the  $N_{ax}$  groups. Intermediate **4** could relieve this strain by decomposing to **5** via a preferential 1,2 proton shift to an  $Me_2N$  nitrogen (rather than to the heterocyclic  $MeN$  nitrogen) while in reaction 2, intermediate **6**

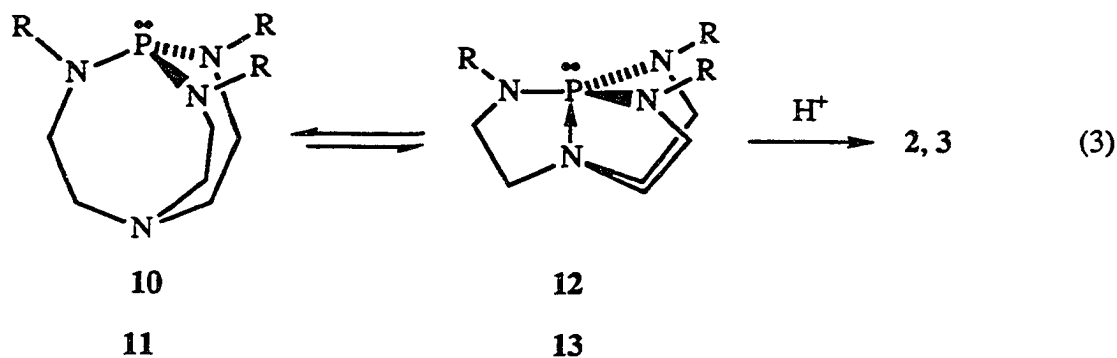


could decompose by prior dissociation of the P- $N_{ax}$  bond followed by H-P<sup>+</sup> dissociation to give  $Ph_2PNMeCH_2CH_2N^+HMe_2$ . Similarly, the N-H bond in the intermediate **7**( $BF_4$ ) in reaction 1 is certainly expected to be stronger than a P-H link in **8**( $BF_4$ ). Moreover, the N-H proton in intermediate **7**( $BF_4$ ) is not expected to ionize appreciably at room temperature in a non-aqueous solvent such as  $CH_2Cl_2$ , and what little might do so would produce even less protonated phosphorus under these conditions. While such a pathway cannot be ruled out, an alternate pathway kinetically favoring **5**( $BF_4$ ) as an intermediate may involve formation of a reactive adduct **9** in a prior equilibrium. Although tricovalent phosphorus

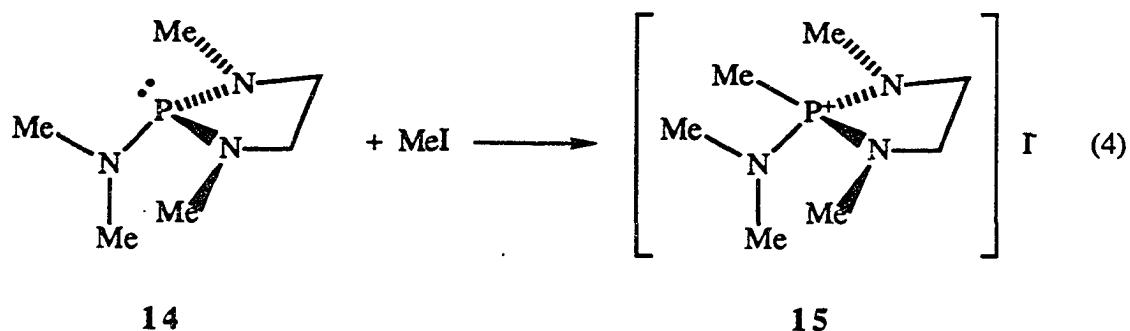


compounds normally are Lewis basic rather than acidic,  $\text{Me}_3\text{NPX}_3$  ( $\text{X} = \text{Cl}, \text{Br}^7$ ),  $\text{Me}_3\text{AsPCl}_3^7$ ,  $\text{PX}_4^-$  ( $\text{X} = \text{Cl}, \text{Br}^8$ ),  $\text{P}(\text{CN})_2\text{Br}_2^-$ ,<sup>8</sup>  $\text{P}(\text{CN})_3\text{Cl}^-$ ,<sup>8</sup> and  $(\text{NC})_3\text{P}(\mu\text{-X})_2\text{P}(\text{CN})_3^{2-}$ <sup>9</sup> have been characterized.

Postulation of reactive intermediate **9** in reaction 1 is also in accord with the rapid and quantitative formation of cations **2** and **3** upon reaction of their corresponding phosphatranes **10** and **11**, respectively.<sup>1,2</sup> Intermediates **9**, **12** and **13** would be favored by chelation and increased nucleophilicity of the phosphorus lone pair would accrue from electron donation by the axial nitrogen.

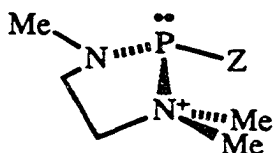


The ease of formation of  $5(\text{BF}_4)$  in reaction 1 prompted us to see if methylation of **14**<sup>10,11</sup> under our conditions would also afford cation **5**. However, its isomer **15** is

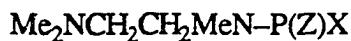


formed quantitatively. Here steric factors and perhaps  $\pi$ -donation to phosphorus from the lone pairs of the nearly planar nitrogens<sup>13</sup> would favor nucleophilicity of the phosphorus over the nitrogens in this reaction. We have been unable to detect isomerization of **5**(BF<sub>4</sub>) or **5**(Cl) (from 17.6 mmol each of Cl<sub>2</sub>PNMe<sub>2</sub> (2.57 g) and MeHN(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub> (1.80 g) using the procedure as reported for the preparation of  $\overline{\text{(Et}_2\text{N)(:)}\text{PNMeCH}_2\text{CH}_2\text{NMe}_2^+\text{Cl}^-$ , lit. **5**) to **15** (or *vice versa*) over a ten hour period in refluxing toluene. The toluene was removed *in vacuo*, and the <sup>31</sup>P NMR spectrum of residue was taken in CH<sub>2</sub>Cl<sub>2</sub>.

The structure of **5**(BF<sub>4</sub>) was confirmed by X-ray crystallography<sup>15</sup> and the ORTEP drawing is shown in Figure 1. The metrics in cation **5** are similar to those in the previously structured cations **16**<sup>17</sup> and **17**.<sup>16</sup> The P-N<sub>quat</sub> distances found in cations **5**, **16** and **17**



**16**, Z = Ph  
**17**, Z = Cl



**18**

(1.901 Å, 1.882 Å and 1.842 Å) decrease as expected, with increasing electronegativity of Z. The other distances and angles of **5** are similar to the corresponding values reported in **16** and **17**. Previously reported species such **16** and **17** were synthesized by Me<sub>3</sub>SiX elimination between a halophosphine and Me<sub>3</sub>SiNMeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>.<sup>16-21</sup>

In cases where the anion (X<sup>-</sup>) is nucleophilic, equilibria between the cyclic form and open-chain species of type **18** have been observed,<sup>14,17,19</sup> which supports the notion that **9** is also in equilibrium with its acyclic conformer. Interestingly, reaction 1 apparently constitutes a new approach to the synthesis of chelation-stabilized phosphonium ions.

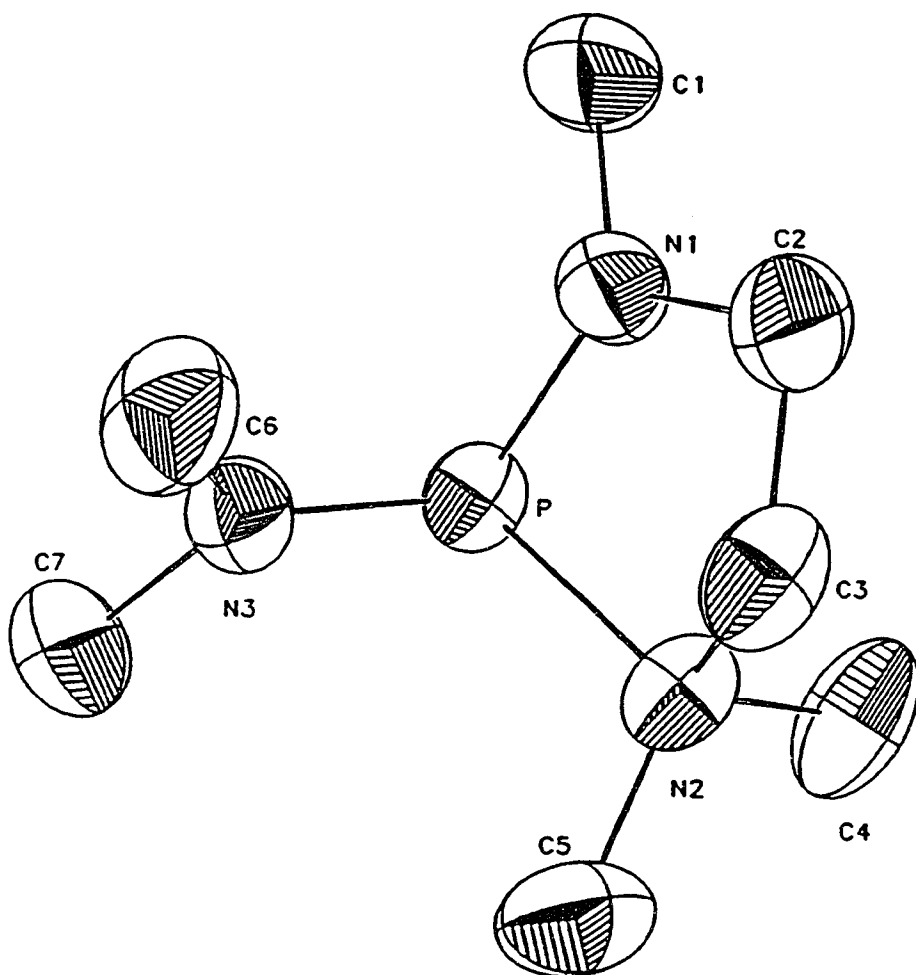


Figure 1. ORTEP drawing of cation 5 with ellipsoids drawn at the 50% probability level



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**Supplementary Material Available.** Tables of X-ray crystallographic data, positional parameters, and bond distances and angles of  $5(\text{BF}_4)$  (9 pages). Ordering information is given on any current masthead page.

## REFERENCES

1. Laramay, M. A. H.; Verkade, J. G. *J. Am. Chem. Soc.* **1990**, *112*, 9421.
2. Lensink, C.; Xi, S.-K.; Daniels, L. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 3478.
3. Laramay, M. A. H.; Verkade, J. G. *Z. anorg. allg. Chem.*, submitted.
4. Method A: To a solution containing 1.84 g (11.3 mmol) of P(NMe<sub>2</sub>)<sub>3</sub> and 1.15 g (11.3 mmol) of HMeNCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> in 25 mL of CH<sub>2</sub>Cl<sub>2</sub> was added 1.82 g (1.13 mmol) of HBF<sub>4</sub>•OMe<sub>2</sub>, via syringe, under an atmosphere of dry argon. After stirring for 16 hours, the volatiles were removed *in vacuo*. The residue was washed with Et<sub>2</sub>O and recrystallized from concentrated CH<sub>2</sub>Cl<sub>2</sub> (1.81 g, 68% yield): <sup>31</sup>P (CD<sub>2</sub>Cl<sub>2</sub>) δ 154.5; <sup>1</sup>H (CD<sub>2</sub>Cl<sub>2</sub>) δ 2.84, δ 2.91 (3H each, d, <sup>3</sup>J<sub>HP</sub> = 10.8 Hz, <sup>3</sup>J<sub>HP</sub> = 6.6 Hz, CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), δ 3.36, δ 3.71 (2H each, m, CH<sub>2</sub>), δ 2.67 (3H, d, <sup>3</sup>J<sub>HP</sub> = 11.1 Hz, NCH<sub>3</sub>), δ 2.82 (6H, d, <sup>3</sup>J<sub>HP</sub> = 11.7 Hz, PN(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C (CD<sub>2</sub>Cl<sub>2</sub>) δ 33.9 (d, <sup>2</sup>J<sub>PC</sub> = 28.7 Hz, PN(CH<sub>3</sub>)<sub>2</sub>), δ 35.2 (d, <sup>2</sup>J<sub>PC</sub> = 9.9 Hz, NCH<sub>3</sub>), δ 44.5, δ 46.1 (d, <sup>2</sup>J<sub>PC</sub> = 21.6 Hz, <sup>2</sup>J<sub>PC</sub> = 9.5 Hz, CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), δ 51.8 (d, <sup>2</sup>J<sub>PC</sub> = 9.0 Hz, CH<sub>2</sub>), δ 58.9 (br, CH<sub>2</sub>). Method B: A neat mixture containing 1.05 g (6.42 mmol) of P(NMe<sub>2</sub>)<sub>3</sub> and 0.595 g (5.83 mmol) of HMeN(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub> was heated to 90 °C under a flow of argon for 10 hours, at which point no more HNMe<sub>2</sub> evolution was detected. After cooling the mixture to 20 °C, the remaining HNMe<sub>2</sub> was removed *in vacuo*. The spectroscopic data of the residue is: <sup>31</sup>P (THF) δ 118 (s); <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>) δ 2.12 (6H, s, CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>), δ 2.3 (2H, m, CH<sub>2</sub>), δ 2.47 (12H, d, <sup>3</sup>J<sub>PH</sub> = 9.3 Hz, P[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>) δ 2.58 (3H, d, <sup>3</sup>J<sub>PH</sub> = 8.7 Hz, NCH<sub>3</sub>), δ 2.6 (2H, m, CH<sub>2</sub>), and ~10% starting materials. To a solution containing 0.274 g (1.26 mmol) of the above residue in 25 mL of CH<sub>2</sub>Cl<sub>2</sub> was added 0.204 g (1.26 mmol) of HBF<sub>4</sub>•OMe<sub>2</sub>. The reaction mixture was worked up as above,

isolated yield = 0.21 g, 72%.

5. To a suspension of 1.04 g (7.80 mmol) of  $\text{AlCl}_3$  in 30 mL of  $\text{CH}_2\text{Cl}_2$  (at  $-78^\circ\text{C}$ , under inert atmosphere) was added a solution containing 1.72 g (7.80 mmol) of  $\text{Ph}_2\text{PCl}$  in 5 mL of  $\text{CH}_2\text{Cl}_2$ . The mixture was warmed to  $20^\circ\text{C}$  and stirred for 1 hour during which time the  $\text{AlCl}_3$  dissolved. The mixture was cooled to  $-78^\circ\text{C}$  and a solution containing 0.724 g (7.10 mmol) of  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NHMe}$  in 5 mL of  $\text{CH}_2\text{Cl}_2$  was added dropwise. The mixture was warmed to  $20^\circ\text{C}$  and stirred for 5 hours. The volatiles were removed *in vacuo* and the residue was washed with  $3 \times 10$  mL of  $\text{C}_5\text{H}_{12}$ :  $^{31}\text{P}$  ( $\text{CHCl}_2$ )  $\delta$  80 ppm (s);  $^1\text{H}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  2.57 (3H, d,  $^3J_{\text{HP}} = 5.2$  Hz,  $\text{NCH}_3$ ),  $\delta$  2.76 (6H, s,  $\text{CH}_2\text{N}(\text{CH}_3)_2$ ),  $\delta$  3.06,  $\delta$  3.45 (2H each, m,  $\text{CH}_2$ ),  $\delta$  7.41 (10H, m,  $\text{C}_6\text{H}_5$ );  $^{13}\text{C}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  36.9 (s,  $\text{CH}_2\text{N}(\text{CH}_3)_2$ ),  $\delta$  43.5 (s,  $(\text{CH}_3)_2\text{N}$ ),  $\delta$  49.1 (d,  $^2J_{\text{PC}} = 20.4$  Hz,  $\text{NCH}_3$ ),  $\delta$  55.2 (br,  $\text{CH}_2\text{N}(\text{CH}_3)$ ),  $\delta$  128.6 (d,  $^2J_{\text{PC}} = 4.83$  Hz, *m*-C on Ph),  $\delta$  129.2 (d,  $^2J_{\text{PC}} = 9.65$  Hz, *o*-C on Ph),  $\delta$  130.4 (s, *p*-C on Ph),  $\delta$  131.9 (d,  $^2J_{\text{PC}} = 17.6$ , *ipso*-C on Ph).
6. Holmes, R. R. *J. Phys. Chem.* 1960, 64, 1295.
7. Holmes, R. R. *J. Am. Chem. Soc.* 1960, 82, 5285.
8. Dillon, K. B.; Platt, A. W. C.; Schmidpeter, A.; Zwaschka, F.; Sheldrick, W. S. Z. *anorg. allg. Chem.* 1982, 488, 7 and, references therein.
9. Sheldrick, W. S.; Zwaschka, Schmidpeter, A. *Angew. Chem. Internat. Ed.* 1979, 91, 1000.
10. Ramirez, F.; Patwardhan, A. V.; Kugler, H. J.; Smith, C. P. *J. Am. Chem. Soc.* 1967, 89, 6276.
11. Synthesized via a new route: To a solution containing 6.68 g (48.8 mmol) of  $\text{PCl}_3$  and 3.98 g (24.4 mmol) of  $\text{P}(\text{NMe}_2)_3$  in 50 mL of  $\text{Et}_2\text{O}$  at  $0^\circ\text{C}$  was slowly added 15.0 g (148 mmol) of  $\text{Et}_3\text{N}$  followed by 6.44 g (73.2 mmol) of  $\text{HMeN}(\text{CH}_2)_2\text{NMeH}$ . After

the reaction mixture was stirred for 20 hours the  $\text{Et}_3\text{NHCl}$  was removed by filtration and the  $\text{Et}_2\text{O}$  removed *in vacuo*. The residue was warmed to 22 °C and **14** was condensed into a  $\text{N}_2(\text{l})$ -cooled trap from a 22 °C pot (0.25 mm Hg). The distillate (6.26 g, 59% yield) was spectroscopically pure (see ref. 16).

12. To a solution containing 0.302 g (4.98 mmol) of **14** in 10 mL of toluene at -78 °C under an inert atmosphere was added dropwise 0.707 g (4.98 mmol) of MeI in 5 mL of toluene. The mixture was warmed to 20 °C, the toluene was evaporated *in vacuo* and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  ( $^{31}\text{P}$  NMR:  $\delta$  58.4 (s);  $^1\text{H}$  ( $\text{CD}_3\text{CN}$ )  $\delta$  2.52 (3H, d,  $^2J_{\text{PH}} = 18.5$  Hz,  $\text{PCH}_3$ ),  $\delta$  3.22,  $\delta$  3.30 (6H, d,  $^3J_{\text{PH}} = 10.8$  Hz,  $^3J_{\text{PH}} = 10.5$  Hz),  $\delta$  3.91 (4H, m,  $\text{CH}_2$ );  $^{13}\text{C}$  ( $\text{CD}_3\text{CN}$ )  $\delta$  8.47 (d,  $^1J_{\text{PC}} = 106.4$  Hz,  $\text{PCH}_3$ ),  $\delta$  30.7,  $\delta$  36.3 (d,  $^2J_{\text{PC}} = 6.49$  Hz,  $^2J_{\text{PC}} = 4.83$  Hz,  $\text{NCH}_3$ ),  $\delta$  48.1 (d,  $^2J_{\text{PC}} = 10.8$  Hz,  $\text{CH}_2$ ).
13. (a) Cowley, A. H.; Cushner, M. C.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 7784. (b) Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789. (c) Pohl, S. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 1342. (d) Pohl, S. *Z. Chem. Ber.* **1979**, *112*, 3519. (e) Friedrich, P.; Huttner, G.; Lubert, J.; Schmidpeter, A. *Chem. Ber.* **1978**, *111*, 1558.
14. Becker, W.; Schmutzler, R. *Phosphorus and Sulfur* **1988**, *37*, 231.
15. Crystal Data: space group  $\text{P}2_1/\text{c}$ ,  $a = 8.100(5)$  Å,  $b = 10.231(3)$  Å,  $c = 15.938$  Å,  $V = 1310.1$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calc}} = 1.368$  g/cm<sup>3</sup>,  $\mu(\text{MoK}\alpha) = 3.2$  cm<sup>-1</sup>; No. data collected: 4984; No. unique data, total: 2310; with  $F_o^2 > 3.0(F_o^2)$ : 1788; No. parameters refined: 154; observed at -50 °C. Refinement of parameters converged with agreement factors of:  $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.050$  and  $R_w = [\sum w(F_o - F_c)^2 / \sum w(F_o^2)]^{1/2} = 0.073$ . The refinement was carried out on a Digital Equipment Corp. Micro VAXII computer using the CAD4-SDP programs. Details of the crystallographic procedures appear in the

## Supplementary Material.

16. Betterman, G.; Schonburg, D.; Schmutzler, R. *Phosphorus and Sulfur* **1986**, *28*, 327.
17. Becker, W.; Schonburg, D.; Schutzler, R. *Phosphorus and Sulfur* **1989**, *42*, 21.
18. Becker, W.; Betterman, G.; Schonburg, D.; Schmutzler, R. *Phosphorus and Sulfur* **1990**, *49*, 109.
19. Kaukorat, T.; Ernst, L.; Schmutzler, R. *Z. Naturforsch., B.: Chem. Soc.* **1989**, *44*, 481.
20. Akiba, K.; Okada, K.; Ohkata, K. *Tett. Lett.* **1986**, *43*, 5221.
21. Kaukorat, T.; Schmutzler, R. *Z. Naturforsch., B.: Chem. Sci.* **1989**, *44*, 481.

## APPENDIX

**Data Collection.** A colorless crystal of the title compound was mounted on the end of a glass fiber in a random orientation. The crystal was then moved to the diffractometer and cooled to  $-50 \pm 1$  °C. The cell constants were determined from a list of 25 reflections found by an automated search routine. The  $P2_1/c$  symmetry of the orthorhombic cell was confirmed by photography. Pertinent data collection and reduction information is given in Table 1.

Lorentz and polarization corrections were applied. A correction based on the decay in the standard reflections of 1.8% was applied to the data. An absorption correction based on a series of psi-scans was applied. The agreement factor for the averaging of the observed reflections was 1.8% (Based on F).

A total of 4984 reflections were collected in the  $hkl$ ,  $hkl$ , and  $hkl$  octants. Equivalent data were merged, leaving 2310 data (1788 with  $F_o^2 \geq 3\sigma(F_o^2)$ ), which included 154 parameters refined. The agreement factor for the averaging of the observed reflections was 2.31% (based on  $F_{obs}$ ). Lorentz and polarization corrections were applied. No decay was detected, and psi-scans of several reflections indicated that an absorption correction was not necessary.

**Structure Solution and Refinement.** The centric space group  $P2_1/c$  was indicated initially by systematic absences and intensity statistics.<sup>1</sup> The positions of all cationic-group atoms were determined by direct methods.<sup>2</sup> All hydrogen atoms were found by difference Fourier techniques and were placed at idealized positions (0.95 Å from the attached atom) with isotropic temperature factors set equal to 1.3 times the

isotropic equivalent of that atom. The  $\text{BF}_4^-$  anion could not be modelled in the normal way using separate atomic positions and anisotropic thermal parameters. The rigid body method was employed using GSAS<sup>3</sup> to model two separate  $\text{BF}_4^-$  groups with nearly the same origin. TLS matrices<sup>4</sup> (18 parameters each), three rotation axes (3 parameters each), a rigid-body origin (3 parameters each) and a linked B-F bond distance (1 parameter) were refined for each  $\text{BF}_4^-$  contributor. S-matrix elements  $S_{AA}$  and  $S_{BB}$  were not refined in this treatment: the librational and translational coordinate systems are assumed to intersect at the origin. Equivalent anisotropic thermal parameters are calculated directly from the rigid-body parameters. This method gave an acceptable refinement of  $R = 0.051$  and  $R_w = 0.075$ , whereas without rigid-body modelling the agreement factors were 2 - 3 times greater. The hydrogen atom isotropic temperature factors were refined in the final cycles of least-squares.

X-ray data collection and the structure solution were carried out at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. MicroVAX II computer using the CAD4-SPD programs.<sup>4</sup>

#### References.

1. SHELXS-86, G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Göttingen. F. R. G.
2. Neutral-atom scattering factors and anomalous scattering corrections were taken from *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.
3. Hamilton, W. C. *Acta Crystallogr.* 1965, 18, 502.
4. Enraf-Nonius Structure Determination Package; Enraf-Noniu: Delft, Holland.

Table 1. X-ray crystallographic data for  $(\text{Me}_2\text{N})(\text{:})\overline{\text{PNMeCH}_2\text{CH}_2\text{NMe}_2}(\text{BF}_4)$ 

Crystal data	
Formula	$[\text{PN}_3\text{C}_7\text{H}_{19}][\text{BF}_4]$
Formula weight	263.08
Space group	$\text{P}2_1/c$
$a, \text{\AA}$	8.100(5)
$b, \text{\AA}$	10.231(3)
$c, \text{\AA}$	15.938(7)
$V, \text{\AA}^3$	1310.1(1)
$Z$	4
$d_{\text{calc}} \text{ g/cm}^3$	1.33
Crystal size, mm	0.40 x 0.30 x 0.30
$\mu(\text{MoK}\alpha), \text{ cm}^{-1}$	2.45
Data collection instrument	Enraf-Nonius CAD4
Radiation	$\text{MoK}\alpha (\lambda = 0.71073 \text{ \AA})$
Orientation reflections, number, range ( $2\theta$ )	25, $21.1 < \theta < 32.2$

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b R_w = [ \sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2 ]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$^c \text{Quality-of-fit} = [ \sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}}) ]^{1/2}$$



Table 1, continued. X-ray crystallographic data;



	Crystal data
Temperature, °C	-50 ± 1
Scan method	θ - 2θ
Data collection range, 2θ, deg	4-50
No. unique data, total:	4984
with $F_o^2 > 3\sigma(F_o^2)$ :	2310
Number of parameters refined	154
R <sup>a</sup>	0.050
R <sub>w</sub> <sup>b</sup>	0.075
Quality-of-fit indicator <sup>c</sup>	1.032
Largest shift/esd, final cycle	0.01
Largest peak, e/Å <sup>3</sup>	0.29(5)

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b R_w = [ \sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2 ]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$^c \text{Quality-of-fit} = [ \sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}}) ]^{1/2}$$

Table 2. Bond distances (Å) for  $(\text{Me}_2\text{N})(\text{:})\overline{\text{PNMeCH}_2\text{CH}_2\text{NMe}_2}(\text{BF}_4)$ 

Atom 1	Atom 2	Distance
P	N(1)	1.6527(26)
P	N(2)	1.9043(25)
P	N(3)	1.6387(25)
N(1)	C(1)	1.445(4)
N(1)	C(2)	1.454(4)
C(2)	C(3)	1.499(5)
N(2)	C(3)	1.485(4)
N(2)	C(4)	1.487(4)
N(2)	C(5)	1.492(4)
N(3)	C(6)	1.463(4)
N(3)	C(7)	1.463(4)
B	F(1)	1.3351(18)
B	F(2)	1.3351(17)
B	F(3)	1.3351(17)
B	F(4)	1.3351(18)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3. Bond angles (deg) for  $(\text{Me}_2\text{N})(\text{:})\overline{\text{PNMeCH}_2\text{CH}_2\text{NMe}_2}(\text{BF}_4)$ 

Atom 1	Atom 2	Atom 3	Angle
P	N(1)	C(1)	121.55(23)
P	N(1)	C(2)	120.61(22)
C(1)	N(1)	C(2)	117.44(27)
N(1)	C(2)	C(3)	105.52(26)
C(2)	C(3)	N(2)	106.73(25)
P	N(2)	C(3)	105.53(17)
P	N(2)	C(4)	106.79(19)
P	N(2)	C(5)	111.67(20)
C(3)	N(2)	C(4)	111.92(26)
C(3)	N(2)	C(5)	110.92(25)
C(4)	N(2)	C(5)	109.88(28)
P	N(3)	C(6)	127.50(22)
P	N(3)	C(7)	118.09(24)
C(6)	N(3)	C(7)	117.24(28)
F(1)	B	F(2)	109.47(4)
F(1)	B	F(3)	109.469(34)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3, continued. Bond angles (deg) for



Atom 1	Atom 2	Atom 3	Angle
F(1)	B	F(4)	109.47(4)
F(2)	B	F(3)	109.48(4)
F(2)	B	F(4)	109.476(28)
F(3)	B	F(4)	109.47(4)
F(1')	B'	F(2')	109.470(30)
F(1')	B'	F(3')	109.469(31)
F(1')	B'	F(4')	109.47(4)
F(2')	B'	F(3')	109.48(4)
F(2')	B'	F(4')	109.476(35)
F(3')	B'	F(4')	109.469(26)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 4. Positional parameters and their standard deviations ( x 100) for



Atom	x	y	z	$U_{\text{equ}}(\text{\AA}^2)$
P	0.73184(9)	0.13266(7)	0.43902(4)	4.16
N(1)	0.62860(32)	0.06725(24)	0.35307(15)	5.19
N(2)	0.89086(27)	0.18957(24)	0.36862(14)	4.54
N(3)	0.62560(30)	0.26340(23)	0.45781(15)	4.92
C(1)	0.5037(5)	-0.3234(37)	0.35810(25)	7.58
C(2)	0.6749(5)	0.09676(38)	0.26995(21)	6.61
C(3)	0.7960(4)	0.20787(34)	0.28338(18)	5.59
C(4)	1.0170(4)	0.08381(40)	0.36961(25)	7.29
C(5)	0.9732(5)	0.31378(38)	0.40008(26)	7.46
C(6)	0.5011(5)	0.33178(36)	0.39915(26)	7.09
C(7)	0.6650(5)	0.32770(41)	0.53991(25)	7.85
B	0.1830(4)	0.18931(33)	0.14844(17)	5.76
F(1)	0.0311(4)	0.18931(33)	0.13318(36)	9.67
F(2)	0.1885(8)	0.2721(5)	0.21348(30)	11.10
F(3)	0.2948(6)	0.0944(5)	0.16717(57)	17.19
F(4)	0.2177(11)	0.2535(7)	0.7991(22)	15.54
B'	0.1733(5)	0.18206(42)	0.15113(26)	5.72
F(1')	0.0714(11)	0.0852(7)	0.16711(56)	14.08

Table 4, continued. Positional parameters and their standard deviations ( x 100) for  
 $(\text{Me}_2\text{N})(\text{:})\overline{\text{PNMeCH}_2\text{CH}_2\text{NMe}_2}(\text{BF}_4)$ , 5

Atom	x	y	z	$U_{\text{equ}}(\text{\AA}^2)$
F(2')	0.2609(11)	0.2215(9)	0.22334(35)	14.26
F(3')	0.2770(9)	0.1397(8)	0.09833(57)	13.03
F(4')	0.0839(10)	0.2819(5)	0.11571(57)	12.74

**PART IV: METAL COORDINATION OF P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N AND ITS NOVEL  
REDOX CHEMISTRY WITH MERCURY(II).**

## ABSTRACT

The pro-azaphosphatane  $\text{P}(\text{NMeCH}_2\text{CH}_2)_3\text{N}$  (**2**) reacts differently with different Lewis acidic metal-containing starting materials. The title compound replaces a CO in  $\text{Re}(\text{CO})_5\text{Br}$ , giving  $(\text{CO})_4\text{Re}(\text{2})\text{Br}$  (**10**); coordinates to  $\text{MeHgX}$  then undergoes disproportionates with another molecule of  $\text{MeHg}(\text{2})\text{X}$ , giving  $(\text{2})_2\text{HgX}_2$  ( $\text{X} = \text{Cl}$  (**11**),  $\text{I}$  (**13**)); and reduces the mercury in  $[\text{Hg}(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{OTf})_2$  to give  $\text{Hg}_2^{2+}$  and  $[\text{H}_2\text{MeNCH}_2\text{CH}_2\text{N}(\overline{\text{CH}_2\text{CH}_2\text{NMe}})_2\text{PO}]_2(\text{OTf})_4$  (**15**). It is shown shown that  $(\text{2})_2\text{HgX}_2$  hydrolyzes to give  $\text{Hg}^0$ ,  $[\overline{\text{HP}(\text{NMeCH}_2\text{CH}_2)_3\text{N}}]_2(\text{HgI}_4)$  (**12**), and the novel peroxide,  $[\overline{\text{HP}(\text{NMeCH}_2\text{CH}_2)_3\text{N}}]_2(\text{O}_2)$ . The latter compound is the first phosphorus(III)-containing compound reported to be stable in the presence of peroxide. Reported herein are the syntheses, characterizations, and solid state molecular structures of **10**, **11**, **12**, and **15**; the synthesis and characterization of  $[\overline{\text{ClP}(\text{NMeCH}_2\text{CH}_2)_3\text{N}}]\text{Cl}$ , **16(Cl)**, another precursor to **15**; and spectroscopic evidence for the existence of  $[\overline{\text{HP}(\text{NMeCH}_2\text{CH}_2)_3\text{N}}]_2(\text{O}_2)$ .

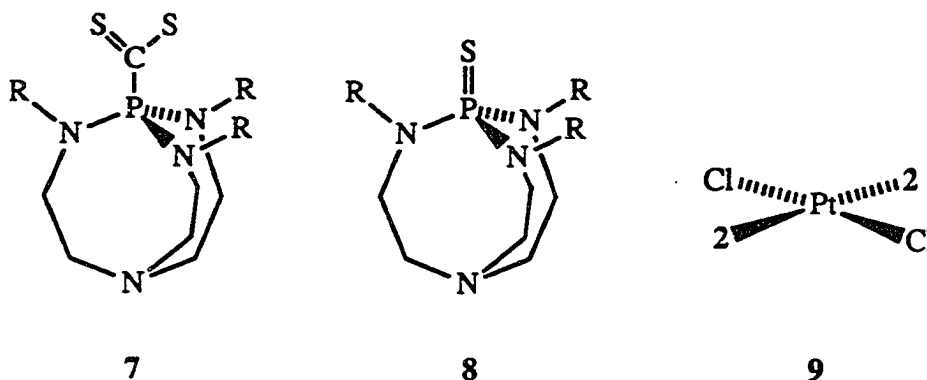


## INTRODUCTION

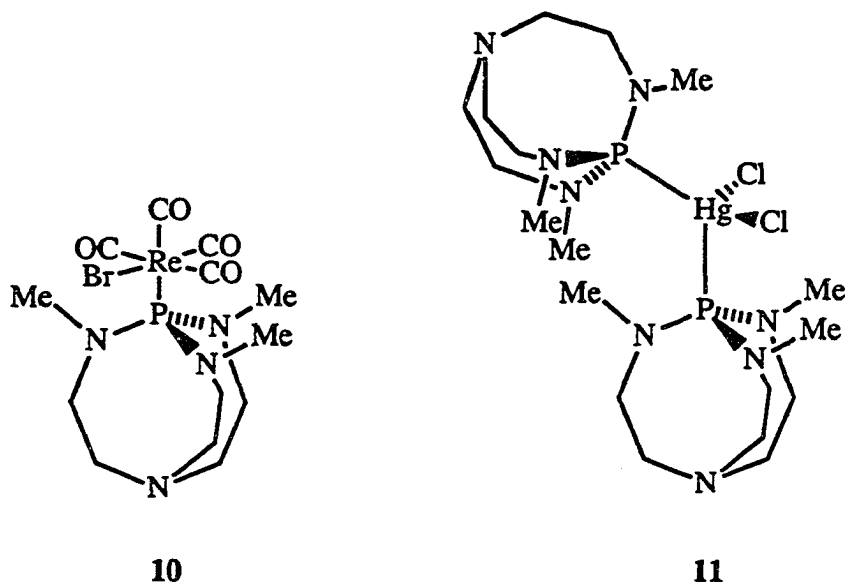
In recent publications from our laboratories we have demonstrated that prophosphatranes **1 - 3** are extraordinarily basic to protons.<sup>1-6</sup> The corresponding conjugate acids **4 - 6** possess  $pK_a$  values in DMSO ranging from 26.8 to 29.6 and feature



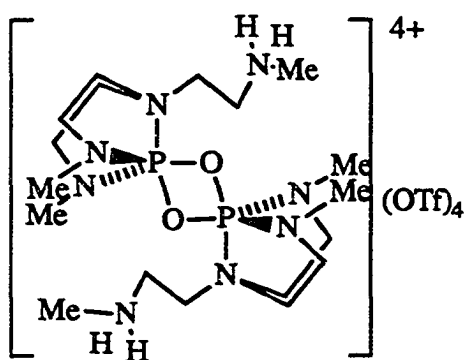
transannulated structures as was shown by X-ray crystallography for **4(Cl)**<sup>1</sup> and **5(BF<sub>4</sub>)**.<sup>2</sup> In cations **4** and **5** the P-N<sub>ax</sub> bond lengths are 2.0778 Å and 1.976 Å, respectively. With the Lewis acids CS<sub>2</sub> (**7**), S (**8**) and PtCl<sub>2</sub> (**9**), the P-N<sub>ax</sub> bond lengths in these phosphorus-ligating species increase from 3.008 Å to 3.250 Å to 3.33 Å, respectively; the last value corresponding closely with the sum of the van der Waals radii of phosphorus and nitrogen (3.35 Å).<sup>3</sup>



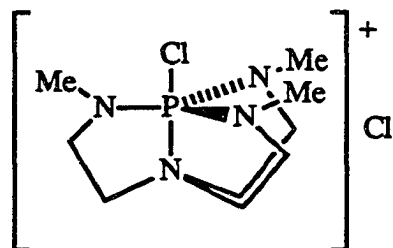
During further attempts to define the conditions required for transannulation in **1-3**, we began an exploration of the metal coordination chemistry of **2**. Herein we report the synthesis and structural characterization of *cis*-Re(CO)<sub>4</sub>(**2**)Br (**10**), Hg(**2**)<sub>2</sub>Cl<sub>2</sub> (**11**) and (5)<sub>2</sub>(HgI<sub>4</sub>) (**12**); the last compound having been formed in the hydrolysis of I<sub>2</sub>Hg(**2**)<sub>2</sub> (**13**).



We also report that this hydrolysis is a redox reaction that produces free mercury and the novel apparently stable phosphorus(III) peroxide (5)<sub>2</sub>O<sub>2</sub> (**14**). In contrast, when [Hg(NCMe)(H<sub>2</sub>O)<sub>2</sub>](OTf)<sub>2</sub> is reacted with **2**, a hydrolytic redox reaction occurs that produces Hg<sub>2</sub><sup>2+</sup> as the ultimate reduction product. The novel transannulated dioxaphosphetane dimer **15**, the ultimate oxidation product, was structured by X-ray crystallographic means. The novel cation **15** also forms quantitatively by hydrolysis of the new cation **16** whose synthesis we report herein as the chloride.



15



16(Cl)

## EXPERIMENTAL

All reactions were carried out under dry argon. Solids were weighed under dry nitrogen and solvents were dried under nitrogen using standard methods.<sup>7</sup> Commercial  $\text{Re}(\text{CO})_5\text{Br}$ ,  $\text{MeHgCl}$ ,  $\text{HgO}$ ,  $\text{HgI}_2$ ,  $\text{AgBF}_4$ ,  $\text{Ag}(\text{OSO}_2\text{CF}_3)$ , and  $\text{Zn}(\text{OSO}_2\text{CF}_3)_2$  were used without purification. Methylmercury iodide, mercuric triflate, and mercuric tetrafluoroborate were prepared using standard methods starting with  $\text{HgI}_2$ ,<sup>8</sup>  $\text{HgO}$ ,<sup>9</sup> and  $\text{HgCl}_2$ ,<sup>10</sup> respectively. Compounds  $2,2,5(\text{Cl})_2$ ,  $\text{O}=\text{P}(\text{NMeCH}_2\text{CH}_2)_3\text{N}$ , and  $\text{Hg}[\text{P}(\text{NMe}_2)_3]_2\text{I}_2$ <sup>11</sup> were prepared using previously reported procedures. Trisdimethylaminophosphine was distilled at room temperature (0.05 mm Hg) before use. Proton and carbon-13 NMR spectra were recorded on a Varian VXR-300 instrument or a Nicolet NT-300 instrument and the  $^{31}\text{P}$  NMR spectra were recorded on a Bruker WM-200 instrument using  $\text{PPh}_3$  in  $\text{C}_6\text{D}_6$  as an external standard ( $\delta$  -4.9 ppm) and external lock solvent, respectively, unless otherwise indicated. Mercury-199 spectra were recorded on a Bruker WM-200 instrument using  $\text{CD}_3\text{CN}$  as an internal lock solvent. The  $^{199}\text{Hg}$  chemical shifts are reported with respect to that of  $\text{MeHgCl}$  which was set to -862 ppm<sup>12</sup> prior to recording the other samples. Infrared spectra were recorded in methylene chloride on an IBM IR/98 Spectrometer.

***cis*- $\text{Re}(\text{CO})_4[\text{PNMeCH}_2\text{CH}_2)_3\text{N}]\text{Br}$ , 10.** A solution containing 0.818 g (3.79 mmol) of 2 in 10 mL of THF was added dropwise to a suspension of 1.54 g (3.79 mmol) of  $\text{Re}(\text{CO})_5\text{Br}$  in 20 mL of THF. The supernatant turned light yellow and the  $\text{Re}(\text{CO})_5\text{Br}$  slowly went into solution with the visible evolution of CO. The reaction was complete after 16 hours. The solvent was removed *in vacuo* and 15 mL of  $\text{CH}_2\text{Cl}_2$  was added to dissolve the residue. Upon slow evaporation of  $\text{CH}_2\text{Cl}_2$ , light yellow crystals of 6 suitable for X-ray determination formed (1.84 g, 81.8% yield). The spectroscopic data are as

follows:  $^{31}\text{P}$  ( $\text{CH}_2\text{Cl}_2$ )  $\delta$  98.6;  $^1\text{H}$  ( $\text{CD}_3\text{CN}$ )  $\delta$  2.83 (9H, d,  $^3J_{\text{PH}} = 9.6$  Hz,  $\text{CH}_3$ ),  $\delta$  2.93 (12H, br,  $\text{CH}_2$ );  $^{13}\text{C}$  ( $\text{CD}_3\text{CN}$ )  $\delta$  36.2 (d,  $^2J_{\text{PC}} = 10.6$  Hz,  $\text{CH}_3$ ),  $\delta$  49.7 (d,  $^{2,3}J_{\text{PC}} = 1.6$  Hz,  $\text{N}_{\text{ax}} \text{CH}_2$ ),  $\delta$  51.34 (d,  $^2J_{\text{PC}} = 2.7$  Hz,  $\text{N}_{\text{eq}} \text{CH}_2$ ),  $\delta$  184.1,  $\delta$  185.1 (s, CO's cis to 2),  $\delta$  185.9 (d,  $^2J_{\text{PC}} = 9.1$  Hz, CO trans to 2); IR ( $\text{CH}_2\text{Cl}_2$ , CO Region)  $2100 \text{ cm}^{-1}$ ,  $1996 \text{ cm}^{-1}$ ,  $1936 \text{ cm}^{-1}$ ,  $1884 \text{ cm}^{-1}$ ; m/e 594 amu (isotopic abundances found match those calculated).

**cis-Re(CO) $_4$ [P(NMe $_2$ ) $_3$ ]Br, 17.** A solution containing 0.142 g (0.875 mmol) of P(NMe) $_3$  in 5 mL of  $\text{CH}_2\text{Cl}_2$  was added dropwise to a suspension of 0.356 g (0.876 mmol) of Re(CO) $_5$ Br in 15 mL of  $\text{CH}_2\text{Cl}_2$ . Upon stirring for 24 hours, the solids dissolved giving a yellow solution. The  $\text{CH}_2\text{Cl}_2$  was removed *in vacuo* and the residue was washed with 15 mL of THF. The THF solution was decanted from the undissolved material and the solvent was removed *in vacuo*. The resulting yellow residue was washed with 25 mL of *n*-pentane to remove any unreacted P(NMe) $_2$  $_3$ , and was then dried *in vacuo* (0.279 g, 59% yield). The spectroscopic data are as follows:  $^{31}\text{P}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  103.3;  $^1\text{H}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  2.71 (d,  $^3J_{\text{PH}} = 10.2$  Hz);  $^{13}\text{C}$  ( $\text{CD}_3\text{CN}$ )  $\delta$  39.1 (d,  $^1J_{\text{PC}} = 2.9$  Hz,  $\text{CH}_3$ ),  $\delta$  184.3 (s, CO trans to Br)  $\delta$  186.4 (d,  $^2J_{\text{PC}} = 4.5$  Hz, CO trans to CO),  $\delta$  187.0 (d,  $^2J_{\text{PC}} = 12.1$  Hz, CO trans to P(NMe) $_2$  $_3$ ); IR ( $\text{CH}_2\text{Cl}_2$ , CO region)  $2100 \text{ cm}^{-1}$ ,  $1996 \text{ cm}^{-1}$ ,  $1938 \text{ cm}^{-1}$ ,  $1896 \text{ cm}^{-1}$ . Elemental analysis calculated for C $_{10}$ H $_{18}$ O $_4$ BrN $_3$ PRE: C, 22.2; H, 3.35; N, 7.76. Found: C, 22.7; H, 3.55; N, 7.91.

**Hg[P(NMeCH $_2$ CH $_2$ ) $_3$ N] $_2$ Cl $_2$ , 11.** A solution containing 0.324 g (1.50 mmol) of 2 in 10 mL of THF was added dropwise to a solution containing 0.377 g (1.50 mmol) of MeHgCl in 15 mL of THF. After 60 minutes a white solid began to precipitate and the process was quantitative after 5 minutes. The supernatant was decanted and the precipitate was washed with 2 x 10 mL portions of THF, leaving 0.519 g of 7 (98.3% yield). The spectroscopic data are as follows:  $^{31}\text{P}$  ( $\text{CH}_2\text{Cl}_2$ )  $\delta$  118 ( $^1J_{\text{HgP}} = 7869$  Hz);  $^1\text{H}$  ( $\text{CD}_3\text{CN}$ )  $\delta$  2.79 (6H, m,  $\text{CH}_2$ )  $\delta$  2.91 (6H, m,  $\text{CH}_2$ ),  $\delta$  2.95 (9H, "t", separation between outer peaks

of the AA'X<sub>9</sub>X<sub>9</sub>' system = 13.2 Hz); <sup>13</sup>C (CD<sub>3</sub>CN) δ 34.9 ("t", separation between outer peaks = 18 Hz), δ 50.9 (s, CH<sub>2</sub>N<sub>ax</sub>) δ 51.04 (s, CH<sub>2</sub>N<sub>eq</sub>). Elemental analysis calculated for C<sub>18</sub>H<sub>42</sub>Cl<sub>2</sub>HgN<sub>3</sub>P<sub>2</sub>: C, 30.7; H, 6.01; N, 15.9. Found: C, 29.7; H, 6.13; N, 15.9. Crystals suitable for X-ray diffraction were grown from a concentrated CH<sub>2</sub>Cl<sub>2</sub> solution. Hg[P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]<sub>2</sub>I<sub>2</sub>, **13**. A solution containing 0.146 g (0.678 mmol) of **2** in 5 mL of THF was added dropwise to a solution containing 0.232 g (0.678 mmol) of MeHgI in 10 mL of THF. A white precipitate began forming after 20 minutes; a process which was complete after 5 minutes. The supernatant was decanted off and the white precipitate was washed with 2 x 10 mL portions of THF, leaving 0.209 g of **13** (69.3% yield). The spectroscopic data are as follows: <sup>31</sup>P (CH<sub>2</sub>Cl<sub>2</sub>) δ 118.6 (<sup>1</sup>J<sub>HgP</sub> = 7050 Hz); <sup>1</sup>H (CD<sub>3</sub>CN) δ 2.79 (6H, m, CH<sub>2</sub>) δ 2.91 (6H, m, CH<sub>2</sub>), δ 2.95 (9H, "t", separation between outer peaks of the AA'X<sub>9</sub>X<sub>9</sub>' system = 6.6 Hz).

[Hg(CH<sub>3</sub>CN)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](OTf)<sub>2</sub>, analysis, a. Elemental analysis of the title compound, prepared from HgO and HOTf in CH<sub>3</sub>CN (see ref. 9), gave: calculated for C<sub>6</sub>H<sub>10</sub>O<sub>8</sub>N<sub>2</sub>HgS<sub>2</sub> C, 11.68; H, 1.63; N, 4.54; Hg, 32.52. Found: C, 11.27; H, 1.72; N, 4.01; Hg, 32.48.

[Hg(CH<sub>3</sub>CN)<sub>2</sub>(H<sub>2</sub>O)](OTf)<sub>2</sub>, analysis b. The <sup>31</sup>P NMR spectrum of a solution containing 0.526 g (2.23 mmol) of (Ph)<sub>2</sub>P(O)Cl, 0.298 g (0.739 mmol) of Ph<sub>3</sub>PMe<sup>+</sup>I<sup>-</sup> (as an internal standard), and 0.0122 g (0.0350 mmol) of Cr(acac)<sub>3</sub> (as a relaxation agent) showed the following: δ 21.4 (Ph<sub>3</sub>PMe<sup>+</sup>I<sup>-</sup>), δ 28.8 (Ph<sub>2</sub>P(O)OP(O)Ph<sub>2</sub>, hydrolysis product, intensity relative to standard = 0.0927), δ 44.4 (Ph<sub>2</sub>P(O)Cl). The <sup>31</sup>P NMR spectrum of a solution containing 0.526 g (2.23 mmol) of Ph<sub>2</sub>P(O)Cl, 0.286 g (0.710 mmol) of Ph<sub>3</sub>PMe<sup>+</sup>I<sup>-</sup>, 0.0145 g (0.0416 mmol) of Cr(acac)<sub>3</sub>, and 0.116 g (0.188 mmol) of [Hg(CH<sub>3</sub>CN)<sub>2</sub>(H<sub>2</sub>O)](OTf)<sub>2</sub> in 2.0 mL of CD<sub>3</sub>CN and 0.5 mL of pyridine gave the same signals as above, however the intensity of the signal at 28.8 ppm relative to the standard

was 0.640, implying that there is 1.16 moles of H<sub>2</sub>O in every mole of mercuric triflate. Due to the reaction of one of the materials with the mercuric triflate, as seen by the precipitation of HgO before the addition of pyridine, this value may be low.  $\{\text{MeH}_2\text{NCH}_2\text{CH}_2\text{N}(\overline{\text{CH}_2\text{CH}_2\text{NMe}})_2\text{PO}\}_2(\text{OTf})_4$ , **15**. A solution containing 0.141 g (0.653 mmol) of **2** in 5 mL of CH<sub>3</sub>CN was added dropwise to a solution containing 0.806 g (1.31 mmol) of [Hg(H<sub>2</sub>O)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>](OTf)<sub>2</sub> in 15 mL of CH<sub>3</sub>CN. Each drop of solution of **2** precipitated what appeared to be black Hg<sup>0</sup> which then dissolved immediately. The reaction mixture was stirred for 24 hours followed by the removal of CH<sub>3</sub>CN *in vacuo*. The residue was washed with 10 mL of toluene and was then redissolved in 15 mL of CH<sub>3</sub>CN. Crystals of **15** suitable for X-ray diffraction were grown from this solution, upon the slow evaporation of CH<sub>3</sub>CN (0.22 g, 64% yield). The spectroscopic data are as follows: <sup>31</sup>P (CH<sub>3</sub>CN) δ -48.6; <sup>1</sup>H (CD<sub>3</sub>CN) δ 2.76 (s, CH<sub>3</sub>NH<sub>2</sub>, 12H), δ 2.89 ("t", N<sub>eq</sub>CH<sub>3</sub>, separation between outer peaks of the AA'X<sub>9</sub>X<sub>9</sub>' system = 12.3 Hz), δ 3.24, δ 3.41, δ 3.55 (m, CH<sub>2</sub>); <sup>13</sup>C (CD<sub>3</sub>CN) δ 35.2 (s, CH<sub>3</sub>NH<sub>2</sub>), δ 37.1 ("t", separation between outer peaks = 6.11 Hz, N<sub>eq</sub>CH<sub>3</sub>), δ 44.2 (s, N<sub>ax</sub>CH<sub>2</sub> (free arm)), δ 44.6 ("t", separation between outer peaks = 12.5 Hz, N<sub>ax</sub>CH<sub>2</sub>), δ 47.2 ("t", separation between outer peaks = 9.73 Hz, N<sub>eq</sub>CH<sub>2</sub>), δ 49.7 (s, NH<sub>2</sub>CH<sub>2</sub>).

The above reaction was also monitored by NMR spectroscopy. a) Loaded in a 10 mm NMR tube were 0.071 g (0.324 mmol) of **2** and 0.400 g (0.648 mmol) of [Hg(CH<sub>3</sub>CN)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](OTf)<sub>2</sub> with no external standard. Acetonitrile and CD<sub>3</sub>CN were added using trap-to-trap techniques *in vacuo* with liquid N<sub>2</sub> cooling. The tube was flame sealed and warmed to -35 °C. The <sup>31</sup>P NMR spectrum of the reaction mixture was taken at -35 °C, 0 °C, then at room temperature after 10 minutes, 30 minutes and 24 hours (Table 1). The Mercury-199 spectrum was taken after 5 days. b) Loaded into a 10 mm NMR tube were 0.112 g (0.518 mmol) of **2** and 0.639 g (1.04 mmol) of

$[\text{Hg}(\text{H}_2\text{O})_2(\text{CH}_3\text{CN})_2](\text{OTf})_2$ . Acetonitrile was added (2.5 mL) *via* syringe. The  $^{31}\text{P}$  NMR spectrum of this mixture was taken after 10 minutes then after 24 hours (Table 1).

c) Loaded in a 10 mm NMR tube were 0.16 g (0.74 mmol) of **1** and 0.27 g (0.44 mmol) of  $[\text{Hg}(\text{H}_2\text{O})_2(\text{CH}_3\text{CN})_2](\text{OTf})_2$ . Acetonitrile (2.5 mL) was added *via* syringe. The  $^{31}\text{P}$  NMR spectrum was taken after 24 hours (see text). The supernatant was decanted from the  $\text{Hg}^0$  which precipitated from the reaction mixture. The  $\text{Hg}^0$  was washed with 2 x 3 mL of  $\text{CH}_3\text{CN}$  then dried *in vacuo* (0.088 g, 0.44 mmol).

**Reaction of  $\text{P}(\text{NMeCH}_2\text{CH}_2)_3\text{N}$  (**2**) with  $\text{Hg}(\text{BF}_4)_2(\text{CH}_3\text{CN})_n$  and  $\text{H}_2\text{O}$ .** To a solution containing 0.37 g of the title mercury compound (0.99 mmol for  $n = 0$  to 0.60 mmol for  $n = 6$ ) in 2 mL of  $\text{CH}_3\text{CN}$  was added 0.60 mL of a 1.0 M solution of  $\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$ , followed by a solution containing 0.13 g (0.60 mmol) of **2** in 1 mL of  $\text{CH}_3\text{CN}$ . The  $^{31}\text{P}$  NMR spectrum was taken after 5 days (see text).

**Reaction of  $\text{P}(\text{NMe}_2)_3$  with  $\text{Hg}(\text{OTf})_2(\text{H}_2\text{O})_2(\text{CH}_3\text{CN})_2$ .** A solution containing 0.074 g (0.45 mmol) of  $\text{P}(\text{NMe}_2)_3$  in 0.5 mL of  $\text{CH}_3\text{CN}$  was added to a solution containing 0.56 g (0.90 mmol) of  $[\text{Hg}(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})_2](\text{OTf})_2$ . No  $\text{Hg}^0$  precipitation was observed. The  $^{31}\text{P}$  NMR of the reaction mixture was taken after 24 hours:  $\delta$  92 ( $^1J_{\text{HgP}} = 13855$  Hz).

**Hydrolysis of  $\text{Hg}\{\text{P}(\text{NMeCH}_2\text{CH}_2)_3\text{N}\}_2\text{I}_2$ , **13**.** A solution containing 0.101 g (0.114 mmol) of  $\text{I}_2\text{Hg}(\text{2})$  in 10 mL of  $\text{CH}_3\text{CN}$  was added all at once to 50 mL of undried  $\text{CH}_3\text{CN}$ . The supernatant was decanted from the  $\text{Hg}^0$  and all but 2 mL of  $\text{CH}_3\text{CN}$  was removed *in vacuo*. A  $^{31}\text{P}$  NMR spectrum of this solution showed only a signal at -10 ppm (**5**). From such a solution, yellow crystals of  $(\text{5})_2\text{HgI}_4$  (**12**) grew over a period of months which were suitable for X-ray diffraction.

**Hydrolysis of  $\text{Hg}\{\text{P}(\text{NMeCH}_2\text{CH}_2)_3\text{N}\}_2\text{Cl}_2$ , **11**.** a) To a solution containing 0.101 g (0.144 mmol) of **11** in 10 mL of  $\text{CH}_2\text{Cl}_2$  was added 2.15 mL of a 0.1 M solution of  $\text{H}_2\text{O}$  in THF (0.215 mmol of  $\text{H}_2\text{O}$ ). A  $^{31}\text{P}$  NMR spectrum of the reaction mixture revealed



only a signal at -10 ppm (5). The volatiles were removed *in vacuo*, leaving a residue which was washed with THF, dried *in vacuo*, and dissolved in 3 mL of CH<sub>2</sub>Cl<sub>2</sub>. The methylene chloride solution was decanted from the Hg<sup>0</sup>. After an IR spectrum was collected (see text), 0.01 g of PPh<sub>3</sub> was dissolved in the solution. The <sup>31</sup>P NMR spectrum was as follows: δ 27 (s, O=PPh<sub>3</sub>), δ -10 (d, <sup>1</sup>J<sub>HP</sub> = 493 Hz, 5). The intensity of the signal at 27 ppm was enhanced upon the addition of previously isolated O=PPh<sub>3</sub>. b) To a solution containing 0.10 g (0.14 mmol) of **11** in 0.5 mL of CH<sub>3</sub>CN was added 0.22 mL of 1.0 M solution of H<sub>2</sub>O in CH<sub>3</sub>CN. The <sup>31</sup>P NMR of the solution gave one signal at -10 ppm (d, <sup>1</sup>J<sub>HP</sub> = 493 Hz, 5). c) A small quantity of **11** was exposed to the atmosphere for 7 days. The resulting grey solids were washed with 2.5 mL of CH<sub>2</sub>Cl<sub>2</sub>. The <sup>31</sup>P NMR spectrum of the washings gave one signal (-10 ppm, d, <sup>1</sup>J<sub>HP</sub> = 493 Hz, 5).

**Reaction of O=P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N with [Hg(CH<sub>3</sub>CN)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](OTf)<sub>2</sub>.** Loaded into a 10 mm NMR tube were 0.15 g (0.65 mmol) of O=P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N, 0.40 g (0.65 mmol) of [Hg(H<sub>2</sub>O)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>](OTf)<sub>2</sub> and 2.5 mL of CH<sub>3</sub>CN. The <sup>31</sup>P NMR spectra after 10 minutes and after 5 days both showed only a singlet at 20.3 ppm (s, O=P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N).

**Reaction of O=P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N with HOTf.** To a solution containing 0.15 g (0.65 mmol) of O=P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N in 2.5 mL of CH<sub>3</sub>CN was added 0.195 g (1.3 mmol) of HOTf. The <sup>31</sup>P NMR taken of this mixture after 10 minutes was as follows: δ -31 (s), δ 20.3 (s, O=P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N). After 5 days, the <sup>31</sup>P NMR was as follows: δ 12 (s), δ 20.3 (s, O=P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N).

**Reaction of [HP(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]Cl with HOTf.** To a solution containing 0.146 g (0.573 mmol) of **2(Cl)** in 2.5 mL of CH<sub>3</sub>CN was added 0.112 g (0.747 mmol) of HOTf. The <sup>31</sup>P NMR of this solution after 10 minutes and after 5 days showed only one signal at -10 ppm (<sup>1</sup>J<sub>HP</sub> = 493 Hz, 5).

**Reaction of  $\text{O}=\text{P}(\text{NMeCH}_2\text{CH}_2)_3\text{N}$  with  $\text{Zn}(\text{OTf})_2$ .** Loaded in a 10 mm NMR tube were 0.19 g (0.82 mmol) of  $\text{O}=\text{P}(\text{NMeCH}_2\text{CH}_2)_3\text{N}$ , 0.30 g (0.82 mmol) of  $\text{Zn}(\text{OTf})_2$ , and 2.5 mL of  $\text{CH}_3\text{CN}$ . The  $^{31}\text{P}$  NMR spectra after 10 minutes and after 5 days both showed only a signal at +20.3 ppm (s,  $\text{O}=\text{P}(\text{NMeCH}_2\text{CH}_2)_3\text{N}$ ).

**Reaction of  $[\overline{\text{HP}(\text{NMeCH}_2\text{CH}_2)_3\text{N}}]\text{Cl}$  with  $\text{Zn}(\text{OTf})_2$ .** Loaded in a 10 mm NMR tube were 0.21 g (0.82 mmol) of **2**(Cl), 0.30 g (0.82 mmol) of  $\text{Zn}(\text{OTf})_2$ , and 2.5 mL of  $\text{CH}_3\text{CN}$ . The  $^{31}\text{P}$  NMR spectra after 10 minutes and after 5 days showed only a signal at -10 ppm (d,  $^1J_{\text{HP}} = 493$  Hz, **5**).

**$[\overline{\text{CIP}(\text{NCH}_3\text{CH}_2\text{CH}_2)_3\text{N}}]\text{Cl}$ , **16**.** To a suspension of 0.421 g (1.78 mmol) of  $\text{Cl}_6\text{C}_2$  in 10 mL of  $\text{Et}_2\text{O}$  was added all at once a solution containing 0.384 g (1.78 mmol) of **2** in 5 mL of  $\text{Et}_2\text{O}$ . The mixture was stirred for 20 hours. The resulting white precipitate was isolated by filtration (0.430 g, 84.2% yield). The spectroscopic data are as follows:  $^{31}\text{P}$  ( $\text{CH}_3\text{CN}$ )  $\delta$  -20.6;  $^1\text{H}$  ( $\text{CD}_3\text{CN}$ )  $\delta$  2.09 (9H, d,  $^3J_{\text{PH}} = 14.5$  Hz,  $\text{CH}_3$ ),  $\delta$  3.22 (6H, br,  $\text{CH}_2\text{N}_{\text{ax}}$ ),  $\delta$  3.35 (6H, d/t,  $^3J_{\text{PH}} = 6.43$  Hz,  $^3J_{\text{HH}} = 3.21$  Hz,  $\text{CH}_2\text{N}_{\text{eq}}$ );  $^{13}\text{C}$  ( $\text{CD}_3\text{CN}$ )  $\delta$  39.7 (d,  $^2J_{\text{PC}} = 5.7$  Hz,  $\text{CH}_3$ ),  $\delta$  46.2 (d,  $^2J_{\text{PC}} = 9.1$  Hz,  $\text{CH}_2\text{N}_{\text{ax}}$ ),  $\delta$  46.8 (d,  $^2J_{\text{PC}} = 8.7$  Hz,  $\text{CH}_2\text{N}_{\text{eq}}$ ).

**Reaction of  $[\overline{\text{CIP}(\text{NMeCH}_2\text{CH}_2)_3\text{N}}]\text{Cl}$  (**16**) with  $\text{Zn}(\text{OTf})_2$ .** Loaded in a 10 mm NMR tube were 0.10 g (0.35 mmol) of **16**, 0.13 g (0.35 mmol) of  $\text{Zn}(\text{OTf})_2$ , and 2.5 mL of undried  $\text{CH}_3\text{CN}$ . The  $^{31}\text{P}$  NMR spectrum after 24 hours gave only a singlet at -48.6 ppm (**15**) (the  $^{13}\text{C}$  NMR of this spectrum also matched that of cation **15**).

**Reaction of  $[\overline{\text{CIP}(\text{NMeCH}_2\text{CH}_2)_3\text{N}}]^+\text{Cl}^-$  with  $\text{H}_2\text{O}$ .** Loaded in a 10 mm NMR tube were 0.10 g (0.35 mmol) of **16** 0.70 mL of a 1 M solution of  $\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$  (0.70 mmol  $\text{H}_2\text{O}$ ), and 2.0 mL of  $\text{CH}_3\text{CN}$ . The  $^{31}\text{P}$  NMR spectrum of this mixture after 24 hours showed ~20% **5** ( $\delta$  -10 ppm) and ~80% **16** ( $\delta$  -20 ppm).

**Stability of  $[\overline{\text{HP}(\text{NMeCH}_2\text{CH}_2)_3\text{N}]\text{Cl}$  in the presence of HOO-*t*-Bu.** A 3 M solution of HOO-*t*-Bu in toluene (0.14 mL, 0.43 mmol HOO-*t*-Bu) was added to a solution containing 0.092 g (0.36 mmol) of **5(Cl)** in 2.5 mL of  $\text{CH}_2\text{Cl}_2$ . The mixture was cooled to 5 °C for 36 hours to prevent thermal decomposition of the hydroperoxide. The  $^{31}\text{P}$  NMR spectrum of the resulting mixture showed only a signal at -10 ppm (d,  $^1J_{\text{HP}} = 493$  Hz). The volatiles were removed *in vacuo* and the residues were dissolved in  $\text{CD}_2\text{Cl}_2$ . The  $^1\text{H}$  NMR spectrum corresponded to that of **5**.<sup>2</sup>

**Attempted synthesis of  $[\overline{\text{HP}(\text{NMeCH}_2\text{CH}_2)_3\text{N}]\text{OO-}t\text{-Bu}$ , (**5**)OO-*t*-Bu.** Two of the following reaction mixtures were prepared; one was kept at room temperature, the other at 5 °C for 36 hours. The resulting spectroscopic data for both reactions were the same. To a solution containing 0.144 g (0.565 mmol) of **5(Cl)** and 0.20 mL of 3 M HOO-*t*-Bu solution in toluene (0.60 mmol HOO-*t*-Bu) in 10 mL of  $\text{CH}_2\text{Cl}_2$  was added 0.60 mL of 1 M solution of NaOEt in EtOH (taken from a solution containing 0.713 g (31.0 mmol) of Na in 31 mL of EtOH). The reaction mixture became cloudy, but due to our uncertainty about the stability of (**5**)OO-*t*-Bu, filtration was not attempted. The  $^{31}\text{P}$  NMR spectrum of the reaction mixture showed only a signal at -10 ppm (d,  $^1J_{\text{HP}} = 493$  Hz, **5**). The volatiles were removed, the resulting residue was washed with 2 x 15 mL portions of  $\text{Et}_2\text{O}$  and dried *in vacuo*. The  $^1\text{H}$  NMR of the residue ( $\text{CD}_2\text{Cl}_2$ ) corresponded to **5** plus a singlet at 1.21 ppm (s, 2H, (not the expected integration for 9H), *t*-Bu). The  $^1\text{H}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ ) was taken after the addition of HOO-*t*-Bu and again after the addition of HO-*t*-Bu (see text). The infrared spectrum of the residue was recorded in  $\text{CH}_2\text{Cl}_2$  (see text). After  $\text{PPh}_3$  was added to the  $\text{CH}_2\text{Cl}_2$  solution of the residue, in addition to the signal at -10 ppm (**5**) the  $^{31}\text{P}$  NMR showed enhancement of the signal at -4.9 ppm ( $\text{PPh}_3$ , external standard) and a new signal at 27 ppm ( $\text{OPPh}_3$ ). The infrared spectrum showed a new band at  $1120\text{ cm}^{-1}$  ( $\nu(\text{P}=\text{O})$ ) and a decrease in intensity of the signal at  $840\text{ cm}^{-1}$  ( $\nu(\text{OOR})$ ).

**X-ray structural determination of  $\text{Re}(\text{CO})_4\text{Br}[\text{P}(\text{NMeCH}_2\text{CH}_2)_3\text{N}]$ , 10.** A colorless crystal of the title compound was mounted on the end of a glass fiber in a random orientation. The crystal was then moved to the diffractometer and cooled to  $-50 \pm 1$  °C. The cell constants were determined from a list of reflections found by an automated search routine. The *Pbca* symmetry of the centric space group was confirmed by photography.

Lorentz and polarization corrections were applied. A correction based on the decay in the standard reflections of 1.3% was applied to the data. An absorption correction based on a series of  $\psi$ -scans was applied. The agreement factor for the averaging of the observed reflections was 2.7% (based on *F*).

A total of 9732 reflections were collected. Equivalent data were merged, leaving 3694 data (2416 with  $F_o^2 \geq 3\sigma(F_o^2)$ ), which included 154 parameters refined.

The centric space group *Pbca* was indicated initially by systematic absences and intensity statistics.<sup>13</sup> The positions of all atoms were determined by direct methods.<sup>14</sup> All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were found by difference Fourier techniques and were placed at idealized positions (0.95 Å from the attached atom) with isotropic temperature factors set equal to 1.3 times the isotropic equivalent of that atom. The hydrogen atom positions and isotropic temperature factors were not refined.

X-ray data collection and the structure solution were carried out at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. MicroVAX II computer using the CAD4-SPD programs.<sup>14</sup>

**X-ray structural determination of  $[\text{N}(\text{CH}_2\text{CH}_2\text{NMe})_3\text{P}]_2\text{HgCl}_2$ , 11.** A colorless cubic crystal of  $\text{HgCl}_2\text{P}_2\text{N}_8\text{C}_{18}\text{H}_{42}$  having approximate dimensions of 0.400 x 0.300 x 0.300 mm was mounted in a glass capillary. All measurements were made on a Rigaku AFC6R

diffractometer with graphite monochromated  $\text{MoK}\alpha$  radiation and a 12KW rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range  $12.34 < 2\theta < 15.09^\circ$  corresponded to an orthorhombic cell with dimensions:  $a = 15.557(6) \text{ \AA}$ ,  $b = 9.508(7) \text{ \AA}$ ,  $c = 18.218(6) \text{ \AA}$ ,  $V = 2695(4) \text{ \AA}^3$ . For  $Z = 4$  and F.W. = 704.03, the calculated density is  $1.735 \text{ g/cm}^3$ . Based on the systematic absences of:  $0k1: 1 \neq 2n$ ,  $h01: h \neq 2n$  packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be  $\text{Pca}2_1$  (#29).

The data were collected at a temperature of  $25 \pm 1^\circ\text{C}$  using the  $\omega$ - $2\theta$  scan technique to a maximum  $2\theta$  value of  $50.1^\circ$ . Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of  $0.38^\circ$  with a take-off angle of  $6.0^\circ$ . Scans of  $(1.10 + 0.30 \tan \theta)$  were made at a speed of  $16.0^\circ/\text{min}$  (in omega). The weak reflections ( $I < 10.0\sigma(I)$ ) were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 400.0 mm.

**Data reduction.** A total of 2743 reflections was collected. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficient for  $\text{MoK}\alpha$  is  $60.5 \text{ cm}^{-1}$ . An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in

transmission factors ranging from 0.75 to 1.00. The data were corrected for Lorentz and polarization effects.

**Structure solution and refinement.** The positions of the non-hydrogen atoms were determined as follows: Patterson superpositions were carried out using two-mercury-mercury vectors and a mercury-chlorine vector (weighted). The positions of the symmetry elements in the superposition map were determined by a reciprocal space method. The resulting phases were referenced to the electron density map origin.<sup>3</sup> An electron density map was then calculated which yielded the positions of the mercury, chlorine, and nitrogen atoms. The positions of the remaining non-hydrogen atoms were determined from successive structure factor and electron density map calculations. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1889 observed reflections ( $I > 3.00\sigma(I)$ ) and 279 variable parameters and converged (largest parameter shift was 0.09 times its esd) with unweighted and weighted agreement factors of:  $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.028$ ,  $R_w = [(\sum w(|F_o| - |F_c|)^2) / \sum w F_o^2]^{1/2} = 0.033$ .

The standard deviation of an observation of unit weight was 1.28. The weighting scheme was based on counting statistics and included a factor ( $p = 0.03$ ) to downweight the intense reflections. Plots of  $\sum w(|F_o| - |F_c|)^2$  versus  $|F_o|$ , reflection order in data collection,  $\sin \theta/\gamma$ , and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.09 and  $-0.70 \text{ e}^-/\text{\AA}^3$ , respectively.

Neutral atom scattering factors were taken from Cromer and Waber.<sup>6</sup> Anomalous dispersion effects were included in  $F_{calc}$ <sup>7</sup>; the values for  $\ddot{A}f$  and  $\ddot{A}f'$  were those of Cromer.<sup>8</sup> All calculations were performed using the HYPAD,<sup>9</sup> CHES,<sup>10</sup> and TEXSAN<sup>11</sup> crystallographic software packages.

**X-ray structural determination of  $[\overline{\text{HP}(\text{NMeCH}_2\text{CH}_2)_3\text{N}}]_2\text{HgI}_4$ , **12**.** A pale yellow-green crystal of **12** was mounted on the end of a glass fiber. The crystal was then moved to the diffractometer and cooled to  $-70 \pm 1$  °C. The cell constants were determined from a list of reflections found by an automated search routine. Pertinent data collection and reduction information are given in Table 2. A total of 3417 reflections were collected in the  $+h, +k, \pm l$  quadrant. Intensity standards collected once every hour showed only random fluctuations throughout the data collection. An absorption correction based on a series of psi-scans was applied. Lorentz and polarization corrections were applied. Equivalent data were merged, leaving 3310 data (2922 with  $R_{\text{int}} \geq 4\sigma(F_{\text{int}})$ ). The agreement factor for the averaging of 198 observed reflections was 3.2%.

The choice of the centric space group  $C2/c$  was indicated by intensity statistics, and verified by the successful refinement of the structure. The positions of the Hg, I, and P atoms were taken from a direct methods E-map<sup>12</sup> and refined with isotropic temperature factors along with a scale factor in full-matrix least-squares calculations. The remainder of the non-hydrogen atoms of the P-complex were located in a subsequent difference Fourier map. One molecule of  $\text{CH}_3\text{CN}$  was later located in the lattice and included in the refinement. The Hg atom lies on the two-fold axis, with the remainder of the atoms on general positions. An axial hydrogen atom bound to the P atom was indicated in a later difference map. The position and isotropic thermal parameter of the axial hydrogen atom was included in further refinement, but the thermal parameter persisted in refining to a negative value. The value was therefore fixed ( $U = 0.01$ ) in further cycles of refinement. Other hydrogen atoms were indicated in difference Fourier maps, and in the final stages of refinement all expected hydrogen atoms were included in idealized positions for the calculation of structure factors. One common isotropic temperature factor was refined for the methyl hydrogen atoms, and another for the methylene hydrogen atoms. All non-

hydrogen atoms were refined with anisotropic temperature factors, and an extinction coefficient refined to a value of  $3.4(1) \times 10^{-7}$  (in absolute units).

The final refinement cycles involved 196 parameters fitted to 2922 observed data. The residuals were:  $R = 0.027$ ;  $R_w = 0.049$ ; quality-of-fit indicator, 0.805.<sup>13</sup> The largest positive peak in the final difference electron density map had a height of  $1.1(1) \text{ e}/\text{\AA}^3$ . Refinement calculations were performed on a Digital Equipment Corp. Micro VAX II computer using the SHELX-76 programs.<sup>14</sup>

**X-ray structural determination of  $[\text{MeH}_2\text{NCH}_2\text{CH}_2\text{N}(\overline{\text{CH}_2\text{CH}_2\text{NMe})_2\text{PO}]_2(\text{OTf})_4$ ,  $15(\text{OTf})_4$ .** A colorless crystal of  $15(\text{OTf})_4$  was attached to the tip of a glass fiber, moved into the cold stream of the low-temperature device on the diffractometer, and cooled to  $-25^\circ\text{C}$ . The cell constants for data collection were determined from a list of reflections found by an automated search routine. The final cell constants were determined after data collection using 25 well-centered high-angle reflections. Pertinent data collection and reduction information are given in Table 2. Lorentz and polarization corrections were applied. An absorption correction based on a series of psi-scans was applied. The agreement factor for the averaging of 433 observed reflections was 1.7% (based on F).

The centric space group  $\text{P}\bar{1}$  was initially chosen, as suggested by intensity statistics. This choice was verified by the successful solution and refinement of the structure. The positions of the atoms of the phosphorus complexes and the positions of the sulfur atoms were taken from a direct methods E-map<sup>12</sup>. The phosphorus complexes exist as two independent dimers, each on an inversion center. The remainder of the atoms of the triflate ions along with one molecule of acetonitrile were located in subsequent difference maps.

One of the triflate ions was found to be rotationally disordered about the sulfur-carbon bond, so it was refined with two sets of  $\text{O}_3$  groups and two of  $\text{F}_3$ , with the

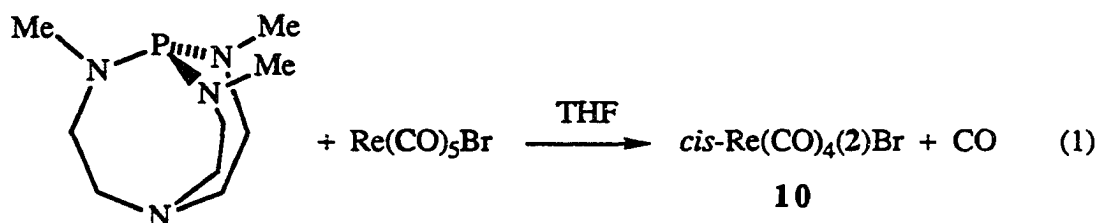


occupancy of each disordered atom set at 0.5. No attempt was made to refine the occupancy. The disordered model improved the residuals but the C-F and S-O bond distances are not necessarily chemically correct.

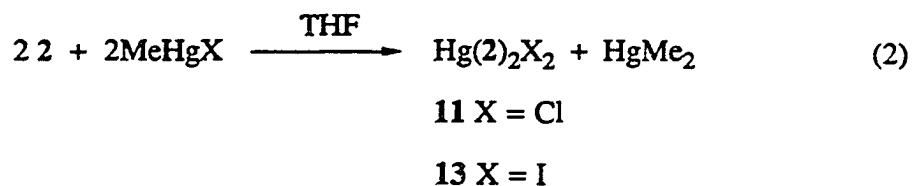
Hydrogen atoms were added in idealized positions (for carbon atoms only) with isotropic temperature factors set equal to 1.3 times the isotropic equivalent of the attached atom. The C-H distance was fixed at 0.95 Å, and the hydrogen positions (for carbon atoms only) with isotropic temperature factors set equal to 1.3 times the isotropic equivalent of the attached atom. The C-H distance was fixed at 0.95 Å, and the hydrogen positions were not refined. The non-carbon atoms were refined with anisotropic temperature factors, except for the disordered O and F atoms and the solvent atoms. Refinement calculations were performed on a Digital Equipment Corp. Micro VAX II computer using the CAD4-SDP programs.<sup>14</sup>

## RESULTS AND DISCUSSION

**Syntheses.** Complex **10** was easily formed at room temperature *via* reaction 1. *Cis*- $\text{Re}(\text{CO})_4[\text{P}(\text{NMe}_2)_3]\text{Br}$  (**17**) was made similarly in  $\text{CH}_2\text{Cl}_2$ . Both reactions proceeded

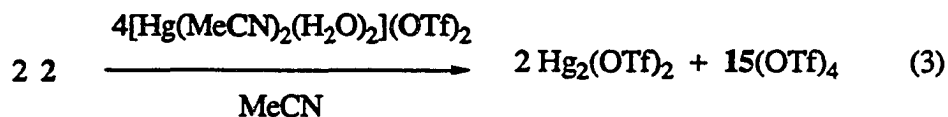


with the visible evolution of CO. The formation of **11** in reaction 2 took 60 minutes before the desired complex began to precipitate. Five minutes after precipitation began, however,



**11** was formed quantitatively. Reactions of this type apparently proceed in two steps with the intermediate formation of a  $[\text{MeHgL}]\text{X}$  complex which then undergoes disproportionation; the latter step increasing in rate with the size of X.<sup>10</sup> Indeed **13** was formed more rapidly than **11** (see Experimental).

The novel dioxaphosphetane **15** was synthesized unexpectedly *via* reaction 3. In this reaction it was observed that free mercury precipitated initially, but redissolved



almost immediately. It was originally assumed that the mercury starting material was anhydrous. However, the elemental analysis of the mercuric triflate used gave values for carbon, hydrogen, nitrogen and mercury that consistently corresponded to the formulation written in reaction 3. Also, a  $^{31}\text{P}$  NMR spectroscopic moisture detection study using  $\text{Ph}_2\text{P}(\text{O})\text{Cl}$  as a reagent<sup>25</sup> corroborated the elemental analysis results in that the mercuric triflate was found to contain water, however, only 1.16 equivalents were found. A side reaction producing  $\text{HgO}$  occurred which may have effected the results, however the  $^{31}\text{P}$  NMR spectrum only showed the expected three signals corresponding to the standard,  $(\text{O})\text{P}(\text{Ph})_2\text{Cl}$ , and  $(\text{Ph})_2(\text{O})\text{P}-\text{O}-\text{P}(\text{O})(\text{Ph})_2$ . Because of this side reaction, we take the results of the elemental analysis to be more accurate (see experimental section).

In an effort to determine whether the acyclic tris-aminophosphine  $\text{P}(\text{NMe}_2)_3$  also led to a redox reaction in the presence of  $[\text{Hg}(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{OTf})_2$ , a reaction analogous to that with **2** in reaction 3 was carried out. However, no  $\text{Hg}^0$  was observed and the  $^{31}\text{P}$  spectrum was indicative only of the presence of  $[\text{HgP}(\text{NMe}_2)_3](\text{OTf})_2$  (*vide infra*).

To determine whether cation **15** could also be formed by the hydrolysis of  $\text{Hg}(\text{2})_2\text{Cl}_2$  (**11**) and/or  $\text{Hg}(\text{2})_2\text{I}_2$  (**13**), reaction 4 was carried out in  $\text{MeCN}$  ( $\text{X} = \text{Cl}, \text{I}$ ),  $\text{CH}_2\text{Cl}_2/\text{THF}$  ( $\text{X} = \text{Cl}$ ) or by exposure to moist air ( $\text{X} = \text{Cl}, \text{I}$ ). However, half of the mercury was



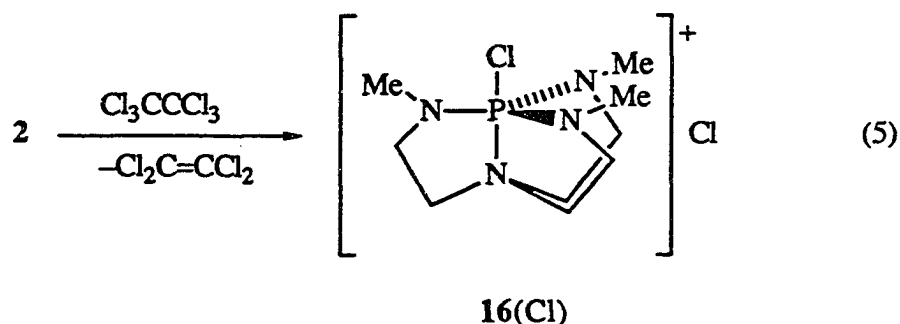
**11**, X = Cl

**14**      **12**, X = I

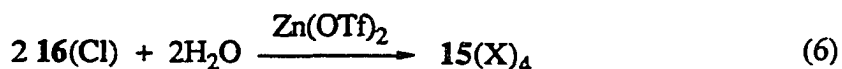
**13**, X = I

precipitated as metallic mercury and in the case of X = I, **12** was isolated and characterized (see later). Spectroscopic evidence for **14** will also be discussed later.

Reaction of the mild chlorinating agent  $\text{Cl}_3\text{CCCl}_3$  with **2** in reaction 5 affords the new phosphatrane cation **16** as the chloride salt. Hydrolysis of **16(Cl)** (reaction 6)



quantitatively yields cation **15** only in the presence of  $\text{Zn}(\text{OTf})_2$ . In the presence of water, **16(Cl)** reacts only partially to give **5** and no **15**.



**Spectroscopic characterizations.** The  $^{31}\text{P}$ ,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for *cis*- $\text{Re}(\text{CO})_4(\mathbf{2})\text{Br}$  (**10**) and *cis*- $\text{Re}(\text{CO})_4[\text{P}(\text{NMe}_2)_3]\text{Br}$  (**17**) are consistent with their formulations as shown. That both have the *cis* configuration is confirmed by the presence

of four CO stretching bands in their IR spectra (2100, 1996, 1936, 1884 and 2100, 1996, 1936, 1896  $\text{cm}^{-1}$ , respectively). From the lower frequency of the last CO band of **10** compared with that of **17**, it may be concluded that **2** is more basic than  $\text{P}(\text{NMe}_2)_3$ ; a conclusion we reached earlier on other considerations.<sup>3</sup> The  $^{31}\text{P}$  NMR chemical shift of **10** (98.6 ppm) lies upfield of **2** (120.8 ppm) by 22.2 ppm. We do not take this result as being indicative of transannulation of ligand **2** in this complex, however, since this chemical shift for **17** (103.3 ppm) is about equally upfield (19.6 ppm) of free  $\text{P}(\text{NMe}_2)_3$  (121.9 ppm<sup>3</sup>). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **10**, however, were suggestive of a  $\text{P-N}_{\text{ax}}$  transannulation interaction. The  $^1\text{H}$  NMR signal for the  $\text{CH}_2$  protons in **10** is broader than those for **2**, and the  $\text{N}_{\text{ax}}\text{C}$  carbon signal is split by a 1.6 Hz coupling to phosphorus. The latter coupling has thus far not been observed if a transannulation interaction is absent. Transannulation, however, was not confirmed in the solid state molecular structure of **10**, thereby providing an exception to the above arguments for transannulation, if the solid state structure reflects that present in solution. The chemical shifts and  $^2\text{J}_{\text{PC}}$  couplings recorded for the CO carbons are consistent with those previously reported for rhenium phosphine complexes.<sup>25-28</sup> The lack of observable P-C couplings for the CO groups *cis* to **2** in **10** has also been observed previously in rhenium phosphine compounds.<sup>25-28</sup>

The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectroscopic parameters for  $\text{Hg}(\mathbf{2})_2\text{Cl}_2$  (**11**) and  $\text{Hg}(\mathbf{2})_2\text{I}_2$  (**13**) are consistent with their formulations as structures in which transannulation in the ligand **2** is absent. In the  $^1\text{H}$  NMR spectra of these complexes the  $\text{N}_{\text{eq}}\text{CH}_3$  proton signal is a pseudo triplet owing to virtual coupling in the  $\text{AA}'\text{X}_9\text{X}'_9$  system wherein  $\text{A} = \text{A}' = \text{P}$  and  $\text{X} = \text{X}' = \text{H}$ .<sup>29</sup> Pseudo triplets were also observed in their  $^{13}\text{C}$  spectra for the  $\text{N}_{\text{eq}}\text{CH}_2$  and  $\text{N}_{\text{eq}}\text{CH}_3$  carbons which display resonances of the  $\text{AA}'\text{X}$  type ( $\text{X} = ^{13}\text{C}$ ).<sup>30</sup> The  $^{31}\text{P}$  chemical shifts of **11** and **13** are virtually identical ( $\delta$  118.0,  $\delta$  118.6, respectively), and the  $^{199}\text{Hg}$ - $^{31}\text{P}$  couplings for **11** and **13** are 7868 Hz and 7050 Hz,

respectively. A decreasing  $^1J_{\text{HgP}}$  from  $(\text{PPh}_3)_2\text{HgCl}_2$  to  $(\text{PPh}_3)_2\text{HgI}_2$  has previously been reported.<sup>31</sup> These  $^1J_{\text{HgP}}$  coupling values are close to those reported for other disubstituted  $\text{HgL}_2(\text{OTf})_2$  complexes ( $\text{L} = \text{P}(\text{OMe})_3$ , 11,123 Hz;  $\text{L} = \text{P}(\text{OEt})_3$ , 10,645 Hz).<sup>32</sup> That a monosubstituted complex  $\text{Hg}(2)\text{X}_2$  is not being formed is also indicated by the larger couplings observed for  $\text{HgL}_2(\text{OTf})_2$  where  $\text{L} = \text{P}(\text{OMe})_3$  (17,528 Hz) and  $\text{L} = \text{P}(\text{OEt})_3$  (17,323 Hz).<sup>32</sup> Unlike **2**,  $\text{P}(\text{NMe}_2)_3$  in the presence of two equivalents of  $[\text{Hg}(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{OTf})_2$  shows only a  $^{31}\text{P}$  NMR resonance indicative of an  $\text{Hg}[\text{P}(\text{NMe}_2)_3]^{2+}$  complex ( $\delta$  92,  $^1J_{\text{HgP}} = 13,855$  Hz).

The upfield  $^{31}\text{P}$  chemical shift of -48.6 ppm observed for cation **15** is the largest thus far observed for a phosphatrane derivative. It should be noted in this regard that in contrast to **4 - 6**, which are formally protonated phosphorus(III) cations, **15** formally contains two phosphorus(V) cations. The  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra also support the dimeric structure of **15**. The  $\text{N}_{\text{eq}}\text{CH}_3$  and  $\text{N}_{\text{eq}}\text{CH}_2$   $^{13}\text{C}$  and  $^1\text{H}$  resonances are pseudo triplets as well as the  $^{13}\text{C}$  resonance of the  $\text{N}_{\text{ax}}\text{CH}_2$  carbon in the five-membered rings. The  $^{13}\text{C}$  resonances of the pendant  $\text{CH}_3\text{N}^+\text{H}_2\text{CH}_2\text{CH}_2$  arms of **15** are singlets, which is expected, except perhaps for the acyclic  $\text{N}_{\text{ax}}\text{CH}_2$  carbon. That reaction 3 produced  $\text{Hg}_2^{2+}$  was confirmed by observing the  $^{199}\text{Hg}$  NMR spectrum of the reaction mixture which exhibited a single signal at -1,570 ppm (relative to external  $\text{MeHgCl}$  (-862 ppm)). This chemical shift (observed at -40 °C in MeCN to reduce broadness)<sup>33</sup> is well within the range recorded for  $\text{Hg}_2^{2+}$  (-2,030 to -1,500 ppm).<sup>33</sup> As expected from previously reported  $\text{Hg}_2^{2+}$  mercury-199 chemical shifts,<sup>12,32,33</sup> the signal for our  $\text{Hg}_2^{2+}$  appears downfield from  $[\text{Hg}(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{OTf})_2$  in an acetonitrile solution of similar concentration.

The  $^{31}\text{P}$  chemical shift of -20.0 ppm for compound **16(Cl)** synthesized *via* reaction 5 is strongly indicative of five-coordinate phosphorus. This was corroborated by the strong

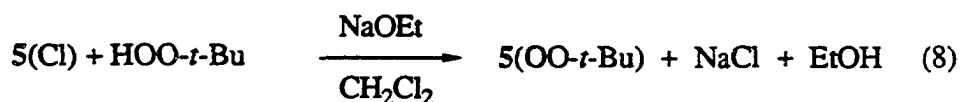
$N_{ax}CH_2P$  coupling observed in the  $^{13}C$  NMR spectrum; a coupling generally observed in phosphatrane structures.<sup>1,2</sup>

**Spectroscopic evidence for the formation of 12 and 14.** The  $^1H$ ,  $^{13}C$  and  $^{31}P$  NMR spectral parameters for isolated **12** virtually duplicated those for **5**.<sup>2</sup> The supernatant  $CH_2Cl_2$  solution from reaction 4 ( $X = Cl$ ) was found by  $^{31}P$  and IR spectroscopies to oxidize  $PPh_3$  ( $\delta$  -4.9,  $\nu(P=O)$  absent) to  $O=PPh_3$  ( $\delta$  27 ppm,  $\nu(P=O)$  1120  $cm^{-1}$ ). Because phosphorus(III) compounds are readily oxidized to phosphorus(V) species in the presence of peroxide<sup>34</sup> and because hydrolysis of **14** by adventitious water could produce potentially dangerous free  $H_2O_2$  (reaction 7) we made no attempt to isolate **14**. Since we did observe,



**14**

however, that according to  $^1H$  and  $^{31}P$  NMR spectroscopies **5(Cl)** is stable for 72 hours in a dry  $CH_2Cl_2$  solution containing 1.2 equivalents of  $HOO-t-Bu$ , we attempted to isolate **5(OO-*t*-Bu)** according to reaction 8. The supernatant was stable for at least three days at

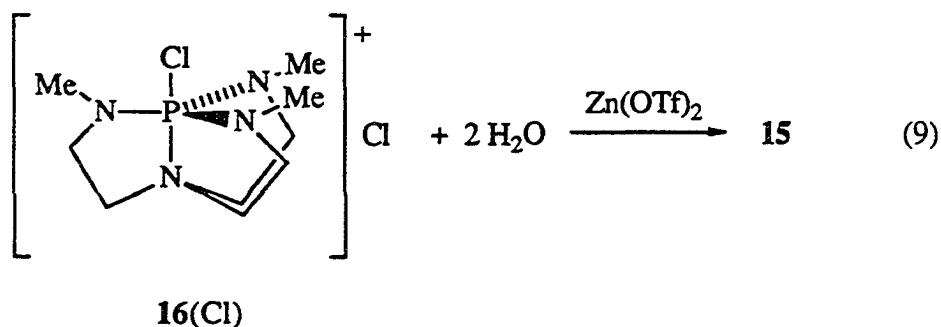


5 °C or room temperature as shown by  $^{31}P$  and  $^1H$  NMR spectroscopies. Evaporation of the solvent and extracting the residue with  $Et_2O$  revealed only  $^1H$  NMR ( $CD_2Cl_2$ ) signals attributable to **5** and **OO-*t*-Bu** ( this signal only integrates to 2H as apposed to the expected

9H); the latter signal (1.21 ppm) was enhanced by added HOO-*t*-Bu. The signal for added HO-*t*-Bu was downfield. Moreover, no  $\nu(\text{OH})$  IR band was observed in this extract. The extract was also found to oxidize  $\text{PPh}_3$  to  $\text{O=PPh}_3$  as shown by  $^{31}\text{P}$  NMR spectroscopy and by the IR spectrum which featured a decrease in the  $840\text{ cm}^{-1}$  band associated with  $-\text{OO-}t\text{-Bu}$  and the appearance of the  $\nu(\text{P=O})$  band at  $1120\text{ cm}^{-1}$ .

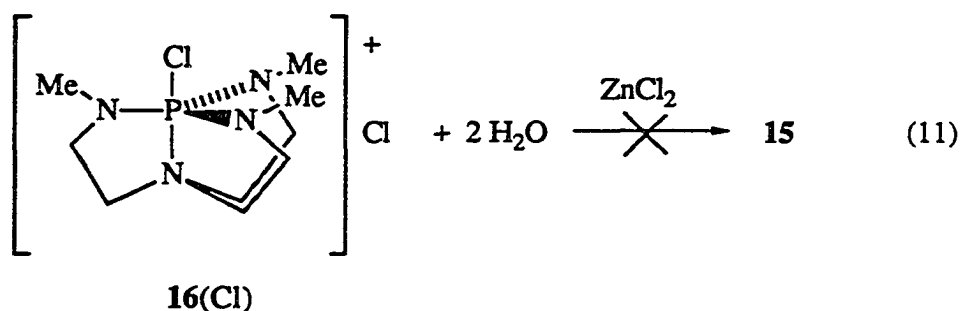
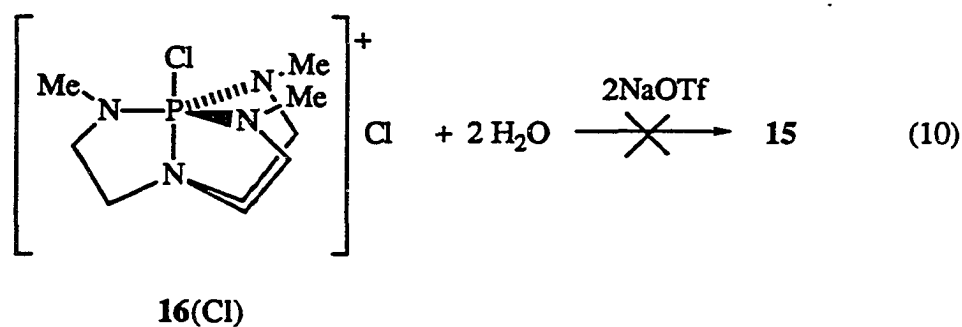
The emf for the reduction of  $\text{HgCl}_4^{2-}$  to  $\text{Hg}^0$  upon the oxidation of  $\text{H}_2\text{O}$  to  $\text{OOH}^-$  is  $-0.01\text{ V}$ ,<sup>35</sup> making the reaction weakly spontaneous in the reverse direction. However, it has been shown that  $\text{Hg}^{2+}$  species are easier to reduce in systems with higher pH.<sup>36,37</sup> It is likely then that the unusual ability of **2** to give **5**<sup>2</sup> allows the oxidation-reduction in reaction 4 to be spontaneous. This conjecture is corroborated by the fact that no reaction occurs (ie no reduction of  $\text{Hg}^{2+}$ ) upon the addition of water to a solution containing  $\text{Cl}_2\text{Hg}\{\text{P}(\text{NMe}_2)_3\}_2$ , an analogue of **11** containing a less basic phosphorus ligand.<sup>2</sup>

**Pathways to dioxaphosphetane 15.** We begin with reaction 9 in which **15** is found to form quantitatively. This reaction does not occur unless  $\text{Zn}(\text{OTf})_2$  is present, indicating

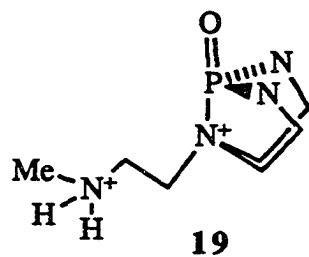


that  $\text{Zn}^{2+}$  and/or  $-\text{OTf}$  is necessary. Our lack of success in detecting **15** in either reaction 10, in which  $\text{NaOTf}$  is the triflate source or in reaction 11, in which no triflate is present,



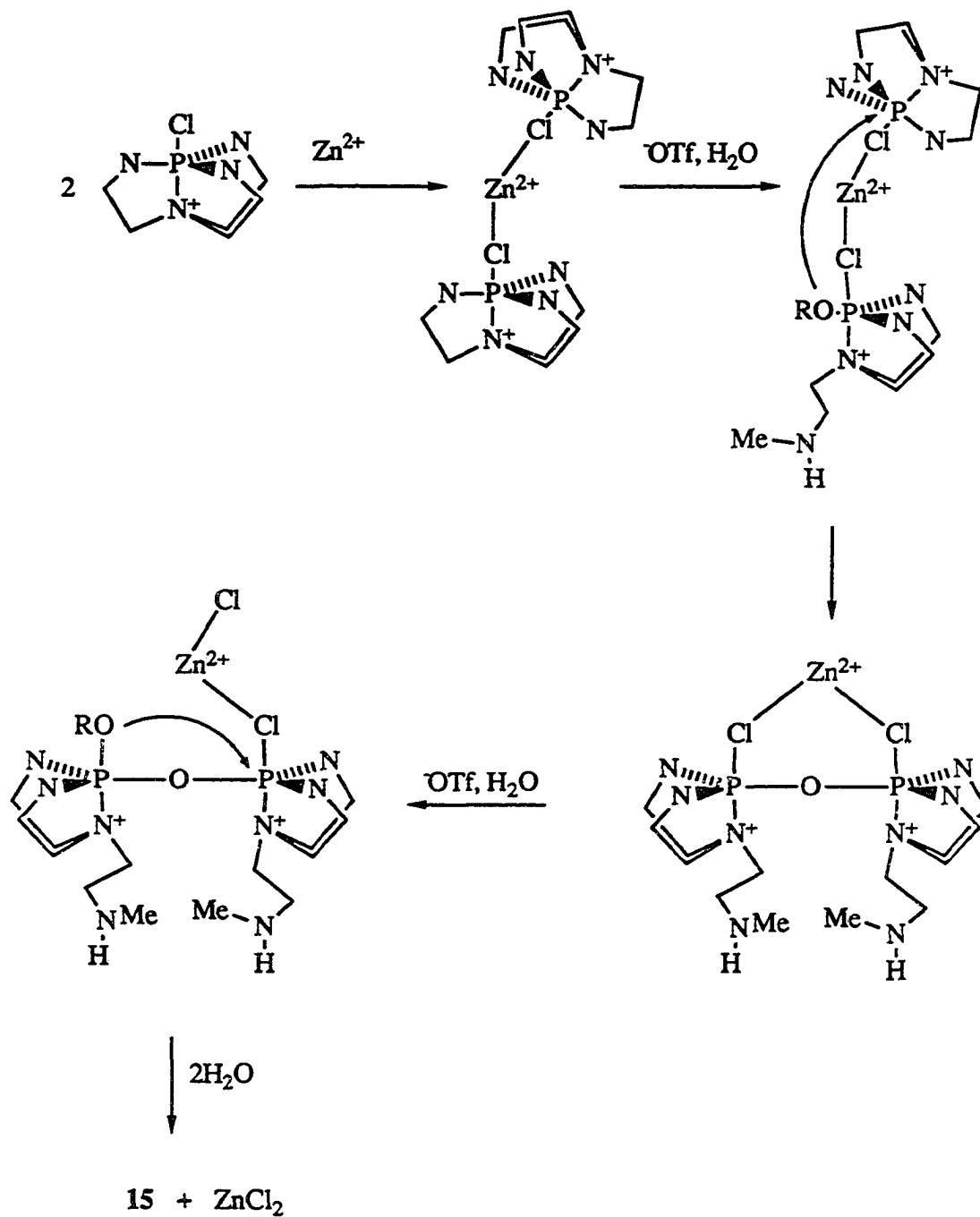


suggests that both  $\text{Zn}^{2+}$ , a coordinating metal center, and  $\text{-OTf}$  are necessary for the hydrolysis of **16** to **15**. It was also found that **15** does not form upon the reaction of **16** with water and triflic acid, supporting the claim that  $\text{Zn}^{2+}$  is necessary for **16** to hydrolyze to **15**. It is also interesting that if  $\text{HOTf}$  is added to the reaction mixture shown in reaction 10, **16** quantitatively converts to a species with a  $^{31}\text{P}$  NMR chemical shift at 8 ppm. It is tempting to assign this signal to **19**, a compound with a similar chemical shift that was detected briefly in the synthesis of **15** *via* reaction 3 (see later). However, the compound formed upon the treatment of the mixture shown in reaction 10 with triflic acid does not dimerize to give **15**, even upon the addition of  $\text{Zn}(\text{OTf})_2$ .

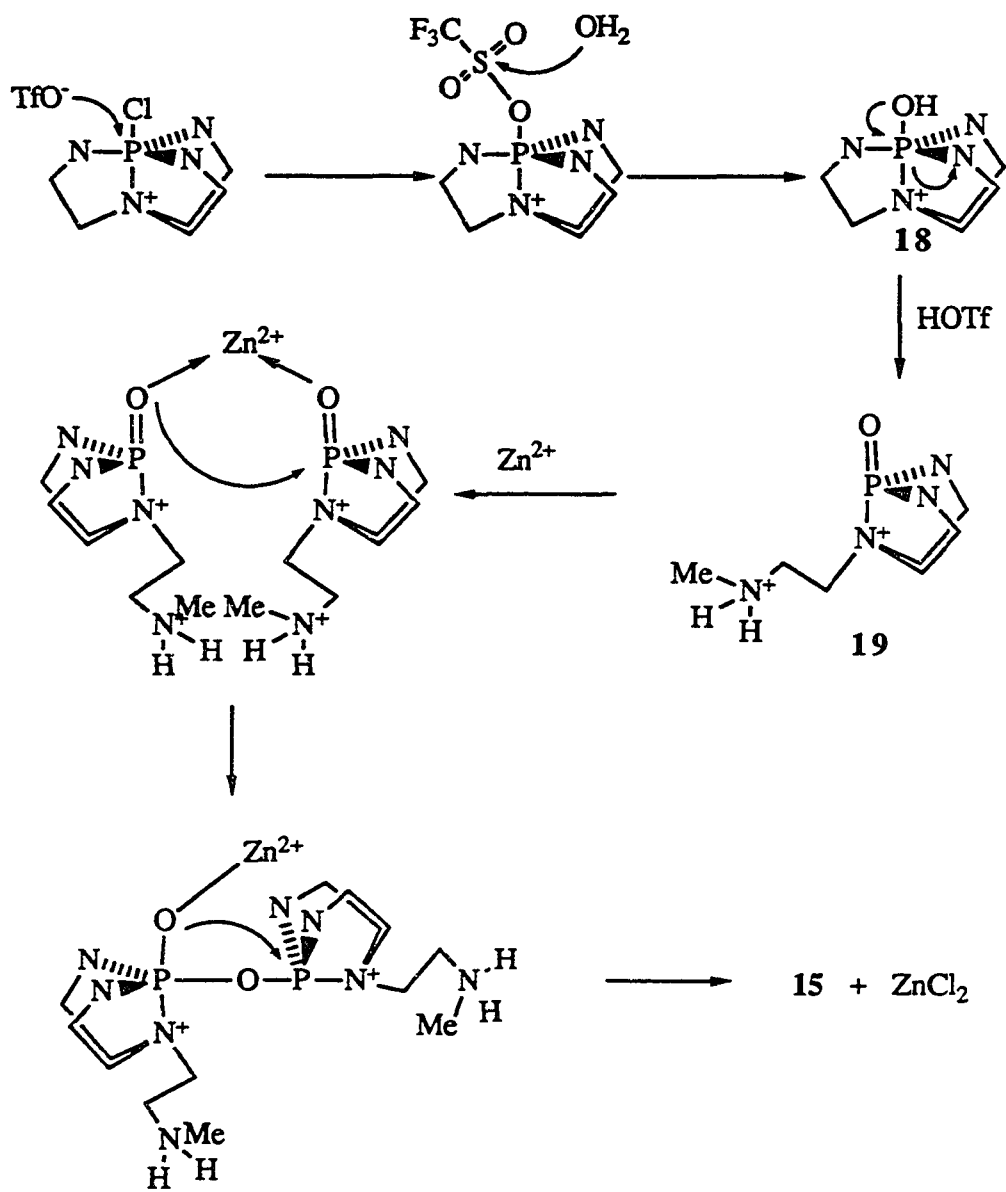


In Scheme 1 is depicted a plausible pathway in which two molecules of **16** initially coordinate through the chlorines to the chlorophilic zinc ion. The P-N bond may be attacked by either the oxygen from the water or an oxygen from the triflate, followed by protonation of the resulting amide with a  $\text{H}_2\text{O}$  proton, Scheme 1.

It is also possible that reaction 9 proceeds through intermediate **19**, which then may dimerize through coordination to the oxophilic  $\text{Zn}^{2+}$ , Scheme 2.

Scheme 1<sup>a</sup>

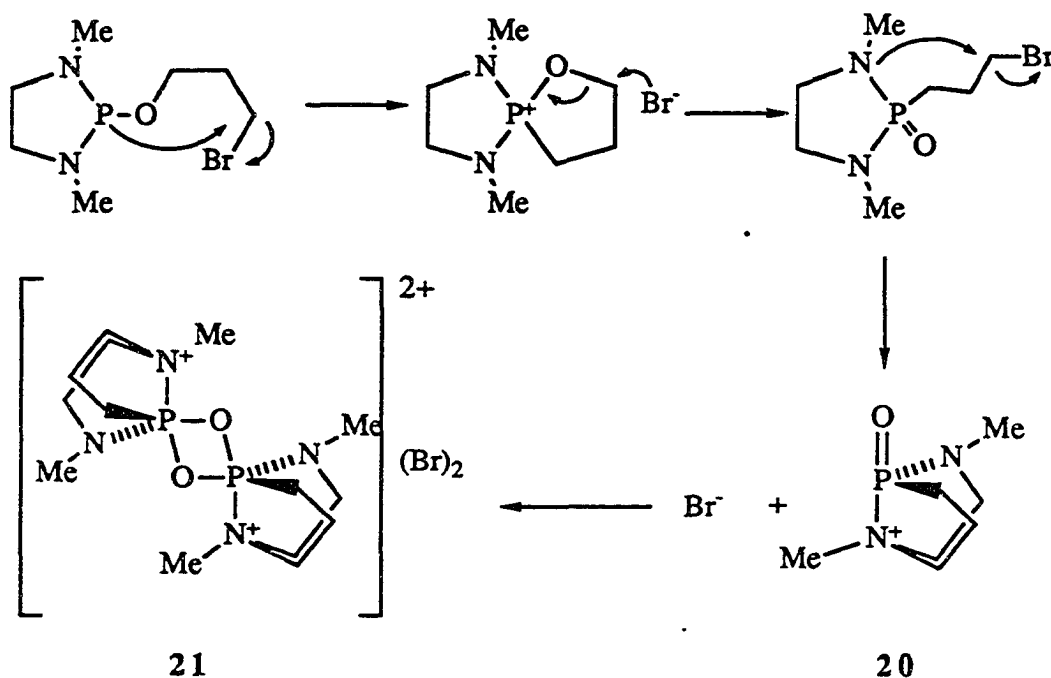
<sup>a</sup>The groups on the NMe nitrogens have been omitted for clarity.

Scheme 2<sup>a</sup>

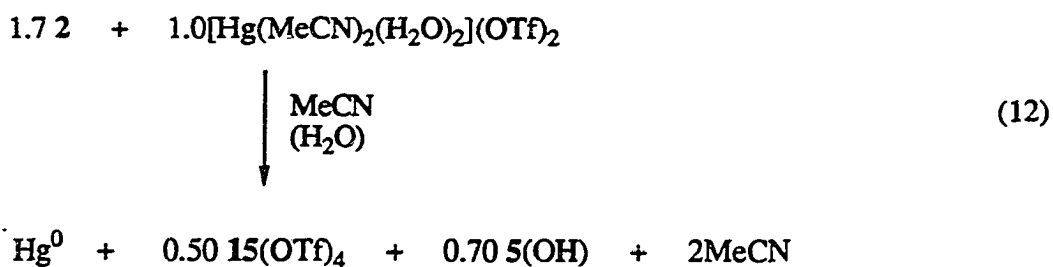
<sup>a</sup>The groups on the NMe nitrogens have been omitted for clarity.

The postulated formation of intermediate **19** is similar to that of **20** in the synthesis of its dioxaphosphetane dimer **21** in Scheme 3.<sup>41</sup>

Scheme 3



The pathway, or pathways, leading to the formation of **15** from **2** and mercury triflate may be similar to those shown in Schemes 1 and 2. In contrast with reaction 3, reaction 12 shows that when insufficient Hg(II) is present, the reduced mercury is quantitatively found



as free mercury (see Experimental). The observation that the stoichiometric excess of **2** is found as **5** is attributable to the presence of adventitious water (see also ref. 2). To help

verify that the triflate ion was also in part responsible for the formation of **15** from **2** and mercury triflate, reaction 3 was carried out with  $[\text{Hg}(\text{MeCN})_n](\text{BF}_4)_2$  (see Experimental). According to the  $^{31}\text{P}$  NMR spectrum, about 10% of the phosphorus was apparently converted to **15**, 60% to **5** and 30% to an unidentified (but probably hypercoordinate phosphorus) species at -37 ppm. Although this reaction produced **5**, **15** and  $\text{Hg}^0$ , as did reaction 12, the conversion to **15** was relatively low. In addition, the reaction involving  $[\text{Hg}(\text{MeCN})_n](\text{BF}_4)_2$  also produced a phosphorus species which may well be an intermediate (with the same  $^{31}\text{P}$  chemical shift) that is also seen in reaction 3 (see next paragraph).

From the  $^{31}\text{P}$  NMR data obtained by monitoring reaction 3 (Table 1), it is seen that a substantial number of intermediates is observed. The singlet observed at 118 ppm ( $^1J_{\text{HgP}} = 7710$  Hz) at room temperature suggests the presence of a  $[\text{Hg}(\text{2})_2]^{2+}$  complex (**22** in Scheme 4). At low temperature, this resonance at the same chemical shift is a doublet with a partner doublet at 9 ppm, although the intensities are not always the same. If these peaks indeed constitute a pair of doublets, an intermediate of type **23** in Scheme 4 may be implicated. The coupling constant of 30.5 Hz is not unreasonable to ascribe to a  $^2J_{\text{PP}}$  value in a tetrahedral metal complex.<sup>38</sup> At 0 °C another pair of doublets appears with a similar coupling value. This time, however, the higher field chemical shift is in the phosphatane

Table 1.  $^{31}\text{P}$  data for reaction 3 starting at  $-35\text{ }^{\circ}\text{C}$  and at room temperature

$\delta\ ^{31}\text{P}$ (ppm); ( $^2J_{\text{PP}}$ in Hz)	Possible source	Relative intensity <sup>a</sup>				
		$-35\text{ }^{\circ}\text{C}$	$0\text{ }^{\circ}\text{C}$	$25\text{ }^{\circ}\text{C}^{\text{b,c}}$	$25\text{ }^{\circ}\text{C}^{\text{d}}$	$25\text{ }^{\circ}\text{C}^{\text{e,e}}$
118, d, (30.5)	<b>23</b>	1	0.8	0	0	0
118, s <sup>f</sup>	<b>22</b>	0	0	0.2(0.4)	0.1	0(0)
17, d, (35)	<b>24</b>	0	0.1	0(0.05)	0	0(0)
12, s	<b>19</b>	0.01	0.05	0.3(0.1)	0.4	0(0)
9, d, (30.5)	<b>23</b>	0.3	0.8	0(0)	0	0(0)
-22, d, (35)	<b>24</b>	0	0.1	0(0.05)	0	0(0)
-31, s	<b>18</b>	0.2	0.2	0.6(0.06)	0.4	0(0)
-35, s		0.01	0.3	0.2(0)	0.05	0(0)
-37, s		0.8	0.5	0.3(0)	0.01	0(0)
-41, s		0	0.3	0.1(0)	0.02	0(0)
-49, s	<b>15g</b>	0	1	1(1)	1	1(1)

<sup>a</sup>Intensities relative to the largest peak in the spectrum, which is taken as 1.

<sup>b</sup>Spectrum taken after 0.2 hrs.

<sup>c</sup>The value in parentheses represents the intensity at the indicated time after the reaction was begun at room temperature.

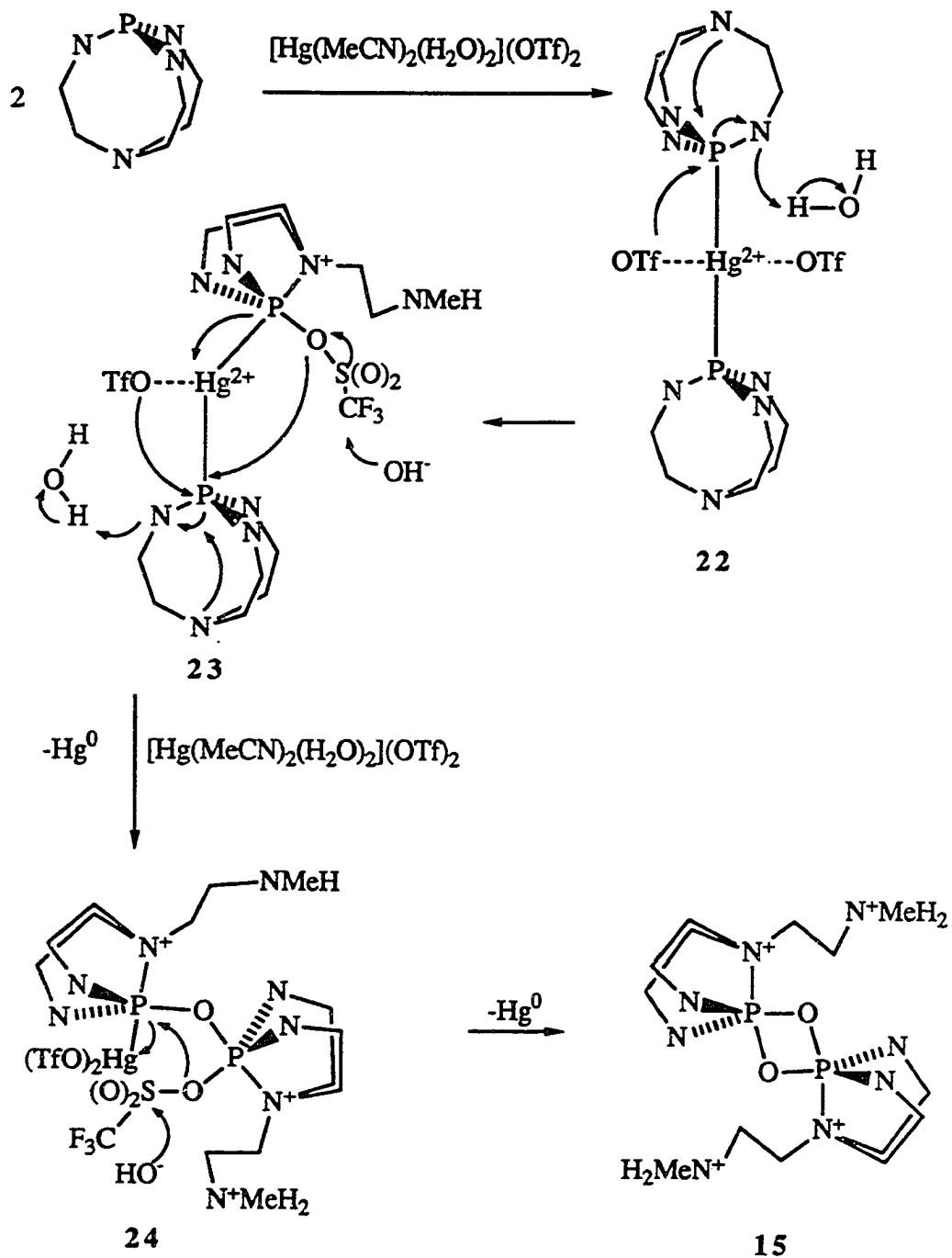
<sup>d</sup>Spectrum taken after 0.5 hrs.

<sup>e</sup>Spectrum taken after 24 hrs.

<sup>f</sup> $^1J_{\text{HgP}} = 7710\text{ Hz}$ .

<sup>g</sup>This assignment was verified by  $^{13}\text{C}$  NMR after 24 hrs.

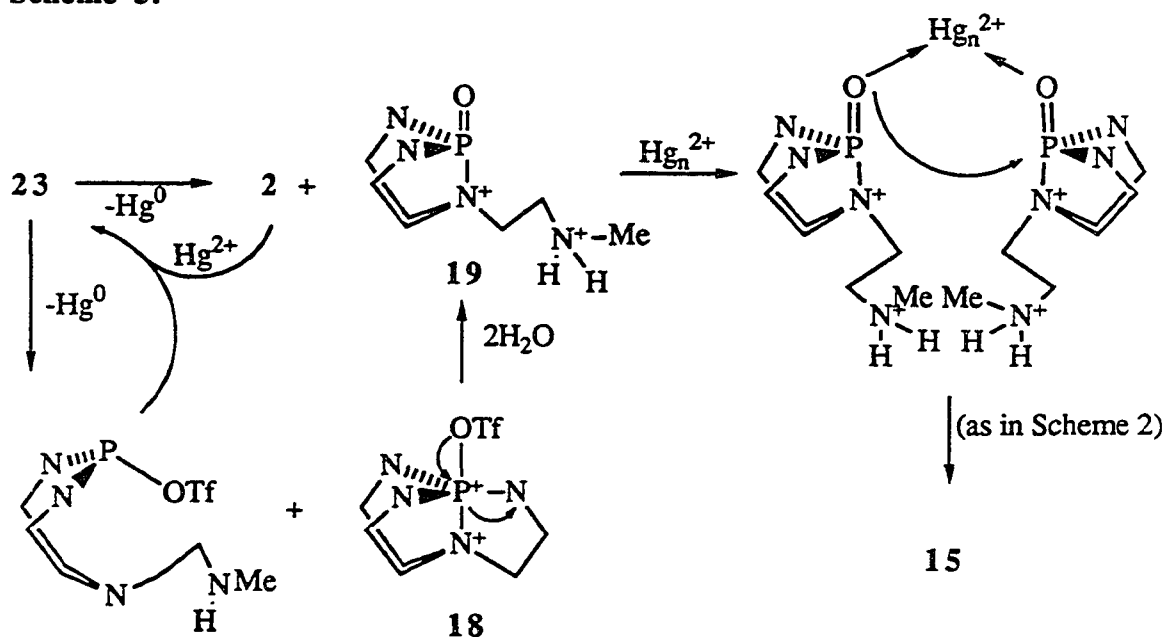
Scheme 4a



<sup>a</sup>The groups on the NMe nitrogens have been omitted for clarity.



range while the lower one is in the same range as one of the peaks in postulated 23. The second pair of doublets may be associated with a complex such as 24. The initial temporary precipitation of  $\text{Hg}^0$  and the existence of several peaks exhibiting no  $^{199}\text{Hg}$  satellites may be a result of a pathway, similar to that shown in Scheme 5, in which 2 reduces rather than coordinates to the mercuric ions, giving  $\text{Hg}^0$  and possibly 18 which, as shown earlier in Scheme 2, can decompose to 19, then 15, Scheme 5. Under preparative conditions, in

Scheme 5.<sup>a</sup>

<sup>a</sup>The groups on the NMe nitrogens have been omitted for clarity.

which a solution of 2 is added dropwise to a solution containing the mercuric triflate, this pathway should be more likely initially when the mercuric cations are in excess, making the initial coordination of two molecules of 2 to one  $\text{Hg}^{2+}$ , as required in Scheme 4, statistically less likely. Our postulate for the involvement of 18 and 19 is supported by the initial

appearance of a signal at -31 ppm in the  $^{31}\text{P}$  NMR of a solution containing two equivalents of HOTf and one of  $\text{O}=\text{P}(\text{NMeCH}_2\text{CH}_2)_3\text{N}$ . This signal disappears quickly with the appearance of a signal at 12 ppm, presumably **19**. This reaction, however, does not result in the formation of **15**, possibly because the mercury is somehow involved in the final coupling step.

As described previously in this paper, attempts to oxidize  $\text{P}(\text{NMe}_2)_3$  with  $[\text{Hg}(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})_2](\text{OTf})$  by adding one equivalent of  $\text{P}(\text{NMe}_2)_3$  to an acetonitrile solution containing  $[\text{Hg}(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})_2](\text{OTf})_2$ , resulted in the formation of the complex  $[\text{HgP}(\text{NMe}_2)_3](\text{OTf})_2$ , with no signs of an oxidation-reduction reaction. This may indicate that, again, the unusually high basicity of **2**<sup>1,2</sup> enhances the oxidative characteristics of  $\text{Hg}(\text{OTf})_2$ .

Our mercury triflate starting material could be made with  $\text{H}_2^{17}\text{O}$  if we started with  $\text{Hg}^{17}\text{O}$ . This labeling could tell us the source of the oxygens in **15** by the expected enhancement of their signal in the  $^{17}\text{O}$  NMR spectrum. Isolation of intermediates occurring in the formation of **15** is also in order.

**Structures determined by X-ray means.** X-ray crystallographic data and positional parameters are found in Tables 2 - 6. From the structures of **10**, **11**, **12**, and **15** shown in Figures 1 - 4, respectively, and the summarized structural data in Table 7, many structural similarities are revealed. In compounds **7** - **11**, in which weak to no  $\text{P}-\text{N}_{\text{ax}}$  interactions are seen, the axial nitrogens are virtually planar; whereas in **15** and **12**, in which strong  $\text{P}-\text{N}_{\text{ax}}$  interactions occur, the axial nitrogens are pyramidal pointing toward the phosphorus. The latter  $\text{P}-\text{N}_{\text{ax}}$  interaction to which we just referred is observed primarily in **15** and **12**, in

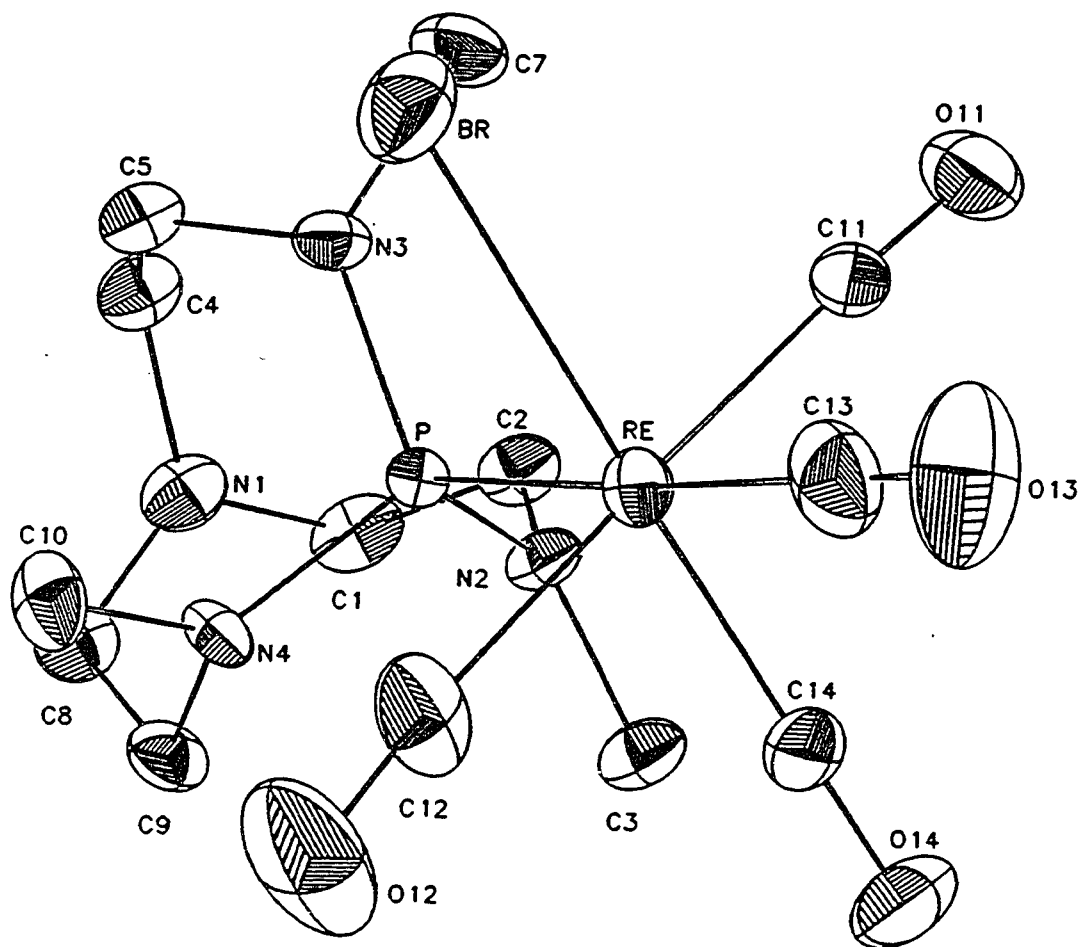


Figure 1. ORTEP drawing of 10: the ellipsoids are drawn at the 50% probability level

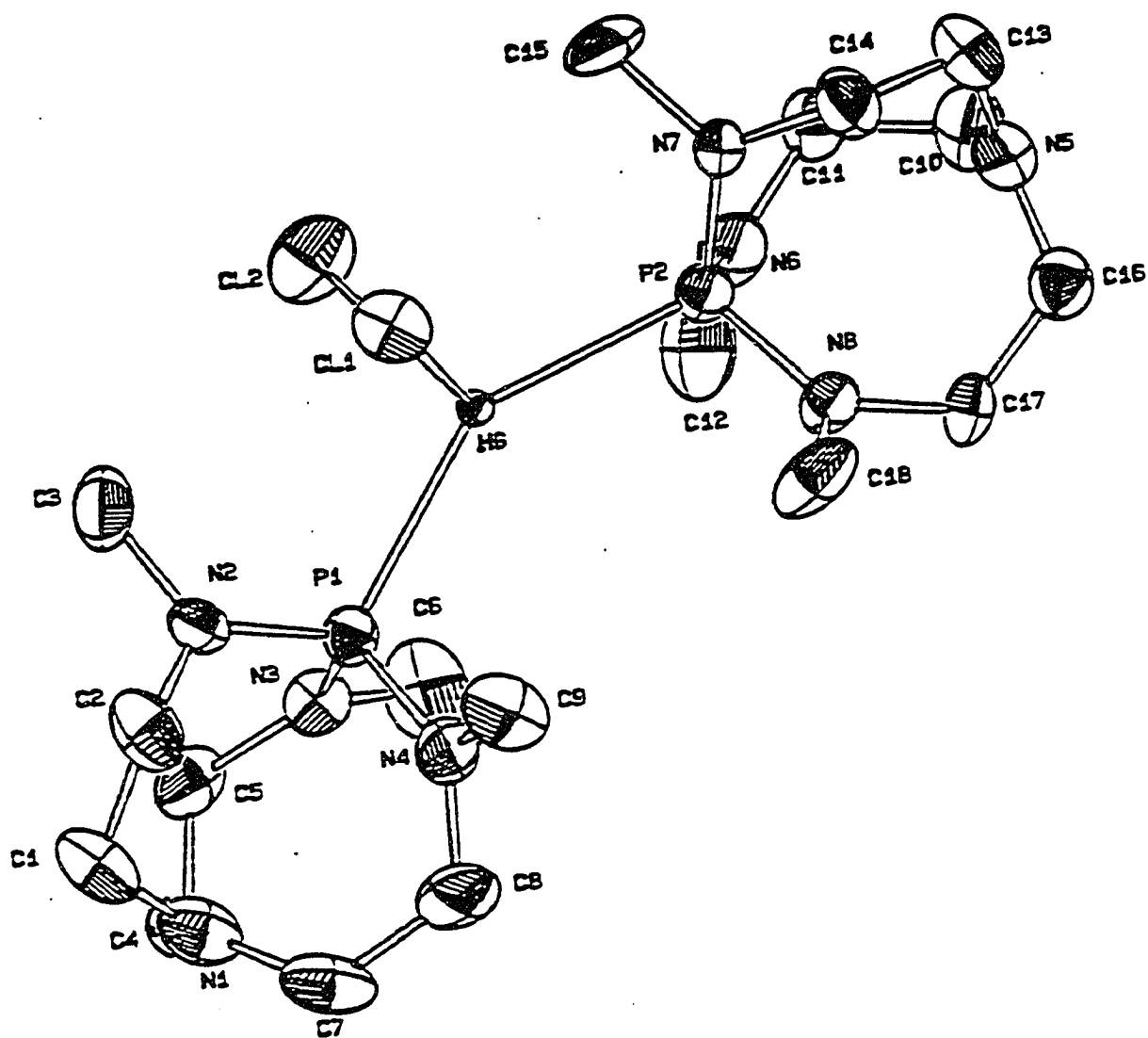


Figure 2. ORTEP drawing of **11**: the ellipsoids are drawn at the 50% probability level

Table 2a. X-ray crystallographic data for **10** and **11**

	<i>cis</i> -Re(CO) <sub>4</sub> (2)Br, <b>10</b>	Hg(2) <sub>2</sub> Cl <sub>2</sub> , <b>11</b>
Formula	C <sub>10</sub> H <sub>21</sub> O <sub>4</sub> N <sub>4</sub> PBr	C <sub>18</sub> H <sub>42</sub> N <sub>8</sub> Cl <sub>2</sub> HgP <sub>2</sub>
F.W	597.22	704.03
Space grp	Pbca	Pca2 <sub>1</sub>
<i>a</i> , Å	16.291(2)	15.557(6)
<i>b</i> , Å	15.269(5)	9.508(7)
<i>c</i> , Å	15.018(6)	18.218(6)
<i>V</i> , Å <sup>3</sup>	3735.8(31)	2695(4)
<i>Z</i>	8	4
<i>d</i> <sub>calc</sub> g/cm <sup>3</sup>	2.112	1.735
Crystal size, mm	0.50 x 0.45 x 0.35	0.40 x 0.30 x 0.30
μ(MoK <sub>α</sub> ), cm <sup>-1</sup>	90.0	60.49
Data collection		
instrument	Enraf-Nonius CAD4	Rigaku AFC6R
Radiation	MoK <sub>α</sub> (λ = 0.71073 Å)	MoK <sub>α</sub> (λ = 0.71069 Å)
Orientation refl's.,		
number, range	25, 24.6 < 2θ < 28.6	25, 12.3 - 15.1
Temperature, °C	-50 °C ± 1	25 ± 1

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b R_w = [ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 ]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$^c \text{Quality-of-fit} = [ \sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}}) ]^{1/2}$$

Table 2a, continued. X-ray crystallographic data for **10** and **11**

	<i>cis</i> -Re(CO) <sub>4</sub> (2)Br, <b>10</b>	Hg(2) <sub>2</sub> Cl <sub>2</sub> , <b>11</b>
Scan method	θ - 2θ	θ - 2θ
Data coll. range,		
2θ, deg	4-50	1.10 - 50.1
Unique data, total:	3694	2743
with $F_o^2 > 3\sigma(F_o^2)$ :	2416	1889
No. param's. refined	217	279
R <sup>a</sup>	0.028	0.028
R <sub>w</sub> <sup>b</sup>	0.035	0.033
Quality-of-fit		
indicator <sup>c</sup>	0.87	1.28
Largest shift/esd,		
final cycle	0.00	0.09
Largest peak, e/Å <sup>3</sup>	1.8(2)	1.09

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b R_w = [ \sum w (|F_o| - |F_c|)^2 / \sum w |F_o|^2 ]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$^c \text{Quality-of-fit} = [ \sum w (|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}}) ]^{1/2}$$

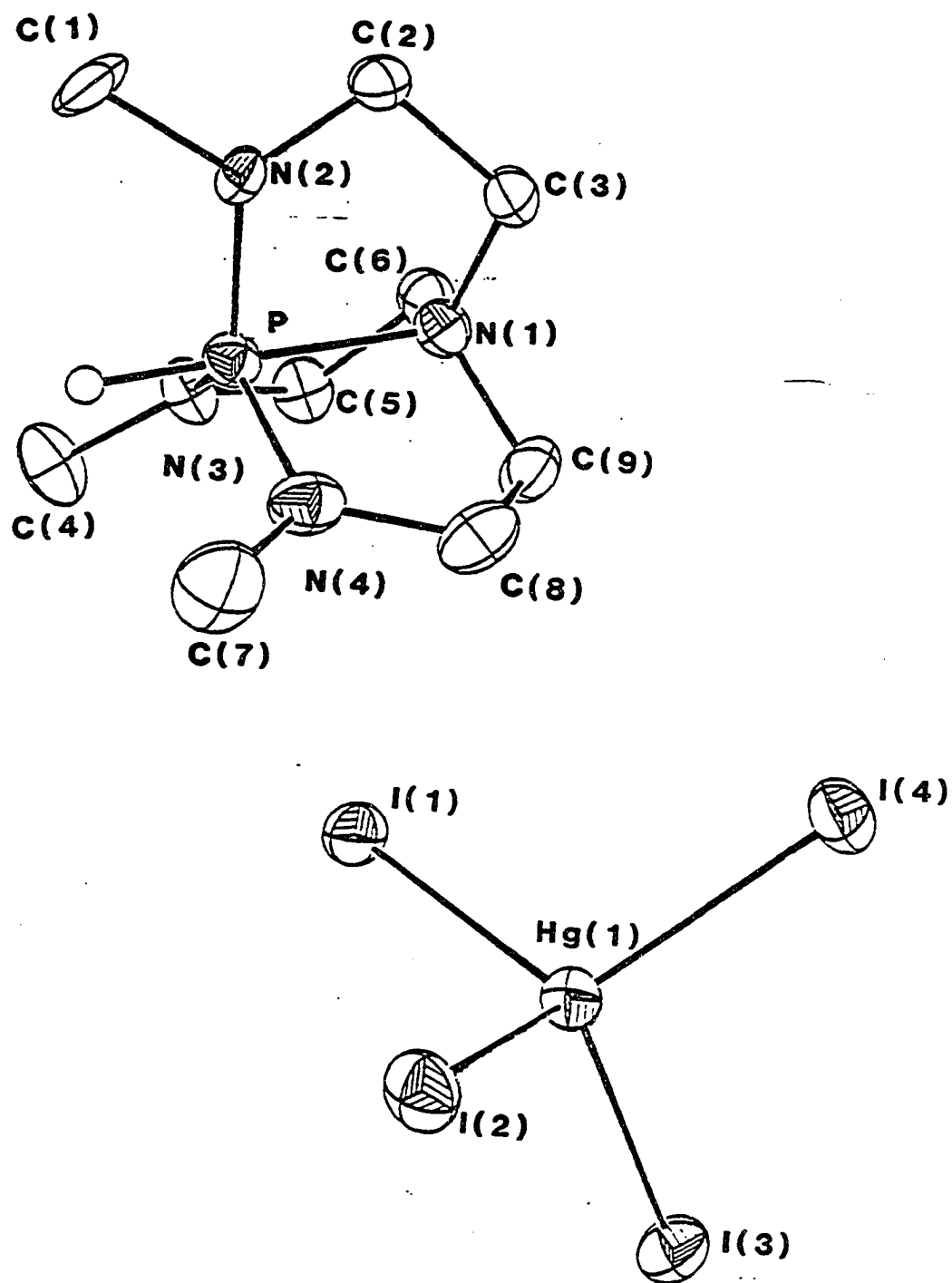


Figure 3. ORTEP drawing of the  $\text{HgI}_4$  ion and one of the nearby 5 cations: ellipsoids drawn at the 50% probability level

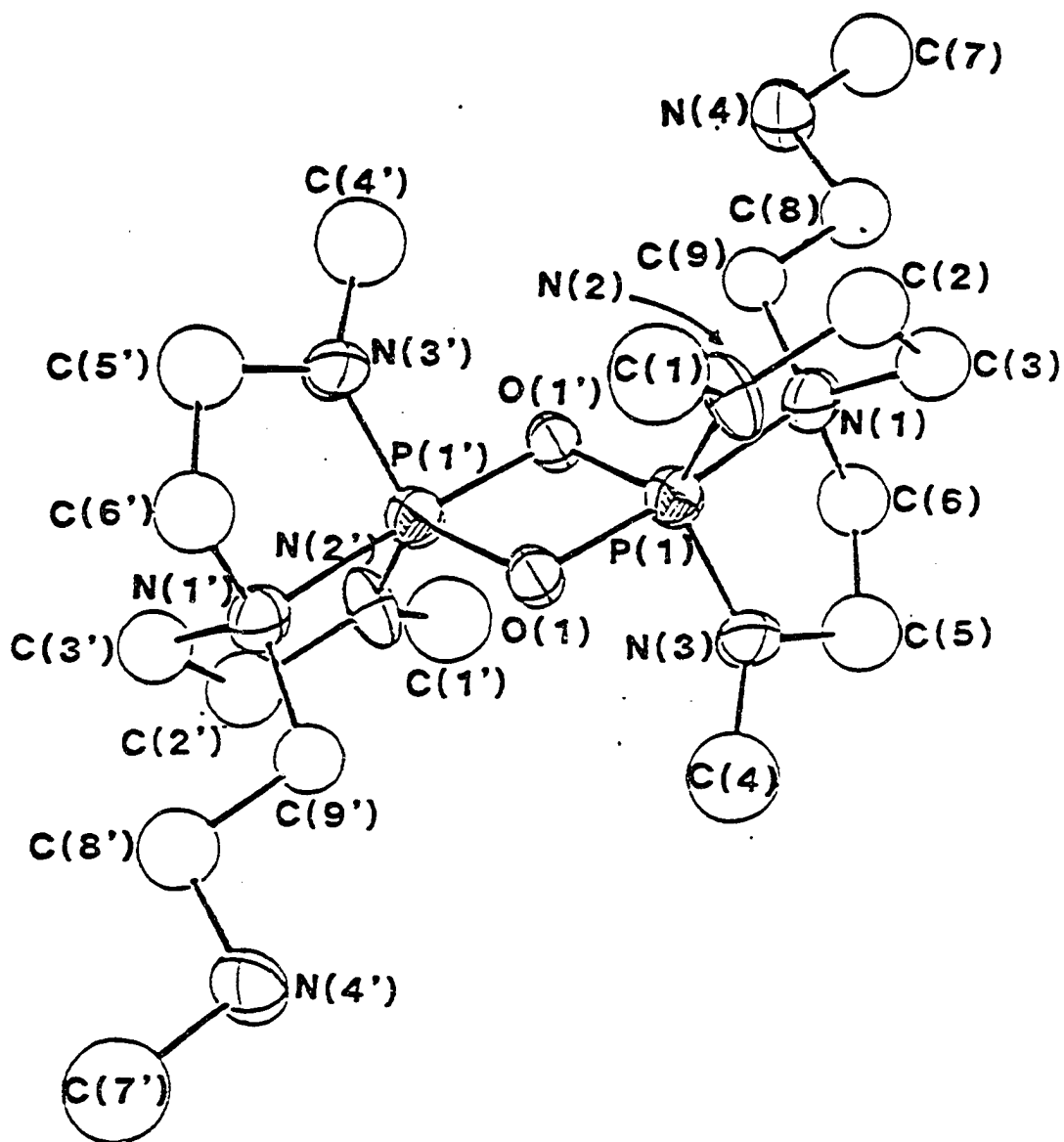


Figure 4. ORTEP drawing of 15, excluding the triflate anions: the ellipsoids drawn at the 50% probability level.



Table 2b. X-ray crystallographic data for 12 and 15

	(5) <sub>2</sub> HgI <sub>4</sub> , 12	15(OTf) <sub>4</sub>
Formula	C <sub>22</sub> H <sub>50</sub> HgI <sub>4</sub> P <sub>2</sub> N <sub>10</sub>	C <sub>22</sub> H <sub>46</sub> N <sub>8</sub> O <sub>14</sub> F <sub>12</sub> P <sub>2</sub> S <sub>4</sub>
F.W	1224.86	1103.8
Space grp	C2/c	P1
<i>a</i> , Å	18.732(3)	13.069(8)
<i>b</i> , Å	11.749(1)	15.148(9)
<i>c</i> , Å	19.640(3)	11.909(5)
α, deg		90.27(4)
β, deg	102.410(7)	95.28(3)
γ, deg		77.74(4)
<i>V</i> , Å <sup>3</sup>	3791.5(9)	2294(2)
<i>Z</i>	4	2
<i>d</i> <sub>calc</sub> g/cm <sup>3</sup>	2.150	1.598
Crystal size, mm	0.51 x 0.51 x 0.56	0.40 x 0.35 x 0.19
μ(MoK <sub>α</sub> ), cm <sup>-1</sup>	74.074	3.781
Data collection		
instrument	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Radiation	MoK <sub>α</sub> (λ = 0.71073 Å)	MoK <sub>α</sub> (λ = 0.71073 Å)

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b R_w = [ \sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2 ]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$^c \text{Quality-of-fit} = [ \sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}}) ]^{1/2}$$

Table 2b, continued. X-ray crystallographic data for 12 and 15

	(5) <sub>2</sub> Hg <sub>4</sub> , 12	15(OTf) <sub>4</sub>
Orientation refl's.,		
number, range	25, 23.0 - 31.2	25, 18.8 - 36.6
Temperature, °C	-70 ± 1	-25 ± 1
Scan method	θ - 2θ	ω - scans
Data coll. range,		
2θ, deg	4.0 - 50.0	4.0 - 45.0
Unique data, total:	3310	5970
with $F_0^2 > 3\sigma(F_0^2)$ :	2922	3698
No. param's. refined	196	455
R <sup>a</sup>	0.027	0.085
R <sub>w</sub> <sup>b</sup>	0.049	0.116
Quality-of-fit <sup>c</sup>	0.805	3.02
Largest shift/esd,		
final cycle	0.03	0.05
Largest peak, e/Å <sup>3</sup>	1.1(1)	0.9(1)

$$^a R = \sum ||F_0| - |F_C|| / \sum |F_0|$$

$$^b R_w = [ \sum w (|F_0| - |F_C|)^2 / \sum w |F_0|^2 ]^{1/2}; w = 1/\sigma^2 (|F_0|)$$

$$^c \text{Quality-of-fit} = [ \sum w (|F_0| - |F_C|)^2 / (N_{\text{obs}} - N_{\text{parameters}}) ]^{1/2}$$

Table 3. Positional parameters and their estimated standard deviations for

Table 3. Positional parameters and their estimated standard deviations for  
*cis*-Re(CO)<sub>4</sub>(2)Br, 10

Atom	x	y	z	B(Å <sup>2</sup> )
Re	0.53135(1)	0.79334(1)	0.04119(1)	1.698(4)
Br	0.48883(4)	0.69835(4)	-0.09730(4)	2.98(1)
P	0.61265(8)	0.66693(9)	0.10288(8)	1.42(2)
N(1)	0.7156(3)	0.5035(3)	0.1944(3)	2.6(i)
C(1)	0.7737(3)	0.5708(5)	0.2194(4)	2.9(1)
C(2)	0.7710(3)	0.6534(4)	0.1630(4)	2.4(1)
N(2)	0.6930(3)	0.6995(3)	0.1635(3)	1.88(9)
C(3)	0.6833(3)	0.7619(4)	0.2370(4)	2.5(1)
C(4)	0.7202(4)	0.4706(4)	0.1042(4)	2.5(1)
C(5)	0.6546(4)	0.5038(4)	0.0407(3)	2.3(1)
N(3)	0.6520(3)	0.5985(3)	0.0276(3)	1.89(9)
C(7)	0.6961(4)	0.6313(5)	-0.0504(4)	3.1(1)
C(8)	0.6423(4)	0.4891(4)	0.2456(4)	2.7(1)
C(9)	0.5868(3)	0.5692(4)	0.2531(4)	2.3(1)
N(4)	0.5566(3)	0.6040(3)	0.1696(3)	1.77(8)
C(10)	0.4812(3)	0.5629(4)	0.1348(4)	2.5(1)
C(11)	0.6318(3)	0.8368(4)	-0.0199(3)	2.0(1)
O(11)	0.6877(3)	0.8650(3)	-0.0525(3)	3.37(9)

Table 3, continued. Positional parameters and their estimated standard deviations for  
*cis*-Re(CO)<sub>4</sub>(2)Br, 10

Atom	x	y	z	B(Å <sup>2</sup> )
C(12)	0.4296(3)	0.7542(4)	0.1037(5)	3.3(1)
O(12)	0.3703(3)	0.7387(4)	0.1392(4)	6.4(1)
C(13)	0.4664(3)	0.8874(5)	-0.0128(4)	2.9(1)
O(13)	0.4283(3)	0.9420(3)	-0.437(3)	4.3(1)
C(14)	0.5534(4)	0.8700(4)	0.1396(4)	2.4(1)
O(14)	0.5624(3)	0.9187(3)	0.1967(3)	3.6(1)

Table 4. Positional parameters and their estimated standard deviations for  
 $(2)_2\text{HgCl}_2$ , 11

Atom	x	y	z	B(Å <sup>2</sup> )
Hg	0.22391(2)	0.21814(4)	0	2.91(2)
Cl(1)	0.3338(2)	0.1177(4)	-0.0982(2)	3.8(2)
Cl(2)	0.3051(3)	0.4429(4)	0.0488(3)	5.0(2)
P(1)	0.2586(2)	0.0373(3)	0.927(2)	2.4(1)
P(2)	0.1079(2)	0.3224(3)	-0.0732(2)	2.6(1)
N(1)	0.2990(9)	-0.202(1)	0.2089(6)	4.1(6)
N(2)	0.3607(6)	-0.006(1)	0.0923(6)	3.1(5)
N(3)	0.2349(7)	0.088(1)	0.1765(6)	2.8(5)
N(4)	0.2037(7)	-0.108(1)	0.0765(7)	3.9(6)
N(5)	-0.0415(7)	0.0442(1)	-0.1673(7)	3.8(6)
N(6)	0.0667(9)	0.460(1)	-0.033(1)	3.9(6)
N(7)	0.1419(6)	0.371(1)	-0.1550(6)	1.0(5)
N(8)	0.0308(6)	0.205(1)	-0.0821(6)	2.7(4)
C(1)	0.384(1)	-0.206(2)	0.180(1)	6(1)
C(2)	0.392(1)	-0.147(23)	0.102(1)	4.4(8)
C(3)	0.4260(9)	0.108(2)	0.0892(9)	4.9(8)
C(4)	0.276(1)	-0.101(2)	0.2641(7)	4.4(8)
C(5)	0.2866(9)	0.049(2)	0.2398(7)	3.9(7)
C(6)	0.156(1)	0.165(2)	0.188(1)	6(1)
C(7)	0.232(1)	-0.284(1)	0.1754(7)	4.0(7)

Table 4, continued. Positional parameters and their estimated standard deviations for  
 $(2)_2\text{HgCl}_2$ , 11

Atom	x	y	z	B(Å <sup>2</sup> )
C(8)	0.166(1)	-0.195(1)	0.133(1)	4.8(8)
C(9)	0.206(1)	-0.170(1)	0.003(2)	4.5(7)
C(10)	-0.0469(9)	0.558(1)	-0.117(1)	4.5(7)
C(11)	0.0341(8)	-0.583(1)	-0.0736(8)	3.2(6)
C(12)	0.047(1)	0.459(3)	0.044(1)	5(1)
C(13)	0.016(1)	0.454(2)	-0.2286(9)	4.8(8)
C(14)	0.0927(8)	0.357(2)	-0.2209(8)	4.0(7)

Table 5. Positional parameters and their estimated standard deviations for  
 $(5)_2\text{HgI}_4$ , 12

Atom	x	y	z	B(Å <sup>2</sup> )
C(15)	0.2214(8)	0.457(2)	-0.159(1)	5.4(9)
C(16)	-0.0851(8)	0.316(1)	-0.1549(8)	3.5(7)
C(17)	-0.0607(7)	0.242(1)	-0.0854(7)	2.7(5)
C(18)	0.0526(8)	0.064(1)	-0.103(1)	4.6(8)
Hg	0.500	0.12714(3)	0.750	2.348(8)
I(1)	0.50523(2)	0.26397(3)	0.62196(2)	2.89(1)
I(2)	0.37302(2)	-0.00320(3)	0.70323(2)	2.96(1)
P	0.28316(8)	0.5052(1)	0.57655(8)	1.89(3)
N(1)	0.3436(2)	0.5727(4)	0.6715(3)	2.1(1)
N(2)	0.2201(3)	0.6026(4)	0.5851(3)	2.4(1)
N(3)	0.2882(3)	0.3844(4)	0.6270(3)	2.7(1)
N(4)	0.3502(3)	0.5422(4)	0.5333(3)	2.5(1)
N(5)	0.0643(3)	0.2170(5)	0.6502(3)	3.7(1)
C(1)	0.1664(3)	0.6389(6)	0.5156(4)	3.0(1)
C(2)	0.2332(3)	0.6852(5)	0.6476(3)	2.5(1)
C(3)	0.2904(3)	0.6315(5)	0.7113(4)	2.6(1)
C(4)	0.2419(4)	0.2859(6)	0.6027(5)	4.2(2)

Table 5, continued. Positional parameters and their estimated standard deviations for  
 $(5)_2\text{HgI}_4$ , 12

Atom	x	y	z	B(Å <sup>2</sup> )
C(5)	0.3269(4)	0.3796(5)	0.7081(4)	3.2(2)
C(6)	0.3822(3)	0.4782(5)	0.7196(3)	2.6(1)
C(7)	0.3571(4)	0.4910(6)	0.4592(4)	3.1(1)



Table 6. Positional parameters and their estimated standard deviations for  
 $15(\text{OTf})_4$

Atom	x	y	z	B(Å <sup>2</sup> )
C(8)	0.4162(3)	0.5943(5)	0.5783(3)	2.4(1)
C(9)	0.3963(3)	0.6512(5)	0.6474(3)	2.4(1)
C(10)	0.0564(4)	0.3016(6)	0.6207(4)	3.2(2)
C(11)	0.0498(5)	0.4149(7)	0.5820(4)	4.4(2)
H(1)	0.248(2)	0.462(4)	0.512(3)	0.8 <sup>a</sup>
P(1)	0.0939(2)	0.0032(2)	0.0017(2)	2.66(5)
P(2)	0.4520(2)	-0.4215(2)	0.4810(2)	2.75(5)
O(1)	0.0034(4)	-0.0021(4)	0.0921(4)	2.6(1)
O(2)	0.5578(4)	-0.4871(4)	0.4460(5)	2.8(1)
N(1)	0.1837(5)	0.0103(4)	-0.1163(6)	2.8(2)
N(2)	0.1174(5)	0.0991(5)	0.0474(6)	3.4(2)
N(3)	0.1688(5)	-0.037(5)	0.0366(6)	3.3(2)
N(4)	0.1270(6)	0.1015(5)	-0.4165(6)	3.8(2)
N(5)	0.4796(5)	-0.3251(4)	0.3892(6)	2.7(2)
N(6)	0.4649(5)	-0.3573(5)	0.5901(6)	3.2(2)
N(8)	0.5917(6)	-0.3242(5)	0.1055(6)	3.7(2)
C(1)	0.0620(9)	0.1592(8)	0.130(1)	6.1(3)
C(2)	0.1998(8)	0.1348(7)	0.0004(8)	4.2(2)

<sup>a</sup>Atoms refined isotropically.

Table 6, continued. Positional parameters and their estimated standard deviations for  
 $15(\text{OTf})_4$

Atom	x	y	z	B(Å <sup>2</sup> )
C(3)	0.2614(7)	0.0601(6)	-0.0621(8)	3.7(2)
C(4)	0.1741(9)	-0.1379(8)	0.147(1)	5.6(3)
C(5)	0.2563(8)	-0.1329(7)	-0.0297(9)	4.6(2)
C(6)	0.2348(7)	-0.0847(6)	-0.1410(8)	3.9(2)
C(7)	0.1923(9)	0.1056(8)	-0.513(1)	5.7(3)
C(8)	0.1960(7)	0.0630(6)	-0.3158(8)	3.9(2)
C(9)	0.1256(7)	0.0580(6)	-0.2219(7)	3.0(2)
C(10)	0.4329(8)	-0.3706(7)	0.7016(9)	4.5(2)
C(11)	0.5036(7)	-0.2747(6)	0.5783(8)	3.7(2)
C(12)	0.5467(7)	-0.2783(6)	0.4656(8)	3.5(2)
C(13)	0.2799(8)	-0.4826(6)	0.3870(8)	4.2(2)
C(14)	0.3035(7)	-0.3331(6)	0.3273(8)	3.2(2)
C(15)	0.3722(7)	-0.2689(6)	0.3638(8)	3.2(2)
C(16)	0.5732(7)	-0.2634(7)	0.0049(9)	4.8(2)
C(17)	0.5265(7)	-0.2843(6)	0.1980(8)	3.2(2)
C(18)	0.5265(6)	-0.3599(6)	0.2841(7)	3.0(2)
S(1)	0.3420(2)	-0.4473(2)	-0.4669(2)	3.93(6)
S(2)	0.1333(2)	-0.1489(2)	0.0101(2)	3.0(2)

<sup>a</sup>Atoms refined isotropically.

Table 6, continued. Positional parameters and their estimated standard deviations for  
 $15(\text{OTf})_4$

Atom	x	y	z	B(Å <sup>2</sup> )
S(3)	0.4769(3)	-0.146(3)	0.2113(3)	7.3(1)
S(4)	-0.1541(3)	0.6822(2)	0.2725(3)	6.69(8)
F(1)	0.1557(5)	-0.4727(5)	-0.0544(7)	9.4(2)
F(2)	0.1565(6)	-0.3698(6)	0.0636(7)	10.2(2)
F(3)	0.1815(7)	-0.3474(6)	-0.1045(7)	11.0(3)
F(4)	0.1370(7)	-0.2499(5)	-0.2922(6)	9.3(2)
F(5)	0.0193(6)	-0.2634(4)	-0.4252(7)	8.2(2)
F(6)	0.1813(6)	-0.3231(4)	-0.4363(6)	7.7(2)
F(7)	0.441(1)	0.0809(9)	0.394(1)	7.3(3)
F(7)	0.543(2)	0.046(2)	0.391(2)	14.1(7)
F(8)	0.424(1)	-0.038(1)	0.408(1)	9.2(4)
F(8)	0.387(1)	0.1044(9)	0.359(1)	7.3(3)
F(9)	0.310(1)	0.074(1)	0.269(2)	10.2(5)
F(9)	0.374(1)	-0.047(1)	0.363(1)	9.8(4)
F(10)	-0.1747(8)	0.5254(5)	0.3313(9)	12.9(3)
F(11)	-0.0235(9)	0.5349(7)	0.313(1)	17.8(5)
F(12)	-0.087(1)	0.5877(7)	0.4477(8)	19.9(5)
O(3)	0.3457(6)	-0.5074(6)	0.1028(7)	7.2(2)

<sup>a</sup>Atoms refined isotropically.

Table 6, continued. Positional parameters and their estimated standard deviations for  
**15(OTf)<sub>4</sub>**

Atom	x	y	z	B(Å <sup>2</sup> )
O(4)	0.3780(6)	-0.4889(5)	-0.0905(6)	5.7(2)
O(5)	0.3764(6)	-0.3659(5)	0.0365(7)	6.1(2)
O(6)	0.1075(6)	-0.1613(5)	-0.5831(6)	5.3(2)
O(7)	0.2399(5)	-0.1472(5)	-0.4342(6)	6.1(2)
O(8)	0.0587(5)	-0.0807(4)	-0.4169(6)	4.8(2)
O(9)	0.571(1)	-0.076(1)	0.271(1)	6.5(4)
O(9')	0.555(2)	-0.079(1)	0.206(2)	11.3(6)
O(10)	0.532(2)	0.076(3)	0.211(4)	21(1)
O(10')	0.441(1)	-0.065(1)	0.135(2)	8.2(5)
O(11)	0.384(2)	-0.050(1)	0.179(2)	10.6(6)
O(11')	0.287(1)	0.066(1)	0.147(1)	6.8(4)
O(12)	-0.0742(6)	0.7326(5)	0.2944(8)	7.9(2)
O(13)	-0.1903(9)	0.6668(7)	0.1657(9)	12.6(3)
O(14)	-0.2488(8)	0.7218(8)	0.330(1)	13.9(5)
C(19)	0.2010(9)	-0.4075(8)	-0.023(1)	6.1(3) <sup>a</sup>
C(20)	0.1172(9)	-0.2507(7)	-0.4017(9)	5.4(3) <sup>a</sup>
C(21)	0.422(2)	0.031(2)	0.331(2)	15.1(7) <sup>a</sup>
C(22)	-0.107(1)	0.579(1)	0.344(1)	8.8(4) <sup>a</sup>

<sup>a</sup>Atoms refined isotropically.

Table 6, continued. Positional parameters and their estimated standard deviations for  
**15(OTf)<sub>4</sub>**

Atom	x	y	z	B(Å <sup>2</sup> )
N(9)	0.231(1)	0.301(1)	0.283(1)	13.9(5) <sup>a</sup>
C(23)	0.111(1)	0.401(1)	0.137(2)	10.7(5) <sup>a</sup>
C(24)	0.186(1)	0.344(1)	0.217(1)	9.7(4) <sup>a</sup>

<sup>a</sup>Atoms refined isotropically.

Table 7. Selected bond distances and angles in 10, 11, 12, and 15.

	P-N <sub>ax</sub>	C-N <sub>ax</sub> -C, deg. <sup>a</sup>	N <sub>eq</sub> -P-N <sub>eq</sub> ', deg. <sup>a</sup>	M-P <sup>a</sup>	P-N <sub>ax</sub> shorter than van der Waals radii(%)
9 <sup>b,d</sup>	3.33	119	105	2.349 <sup>c</sup>	0.6
8 <sup>b</sup>	3.250	119.6	106.8		3.0
7 <sup>b</sup>	3.008	120.0	110.3		10
10	3.307	119.6	105.5	2.518	1.3
11 <sup>e,f</sup>	3.143	120	108.3	2.461	6
12 <sup>g</sup>	1.973	112	119.9		40
15	1.934 <sup>a</sup>	111.3	120		42

<sup>a</sup>Average value.

<sup>b</sup>See ref. 3.

<sup>c</sup>Average for two independent molecules.

<sup>d</sup>P-Pt-P angle is 180°.

<sup>e</sup>P-Hg-P angle is 144°.

<sup>f</sup>Average for two different distances in the same molecule.

<sup>g</sup>Similar to those values found in 5(BF<sub>4</sub>), See ref. 2.

which the P-N<sub>ax</sub> distances are considerably shorter than the sum of the sum of the van der Waals radii (42% and 40%, respectively). Compounds **7-9** and **11** show only up to 10% shortening (Table 7).

It can also be seen from Table 7 that when the P-N<sub>ax</sub> interaction is strong, the geometry around the phosphorus is approximately trigonal bi-pyramidal (as in **15** and **5**),<sup>42</sup> whereas when the interaction is weak to non-existent the phosphorus geometry is more trigonal pyramidal (as in **7-11**).

The geometries at the metal centers for **10** and **11** are what would be predicted considering the respective metal coordination spheres. The approximately octahedral geometry around the rhenium in **10** is expected, as is the bending of the ligands *cis*- to **2** away from **2** due to its large size. The normal geometry in Hg(L)<sub>2</sub><sup>2+</sup> complexes (where L = PR<sub>3</sub> or P(OR)<sub>3</sub>) is primarily tetrahedral with distortions accommodating the size of the ligands (ie the larger the cone angle of the phosphorus ligand, the larger the P-Hg-P angle).<sup>43</sup> The P-Hg-P angle in **11** of 144°, is therefore not surprising.

The sum of the angles around all of the equatorial nitrogens in **10 - 12** and **15** are approximately 360°. This planarity was also seen in **7-9**, and in analogous silatranyl species.<sup>44</sup>

It has been recently calculated for silatranyl systems of the type shown in Figure 5, that the bridgehead-bridgehead bond distance decreases with the number of chelate rings (ie as n decreases, Si-N<sub>ax</sub> decreases).<sup>45</sup> The magnitude of the shortening in this Si-N distance was calculated to be 0.05 Å by AM1 calculations and 0.11 Å by 6-31G(d) calculations for Δn = 1. It is conceivable that this increase of bridgehead-bridgehead interaction with decreasing n may

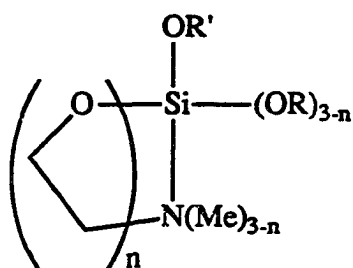


Figure 5

also be invoked in isoelectronic and isostructural phosphatranyl systems such as **15** and **5**. As can be seen from Table 7, the P-N<sub>ax</sub> distance in **15** (where n = 2) is 0.04 Å shorter than that in **5**<sup>+</sup> (where n = 3). Although the substitution of a nitrogen for an oxygen in going from **5** to **15** (conceptually, not chemically) makes these systems less analogous, the bridgehead-bridgehead distance difference is similar in **15** and **5** to that calculated for the Si-N<sub>ax</sub> using AM1 calculations.<sup>45</sup>

The structure of **15** was found to be very similar to the previously reported analogous dioxaphosphetane, **21**,<sup>41</sup> see Table 8. The angles in the P<sub>2</sub>O<sub>2</sub> plane are distorted from 90



Table 8. Selected bond distances and angles for **15** and **21**

Angles, deg <sup>b</sup>	<b>15</b>	<b>21</b> <sup>a</sup>	Bond	<b>15</b>	<b>21</b> <sup>a</sup>
			Distances, Å		
O-P-O	82.8	82.6	P-O <sub>ax</sub>	1.685	1.735
P-O-P	97.4	97.2	P-N <sub>ax</sub>	1.935	1.934
O <sub>ax</sub> -P-N <sub>ax</sub>	172.9	173.2	P-O <sub>eq</sub>	1.613	1.593
O <sub>ax</sub> -P-N <sub>eq</sub>	95.1	95.0			
O <sub>ax</sub> -P-E <sup>c</sup>	96.0	94.3			

<sup>a</sup>See Ref. 41.

<sup>b</sup>Values are averaged.

<sup>c</sup>E = CH<sub>2</sub> for **21**, E = NMe for **15**.

degrees in both structures, and the analogous distances and angles from and around the phosphorus in **15**, respectively, are similar to the corresponding values in **21**.

**Conclusions.** We have demonstrated that **2** can react very differently with different metal starting materials: simple coordination to the metal, as demonstrated in **10**; ligand disproportionation upon the formation of **11**; and unusual oxidation-reduction reactions, as seen in the formation of **15**. It seems likely that the source of the unusual behavior of **2** is in its high basicity. In the Lewis view of basicity, the strong ability of the pro-azaphosphatrane to donate the lone pair on the phosphorus is conceivably the reason why under the same conditions, **2** will completely transfer its electrons to mercury(II) in the presence of triflate, whereas the less electron-donating P(NMe<sub>2</sub>)<sub>3</sub> will only coordinate to the mercuric ions. In the Bronsted-Lowry view of basicity, the high stability of the protonation product of **2** (**5**), due in part to the 3-center-4-electron molecular orbital system and the three chelate rings, is likely

responsible for the stability of **5** with respect to oxidation in the presence of peroxides. Because of the bridgehead-bridgehead interaction in **5**, the phosphorus is 5-coordinate, a geometry usually reserved for phosphorus(V) compounds, and is stable (more like a phosphorus(V)-containing species ) in the presence of oxidants.

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## REFERENCES

1. Laramay, M. A. H.; Verkade, J. G. *J. Amer. Chem. Soc.*, **1990**, *112*, 9421.
2. Lensink, C.; Xi, S. K.; Daniels, L. M.; Verkade, J. G. *J. Amer. Chem. Soc.*, **1989**, *111*, 3478.
3. Xi, S. K.; Schmidt, H.; Lensink, C.; Kim, S.; Wintergrass, D.; Daniels, L. M.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.*, **1990**, *29*, 2214 and references therein.
4. Schmidt, H.; Lensink, C.; Xi, S. K.; Verkade, J. G. *Z. anorg. allg. Chem.*, **1989**, *587*, 75.
5. Laramay, M. A. H.; Verkade, J. G. *Z. anorg. allg. Chem.*, submitted.
6. Gudat, D.; Lensink, C.; Schmidt, H.; Xi, S. K.; Verkade, J. G. *Phosphorus, Sulfur and Silicon*, **1989**, *41*, 21.
7. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals, Third Edition*, Pergamon Press: New York, NY 1988.
8. Marvel, C. S.; Gauerke, C. G.; Hill, E. L. *J. Amer. Chem. Soc.*, **1925**, *47*, 3009.
9. Peringer, P.; Obendorf, D. *Inorg. Nucl. Chem. Lett.*, **1980**, *42*, 1501.
10. Coates, G. E.; Lauder, A. J. *J. Chem. Soc.*, **1965**, 1857.
11. Noth, H.; Vetter, H.-J. *Chem. Ber.*, **1963**, *96*, 1479.
12. Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*, Academic Press: New York, NY, 1978.
13. SHELXS-86, Sheldrick, G. M., Institut Fur Anorganische Chemie der Universitat, Gottingen, F. G. R.
14. Enraf-Nonius Structure Determination Package; Enraf-Nonius: Delft-Holland.  
Neutral-atom scattering factors and anomalous scattering corrections were taken

- from *International Tables for X-ray Crystallography*, The Kynoch Press:  
Birmingham, England, 1974, Vol. IV.
15. Sheldrick, G. M. in *Computing in Crystallography*, Schenk, H.; Olthof-Hazekamp, R.; Van Koningsveld, H.; Bassi, G. C.; Eds.; Delft University: Delft, 1978.
  16. Motherwell, S.; Clegg, W.; PLUTO; Program for plotting molecular crystal structures; Univ. of Cambridge, England, 1978.
  17. Johnson, C. K.; ORTEP II; Report ORNL-5138; Oak Ridge National Laboratory, Tennessee, 1976.
  18. Hendrixson, T. L.; A reciprocal space approach for locating symmetry elements in Patterson superposition maps, Part I; Iowa State University, Ph.D. Thesis, 1989.
  19. Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*, The Kynoch Press: Birmingham, England, 1974, Vol. IV.
  20. Ibers, J. A.; Hamilton, W. C. *Acta Crystallographica*, 1964, 17, 781.
  21. Cromer, D. T. *International Tables for X-ray Crystallography*, Table 2.3.1., The Kynoch Press: Birmingham, England, 1974, Vol. IV.
  22. Hendrixson, T. L.; A reciprocal space approach for locating symmetry elements in Patterson superposition maps, Part II; Iowa State University, Ph.D. Thesis, 1989.
  23. Powell, D. R.; Jacobson, R. A. *FOUR: A Generalized Crystallographic Fourier Program*, U.S. DOE Report IS-4737, Iowa State University, Ames, IA, 1980.
  24. TEXSAN - TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.
  25. Reinartz, K.; Wroblewski, A. E.; Verkade, J. G. *Energy and Fuels*, submitted.
  26. Casey, C. P.; O'Connor, J. M.; Jones, W. D.; Haller, K. J. *Organometallics*, 1983, 2, 535.
  27. Casey, C. P.; Bullock, R. M. *J. Organomet. Chem.*, 1983, 251, 245.

28. Lee, K.-W.; Brown, T. L. *Organometallics*, **1985**, *4*, 1025.
29. Ogilvie, F. B.; Jenkins, J. M.; Verkade, J. G. *J. Amer. Chem. Soc.*, **1970**, *92*, 1916.
30. Redfield, D. A.; Nelson, J. H.; Cary, L. W. *Inorg. Nucl. Chem. Lett.*, **1974**, *10*, 727.
31. Alyea, E. C.; Dias, S. A.; Goel, R. G.; Ogini, W. O.; Pilon, P.; Meek, D. M. *Inorg. Chem.*, **1978**, *17*, 1697.
32. Peringer, P.; Obendorf, D. *Inorg. Chem. Acta.*, **1983**, 1147.
33. Gillespie, D. J.; Granger, P. J.; Morgan, K. R.; Schrobilen, G. L. *Inorg. Chem.*, **1984**, *23*, 887.
34. Reinartz, K.; Verkade, J. G. in press.
35. Huheey, J. E. *Inorganic Chemistry, Third Edition*, Harper and Row: New York, NY, 1983.
36. Lyashenko, S. D.; Stepanov, A. S. *Khim. Elementoorg. Soedin.*, **1976**, *4*, 50.
37. Zeilen, A. J.; Sullivan, J. C. *J. Phys. Chem.*, **1962**, *66*, 1065.
38. Coskran, K. J.; Bertrand, R. D.; Verkade, J. G. *J. Amer. Chem. Soc.*, **1967**, *89*, 4535.
39. Cullis, P. M.; Kay, P. B.; Trippet, S. *J. Chem. Soc., Chem. Comm.*, **1985**, 1329.
40. Cullis, P. M.; Kaye, A. D.; Trippet, S. *J. Chem. Soc., Chem. Comm.*, **1987**, 1464.
41. Powell, J.; Ng, K. S.; Sawyer, J. F. *J. Chem. Soc., Chem. Comm.*, **1987**, 1131.
42. Bondi, A. *J. Phys. Chem.*, **1964**, *68*, 441.
43. Dakternieks, D. *Inorg. Chem. Acta.*, **1984**, *89*, 209.
44. Gudat, D.; Verkade, J. G. *Organometallics*, **1989**, *8*, 2772.
45. Gordon, M. S.; Carrol, M. T.; Jensen, J. H.; Davis, L. P.; Burggraf, L. W.;

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## APPENDIX

Table 9. Bond distances (Å) for *cis*-(CO)<sub>4</sub>Re[P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]Br, 10

Atom 1	Atom 2	Distance
Re	Br	2.6286(7)
Re	P	2.518(2)
Re	C(11)	1.990(7)
Re	C(12)	1.997(7)
Re	C(13)	1.959(8)
Re	C(14)	1.919(7)
P	N(2)	1.670(5)
P	N(3)	1.667(5)
P	N(4)	1.662(5)
P	N(1)	3.307(6)
N(1)	C(3)	1.447(9)
N(1)	C(6)	1.446(8)
N(1)	C(9)	1.436(8)
C(1)	N(2)	1.466(7)
N(2)	C(2)	1.452(7)
C(2)	C(3)	1.52(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 9, continued. Bond distances (Å) for *cis*-(CO)<sub>4</sub>Re[P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]Br

Atom 1	Atom 2	Distance
N(3)	C(4)	1.462(8)
N(3)	C(5)	1.460(8)
C(6)	C(5)	1.521(9)
N(4)	C(7)	1.475(7)
N(4)	C(8)	1.448(7)
C(9)	C(8)	1.525(9)
O(11)	C(11)	1.120(7)
O(12)	C(12)	1.128(8)
O(13)	C(13)	1.139(9)
O(14)	C(14)	1.144(8)

Numbers in parentheses are estimated standard deviations in the least significant digits.



Table 10. Bond distances (Å) for Cl<sub>2</sub>Hg[P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]<sub>2</sub>, 11

Atom 1	Atom 2	Distance
Hg	Cl(1)	2.652(4)
Hg	Cl(2)	2.637(4)
Hg	P(1)	2.470(3)
Hg	P(2P)	2.454(3)
P(1)	N(2)	1.64(1)
P(1)	N(3)	1.64(1)
P(1)	N(4)	1.65(1)
P(2)	N(6)	1.63(1)
P(2)	N(7)	1.65(1)
P(2)	N(8)	1.64(1)
N(1)	C(1)	1.42(2)
N(1)	C(4)	1.44(2)
N(1)	C(7)	1.44(2)
N(2)	C(2)	1.44(2)
N(2)	C(3)	1.49(2)
N(3)	C(5)	1.46(2)
N(3)	C(6)	1.45(2)
N(4)	C(8)	1.45(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 10, continued. Bond distances (Å) for Cl<sub>2</sub>Hg[P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]<sub>2</sub>, 11

Atom 1	Atom 2	Distance
N(4)	C(9)	1.47(3)
N(5)	C(10)	1.44(2)
N(5)	C(13)	1.44(2)
N(5)	C(16)	1.40(2)
N(6)	C(11)	1.47(2)
N(6)	C(12)	1.44(2)
N(7)	C(14)	1.43(2)
N(7)	C(15)	1.48(2)
N(8)	C(17)	1.47(1)
N(8)	C(18)	1.44(2)
C(1)	C(2)	1.53(2)
C(4)	C(5)	1.50(2)
C(7)	C(8)	1.53(2)
C(10)	C(11)	1.50(2)
C(13)	C(14)	1.51(2)
C(16)	C(17)	1.50(2)
Hg	I(1)	2.7884(4)
Hg	I(2)	2.7991(4)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 11. Bond distances (Å) for  $[\overline{\text{HP}(\text{NMeCH}_2\text{CH}_2)_3\text{N}}]_2\text{HgI}_4$ , **12**

Atom 1	Atom 2	Distance
P	N(1)	1.973(4)
P	N(2)	1.676(5)
P	N(3)	1.667(5)
P	N(4)	1.660(5)
P	H(1)	1.29(4)
N(1)	C(3)	1.503(8)
N(1)	C(6)	1.487(7)
N(1)	C(9)	1.478(8)
N(2)	C(1)	1.469(7)
N(2)	C(2)	1.448(7)
N(3)	C(4)	1.454(9)
N(3)	C(5)	1.457(8)
N(4)	C(7)	1.468(8)
N(4)	C(8)	1.453(7)
C(2)	C(3)	1.512(8)
C(5)	C(6)	1.538(9)
C(8)	C(9)	1.504(9) N(5)
	C(10)	1.116(9)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 12. Bond distances (Å) for  $[\text{MeH}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NMe})_2\text{PO}]_2(\text{OTf})_4$ ,  
15

Atom 1	Atom 2	Distance
C(10)	C(11)	1.48(1)
P(1)	O(1)	1.685(3)
P(1)	O(1')	1.616(3)
P(2)	O(2)	1.610(3)
P(2)	O(2')	1.673(3)
P(1)	N(1)	1.930(4)
P(1)	N(2)	1.628(4)
P(1)	N(3)	1.614(4)
P(2)	N(5)	1.941(4)
P(2)	N(6)	1.637(4)
P(2)	N(7)	1.614(4)
N(1)	C(3)	1.489(7)
N(1)	C(6)	1.493(7)
N(1)	C(9)	1.510(6)
N(2)	C(1)	1.468(8)
N(2)	C(2)	1.459(7)
N(3)	C(4)	1.468(8)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 12, continued. Bond distances (Å) for



Atom 1	Atom 2	Distance
N(3)	C(5)	1.468(7)
N(4)	C(7)	1.501(8)
N(4)	C(8)	1.476(7)
N(5)	C(12)	1.487(6)
N(5)	C(15)	1.484(6)
N(5)	C(18)	1.502(6)
N(6)	C(10)	1.456(7)
N(6)	C(11)	1.458(7)
N(7)	C(13)	1.454(7)
N(7)	C(14)	1.495(7)
N(8)	C(16)	1.485(7)
N(8)	C(17)	1.501(7)
C(2)	C(3)	1.483(8)
C(5)	C(6)	1.491(8)
C(8)	C(9)	1.523(8)
C(11)	C(12)	1.499(8)
C(14)	C(15)	1.495(7)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 12, continued. Bond distances (Å) for



Atom 1	Atom 2	Distance
C(17)	C(18)	1.535(7)
S(1)	O(3)	1.425(5)
S(1)	O(4)	1.422(4)
S(1)	O(5)	1.423(4)
S(1)	C(19)	1.820(8)
S(2)	O(6)	1.415(4)
S(2)	O(7)	1.418(4)
S(2)	O(8)	1.430(4)
S(2)	C(20)	1.790(7)
S(3)	O(9)	1.50(1)
S(3)	O(9')	1.26(2)
S(3)	O(10)	1.67(3)
S(3)	O(10')	1.30(1)
S(3)	O(11)	1.45(2)
S(3)	O(11')	1.48(1)
S(3)	C(21)	1.73(2)
S(4)	O(12)	1.425(5)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 12, continued. Bond distances (Å) for



Atom 1	Atom 2	Distance
S(4)	O(13)	1.352(7)
S(4)	O(14)	1.481(8)
S(4)	C(22)	1.75(1)
F(1)	C(19)	1.292(8)
F(2)	C(19)	1.303(8)
F(3)	C(19)	1.303(8)
F(4)	C(20)	1.306(8)
F(5)	C(20)	1.338(8)
F(6)	C(20)	1.320(8)
F(7)	C(21)	1.12(2)
F(7')	C(21)	1.73(2)
F(8')	C(21)	1.17(2)
F(9)	C(21)	1.59(2)
F(9')	C(21)	1.51(2)
F(10)	C(22)	1.32(1)
F(11)	C(22)	1.24(1)
F(12)	C(22)	1.25(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 12, continued. Bond distances (Å) for



Atom 1	Atom 2	Distance
F(8)	C(21)	1.38(2)
N(9)	C(24)	1.07(1)
C(23)	C(24)	1.45(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.



Table 13. Bond angles (deg) for *cis*-(CO)<sub>4</sub>Re[P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]Br, 10

Atom 1	Atom 2	Atom 3	Angle
Br	Re	P	90.39(4)
Br	Re	C(11)	92.1(2)
Br	Re	C(12)	89.3(2)
Br	Re	C(13)	86.3(2)
Br	Re	C(14)	174.4(2)
P	Re	C(11)	89.6(2)
P	Re	C(12)	92.0(2)
P	Re	C(13)	176.6(2)
P	Re	C(14)	94.9(2)
C(11)	Re	C(12)	177.9(3)
C(11)	Re	C(13)	90.5(3)
C(11)	Re	C(14)	89.9(3)
C(12)	Re	C(13)	88.0(3)
C(12)	Re	C(14)	88.6(3)
C(13)	Re	C(14)	88.4(3)
Re	P	N(2)	112.6(2)
Re	P	N(3)	115.7(2)
Re	P	N(4)	112.1(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 13, continued. Bond angles (deg) for *cis*-(CO)<sub>4</sub>Re[P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]Br

Atom 1	Atom 2	Atom 3	Angle
N(2)	P	N(3)	104.8(2)
N(2)	P	N(4)	104.9(2)
N(3)	P	N(4)	105.9(3)
C(3)	N(1)	C(6)	117.0(6)
C(3)	N(1)	C(9)	120.9(5)
C(6)	N(1)	C(9)	119.5(6)
P	N(2)	C(1)	121.3(4)
P	N(2)	C(2)	122.6(4)
C(1)	N(2)	C(2)	114.4(5)
N(2)	C(2)	C(3)	115.2(5)
N(1)	C(3)	C(2)	115.2(5)
P	N(3)	C(4)	121.2(5)
P	N(3)	C(5)	122.7(4)
C(4)	N(3)	C(5)	115.6(5)
N(3)	C(5)	C(6)	115.8(5)
N(1)	C(6)	C(5)	115.8(5)
P	N(4)	C(7)	119.3(4)
P	N(4)	C(7)	123.2(4)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 13, continued. Bond angles (deg) for *cis*-(CO)<sub>4</sub>Re[P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]Br

Atom 1	Atom 2	Atom 3	Angle
C(7)	N(4)	C(8)	115.7(5)
N(4)	C(8)	C(9)	115.6(5)
N(1)	C(9)	C(8)	114.1(6)
Re	C(11)	O(11)	176.8(6)
Re	C(12)	O(12)	174.6(6)
Re	C(13)	O(13)	179.5(6)
Re	C(14)	O(14)	175.7(6)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 14. Bond angles (deg) for Cl<sub>2</sub>Hg[P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]<sub>2</sub>, 11

Atom 1	Atom 2	Atom 3	Angle
Cl(1)	Hg	Cl(2)	102.1(1)
Cl(1)	Hg	P(1)	94.0(1)
Cl(1)	Hg	P(2)	104.7(1)
Cl(2)	Hg	P(1)	103.3(1)
Cl(2)	Hg	P(2)	102.0(1)
P(1)	Hg	P(2)	144.5(1)
Hg	P(1)	N(2)	112.5(4)
Hg	P(1)	N(3)	112.3(4)
Hg	P(1)	N(4)	110.4(4)
N(2)	P(1)	N(3)	107.1(5)
N(2)	P(1)	N(4)	106.9(6)
N(3)	P(1)	N(4)	107.3(6)
Hg	P(2)	N(6)	111.8(5)
Hg	P(2)	N(7)	111.6(4)
Hg	P(2)	N(8)	108.4(4)
N(6)	P(2)	N(7)	107.9(7)
N(6)	P(2)	N(8)	107.5(6)
N(7)	P(2)	N(8)	109.6(5)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 14, continued. Bond angles (deg) for Cl<sub>2</sub>Hg[P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]<sub>2</sub>, 11

Atom 1	Atom 2	Atom 3	Angle
C(1)	N(1)	C(4)	121(1)
C(1)	N(1)	C(7)	120(1)
C(4)	N(1)	C(7)	119(1)
P(1)	N(2)	C(2)	124.0(9)
P(1)	N(2)	C(3)	118.7(9)
C(2)	N(2)	C(3)	117(1)
P(1)	N(3)	C(5)	122.4(9)
P(1)	N(3)	C(6)	118(1)
C(5)	N(3)	C(6)	119(1)
P(1)	N(4)	C(8)	124(1)
P(1)	N(4)	C(9)	119(1)
C(8)	N(4)	C(9)	116(1)
C(10)	N(5)	C(13)	118(1)
C(10)	N(5)	C(16)	122(1)
C(13)	N(5)	C(16)	120(1)
P(2)	N(6)	C(11)	124(1)
P(2)	N(6)	C(12)	121(2)
C(11)	N(6)	C(12)	115(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 14, continued. Bond angles (deg) for Cl<sub>2</sub>Hg[P(NMeCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]<sub>2</sub>, 11

Atom 1	Atom 2	Atom 3	Angle
P(2)	N(7)	C(14)	124.4(8)
P(2)	N(7)	C(15)	118(1)
C(14)	N(7)	C(15)	117(1)
P(2)	N(8)	C(17)	123.6(8)
P(2)	N(8)	C(18)	119.2(8)
C(17)	N(8)	C(18)	116(1)
N(1)	C(1)	C(2)	114(1)
N(2)	C(2)	C(1)	116(1)
N(1)	C(4)	C(5)	114(1)
N(3)	C(5)	C(4)	115(1)
N(1)	C(7)	C(8)	113(1)
N(4)	C(8)	C(7)	114(1)
N(5)	C(10)	C(11)	114(1)
N(6)	C(11)	C(10)	115(1)
N(5)	C(13)	C(14)	112(1)
N(7)	C(14)	C(13)	116(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 14, continued. Bond angles (deg) for  $\text{Cl}_2\text{Hg}[\text{P}(\text{NMeCH}_2\text{CH}_2)_3\text{N}]_2$ , 11

Atom 1	Atom 2	Atom 3	Angle
N(5)	C(16)	C(17)	115(1)
N(8)	C(17)	C(16)	113(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 15. Bond angles (deg) for  $[\text{HP}(\text{NMeCH}_2\text{CH}_2)_3\text{N}]_2\text{HgI}_4$ , 12

Atom 1	Atom 2	Atom 3	Angle
I(1)	Hg	I(1')	109.55(2)
I(1)	Hg	I(2)	104.66(1)
I(1)	Hg	I(2')	112.23(1)
I(2)	Hg	I(2')	113.63(2)
N(1)	P	N(2)	86.3(2)
N(1)	P	N(3)	86.2(2)
N(1)	P	N(4)	86.0(2)
N(1)	P	H(1)	175(2)
N(2)	P	N(3)	119.6(3)
N(2)	P	N(4)	118.6(3)
N(2)	P	H(1)	97(2)
N(3)	P	N(4)	120.4(3)
N(3)	P	H(1)	96(2)
N(4)	P	H(1)	89(2)
P	N(1)	C(3)	105.2(3)
P	N(1)	C(6)	107.6(3)
P	N(1)	C(9)	107.7(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.



Table 15, continued. Bond angles (deg) for  $[\text{HP}(\overline{\text{NMeCH}_2\text{CH}_2})_3\text{N}]_2\text{HgI}_4$ , 12

Atom 1	Atom 2	Atom 3	Angle
C(3)	N(1)	C(6)	111.6(4)
C(3)	N(1)	C(9)	113.4(5)
C(6)	N(1)	C(9)	111.0(4)
P	N(2)	C(1)	119.5(4)
P	N(2)	C(2)	121.2(3)
C(1)	N(2)	C(2)	114.4(5)
P	N(3)	C(4)	124.0(4)
P	N(3)	C(5)	121.0(4)
C(4)	N(3)	C(5)	113.4(5)
P	N(4)	C(7)	121.3(4)
P	N(4)	C(8)	119.9(4)
C(7)	N(4)	C(8)	115.5(5)
N(2)	C(2)	C(3)	105.2(4)
N(1)	C(3)	C(2)	106.3(5)
N(3)	C(5)	C(6)	106.2(5)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 15, continued. Bond angles (deg) for  $[\text{HP}(\overline{\text{NMeCH}_2\text{CH}_2})_3\text{N}]_2\text{HgI}_4$ , 12

Atom 1	Atom 2	Atom 3	Angle
N(1)	C(6)	C(5)	104.9(4)
N(4)	C(8)	C(9)	107.9(6)
N(1)	C(9)	C(8)	104.6(5)
N(5)	C(10)	C(11)	177.2(7)

Numbers in parentheses are estimated standard deviations in the least significant digits.

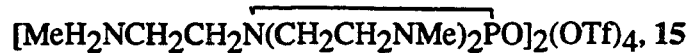
Table 16. Bond angles (deg) for  $[\text{MeH}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NMe})_2\text{PO}]_2(\text{OTf})_4$ .

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Atom 1	Atom 2	Atom 3	Angle
O(1)	P(1)	O(1')	83.0(2)
O(1)	P(1)	N(1)	172.9(2)
O(1)	P(1)	N(2)	95.1(2)
O(1)	P(1)	N(3)	96.0(2)
O(1')	P(1)	N(1)	90.0(2)
O(1')	P(1)	N(2)	119.9(2)
O(1')	P(1)	N(3)	116.1(2)
N(1)	P(1)	N(2)	88.0(2)
N(1)	P(1)	N(3)	87.5(2)
N(2)	P(1)	N(3)	123.7(2)
O(2)	P(2)	O(2')	82.7(2)
O(2)	P(2)	N(5)	89.9(2)
O(2)	P(2)	N(6)	116.5(2)
O(2)	P(2)	N(7)	119.3(2)
O(2')	P(2)	N(5)	172.6(2)
O(2')	P(2)	N(6)	96.4(2)
O(2')	P(2)	N(7)	95.8(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 16, continued. Bond angles (deg) for



Atom 1	Atom 2	Atom 3	Angle
N(5)	P(2)	N(6)	87.2(2)
N(5)	P(2)	N(7)	87.5(2)
N(6)	P(2)	N(7)	123.9(2)
P(1)	O(1)	P(1')	97.0(2)
P(2)	O(2)	P(2')	97.3(2)
P(1)	N(1)	C(3)	102.9(3)
P(1)	N(1)	C(6)	106.3(3)
P(1)	N(1)	C(9)	113.5(3)
C(3)	N(1)	C(6)	111.3(4)
C(3)	N(1)	C(9)	111.9(4)
C(6)	N(1)	C(9)	110.6(4)
P(1)	N(2)	C(1)	127.9(4)
P(1)	N(2)	C(2)	118.8(4)
C(1)	N(2)	C(2)	113.2(5)
P(1)	N(3)	C(4)	124.0(4)
P(1)	N(3)	C(5)	120.6(4)
C(4)	N(3)	C(5)	113.6(4)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 16, continued. Bond angles (deg) for



Atom 1	Atom 2	Atom 3	Angle
C(7)	N(4)	C(8)	109.5(5)
P(2)	N(5)	C(12)	104.8(3)
P(2)	N(5)	C(15)	101.5(3)
P(2)	N(5)	C(18)	112.2(3)
C(12)	N(5)	C(15)	111.7(4)
C(12)	N(5)	C(18)	113.6(4)
C(15)	N(5)	C(18)	112.1(4)
P(2)	N(6)	C(10)	125.7(4)
P(2)	N(6)	C(11)	120.2(3)
C(10)	N(6)	C(11)	113.9(4)
P(2)	N(7)	C(13)	127.5(4)
P(2)	N(7)	C(14)	118.9(3)
C(13)	N(7)	C(14)	113.4(4)
C(16)	N(8)	C(17)	111.7(4)
N(2)	C(2)	C(3)	106.6(5)
N(1)	C(3)	C(2)	105.9(4)
N(3)	C(5)	C(6)	106.5(5)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 16, continued. Bond angles (deg) for



Atom 1	Atom 2	Atom 3	Angle
N(1)	C(6)	C(5)	105.5(5)
N(4)	C(8)	C(9)	107.3(4)
N(1)	C(9)	C(8)	113.7(4)
N(6)	C(11)	C(12)	106.7(5)
N(5)	C(12)	C(11)	106.3(5)
N(7)	C(14)	C(15)	104.8(5)
N(5)	C(15)	C(14)	106.0(4)
N(8)	C(17)	C(18)	107.7(4)
N(5)	C(18)	C(17)	112.5(4)
O(3)	S(1)	O(4)	115.4(4)
O(3)	S(1)	O(5)	115.7(4)
O(3)	S(1)	C(19)	101.8(3)
O(4)	S(1)	O(5)	114.4(3)
O(4)	S(1)	C(19)	104.5(3)
O(5)	S(1)	C(19)	102.6(3)
O(6)	S(2)	O(7)	116.1(3)
O(6)	S(2)	O(8)	114.0(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 16, continued. Bond angles (deg) for



Atom 1	Atom 2	Atom 3	Angle
O(6)	S(2)	C(20)	103.9(3)
O(7)	S(2)	O(8)	114.6(3)
O(7)	S(2)	C(20)	103.1(3)
O(8)	S(2)	C(20)	102.9(3)
O(9)	S(3)	O(9')	31.8(8)
O(9)	S(3)	O(10)	95(1)
O(9)	S(3)	O(10')	104.4(7)
O(9)	S(3)	O(11)	118.8(7)
O(9)	S(3)	O(11')	121.7(6)
O(9)	S(3)	C(21)	96.4(8)
O(9')	S(3)	O(10)	102(1)
O(9')	S(3)	O(10')	78(1)
O(9')	S(3)	O(11)	107(1)
O(9')	S(3)	O(11')	112.0(9)
O(9')	S(3)	C(21)	128(1)
O(10)	S(3)	O(10')	136(1)
O(10)	S(3)	O(11)	146(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 16, continued. Bond angles (deg) for



Atom 1	Atom 2	Atom 3	Angle
O(10)	S(3)	O(11')	34(1)
O(10)	S(3)	C(21)	86(1)
O(10')	S(3)	O(11)	39.7(7)
O(10')	S(3)	O(11')	103.9(7)
O(10')	S(3)	C(21)	129.3(9)
O(11)	S(3)	O(11')	115.6(8)
O(11)	S(3)	C(21)	89.8(9)
O(11')	S(3)	C(21)	103.2(7)
O(12)	S(4)	O(13)	121.1(4)
O(12)	S(4)	O(14)	111.2(4)
O(12)	S(4)	C(22)	105.8(4)
O(13)	S(4)	O(14)	105.3(5)
O(13)	S(4)	C(22)	109.3(5)
O(14)	S(4)	C(22)	102.7(5)
S(1)	C(19)	F(1)	111.7(6)
S(1)	C(19)	F(2)	111.3(6)
S(1)	C(19)	F(3)	110.9(6)

Numbers in parentheses are estimated standard deviations in the least significant digits.



Table 16, continued. Bond angles (deg) for



Atom 1	Atom 2	Atom 3	Angle
F(1)	C(19)	F(2)	107.7(6)
F(1)	C(19)	F(3)	107.8(8)
F(2)	C(19)	F(3)	107.3(8)
S(2)	C(20)	F(4)	111.9(5)
S(2)	C(20)	F(5)	111.0(4)
S(2)	C(20)	F(6)	112.5(6)
F(4)	C(20)	F(5)	108.3(6)
F(4)	C(20)	F(6)	106.0(6)
F(5)	C(20)	F(6)	106.8(6)
S(3)	C(21)	F(7)	134(2)
S(3)	C(21)	F(8)	110(1)
S(3)	C(21)	F(8')	134(1)
S(3)	C(21)	F(9)	96(1)
S(3)	C(21)	F(9')	99(1)
F(7)	C(21)	F(8)	96(2)
F(7)	C(21)	F(8')	40.6(9)
F(7)	C(21)	F(9)	106(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 16, continued. Bond angles (deg) for



Atom 1	Atom 2	Atom 3	Angle
F(7)	C(21)	F(9')	122(2)
F(8)	C(21)	F(8')	117(2)
F(8)	C(21)	F(9)	116(1)
F(8)	C(21)	F(9')	33.5(7)
F(8')	C(21)	F(9)	66(1)
F(8')	C(21)	F(9')	121(1)
F(9)	C(21)	F(9')	87(1)
S(4)	C(22)	F(10)	111.9(8)
S(4)	C(22)	F(11)	113.9(9)
S(4)	C(22)	F(12)	112.9(8)
F(10)	C(22)	F(11)	106(1)
F(10)	C(22)	F(12)	107.4(9)
F(11)	C(22)	F(12)	104(1)
N(9)	C(24)	C(23)	171(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

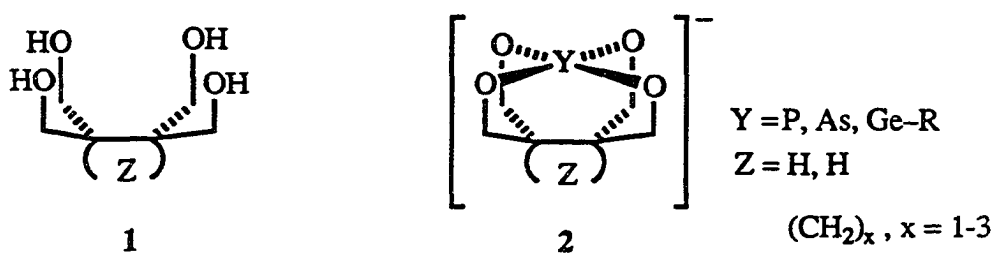
**PART V: THE UNEXPECTED SYNTHESIS OF TRICYCLO-[4.2.1.1.2,5]-1,2,5,6-  
TETRAETHYL CARBOXYLATODECANE-9,10-DIONE**

**ABSTRACT**

Tricyclo-[4.2.1.1.<sup>2,5</sup>]-1,2,5,6-tetraethyl carboxylatodecane-9,10-dione (**5**) was prepared unexpectedly by reacting ethylene dimalonic ester with sodium ethoxide and bromine. It was initially assumed that **5** was formed from the deprotonation and subsequent dimerization of 2,5-diethylcarboxycyclopentanone (**7**), however our attempts to prepare **5** from isolated **7** failed. The synthesis, characterization, and X-ray determination of **5** is presented. Also, our attempts to dimerize **7** using conditions similar to those used in the initial synthesis of **5** and with modification of those conditions are described.

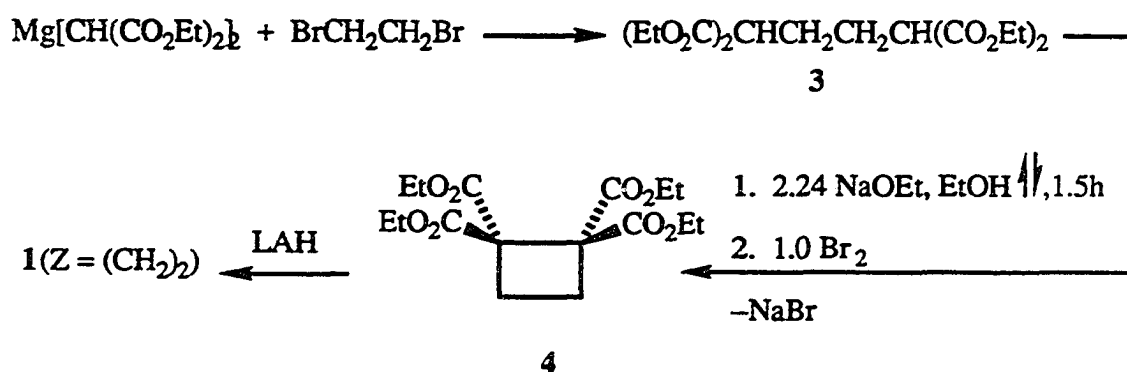
## INTRODUCTION

Recently we have been investigating tetraols of type **1** with respect to their ability to form polycyclic anionic esters of nonmetals and alkoxides of metals such as **2**.<sup>1-3</sup>

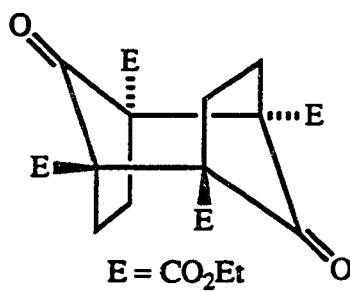


In Scheme 1 is shown a facile route to **4**,<sup>4-6</sup> the precursor to **1** wherein  $\text{Z} = (\text{CH}_2)_2$ . Precursor **4** is usually isolated in 74% yield by filtering off the NaBr byproduct, evaporating the EtOH, extracting the residue with water and ether, drying the ether

## Scheme 1



solution, evaporating the ether and vacuum distilling the oil. In a reaction in which the mixture of **3** and NaOEt/EtOH had been refluxed for a much longer period of time (16 hours) before bromine addition and work-up, a fraction that distilled following some starting material in 26% yield and **4** in 42% yield was unexpectedly found to be the novel title compound **5**.

**5**

## RESULTS AND DISCUSSION

By extending the reflux time in step 2 of Scheme 1 from 1.5 to 16 hours, **5** is obtained by vacuum distillation in ca. 13% yield. Upon standing, **5** crystallizes from the melt in pure form as prisms suitable for X-ray analysis as well as  $^1\text{H}$ ,  $^{13}\text{C}$  and mass spectroscopies (see Experimental Section). The positional parameters for **5** are given in Table 1 and an ORTEP drawing is shown in Figure 1. The bond lengths and angles are unremarkable. In Table 2 are collected the crystal and refinement data.

Table 1. Positional parameters and their estimated standard deviations for  $\text{C}_{22}\text{H}_{28}\text{O}_{10}$ , **5**

Atom	x	y	z	B(Å <sup>2</sup> )
O(1)	-0.06136(8)	-0.13276(6)	-0.0081(2)	4.03(3)
O(2)	-0.18876(7)	-0.01522(7)	0.2351(2)	4.17(3)
O(3)	-0.14250(8)	0.16449(6)	0.0876(2)	4.48(3)
O(4)	-0.10235(7)	-0.09281(7)	0.3721(2)	3.86(2)
O(5)	-0.07702(7)	0.11586(6)	0.3156(2)	3.77(3)
C(1)	-0.04432(9)	-0.01762(8)	0.1571(2)	2.53(3)
C(2)	0.0398(1)	-0.1372(9)	0.2541(2)	2.92(3)
C(3)	0.1077(1)	-0.0374(1)	0.1216(2)	3.18(3)

<sup>a</sup>Atoms were refined isotropically.

Table 1, continued. Positional parameters and their estimated standard deviations for  
 $C_{22}H_{28}O_{10} \cdot 5$

Atom	x	y	z	B(Å <sup>2</sup> )
C(4)	-0.6177(9)	0.05424(8)	0.0480(2)	2.63(3)
C(5)	-0.0230(1)	-0.07777(8)	0.0246(2)	2.67(3)
C(6)	-0.1206(1)	-0.04007(9)	0.2592(2)	2.99(3)
C(7)	-0.1720(1)	-0.1247(1)	0.4672(3)	4.23(4)
C(8)	-0.1388(1)	-0.1876(1)	0.5705(3)	5.08(5)
C(9)	-0.1000(1)	0.11746(8)	0.1503(2)	3.17(3)
C(10)	-0.1105(1)	0.1738(1)	0.4268(3)	4.79(5)
C(11)	-0.1943(1)	0.1531(1)	0.4904(3)	5.87(5)
H(1)	0.049(1)	0.0382(9)	0.297(2)	1.3(4) <sup>a</sup>
H(2)	0.039(1)	-0.0463(8)	0.352(2)	0.8(3) <sup>a</sup>
H(3)	0.152(1)	0.0011(9)	0.104(2)	1.5(4) <sup>a</sup>
H(4)	0.136(1)	-0.084(1)	0.158(2)	1.9(4) <sup>a</sup>
H(5)	-0.195(1)	-0.0841(9)	0.536(2)	2.6(4) <sup>a</sup>
H(6)	-0.212(1)	-0.1391(9)	0.384(2)	2.5(4) <sup>a</sup>
H(7)	-0.113(1)	-0.223(1)	0.494(3)	4.0(5) <sup>a</sup>

<sup>a</sup>Atoms were refined isotropically.



Table 1, continued. Positional parameters and their estimated standard deviations for  
 $C_{22}H_{28}O_{10} \cdot 5$

Atom	x	y	z	B(Å <sup>2</sup> )
H(8)	-0.182(1)	-0.210(1)	0.629(3)	3.5(5) <sup>a</sup>
H(9)	-0.095(1)	-0.169(1)	0.660(3)	4.5(6) <sup>a</sup>
H(10)	-0.112(1)	0.218(1)	0.359(3)	3.3(5) <sup>a</sup>
H(11)	-0.070(1)	0.177(1)	0.523(3)	3.6(5) <sup>a</sup>
H(12)	-0.196(1)	0.101(1)	0.538(3)	4.7(6) <sup>a</sup>
H(13)	-0.209(2)	0.190(1)	0.570(3)	5.0(6) <sup>a</sup>
H(14)	-0.234(2)	0.153(1)	0.393(3)	5.6(6) <sup>a</sup>

<sup>a</sup>Atoms were refined isotropically.

Table 2. Crystal and refinement data for C<sub>22</sub>H<sub>28</sub>O<sub>10</sub>, 5

	Data
Formula	C <sub>22</sub> O <sub>10</sub> H <sub>28</sub>
Formula weight	452.46
Space Group	Pbca
<i>a</i> , Å	16.085(2)
<i>b</i> , Å	18.028(2)
<i>c</i> , Å	7.759(1)
<i>V</i> , Å <sup>3</sup>	2250.0(8)
<i>Z</i>	4
<i>d</i> <sub>calc.</sub> g/cm <sup>3</sup>	1.336
μ(MoK <sub>α</sub> ), cm <sup>-1</sup>	0.990
Data collection instrument	Enraf-Nonius CAD4
Radiation (monoch.; inc. beam)	MoK <sub>α</sub> (λ = 0.71073 Å)
Orientation reflections, no., mg., (2θ)	25, 20-34°
Temperature, °C	22 ± 1
Scan method	θ-2θ
Data col. range, 2θ, deg	0-55
No. unique data, total:	2569

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b R_w = [ \sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2 ]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$^c \text{Quality-of-fit} = [ \sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}}) ]^{1/2}$$

Table 2, continued. Crystal and refinement data for C<sub>22</sub>H<sub>28</sub>O<sub>10</sub>, 5

	Data
with $F_o^2 > 3\sigma(F_o^2)$ :	1408
Number of parameters refined	201
R <sup>a</sup>	0.0324
R <sub>w</sub> <sup>b</sup>	0.0413
Quality-of-fit indicator <sup>c</sup>	1.11

$$^aR = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^bR_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$^c\text{Quality-of-fit} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

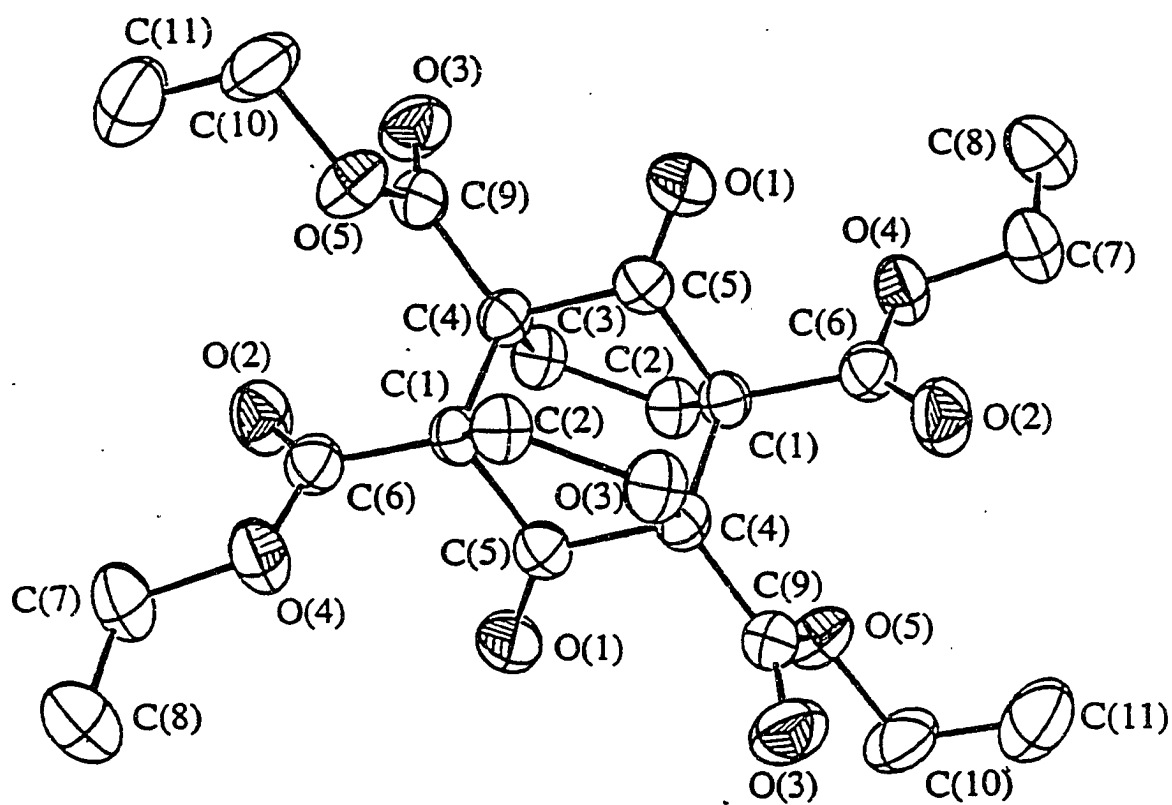
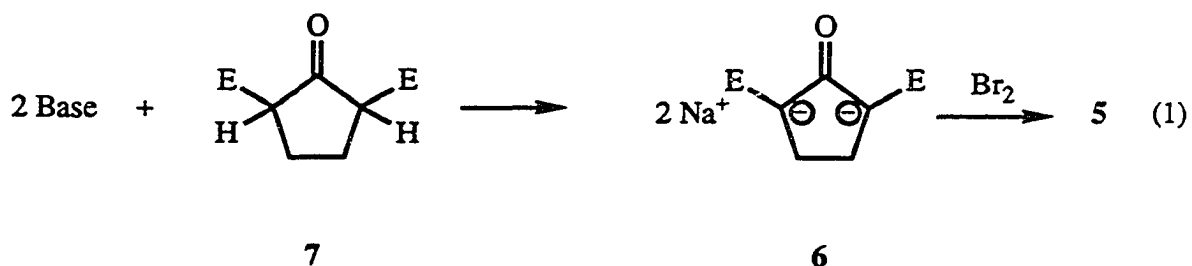


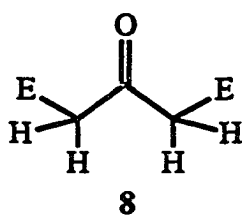
Figure 1. ORTEP drawing of the title molecule, 5: the ellipsoids drawn at the 50% probability level

Yields of **5** up to 22% have been obtained by distillation of the reaction mixture, whereas recrystallization of the oils obtained upon work-up from pentane/ether afforded yields up to 45%.

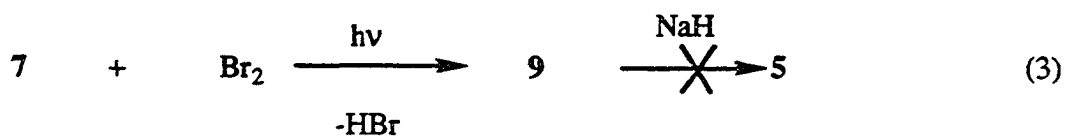
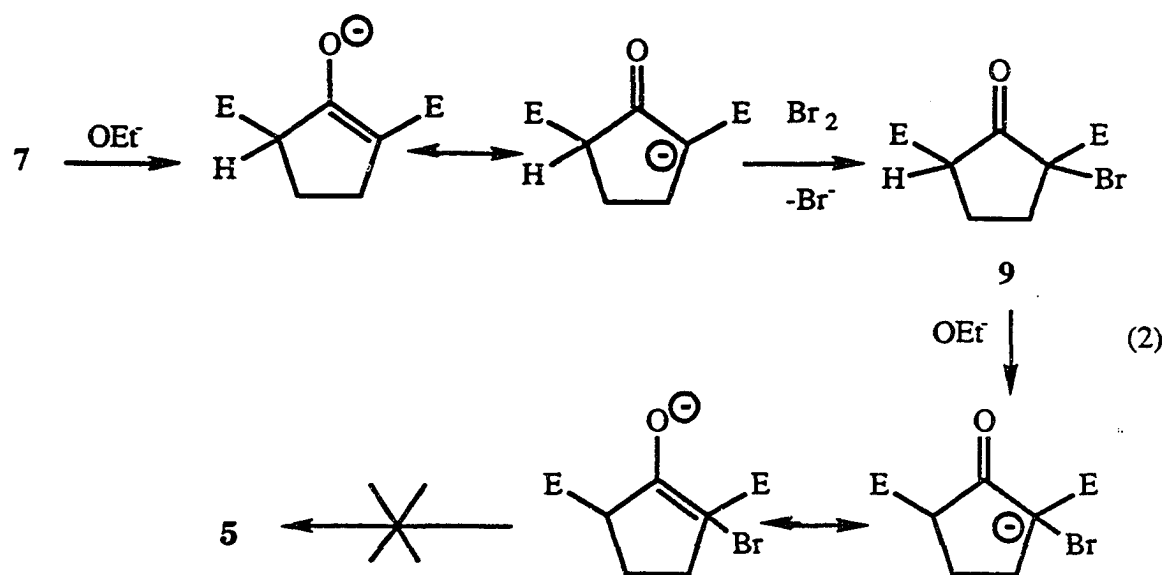
The novel compound **5** can be considered as the oxidatively coupled dimer of dianion **6** (reaction 1) obtained by deprotonation of **7**. Indeed, **7** has been synthesized by aqueous work-up of the reaction mixture obtained by refluxing **3** in EtOH with one

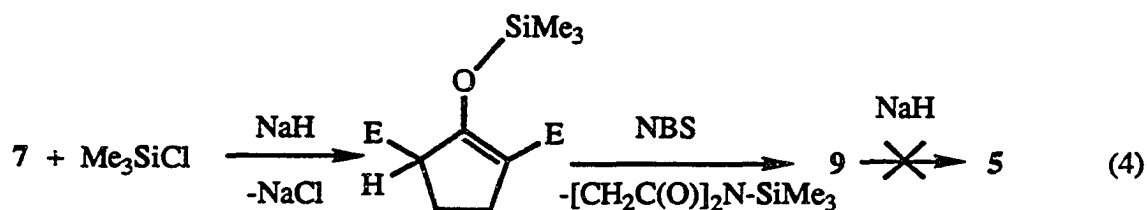


equivalent of NaOEt for 13 hours.<sup>7-10</sup> In this work we prepared dianion **6** by deprotonating **7** with NaH in either THF or DMSO. The formation of **6** was indicated by the disappearance of the resonance associated with the methine proton in **7** in the <sup>1</sup>H NMR spectrum of **6** prepared in THF, and by the shift of the methine carbon signal from 60.8 ppm to 84.1 ppm in the <sup>13</sup>C NMR spectrum of **6**, prepared in DMSO, a shift similar to that reported previously in the dianion of **8**.<sup>11</sup> However, the final step in reaction 1 was



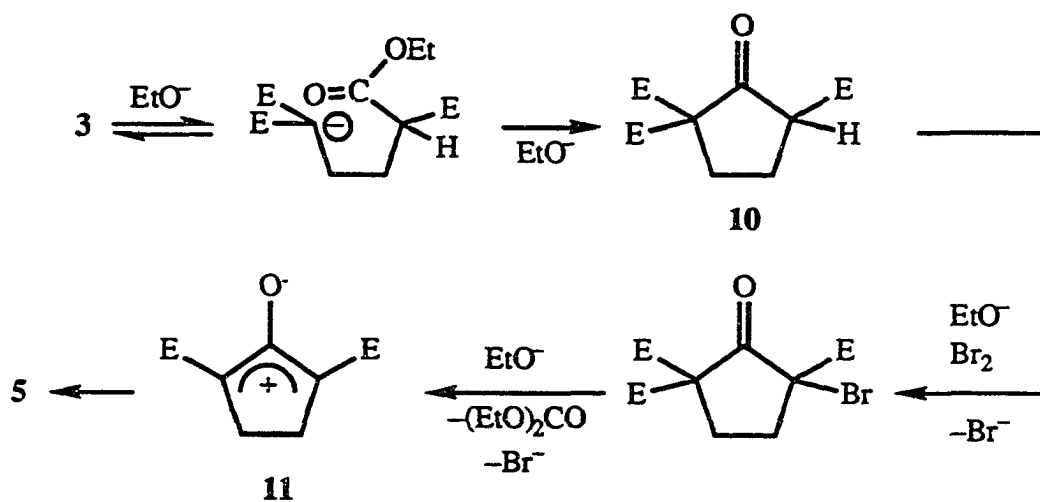
unsuccessful in our hands. Similarly, treatment of **9** in reaction 1 (formed by means of previously reported bromination procedures)<sup>12-14</sup> with bases in reactions 2 - 4 gave no evidence of **5**





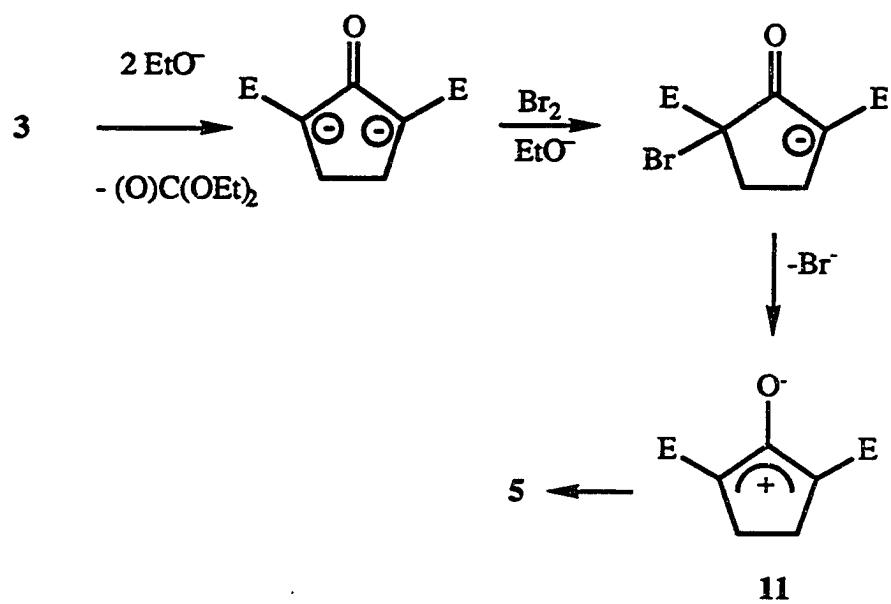
in the  $^1\text{H}$  NMR spectra of the reaction mixtures. It thus becomes tempting to postulate the participation of triester **10** in a pathway such as that shown in Scheme 2.<sup>15</sup> However, we were unable to detect any triester **10** in the GC/mass spectrum of the crude oil obtained after work-up in the synthesis of **7** (see Experimental section). Pending further efforts

Scheme 2



to define the pathway of the novel transformation reported herein, however, other viable pathways such as that shown in Scheme 3 cannot be ruled out.

Scheme 3





## EXPERIMENTAL

All reactions were carried out under dry argon. Ethanol was dried and distilled under nitrogen using a standard procedure.<sup>16</sup> Commercial sodium and bromine were used without further purification. Ethylene dimalonic ester was prepared using a previously reported synthesis.<sup>17</sup> Proton and <sup>13</sup>C spectra were obtained on a Nicolet NT300 instrument.

**Syntheses of 5.** a) This approach duplicates that reported earlier except that the solution of 3, NaOEt and EtOH was refluxed for 16 h. After normal work-up, the final oil was distilled at 0.05 Torr. After collecting a 26% yield of the starting 3 (bp 110 - 115°C) and a 46% yield of 4 (bp 128 - 130 °C), a 13% yield of 5 (bp 190-200°) was obtained. The colorless crystals are air stable and soluble in most organic solvents (m.p. 112-114 °C). The spectroscopic data are as follows: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.23 (12 H, t, <sup>3</sup>J<sub>HH</sub> = 7.12 Hz, CH<sub>3</sub>), δ 2.67 (8H, AA'BB' system, CH<sub>2</sub>CH<sub>2</sub>, <sup>3</sup>J<sub>AA'</sub> = 11.1 Hz, <sup>2</sup>J<sub>A-B</sub> = -5.90 Hz, <sup>3</sup>J<sub>AB'</sub> = 13.9 Hz, <sup>3</sup>J<sub>A'B'</sub> = 12.9 Hz), δ 4.22 ppm (8 H, q, CH<sub>2</sub>-CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.11 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.93 ppm (C-8, C-11, qt, <sup>1</sup>J<sub>CH</sub> = 127.23 Hz, <sup>2</sup>J<sub>CH</sub> = 4.04 Hz), δ 25.4 ppm (C-2, C-3), tt, <sup>1</sup>J<sub>CH</sub> = 138.03 Hz, <sup>2</sup>J<sub>CH</sub> = 5.21 Hz), δ 61.96 ppm (C-7, C-10, tq, <sup>1</sup>J<sub>CH</sub> = 148.32 Hz, <sup>2</sup>J<sub>CH</sub> = 4.05 Hz), δ 64.89 ppm (C-1, C-4, s), δ 167.27 ppm (C-6, C-9, s), δ 201.91 ppm (C-5, t, <sup>3</sup>J<sub>CH</sub> = 6.49 Hz), HRMS- measured m/e: 452.16864 amu, calculated: 452.16825 amu for C<sub>22</sub>H<sub>28</sub>O<sub>10</sub>, error: 0.88 ppm. The AA'BB' <sup>1</sup>H NMR pattern was simulated by computer means. Elemental analysis calculated for C<sub>22</sub>H<sub>28</sub>O<sub>10</sub>: C, 58.4; H, 6.19. Found: C, 57.8; H, 6.16. b) This approach duplicates that reported above, accept that the final oils produced were dissolved in a 1:1 mixture of pentane/Et<sub>2</sub>O. The crystals retrieved from this solution after cooling to -25 °C for 2 days gave a 45% overall yield.

**Preparation of Na<sub>2</sub>(6) in DMSO.** Into a dry 5 mm NMR tube was syringed 0.5 mL of d<sub>6</sub>-DMSO. To this was added 0.010 g (0.42 mmol) of NaH and 0.048 g (0.21 mmol) of 7. The <sup>13</sup>C NMR spectrum of this mixture was collected after the evolution of H<sub>2</sub> was complete: δ 13.9 ppm (CH<sub>3</sub>), δ 24.9 ppm (CH<sub>2</sub>, ring), δ 54.6 ppm (CH<sub>2</sub>, ethyl), δ 84.1 ppm (C, see reference 1), δ 168.27 ppm (CO, ester), δ 205.7 ppm (CO).

**Reaction of Na<sub>2</sub>(6) and bromine.** A solution containing 1.00 g (4.38 mmol) in 10 mL of THF was added dropwise to a suspension containing 0.202 g (8.77 mmol) of sodium in 25 mL of THF. The sodium completely dissolved. An aliquot of this mixture was removed and the volatiles evaporated *in vacuo*. The <sup>1</sup>H NMR spectrum was consistent with Na<sub>2</sub>(6) in that there was no signal corresponding to the methine protons: (CDCl<sub>3</sub>), δ 1.26, δ 1.28 (6H, t, <sup>3</sup>J<sub>HH</sub> = 7.12 Hz, CH<sub>3</sub>), δ 2.31 (4H, m, CH<sub>2</sub>), δ 4.22, δ 4.26 (4H, q, <sup>3</sup>J<sub>HH</sub> = 7.12 Hz, CH<sub>2</sub>). The CDCl<sub>3</sub> was removed *in vacuo*, and the Na<sub>2</sub>(6) was returned to the supernatant before the addition of 0.408 g (4.42 mmol) of bromine. The NaBr was filtered off, the THF was removed *in vacuo*, and the residues were extracted with water and Et<sub>2</sub>O. The organic layers were combined and dried over MgSO<sub>4</sub>, and then the Et<sub>2</sub>O was removed *in vacuo*. There were several ethyl ester signals detected in the <sup>1</sup>H NMR spectrum of the crude oils, but the characteristic AA'BB' pattern corresponding to 5 was undetectable (see the spectroscopic characterization of 5 in the preparation of 5).

**Preparation of 9 and its attempted dimerization, a).** To a solution containing 0.369 g (1.62 mmol) of 7 in 10 mL of CCl<sub>4</sub> in a quartz tube was added 0.130 g (0.81 mmol) of Br<sub>2</sub>. The reaction mixture was exposed to a 254 nm light source. After the mixture had become colorless (~15 minutes) the volatiles were removed *in vacuo* and the residues were neutralized with NaHCO<sub>3</sub>(aq) and extracted with water and Et<sub>2</sub>O. The organic layers were combined and dried over MgSO<sub>4</sub>, followed by the removal of the Et<sub>2</sub>O *in vacuo*. This crude mixture was dissolved in 15 mL of THF and added to a suspension of

0.0780 g ( 3.234 mmol) of NaH in 10 mL of THF. The mixture was worked up as previously discussed in the preparation of **5**. b) A solution containing 0.500 g ( 2.45 mmol) of **7** in 10 mL of THF was added to a suspension of 0.0588 g ( 2.45 mmol) of NaH in 10 mL of THF. This mixture was stirred for 15 minutes before the addition of 0.265 g ( 2.45 mmol) of TMS-Cl in 5 mL of THF. The THF was removed *in vacuo* and the residue was dissolved in hexanes and passed through Celite to remove the NaCl. The hexanes were removed *in vacuo*, producing 0.578 g of **9** ( 85% yield). The <sup>1</sup>H MNR of the residue was consistent with **10** and approximately 15% TMS-Cl as an impurity: (CDCl<sub>3</sub>) δ -0.01 ( 3H, s, TMS-Cl), δ 0.41 ( 9H, s, TMS), δ 1.27, δ 1.31 (6H, t, <sup>3</sup>J<sub>HH</sub> = 7.13 Hz, CH<sub>3</sub>), δ 2.31 ( 4H, m, CH<sub>2</sub>), δ 3.26 (1H, m, CH), δ 4.32, δ 4.26 (4H, q, <sup>3</sup>J<sub>HH</sub> = 7.12Hz, CH<sub>2</sub>).

**Reaction of crude 10 with NBS.** To a solution containing 0.726 g ( 2.057 mmol, assuming 85% purity) of **9** in 15 mL of THF was added 0.351 g ( 2.057 mmol) of NBS in 5 mL of THF. The mixture was stirred for 30 minutes. The THF was removed *in vacuo* and the residue was dissolved in 15 mL of hexanes ( the resulting solution was turbid due to the low solubility of the [CH<sub>2</sub>C(O)]<sub>2</sub>N-TMS). This solution was passed through a silica gel column, using a slight over pressure of argon. The TLC experiments of all the fractions removed gave only one spot ( most of the [CH<sub>2</sub>C(O)]<sub>2</sub>N-TMS likely stuck to the column due to its high polarity). The fractions were combined and the hexanes were removed *in vacuo*, producing 0.47 g of **9** ( 74% yield). The <sup>1</sup>H NMR spectrum was consistent with **9** and approximately 5% [CH<sub>2</sub>C(O)]<sub>2</sub>N-TMS as an impurity: (CDCl<sub>3</sub>) δ 1.27, δ 1.31 (6H, t, <sup>3</sup>J<sub>HH</sub> = 7.13 Hz, CH<sub>3</sub>), δ 2.31 ( 4H, m, CH<sub>2</sub>), δ 3.26 (1H, m, CH), δ 4.32, δ 4.26 (4H, q, <sup>3</sup>J<sub>HH</sub> = 7.12Hz, CH<sub>2</sub>), δ 0.41 ( 1H, s, TMS), δ 2.31, δ 3.26 (0.4H, [ CH<sub>2</sub>C(O)]<sub>2</sub>N, ring). All of the residues containing **9** ( 0.47 g, 1.45 mmol, assuming 95% purity) were dissolved in 10 mL of THF and added to a suspension of 0.38 g ( 1.6 mmol) of NaH in 10 mL of THF. The mixture was stirred for 2 hours, then worked

up as was the previous dimerization attempt. There were several ethyl ester signals detected in the  $^1\text{H}$  NMR spectrum of the crude oils, but the characteristic AA'BB' pattern corresponding to **5** was undetectable ( see the spectroscopic characterization of **5** in the preparation of **5**).

**An attempt to detect 10.** A solution containing 52.62 g ( 0.164 mole) of **3** in 150 mL of EtOH was added dropwise to a solution containing 4.11 g ( 0.179 mole) of sodium in 50 mL of EtOH. This mixture was refluxed for 16 hours, followed by the standard aqueous work-up.<sup>7-10</sup> The GC/mass spectrum of the resulting oil gave 4 fractions with the following parent ions: fraction I: m/e 118.2 amu ( (O)C(OEt)<sub>2</sub>); fractions II and III: m/e 228.2 amu ( **7**, *cis*- and *trans*- isomers); fraction IV: 320.1 amu (**3**).

**Crystal structure determination.** A colorless crystal of **5** of dimensions 0.4 x 0.4 x 0.3 nm was mounted on a glass fiber; no precautions against atmospheric moisture and oxygen were employed. The orthorhombic cell parameters were  $a = 16.085(\text{s}) \text{ \AA}$ ,  $b = 18.028(2) \text{ \AA}$  and  $c = 7.759(1) \text{ \AA}$ . A total of 4937 reflections were collected in the +h, +k,  $\pm$ l quadrant, of which 2569 were unique and not systematically absent, indicating a Pbcu space group. The agreement factors for the averaging of the observed and accepted reflections were 1.7% and 1.9% based on the intensity and on  $F_{\text{obs}}$ , respectively. The relevant data collection information is listed in Table 2.

The direct methods E-map revealed all of the 16 unique non-hydrogen atoms.<sup>18</sup> A difference map was used to locate all hydrogen positions following least-squares convergence of the non-hydrogen atoms using isotropic thermal parameters.<sup>19</sup>

The final refinement cycles included 102 variable parameters fitted to 1408 observed data. These parameters converged with unweighted and weighted agreement factors of  $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0324$  and  $R_w = [\sum_w (|F_o| - |F_c|)^2 / \sum_w |F_o|^2]^{1/2} = 0.0413$ , respectively.

Refinement calculations were performed on a Digital Equipment Corp. Micro VAXII computer using the CAD4-SDP programs.<sup>20</sup>

**Acknowledgement.** The authors are grateful to the donors of the Petroleum Research Fund administered by the American Chemical Society and to the National Science Foundation for grant support of this research and to Dr. Lee M. Daniels of the Iowa State Molecular Structure Laboratory for the X-ray structure determination.

**Supplementary Material Available:** Tables of bond lengths, bond distances, general displacement parameters and structure factors (7 pages).

## REFERENCES

1. Davis, R. and Verkade, J. G. *Inorg. Chem.*, accepted.
2. Davis, R. V.; Wintergrass, D. J.; Janikaraman, M. N.; Hyatt, E. M.; Jacobson, R. A.; Daniels, L. M.; Wroblewski, A.; Padmakumari Amma, J.; Das, S. K. and Verkade, J. G. *Inorg. Chem.*, in press.
3. Ye, M.-C.; Verkade, J. G., manuscript in progress.
4. Weinges, K.; Klessing, K.; Kolb, R. *Chem. Ber.* **1973**, *106*, 2298.
5. Buchta, E.; Billenstein, S. *Leibig. Ann. Chem.* **1967**, *702*, 38.
6. Weinges, K.; Wiesenhütter, A. *Leibig. Ann. Chem.* **1971**, *746*, 70.
7. Kierstead, R. W.; Linstead, R. P.; Weedon, B. C. L. *J. Chem. Soc.* **1952**, *155*, 3616.
8. Nandi, J. *J. Indian Chem. Soc.* **1934**, *11*, 277.
9. Muncke, E. R.; Cox, R. F. B.; McElvain, S. M. *J. Am. Chem. Soc.* **1935**, *57*, 1133.
10. Guha, P. C.; Seshadriengar, N. K. *Chem. Ber.* **1936**, *69*, B, 1212.
11. Lambert, J. B.; Wharry, S. M. *J. Chem. Soc., Chem. Comm.*, **1978**, 172.
12. Blanco, L.; Amice, P.; Conia, J. M. *Synthesis*, **1976**, 194.
13. Palmer, C. S.; McWherter, P. W. *Organic Syn., Coll. Vol. I*, **1944**, 245.
14. Reuss, R. H.; Hassner, A. *J. Org. Chem.*, **1974**, *39*, 1785.
15. Baretta, A.; Waegell, B. *Reactive Intermed.*, **1982**, *2*, 527.
16. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, Pergamon Press: New York, 1988, p. 174.
17. Noyes, W. A.; Kyriakides, L. P. *J. Am. Chem. Soc.* **1910**, *32*, 1057.
18. SHELX-86, Sheldrick, G. M. Institute für Anorganische Chemie der Universität, Grotten, F.R.G.

19. Neutral-atom scattering factors and anomalous scattering corrections were taken from *International Tables for X-ray Crystallography*; The Kynock Press: Birmingham, England 1974; Vol. IV.
20. Enraf-Nonius Structure Determination Package; Enraf-Nonius: Delft, Holland.

## APPENDIX

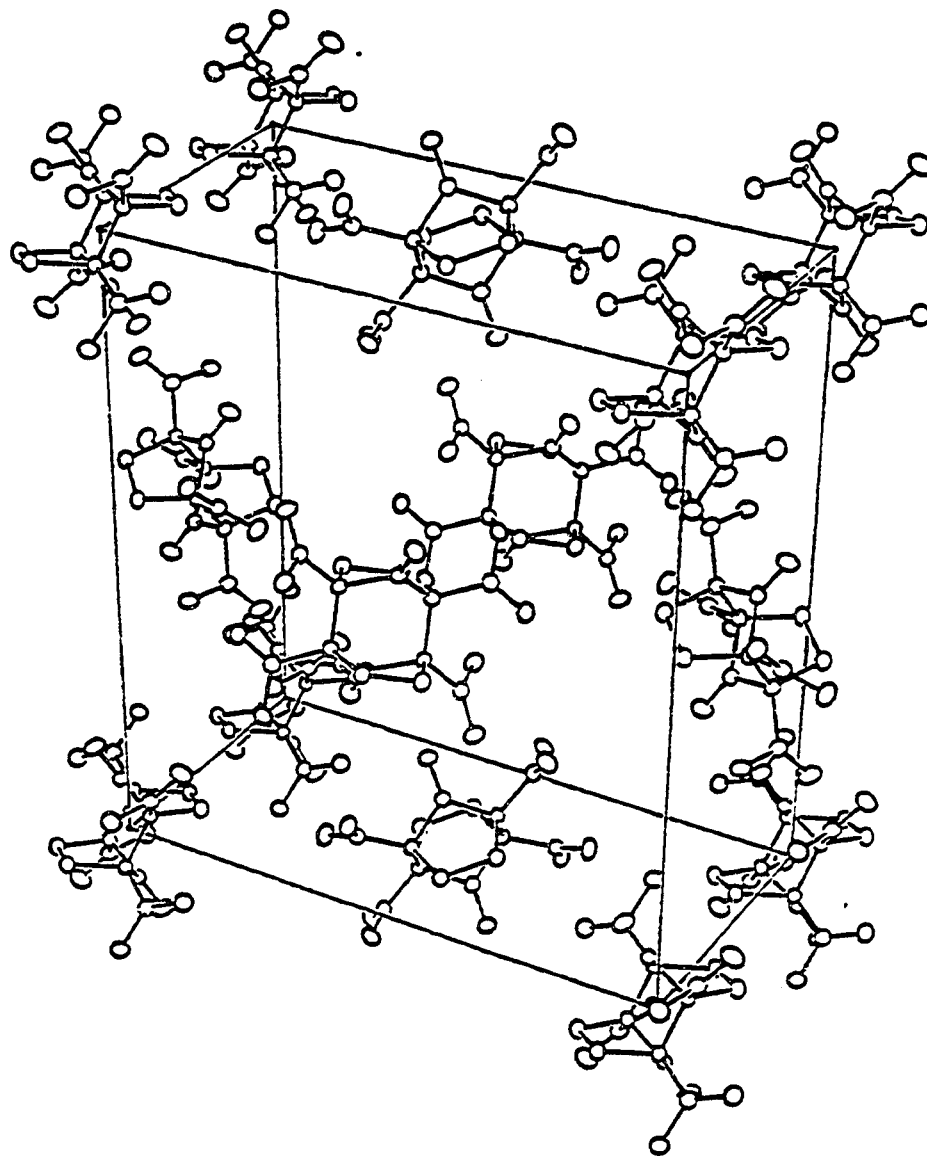


Figure 2. ORTEP representation of the unit cell, with ellipsoids scaled to enclose 30% of the electron density: terminal ethyl groups omitted for clarity.



Table 3. Bond distances (Å) for C<sub>22</sub>H<sub>28</sub>O<sub>10</sub>, 5

Atom 1	Atom 2	Distance
O(1)	C(5)	1.194(2)
O(2)	C(6)	1.199(2)
O(3)	C(9)	1.193(2)
O(4)	C(6)	1.326(2)
O(4)	C(7)	1.460(2)
O(5)	C(9)	1.336(2)
O(5)	C(10)	1.458(2)
C(1)	C(2)	1.550(2)
C(1)	C(4)	1.573(2)
C(1)	C(5)	1.533(2)
C(1)	C(6)	1.515(2)
C(2)	C(3)	1.559(2)
C(2)	H(1)	1.00(2)
C(2)	H(2)	0.96(2)
C(3)	C(4)	1.540(2)
C(3)	H(3)	1.00(2)
C(3)	H(4)	1.00(2)
C(4)	C(5)	1.536(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3, continued. Bond distances (Å) for C<sub>22</sub>H<sub>28</sub>O<sub>10</sub>, 5

Atom 1	Atom 2	Distance
C(4)	C(9)	1.519(2)
C(7)	C(8)	1.487(3)
C(7)	H(5)	0.98(2)
C(7)	H(6)	0.95(2)
C(8)	H(7)	0.97(2)
C(8)	H(8)	0.93(2)
C(8)	H(9)	1.05(2)
C(10)	C(11)	1.483(3)
C(10)	H(10)	0.96(2)
C(10)	H(11)	0.99(2)
C(11)	H(12)	1.00(2)
C(11)	H(13)	0.94(2)
C(11)	H(14)	0.99(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 4. Bond angles (deg) for C<sub>22</sub>H<sub>28</sub>O<sub>10</sub>, 5

Atom 1	Atom 2	Atom 3	Angle
C(6)	O(4)	C(7)	116.5(1)
C(9)	O(5)	C(10)	116.8(1)
C(2)	C(1)	C(4)	112.3(2)
C(2)	C(1)	C(5)	99.4(2)
C(2)	C(1)	C(6)	117.7(2)
C(4)	C(1)	C(5)	105.2(2)
C(4)	C(1)	C(6)	110.9(1)
C(5)	C(1)	C(6)	110.0(1)
C(1)	C(2)	H(1)	109.3(9)
C(1)	C(2)	C(3)	106.2(1)
C(1)	C(2)	H(2)	110(1)
C(3)	C(2)	H(1)	112(1)
C(3)	C(2)	H(2)	112(1)
H(1)	C(2)	H(2)	108(1)
C(2)	C(3)	C(4)	106.4(1)
C(2)	C(3)	H(3)	113(1)
C(2)	C(3)	H(4)	111(1)
C(4)	C(3)	H(3)	111(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 4, continued. Bond angles (deg) for C<sub>22</sub>H<sub>28</sub>O<sub>10</sub>. 5

Atom 1	Atom 2	Atom 3	Angle
C(4)	C(3)	H(4)	107(1)
H(3)	C(3)	H(4)	108(1)
C(1)	C(4)	C(3)	112.5(1)
C(1)	C(4)	C(5)	105.4(1)
C(1)	C(4)	C(9)	114.2(1)
C(3)	C(4)	C(5)	99.6(1)
C(3)	C(4)	C(9)	113.6(1)
C(5)	C(4)	C(9)	110.1(1)
O(1)	C(5)	C(1)	127.9(1)
O(1)	C(5)	C(4)	127.6(1)
C(1)	C(5)	C(4)	104.4(2)
O(2)	C(6)	O(4)	125.0(1)
O(2)	C(6)	C(1)	124.0(2)
O(4)	C(6)	C(1)	111.0(1)
O(4)	C(7)	C(8)	107.3(2)
O(4)	C(7)	H(5)	106(1)
O(4)	C(7)	H(6)	107(1)
C(8)	C(7)	H(5)	114(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 4, continued. Bond angles (deg) for C<sub>22</sub>H<sub>28</sub>O<sub>10</sub>, 5

Atom 1	Atom 2	Atom 3	Angle
H(5)	C(7)	H(6)	114(1)
C(7)	C(8)	H(7)	109(1)
C(7)	C(8)	H(8)	109(1)
C(7)	C(8)	H(9)	111(1)
H(7)	C(8)	H(8)	109(2)
H(7)	C(8)	H(9)	110(2)
H(8)	C(8)	H(9)	109(2)
O(3)	C(9)	O(5)	124.5(2)
O(3)	C(9)	C(4)	123.5(2)
O(5)	C(9)	C(4)	111.9(1)
O(5)	C(10)	C(11)	110.6(2)
O(5)	C(10)	H(10)	106(1)
O(5)	C(10)	H(11)	105(1)
C(11)	C(10)	H(10)	112(1)
C(11)	C(10)	H(11)	111(1)
H(10)	C(10)	H(11)	112(2)
C(10)	C(11)	H(12)	113(1)
C(10)	C(11)	H(13)	106(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

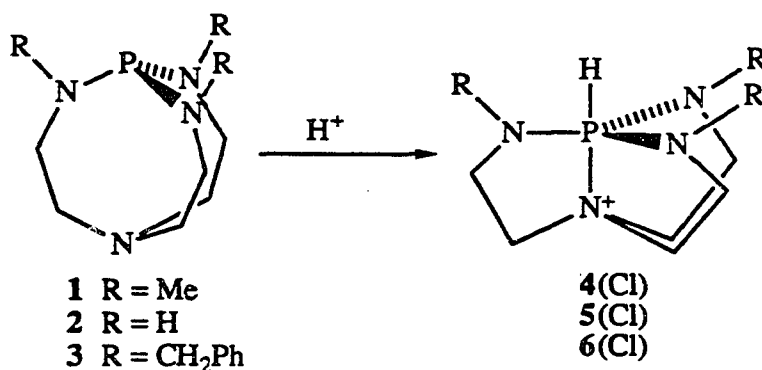
Table 4, continued. Bond angles (deg) for  $C_{22}H_{28}O_{10}$ , 5

Atom 1	Atom 2	Atom 3	Angle
C(10)	C(11)	H(14)	109(1)
H(12)	C(11)	H(13)	114(2)
H(12)	C(11)	H(14)	105(2)
H(13)	C(11)	H(14)	110(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

## THESIS SUMMARY AND SUGGESTIONS FOR FUTURE WORK

The first report of isolated azaphosphatranes and pro-azaphosphatranes was from these laboratories in 1989.<sup>1</sup> Since then, the only reported research on pro-azaphosphatranes (1 - 3) and azaphosphatranes (4 - 6) is presented either in four papers



published from 1989 to 1990, 2-5 or in one of the first four parts presented in this manuscript. The pro-azaphosphatranes feature an unusually high basicity and, in the case of **1**, an unusual redox reactivity, as presented in Part IV. In light of the results reported in this manuscript and of some very preliminary results recently obtained, possibilities for the future direction of this work may be proposed.

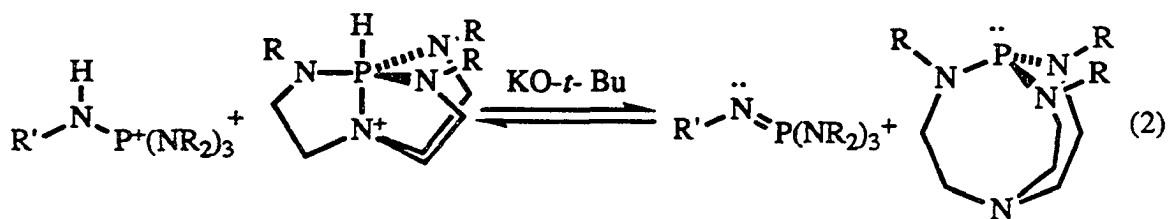
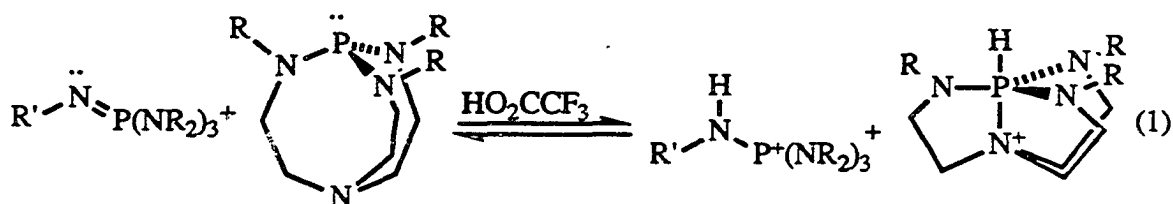
**Relative basicities of pro-azaphosphatranes and triamino(imido)phosphoranes.** As discussed previously in Parts I and II of this thesis, the pro-azaphosphatranes are extremely basic for phosphorus(III) species, with the site of protonation being the phosphorus. The peralkylated triamino(imino)phosphoranes, **7**, have also been reported to feature extremely high basicities,<sup>6</sup> however these are phosphorus(V) species with the site



7

of protonation being the imino nitrogen. Both the pro-azaphosphatranes and the triamino(imino)phosphoranes have been determined to be significantly more basic than DBU (1,4-diazabicyclo[5.4.0]undec-7-ene).<sup>2,6</sup>

It would be interesting to compare the basicities of the pro-azaphosphatranes with the triamino(imino)phosphoranes by both competitive protonations ( reaction 1) and competitive deprotonations ( reaction 2) using an acid such as  $\text{HO}_2\text{CCF}_3$  and a base such as  $\text{KO}-t\text{-Bu}$ , respectively. These reactions could then be monitored by  $^{31}\text{P}$  NMR.

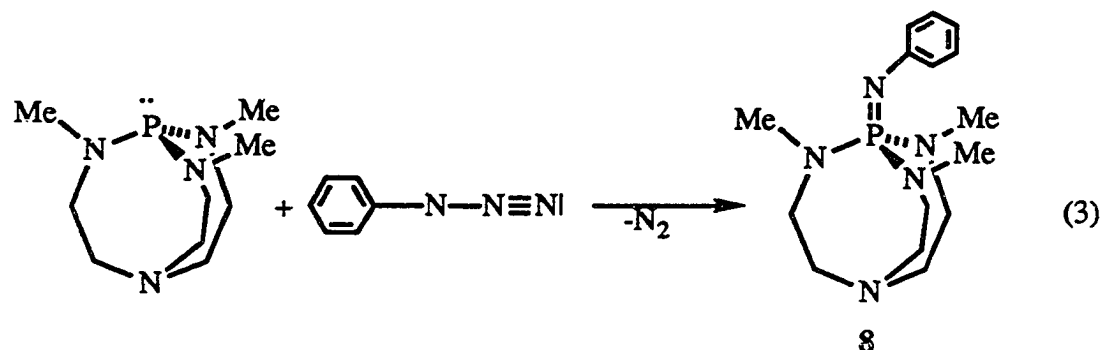


It would also be interesting to determine the relative basicities of the triamino(imino)phosphoranes with an imino derivative of 1 using the above reactions.



Phenyl(imino)trimethyl-azaphosphatrane, **8**, has been prepared according to reaction 3.<sup>7</sup>

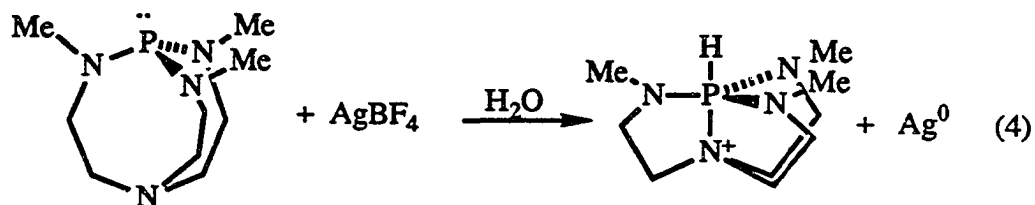
From the unremarkable <sup>31</sup>P NMR chemical shift of **8** ( 15 ppm) and the lack of



heteronuclear spin-spin coupling between the phosphorus and the  $N_{ax}CH_2$  carbons, it has been determined that little, if any, bridgehead-bridgehead interaction exists in the molecule. Upon protonation (likely at the imino nitrogen), however, the increased positive charge at the phosphorus may cause the axial nitrogen to coordinate to the phosphorus, thereby forming the three chelate rings and the 3-center-4-electron molecular orbital system, the likely stabilizing factors in azaphosphatranes.<sup>1-5</sup> The possible ability of **8** to transannulate upon protonation may cause its basicity to be higher than the acyclic triamino(imino)phosphoranes.

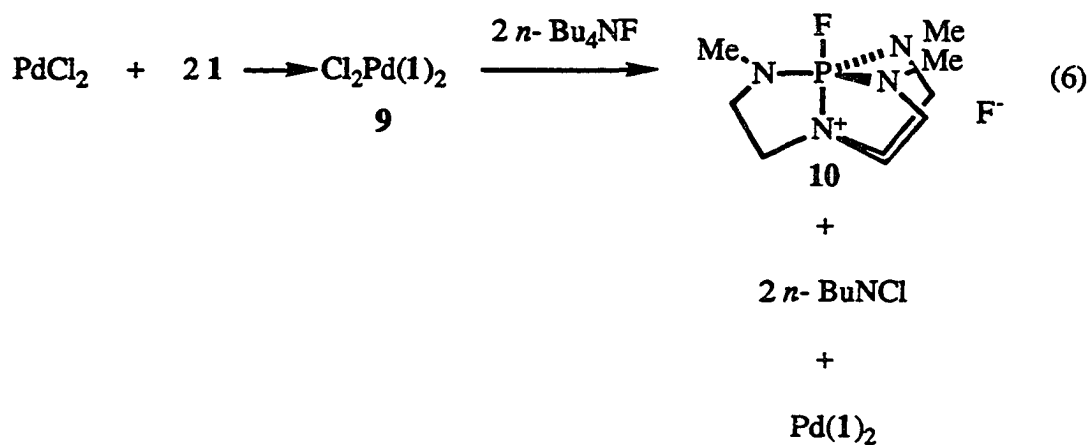
#### Redox chemistry of $P(NMeCH_2CH_2)_3N$ producing new azaphosphatrane derivatives.

The unusually high basicity of **1** is thought to be responsible for the unusual redox behavior it demonstrates with mercury(II), as seen in Part IV. In NMR scale reactions, **1** has also been found to reduce silver(I), reaction 4, and to disproportionate cobalt(II),



reaction 5. The reduction of silver is very similar to what was observed upon the reaction of **1** with mercuric tetrafluoroborate, reported in Part IV, and the cobalt(II) disproportionation was also reported previously in reactions of  $\text{Co}(\text{BF}_4)_2(\text{DMSO})_6$  with phosphites.<sup>8</sup>

The ability of **1** to reduce certain metals also may apply to palladium(II) compounds. A complex such as  $\text{Cl}_2\text{Pd}(\mathbf{1})_2$  (**9**) might be prepared from  $\text{PdCl}_2$  and **1**, a reaction similar to that used in the synthesis of  $\text{Cl}_2\text{Pt}(\mathbf{1})_2$ .<sup>2</sup> In the presence of a fluoride source, **9** may decompose to give  $\text{Pd}(\mathbf{1})_2$  and **10**, the fluoronium fluoride of **1**, reaction 6. A similar



reaction has been recently investigated for phosphines by Mason and Verkade,<sup>9</sup> and may present a convenient route to **9**, **10**, and  $\text{Pd}(\mathbf{1})_2$ , three new derivatives of **1**.

**General summary.** Each section of this manuscript presents results that were surprising. The basicity order found for the prophosphatranes in Parts I and II is anomalous with respect to what would be expected using inductive reasoning. In Part III the attempts to prepare  $(\text{Me}_2\text{N})_2\text{PHNMeCH}_2\text{CH}_2\text{N}^+\text{Me}_2$ , a pseudo phosphatrane with only one chelate ring, gave instead the phosphonium ion  $(\text{Me}_2\text{N})(\text{:})\text{PNMeCH}_2\text{CH}_2\text{N}^+\text{Me}_2$ . The redox chemistry presented in Part IV and the formation of the new tetraester in Part V were also unexpected. As a whole the work that has been presented herein is an excellent example of serendipity.

#### References.

1. Schmidt, H.; Lensink, C.; Xi, S.-K.; Verkade, J. G. *Zeitschr. anorg. allg. Chem.*, **1989**, *578*, 75.
2. Xi, S.-K.; Schmidt, H.; Lensink, C.; Kim, S.; Wintergrass, D.; Daniels, L. M.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1990**, *29*, 2214.

3. Schmidt, H.; Xi, S.-K.; Lensink, C.; Verkade, J. G. *Phosphorus, Sulfur, and Silicon*, **1990**, *49/50*, 163.
4. Gudat, D.; Lensink, C.; Schmidt, H.; Xi, S.-K.; Verkade, J. G. *Phosphorus, Sulfur, and Silicon*, **1989**, *41*, 21.
5. Lensink, C.; Xi, S.-K.; Daniels, L. M.; Verkade, J. G. *J. Amer. Chem. Soc.*, **1989**, *111*, 3478.
6. Scwesinger, R. *Chimia*, **1985**, *39*, 269.
7. Schmidt, H.; Verkade, J. G., to be published.
8. Verkade, J. G.; Piper, T. S. In *Advances in the Chemistry of the Coordination Complexes*; Kirschner, S., Ed.; Macmillan: New York, 1961; p. 634.
9. Mason, M. R.; Verkade, J. G. *Organometallics*, **1990**, *9*, 864.

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