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Synthesis, structure features and application of pro-azaphsphatranes as catalysts and strong non-ionic bases in organic synthesis

Jiansheng Tang
Iowa State University

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Tang, Jiansheng, Ph.D.

Iowa State University, 1994

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

Synthesis, structure features and application of pro-azaphsphatranes as catalysts and strong non-ionic bases in organic synthesis

by

Jiansheng Tang

A Dissertation Submitted to the
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Major: Organic Chemistry

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Signature was redacted for privacy.
In Charge of Major Work

Signature was redacted for privacy.
For the Major Department

Signature was redacted for privacy.
For the Graduate College

Iowa State University
Ames, Iowa

1994

DEDICATION

To my wife, son, parents, brother and sisters for their love

and to the memory of my father

TABLE OF CONTENTS

GENERAL INTRODUCTION

An Explanation of the Dissertation Organization. This dissertation contains nine sections. The first section is a general introduction containing a statement of the project and an outline of the goals of the research described herein. Each of the subsequent seven sections (paper 1 to paper 7) represents research results as they have been published or submitted for journal publication. The numbering of compounds, figures, schemes, tables and references are independent in each paper. The final section is a summary of the results achieved, some suggestions for additional research and references. All contributors to the work presented herein are acknowledged in each chapter and a general acknowledgment is presented in the end of the dissertation.

A Statement of the Research Project. Phosphorus is ubiquitous in our world. It is the key element in the genetic tape that guides the reproduction of all species. It is essential to all forms of life. It is one of the major elements found in many solid-state metal materials such as GaP and InP. Its salts leaven our food , and clean our teeth and water. Its organic derivatives reduce the flammability of materials around us, kill insects and bacteria as highly effective but low toxicity pesticides, and kill cancers as chemo-therapeutics. In other words, the application of phosphorus compounds impacts virtually every area of "everyday living".[1] In a more basic sense, its chemistry, which is so important in life, provides many conceptual challenges in topics from unusual bonding patterns and stereochemistry to reaction kinetics that control important chemical processes.

Since the end of the 19th century, the study of organic phosphorus compounds has developed at an ever increasing rate. One can identify, however, several periods in subsequent years where important discoveries have led to rapid increases in interest in phosphorus compounds. The discovery of the toxic and insecticidal properties of such compounds by

Schrader and others[2] in 1930s has created a whole new industry. Reports[3] in the 1950s of the conversion of carbonyl compounds to alkenes by Wittig opened a completely new area in the use of organic phosphorus compounds in organic synthesis. The Wittig reaction in which triphenyl phosphine is involved was recognized with a Nobel Prize. This reaction along with the Horner-Emmons modification[4] continues to be an important tool for the carbon-carbon bond construction in modern synthetic organic chemistry. Other synthetically useful reactions coupled with phosphorus(III) compounds into phosphorus(V) compounds includes the Michaelis-Abuzov reaction[5], the reactions using reagents formed by the combination of tertiary phosphines or triaryl phosphite with carbon tetrahalides or with halogens,[6] the Mukaiyama redox condensation[7] and the Mitsunobu esterification reaction.[8] The use of effective phosphorus ligands in homogeneous catalysis opened up another new area in the use of phosphorus compounds in synthetic organic chemistry.[9] In fact, use of a chiral phosphorus-Rh(I) complex introduced in Monsanto's L-Dopa synthesis in 1970's is the first commercialized catalytic asymmetric process.[10] In the late 1980's, Schwesinger reported the tetraphosphazene P_4-*t*-Bu (i.e. *t*-BuN=P[N=P(NMe_2)$_3$]$_3$) to be the strongest non-ionic base.[11] This discovery opened up a third area of the use of organophosphorus compounds in synthetic organic chemistry[12] which was recognized with the 1992 Fluka new reagent prize. However, P_4-*t*-Bu is very difficult to synthesize and, though commercially available, it is very expensive.

Since the late 1970s, the chemistry of atranes of groups 13 to 15 and also many metallic examples has been extensively explored by the Verkade group and others[13] because of its intrinsic interest and the possibility that volatile examples may serve as precursors for metal and non-metal nitrides for a variety of electronic applications and as hard-surface coatings for protection against corrosion and wear. In addition, pro-phosphatranes[14] and pro-azaphosphatranes[15] have also been synthesized and found to be bases stronger than the medium strong non-ionic base Proton Sponge.[16] However, their actual basicities were not

measured and their applications as non-ionic superbases and catalysts in synthetic organic chemistry were not yet exploited.

The focus of this dissertation is the development of pro-azaphosphatranes into useful synthetic reagents. We were interested in: (1) determining how the basicity of pro-azaphosphatrane $P(MeNCH_2CH_2)_3N$ compared with P4-*t*-Bu and how the basicity and transannulation capability of $P(MeNCH_2CH_2)_3N$ change when $P(MeNCH_2CH_2)_3N$ is transformed into a phosphazene $RN{=}P(MeNCH_2CH_2)_3N$. In addition, we wished to learn how the basicity of the latter compound compared with their acyclic analogues and with P4-*t*-Bu as well as with DBU which is a medium strong non-ionic base that has been widely used in synthetic organic chemistry.[17] (2) developing a new easier and more economical process for the synthesis of $P(MeNCH_2CH_2)_3N$. (3) exploring the application of $P(MeNCH_2CH_2)_3N$ as a superior non-ionic proton abstraction reagent in organic synthesis to determine if there were any advantages of $P(MeNCH_2CH_2)_3N$ over traditional medium strong non-ionic bases such as DBU or the strong non-ionic base P_4-*t*-Bu. (4) exploring the fundamental chemistry of pro-azaphosphatranes such as their reaction patterns, and the flexibility of the bridgehead P-N_{ax} transannulation bond with an eye toward tuning the interbridgehead distance by varying the steric and electronic properties of the axial substituents. These fundamental studies have led to our discoveries that $P(MeNCH_2CH_2)_3N$ is a superior catalyst for the conversion of isocyanates to industrially important isocyanurates and isocyanurate-based polymers, and that oxide and sulfide derivatives of $P(MeNCH_2CH_2)_3N$ are much stronger catalysts than their acyclic analogues in the selective conversion of isocyanates to carbodiimides.

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PAPER 1. AN IMPROVED SYNTHESIS OF THE STRONG BASE $P(MeNCH_2CH_2)_3N$

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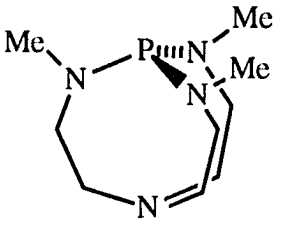
ABSTRACT

The proazaphosphatrane $P(MeNCH_2CH_2)_3N$ is synthesized in high yield from $(HMeNCH_2CH_2)_3N$ and $ClP(NEt_2)_2$. The last compound is synthesized from inexpensive PCl_3 and $HNEt_2$.

COMMUNICATION

Strong non-ionic bases play an important role in organic synthesis because of the milder reaction conditions they generally permit,[1] the enhanced reactivity of the more naked anions in the poorly associated ion pairs formed upon substrate deprotonation by such bases (in contrast to ionic bases),[2] and the better solubility of non-ionic bases in organic solvents at room temperature and below required for some reactions.[3] Compound **1** is a very useful



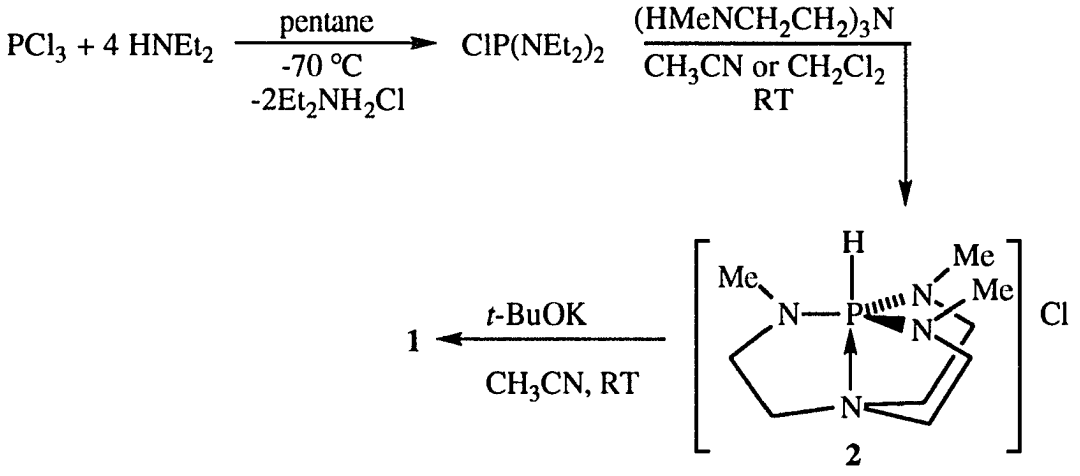
1

exceedingly strong non-ionic base[4] as well as a superior catalyst for the conversion of isocyanates to industrially relevant isocyanurates.[5] We earlier reported the synthesis of **1** from $ClP(NMe_2)_2$,[4] which was formed from PCl_3 and the relatively quite expensive reagent $P(NMe_2)_3$. It was therefore deemed important to design a more economical and efficient method to synthesize **1** in order to facilitate its wider utilization. Here we report that **1** can be synthesized in high yield from $(HMeNCH_2CH_2)_3N$ and $ClP(NEt_2)_2$.[6,7] The latter compound is about 800 times cheaper per mole than $P(NMe_2)_3$, thus rendering the synthesis of $ClP(NEt_2)_2$ over 130 times cheaper than $ClP(NMe_2)_2$ on a molar basis.

The reaction of one molar equivalent of $(HMeNCH_2CH_2)_3N$[4b] with $ClP(NEt_2)_2$ in Scheme 1 gave ^{31}P and ^1H NMR spectroscopically pure **1** in 81% yield In a one-pot synthesis. Although $ClP(NEt_2)_2$ is more sterically hindered than $ClP(NMe_2)_2$, it is still sufficiently reactive to complete its condensation with $(HMeNCH_2CH_2)_3N$ in 1 h. New

applications of **1** and its derivatives in organic synthesis as a potent proton abstractor or catalyst are currently being investigated in our laboratories.

Scheme 1



The one-pot synthesis of **1** is initiated by adding via a syringe to a stirred solution of $ClP(NEt_2)_2$ (5.5 g, 26 mmol) in 100 mL of dry CH_3CN 5.0 g of $(HNMeCH_2CH_2)_3N$ (26 mmol) over 5 min. After stirring the reaction mixture at RT for 1 h, the solution (which showed only a ^{31}P NMR resonance for **2** at -9.53 ppm) was transferred by syringe or cannula to a 500 mL flask containing *t*-BuOK (4.8 g, 42 mmol) in dry CH_3CN (20 mL). After stirring the reaction mixture for 1 h at room temperature, the solvent was removed under vacuum and the residue was extracted overnight while stirring with 480 mL of dry pentane which was transferred in by cannula. The extract was transferred by cannula to another flask and evaporated in vacuo to remove pentane to give a white solid which was purified by vacuum sublimation (50 °C/1 Torr) to give ^{31}P NMR and ^{1}H NMR spectroscopically pure proazaphosphatrane **1** (4.6 g, 81%).

ACKNOWLEDGMENTS

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7. $ClP(NEt_2)_2$ was synthesized according to reference 6 with the modifications that dry benzene was used as the reaction solvent, and the salt formed was removed by filtration under vacuum using a medium frit in a closed system protected from moisture and was washed several times with dry pentane under nitrogen. As a result, the yield was raised from 71% to 85%.

SUPPLEMENTARY MATERIALS

Alternative methods for the synthesis of 1 and 2. To a stirred solution of $ClP(NEt_2)_2$ (5.5 g, 26 mmol) in dry CH_2Cl_2 (50 mL) was added by syringe $(HNMeCH_2CH_2)_3N$ (5.0 g, 26 mmol) over 5 min. After stirring the reaction mixture at room temperature for 1 h, the solvent was removed in vacuo. The residue was recrystallized from $CHCl_3$ (30 mL) and pentane (30 mL) in a freezer overnight. The supernatant was removed by filtration in vacuo. The white solid was dried in vacuo at 60 °C overnight to give [**2**]Cl (6.1 g, 91%). ^{31}P NMR (CD_3CN): δ -9.51; ^1H NMR ($CDCl_3$): δ 2.62 (d, 9 H, NCH_3, $^3J_{PH}$ = 17.4 Hz), 3.03 (dt, 6 H, $N_{ax}CH_2$, $^3J_{PH}$ = 11.0 Hz, $^3J_{HH}$ = 6.2 Hz), 3.59 (dt, 6 H, $N_{eq}CH_2$, $^3J_{PH}$ = 4.7 Hz, $^3J_{HH}$ = 6.2 Hz), 5.20 (d, 1 H, $^1J_{PH}$ = 491 Hz). Compound [**2**]Cl was also synthesized in 85% isolated yield using dry CH_3CN as the reaction solvent. Compound of [**2**]Cl (6.1 g, 24 mmol) dissolved in dry acetonitrile (60 mL) was added by syringe to a suspension of *t*-BuOK (4.4 g, 38 mmol) in acetonitrile (20 mL). After stirring the reaction mixture for 1 h at room temperature, the solvent was removed in vacuo and the residue was extracted with 480 mL of dry pentane overnight while stirring. The extract was transferred by cannula to another flask and evaporated to remove the solvent to give a white solid which was sublimed at 50 °C/1 Torr to give **1** (4.4 g, 85%). ^{31}P NMR (CD_3CN): δ 120.8; ^1H NMR (CD_3CN): δ 2.60 (d, 9 H, NCH_3, $^3J_{PH}$ = 11.0 Hz), 2.76 (br, 12 H, $N_{eq}CH_2$ and $N_{ax}CH_2$). An attempt to synthesize [**2**]Cl using PCl_3 and $P(OCH_3)_3$ was not successful. Thus stirring a mixture of PCl_3 and two molar equivalents of $P(OMe)_3$ in CH_3CN for 2 h at RT followed by addition of one equivalent of $(HMeNCH_2CH_2)_3N$ gave only a barely detectable amount of **2** as monitored by ^{31}P NMR spectroscopy. Similarly, an attempt to synthesize [**2**]Cl from PCl_3 and $(HMeNCH_2CH_2)_3N$ was only partially successful. To a solution of PCl_3 in dry CH_3CN at RT was added 2 equivalents of Et_3N and then one equivalent of $(HMeNCH_2CH_2)_3N$. The mixture was stirred for 2 h at RT and evaporated in vacuo to remove the solvent. The ^{31}P

NMR (CD_3CN) of the mixture showed peaks at -9.34 ppm (**2**, 42.2%), 24.19 ppm (27.6%) and 167.52 ppm (30.2%). Compound [**2**]Cl was difficult to isolate by recrystallization from the Et_3N•HCl formed in the reaction, because both salts have similar solubilities in non-polar and polar solvents.

Because proazaphosphatrane **1** is more basic than any amine, *t*-BuOK must be used to transform **2** to **1**. If CH_2Cl_2 is used as the solvent for the condensation reaction, it must be completely removed in vacuo from the product **2** before the subsequent deprotonation reaction with *t*-BuOK, because halogenated solvents react very rapidly with **1**. It is, however, not necessary to remove CH_3CN when it is used as the solvent. Instead, the solution of the crude product **2** in CH_3CN can be immediately treated with *t*-BuOK to give ^{31}P and ^{1}H NMR spectroscopically pure **1** in 81% yield. This one-pot reaction for the synthesis of **1** from $ClP(NEt_2)_2$ prevents loss of **2** during the purification process, and it also reduces solvent usage and labor.

PAPER 2. STEPWISE TRANSANNULAR BOND FORMATION BETWEEN THE BRIDGEHEAD ATOMS IN $ZP(MeNCH_2CH_2)_3N$ SYSTEMS

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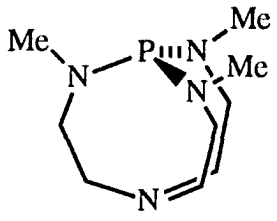
ABSTRACT

The structures of the title systems (Z = H^+ (**2**), 1/2$PtCl_2$ (**3**), S (**4**), S_2C (**5**), $Br(OC)_4Re$ (**6**), Cl_2Hg (**7**), $MeS(S)C^+$ (**8**), $PhN{=}CSMe^+$ (**9**)) determined by X-ray means reveal step-wise closure of the P-N_{ax} bridgehead-bridgehead distance from 3.33 to 1.967 Å from **3** to **9** to **2**, concomitant with incremental opening of the N_{eq}-P-N_{eq} angle from 104.5° to 119.6°. The nearly linear plot (r^2 = 0.98) is interpreted in terms of greater hybridizational flexibility at phosphorus, compared with other atoms tethering the bridgehead atoms, and increasing strain along with decreasing entropy associated with formation of the three five-membered rings in **2**.

COMMUNICATION

We have recently described the extraordinary Lewis basicity of the phosphorus in **1** for protons to produce the unexpectedly weak conjugate acid **2**.[1-7] The transannulation process.



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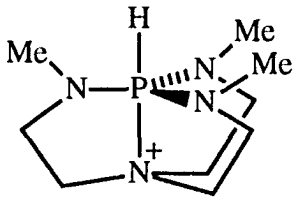

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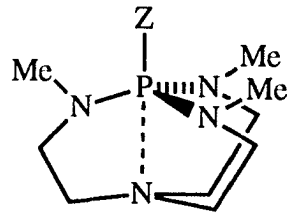
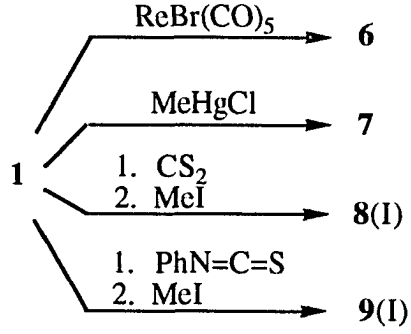


	Z
3	*trans*-$Cl_2Pt(1)$[6]
4	S[6]
5	S_2C[6]
6	*cis*-$Br(OC)_4Re$
7	Cl_2Hg
8	$MeS(S)C^+$
9	$PhN{=}C^+{-}SMe$

that accompanies protonation of **1** to give **2** can be viewed as a model of S_N2 formation of a five-coordinate intermediate, with the unusual feature that the nucleophilic atom is forced to invert by virtue of its bridgehead position in the bicyclic structure **1**. It could be expected that exocyclic electrophiles binding to the phosphorus of **1** would be of two kinds, namely, those that cause transannulation and those that do not. However as we report here, a progression of intermediate P-N_{ax} distances and N_{eq}-P-N_{eq} angles (determined by X-ray means) is observed in **3-9**, marking in a stepwise manner the S_N2 process as a function of the Lewis acidity of the Z substituent.

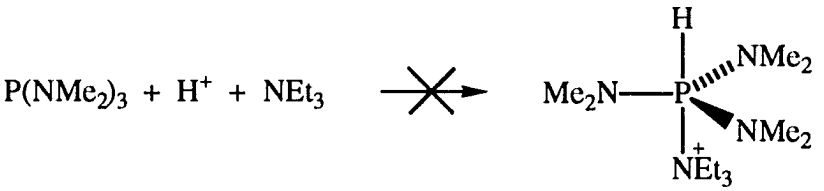
The new compounds **6-9** are synthesized[8] according to reactions 1-4. Because the



ORTEP drawings of **6-9** are similar[9] and those for **2**[1] and **3-5**[6] have been published, only the ORTEP for **8** is shown in Figure. 1.

A plot of P-N_{ax} distance versus the N_{eq}-P-N_{eq} angle in Figure 2 reveals a decrease in P-N_{ax} distance from a value close to the sum of the van der Waals radii (3.34 Å)[10] in **3** (3.33 Å) to a bonded value of 1.967 Å in **2**. Although there is a clearly visible and consistent curvature of this plot, the deviation from linearity ($r^2 = 0.98$) is relatively small. The nearly monotonic response of the N_{eq}-P-N_{eq} angle to transannulation could arise from a lower reorganization energy associated with phosphorus rehybridization than for other atoms in the bridges tethering the phosphorus to N_{ax}.[11] The only related study we were able to find in the literature concerns a group of eleven Cd(II) thiolate and dithiophosphate structures.[12] Here the response of the S_{eq}-Cd-S_{eq} angle to the approaching nucleophile in the Y-CdS_3...Y' moiety (Y, Y' = I, S or O) was roughly linear ($r^2 = 0.88$), with no obvious curvature. The roughness of the plot for the Cd(II) complex data must in part be associated with the variation of the nucleophilic species, which in our system is consistently a tertiary nitrogen.

The stepwise establishment of the P-N_{ax} bond depicted in Figure 2 may reflect increasing strain and decreasing entropy associated with the formation of the three five-membered rings in **2**, which counterbalance the electron-withdrawing power of the Z substituent. We have not seen evidence for reaction 5, however, wherein ring strain would not



(5)

be a factor. Thus only HN^+Et_3 is observed to form. Reaction 5, wherein after electrophilic attack of the proton two molecules condense to one, probably requires a larger decrease in entropy than transannulation, which is intramolecular. Another factor possibly favoring P-N_{ax} interaction when **1** is electrophilically attacked is the already nearly planar

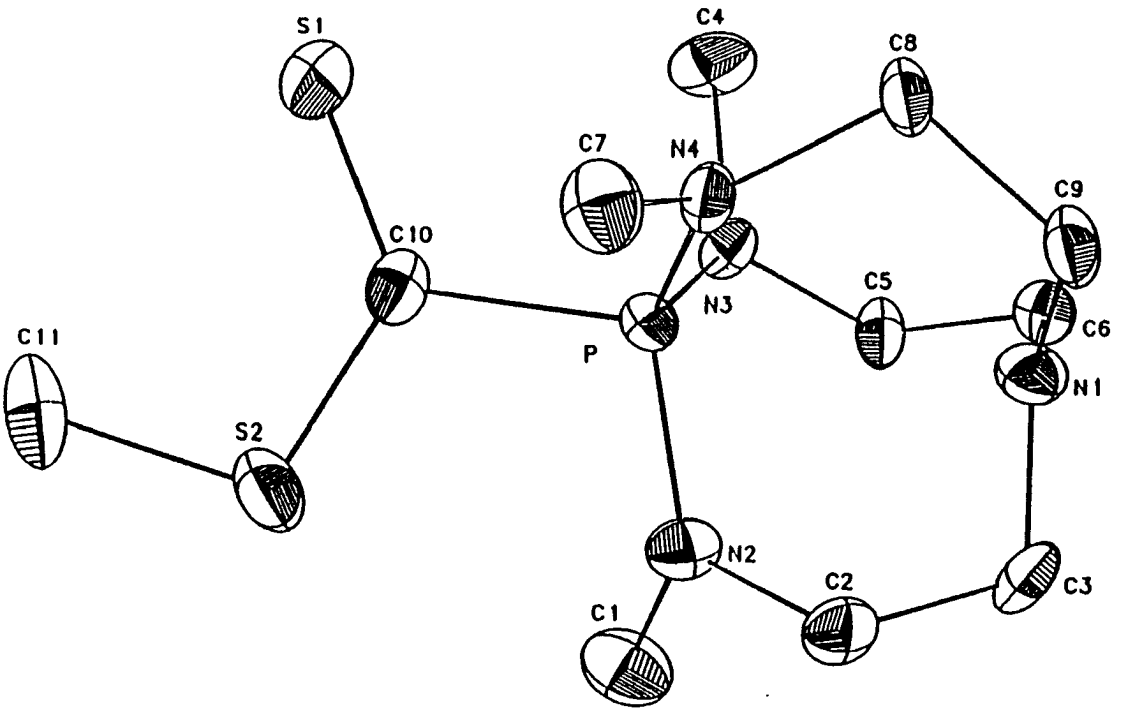


Figure. 1. ORTEP drawing for **8** with ellipsoids drawn at the 50% probability level.

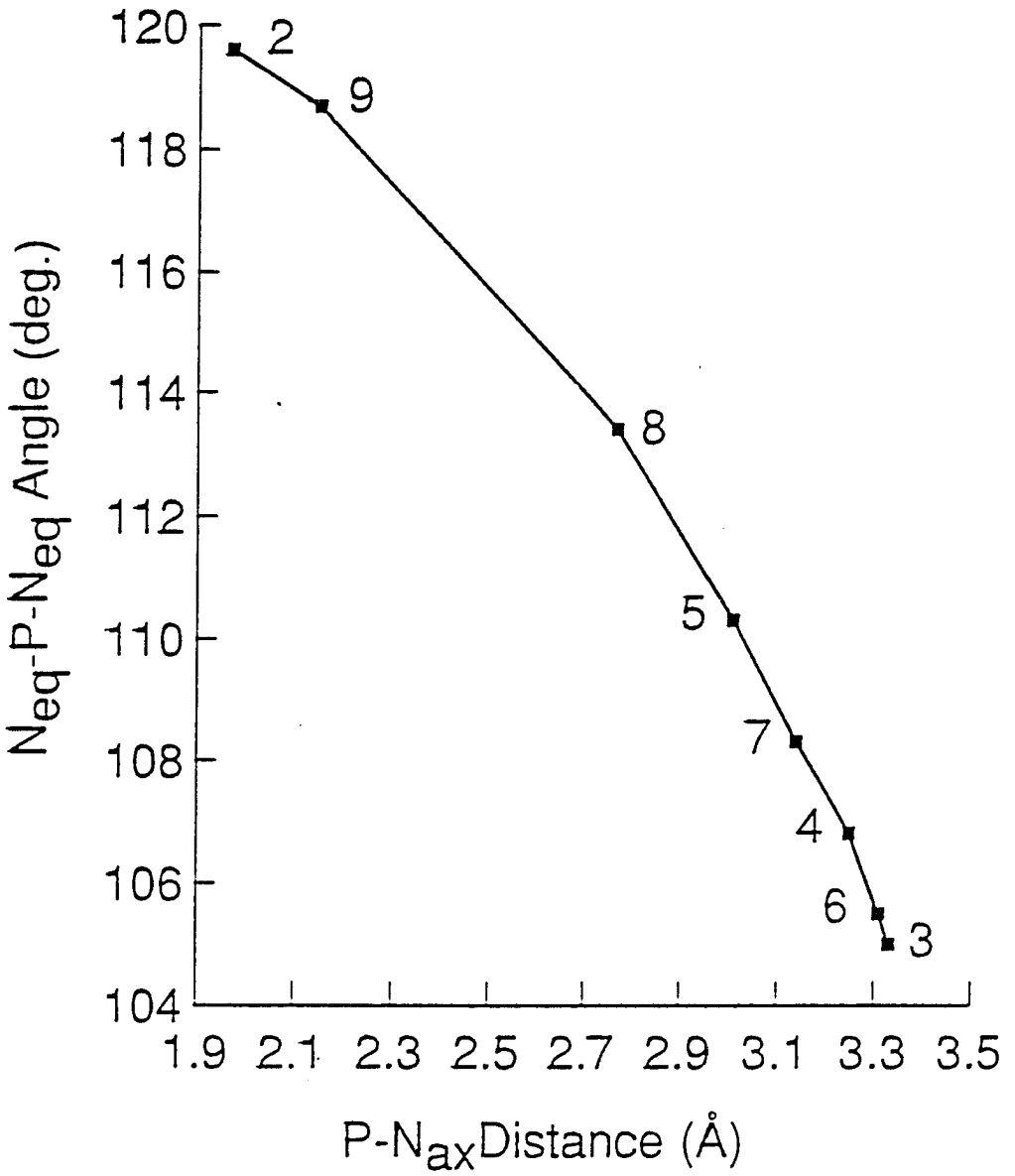


Figure. 2. Plot of P-N_{ax} distances (which decrease in the order 3.33, 3.307, 3.250, 3.143, 3.008, 2.771, 2.184, 1.967 Å) against N_{eq}-P-N_{eq} angles (which correspondingly increase in the order 104.5, 105.5, 106.8, 108.3, 110.3, 113.4, 118.5, 119.6°) in $ZP(MeNCH_2CH_2)_3N$ systems **2-9**.

configuration of N_{ax} in **3** (and very probably in **1**) even though the P and N_{ax} atoms are separated by the sum of the van der Waals radii. The planarity of bridgehead nitrogens in bicyclics of this type is apparently due to van der Waals interactions among the CH_2 hydrogens.[6,13]

ACKNOWLEDGMENTS

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(8) A solution of 0.818 g (3.79 mmol) of **1**[1] in 10 mL of THF was added dropwise to a suspension of 1.54 g (3.79 mmol) of $Re(CO)_5Br$ in 20 mL of THF. After 16 h the solvent was removed under vacuum and the residue dissolved in 15 mL of CH_2Cl_2. Slow evaporation gave light yellow single crystals of **6**: 81.8% yield, Anal. ($C_{10}H_{18}O_4BrN_3PRe$) C, H, N; NMR ^1H, ^{13}C, ^{31}P. A solution of 0.324 g (1.50 mmol) of **1**[1] in 10 mL of THF was added dropwise to a solution of 0.377 g (1.50 mmol) of MeHgCl in 15 mL of THF. After 5 min. the supernatant was decanted and the white precipitate of **7** was washed with 2 x 10 mL portions of THF: 98.3% yield; Anal. ($C_{18}H_{42}Cl_2HgN_3P_2$) C, H, N: calcd. 30.7, 6.01, 15.9; found 29.7, 6.13, 15.9; NMR ^1H, ^{13}C, ^{31}P. Crystals for X-ray diffraction were grown from CH_2Cl_2 solution. To 0.12 g (0.41 mmol of **5**[2] was added 1.88 g (13.2 mmol) of MeI. After the exothermic reaction subsided, the residual red solid was dissolved in a minimum of MeCN and the solution stirred for 2 min. at room temperature. Evaporation of the volatiles under

vacuum gave spectroscopically pure **8**(I) in quantitative yield: Anal. ($C_{11}H_{24}IN_4PS_2$) C, H, N; NMR ^1H, ^{13}C, ^{31}P; FAB (MeCN) 307.1066 (M^+ of **8**). Single crystals of **8** were grown from MeCN at -25 °C. To 0.14 g (0.42 mmol) dissolved in 3 mL of Et_2O was added 0.087 g (0.64 mmol) of PhNCS. After stirring for 5 min., the greenish-yellow solid was collected by filtration, washed with 5 mL of Et_2O and dried under vacuum. To 0.073 g (2.9 mmol) of this adduct in 1 mL of CH_3CN was added 0.2 mL of MeI. After 30 min. of stirring, the volatiles were removed to give **9**(I) quantitatively: MS (FAB, MeCN) 366.3211 (M^+ of **9**, base peak); Anal. ($C_{17}H_{29}N_5PS$) C, H, N: calcd. 41.35, 5.93, 14.19; found 40.82, 5.88, 13.78; NMR ^1H, ^{13}C, ^{31}P. Crystals for X-ray diffraction were grown from MeCN at -20 °C.

(9) Crystal data for **6**. Orthorhombic crystals, space group Pbca; a = 16.291 (2) Å, b = 15.269 (5) Å, c = 15.018 (6) Å, V = 3736 (3) Å,^{3} D_{calc} = 2.112 g/cm^3, Z = 8, anisotropic least-squares refinement (MoK_α radiation, μ (MoK_α) = 90.0 cm^{-1}, 2416 observed reflections, R = 0.028, R_w = 0.035, diffractometer = Enraf-Nonius CAD4, temperature = -50 °C.

Crystal data for **7**. Orthorhombic crystals, space group $Pca2_1$; a = 15.557 (6) Å, b = 9.508 (7) Å, c = 18.218 (6) Å, V = 2695 (4) Å, D_{calc} 1.753 g/cm^3, Z = 4, anisotropic least squares refinement (MoK_α radiation, μ(MoK_α) = 60.49 cm^{-1}, 2743 observed reflections, R = 0.028, R_w = 0.033, diffractometer = Rigaku AFC6R, temperature = 25 °C.

Crystal data for **8**. Orthorhombic crystals, space group $P2_12_12_1$; a = 9.975 (5) Å, b = 11.436 (3) Å, c = 14.722 (5) Å, V = 1679 (2) Å^3, D_{calc} = 1.718 g/cm^3, Z = 4 anisotropic least-squares refinement (MoKα radiation, μ(MoKα) = 22.6 cm^{-1}, 1629 observed reflections, R = 0.034, R_w = 0.061, diffractometer=Enraf-Nonius CAD4, temperature = -50 °C.

Crystal data for **9**. Orthorhombic crystals, space group $Pca2_1$; a = 16.786 (3) Å, b = 10.756 (2) Å, c = 24.328 (4) Å, V = 4392 (2) $Å^3$, D_{calc} = 1.514 g/cm^3, Z = 8 anisotropic least-squares refinement (MoKα radiation, μ(MoKα) = 22.6 cm^{-1}, 6401 observed reflections, R = 0.0422, R_w = 0.1135 diffractometer=Enraf-Nonius CAD4, temperature = 20 °C.

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SUPPLEMENTARY MATERIALS

Table 1. Pertinent Structural Metrics for **2-12**.

Compound	P-N_{ax}(Å)	N_{eq}-P-N_{eq}(°)	C-N_{ax}-C(°)
3	3.33	104.5	119
6	3.307	105.5	119.6
4	3.250	106.8	119.6
7	3.143	108.3	120
10[a]	3.137	107.6	117.8
5	3.008	110.3	120
11[b]	2.773	113.2	119.1
7	2.771	113.4	119.4
12[c]	2.551	115.1	117.1
9[d]	2.209	118.3	113.3
	2.159	118.7	112.1
2	1.967	119.6	111

[a]Compound O=P($MeNCH_2CH_2$)$_3$N, **10**, corresponds to compound **4** in chapter 6.

[b]Compound Me[P($MeNCH_2CH_2$)$_3$N]I, **11**(I): Mohan, T.; Verkade, J.G., to be published.

[c]Compound PhNH[P($MeNCH_2CH_2$)$_3$N](CF_3CO_2), **12**(CF_3CO_2), corresponds to compound **5**(CF_3CO_2) in chapter 3. [d]Two molecules per asymmetric unit.

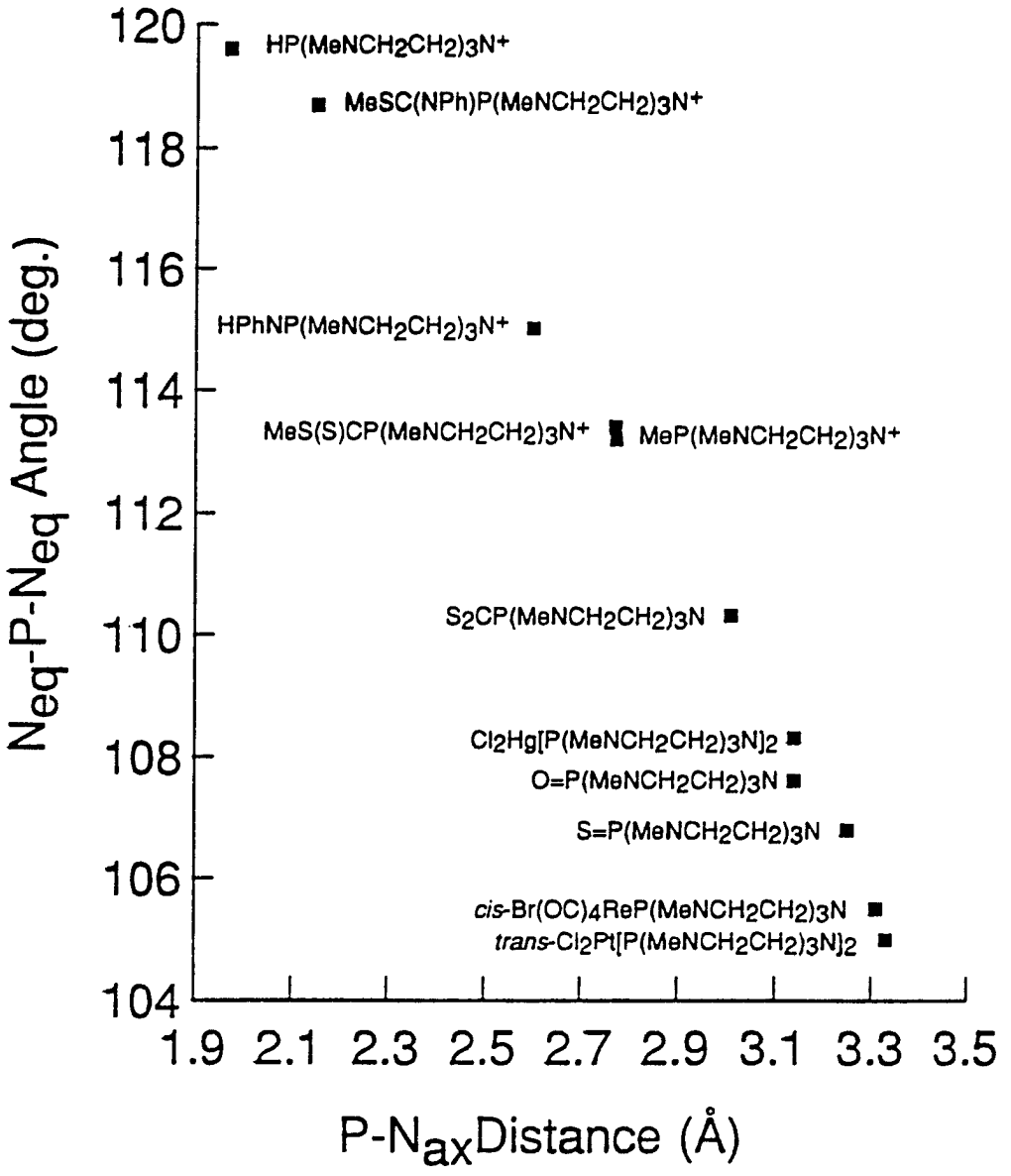

Figure 3. Plot of P-N_{ax} distances against N-$_{eq}$P-N_{eq} angles in ZP(MeNCH$_2$CH$_2$)$_3$N systems with insertion of componds **10-12** to Figure 2. The regression coefficiency R (= 0.98) remains

Table 2. NMR Spectrum Data for New Compounds

Compound	Data
6	^{1}H (CD_3CN) 2.83 (CH_3, $^{3}J_{PH}$ = 9.6 Hz), 2.93 (br, CH_2); ^{13}C (CD_3CN) 36.2 (CH_3, $^{2}J_{PC}$ = 10.6 Hz), 49.7 ($N_{ax}(CH_2)_3$ J_{PC} = 1.6 Hz), 51.3 ($N_{eq}(CH_2)_3$, $^{2}J_{PC}$ = 2.7 Hz), 184.1, 185.1, (CO's cis to **1**), 185.9 (CO trans to **1**, $^{2}J_{PC}$ = 9.1 Hz); ^{31}P (CH_2Cl_2) 98.6; IR (CH_2Cl_2, CO region, cm^{-1}) 2100, 1996, 1936, 1884.
7	^{1}H (CD_3CN) 2.79, 2.91 (m, CH_2), 2.95 (virt. t, CH_3); ^{13}C (CD_3CN) 34.9 (virt. t, CH_3), 50.9 ($N_{ax}(CH_2)_3$), 51.0 ($N_{eq}(CH_2)_3$); ^{31}P (CH_2Cl_2) 118 ($^{1}J_{HgP}$ = 7869 Hz).
8	^{1}H (CD_3CN) 3.01 ($N_{eq}(CH_2)_3$, $^{3}J_{PH}$ = 15.6 Hz, $^{3}J_{HH}$ = 5.7 Hz), 2.85 ($N(CH_2)_3$, $^{3}J_{HH}$ = 5.7 Hz), 2.86 (CH_3N_{eq}, $^{3}J_{PH}$ = 11.1 Hz), 2.72 (CH_3S); ^{13}C (CD_3CN) 50.4 ($N_{eq}(CH_2)_3$, $^{2}J_{PC}$ = 3.5 Hz), 51.8 ($N_{ax}(CH_2)_3$), 38.1 (CH_3N_{eq}, J_{PC} = 2.0 Hz), 232.5 (SCS, $^{1}J_{PC}$ = 154.3 Hz), 21.3 (CH_3S, $^{3}J_{PC}$ = 0.1 Hz); ^{31}P (CD_3CN) 24.1.
9	^{1}H (CD_3CN) 2.18 (CH_3S, $^{4}J_{PH}$ = 0.6 Hz), 2.90 ($N_{ax}(CH_2)_3$, J_{PH} = 5.1 Hz), 2.94 (CH_3N_{eq}, $^{3}J_{PH}$ = 11.4 Hz), 3.08 ($N_{eq}(CH_2)_3$, $^{3}J_{PH}$ = 15.3 Hz, $^{3}J_{HH}$ = 2.3 Hz), 6.89-7.40 (m, C_6H_5); ^{13}C NMR (CD_3CN) 16.9 (CH_3S, $^{3}J_{PC}$ = 2.3 Hz), 38.2 (CH_3N_{eq}, $^{2}J_{PC}$ = 3.3 Hz), 49.7 ($N_{ax}(CH_2)_3$), 50.7 ($N_{eq}(CH_2)_3$, $^{2}J_{PC}$ = 6.0 Hz), 119.01 (*o*-C, $^{4}J_{PC}$ = 1.4 Hz), 125.6, 130.2 (*m*, *p*-C), 150.0 (*ipso*-C, $^{3}J_{PC}$ = 22.5 Hz), 167.3 (PC, $^{1}J_{PC}$ = 186.9 Hz); ^{31}P NMR (CD_3CN) 14.45.

X-Ray Structure Determination of 6 , 7, 8(I) and 9(I)

Data Collection for 6. 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 ± 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 was confirmed by photography.

Lorentz and polarization corrections were applied. A correction based on the decay in the standard reflections of 1.35 was applied to the data. An absorbtion correction based on a series of Ψ–scans was applied. The arrangement 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 217 parameters refined.

Structure Solution and Refinement of 6. The centric space group Pbca was indicated initially by symmetric absences and intensity statistics.[1] The positions of all atoms were determined by direct methods.[2] All non-hydrogen atoms were refined 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 equivaent of the 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 Laboratory. Refinement calculations were performed on a Digital Equipment Corp. Micro VAXII computer using the CAD4-SPD programs.[2]

Data Collection of 7. A colorless cubic crystal of the title compound 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 MoK_α radiation and a 12 KW rotating anode generator.

Cell constants and an orientation for data collection, obtaned from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $12.34 < 2\theta < 15.09^o$ corresponded to an orthorhombic cell with dimensions: a = 15.557(6) Å, b = 9.508(7) Å, c = 18.218(6) Å, V = 2695(4) $Å^3$. For Z = 4 and F.W. = 704.03, the calculated density is 1.735 g/cm^3. Based on the systematic absences of 0k1: $1 \neq 2n$, h01: $h \neq 2n$ packing considerations, a statistic analysis of intensity distribution, and the succesful solution and refinement of the structure, the space group was determined to be $Pca2_1$ (#29).

The data were collected at a temperature of 25 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 50.1°. Omega scans of seval intense reflections, made prior to data collection, had an average width at half-height of 0.38° with a take-off angle of 6.0°. Scans of $(1.10 + 0.30 \tan \theta)$ were made at a speed of 16.0°/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.

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

The linaer absorbtion coefficient for MoK_α is 60.5 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 for 7. The position of the non-hydrogen atoms were determined as follows: Patterson superpositions were carried out using two-

mercury-mercury-vectors and 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.[3] An electron density map was then calculated which yield the positions of the mercury, chlorine and nitrogen atoms. The position 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 > 3.00σ(I)) and 279 variable parameters and converged (largest parameter shift was 0.09 times its esd) with unweighted and weighted agreement factors of R = $\Sigma /\!/ F_o / - / F_c /\!/ / \Sigma / F_o / = 0.028$, $R_w = [\Sigma_w (/ F_o / - / F_c /)^2 / \Sigma_w /] F_o /^2]^{1/2} = 0.033$.

The standard deviation of an observation of unit weight was 1.28. The weighing scheme was based on counting statistics and included a factor (p = 0.03) to downweight the intense reflections. Plots of $\Sigma_w (/ F_o / - / F_c /)^2$ versus $/ F_o /$, reflection in order in data collection, sin θ/γ, 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 $e^-/Å^3$, respevtively.

Neutral atom scattering factors were taken from Cromer and Waber.[4] Anomalous dispersion effects were included in Fcalc;[5] the value for Äf' and Äf'' were those of Cromer.[6] All calculations were performed using the HYPAD,[7] CHES,[8] and TEXAN[9] crystallographic software packages.

Data Collection of 8(I). A colorless crystal of the title compound was attached to the tip of a glass fiber and mounted on the diffractometer for a data collection at -50 ± 1°C. The cell constants for data collection were determined from a list of reflections found by an automated search routine.

Lorentz and polarization corrections were applied. A correction baseed on a decay in the standard reflections of 2.0% was applied to the data. An absorption correction based on a

series of Ψ–scans was applied. The agreement factor for the averaging of observed reflections was 1.8% (based on F).

Structure Solution and Refinement of 8(I). The acentric space group $P2_12_12_1$ was indicated initially by systematic absences and intensity statistics.[1] The positions of all atoms were determined by direct methods.[2] 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.

Since a rather large crystal was used for this data collection, it was found necessary to use an extinction correction. This improved the agreement for the highest intensity reflections. The extinction refined to 1.69 μm.

X-ray data collection and structure solution were carried out at the Iowa State Molecular Laboratory. Refinement calculations were performed on a Digital Equipment Corp. MicroVAX computer using the CAD4-SDP programs.[2]

Data Collection of 9(I). A colorless crystal of the title compound was attached to the tip of a glass fiber and mounted on the diffractometer for a data collection at 20 ± 1 °C. The cell constants for data collection were determined from a list of reflections found by automated search routine.

Lorentz and polarization corrections were applied. A correction baseed on a decay in the standard reflections was not required for this dataset. An absorption correction based on a series of Ψ–scans was applied. The agreement factor for the averaging of observed reflections was 2.6% (based on F).

Structure Solution and Refinement of 9(I). The acentric space group $Pca2_1$ was indicated initially by systematic absences and intensity statistics.[1] The positions of all atoms were determined by Patterson interpretation program.[1] All non-hydrogen atoms were

refined with anisotropic thermal parameters. All hydrogen atoms were placed at idealized positions as reading atoms with isotropic temperature factors set equal to 1.2 times the isotropic eqivalent of that atom.

The $Pca2_1$ space group requires two independent molecules per asymmetric unit. The cations are nearly centrosymmetric, however, the iodine anions are noncentrosymmetric. Attempts to refine this structure in Pbcm failed. The initial refinement in SDP[2] was converted to SHELXL-93.[10] to test for racemic twinning. A twinned crystal was confirmed and therefore refined as such. Difference Fourier maps of the residual peaks indicatedd the presence of water, which was added to the refinement. Noteable hydrogen bonds are O···H (16B) = 2.526Å, H(10)···I(1) = 2.830Å, H(6B)···I(2) = 3.049Å, and H(7A)···I(2) = 3.204Å.

X-ray data collection and structure solution were carried out at the Iowa State Molecular Laboratory. Refinement calculations were performed on a digital Equipment Corp. MicroVAX computer using the CAD4-SDP programs[2] and SHELXL-93.[3] Thermal ellipsoid illustrated were drawn using the SHELXTL-Plus package.[11]

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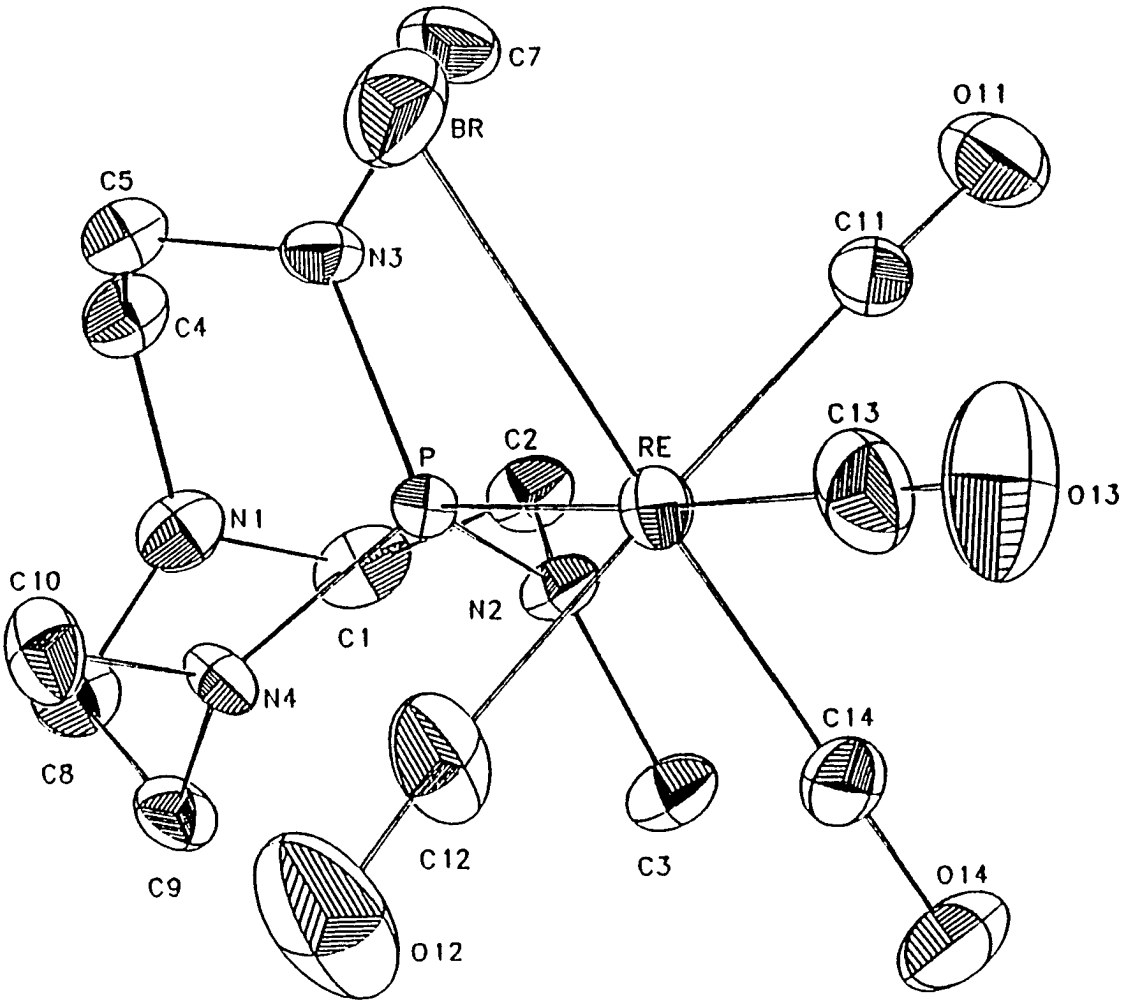

Figure 4. ORTEP drawing for **6** with ellipsoids drawn at the 50% probability level.

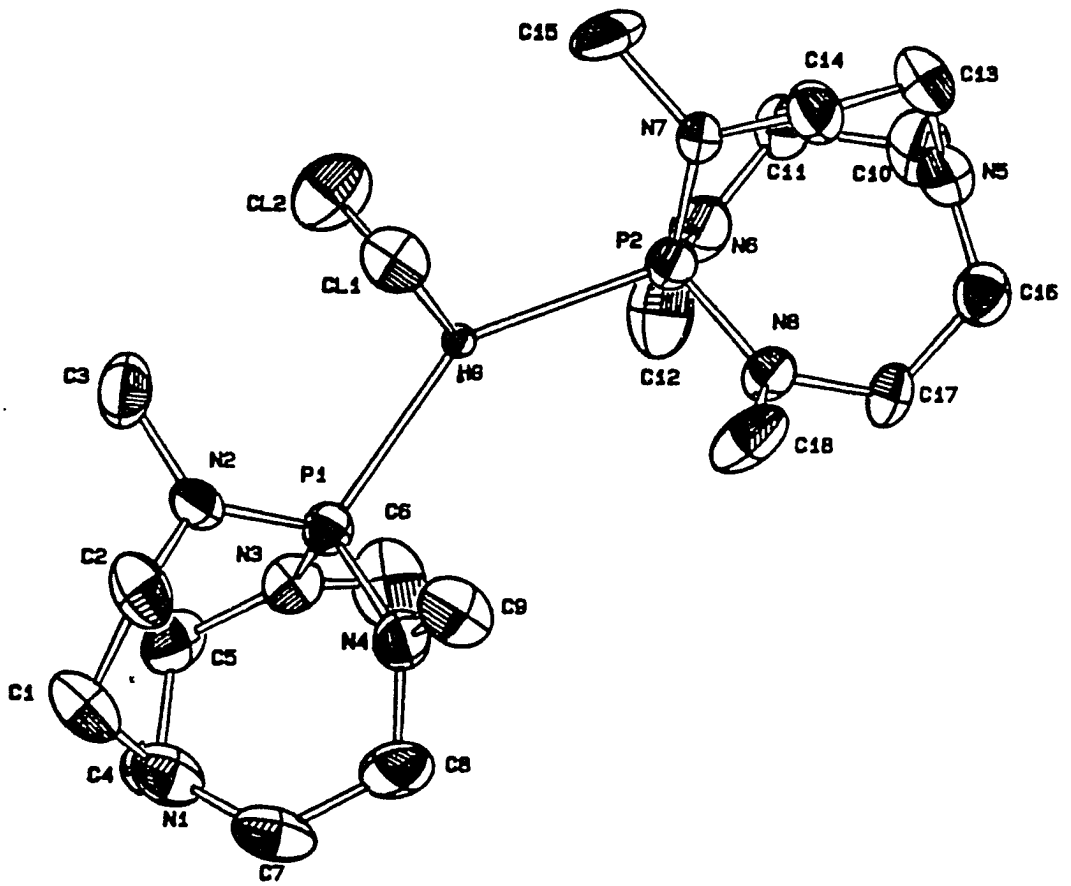

Figure 5. ORTEP drawing for **7** with ellipsoids drawn at the 50% probability level.

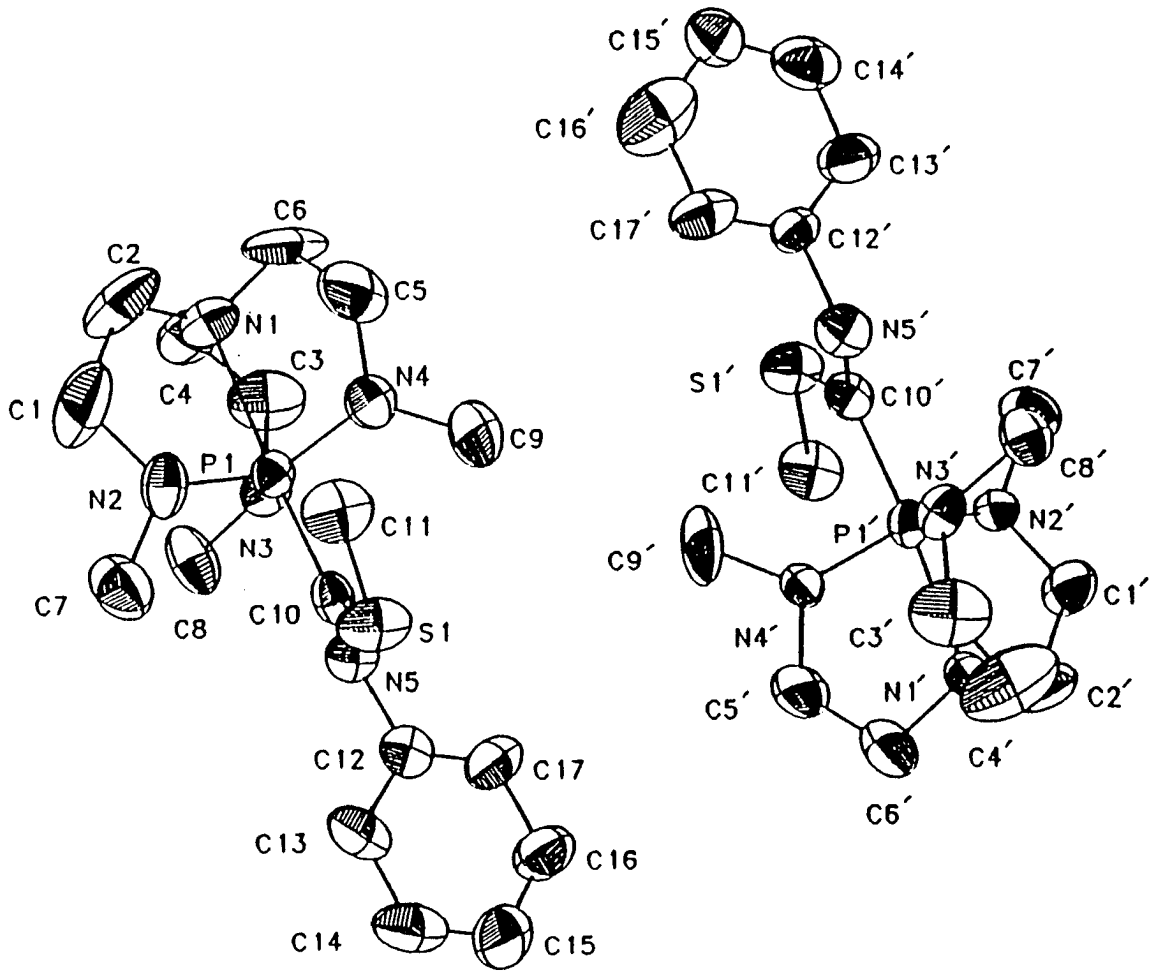

Figure 6. ORTEP drawing for **9** with ellipsoids drawn at the 50% probability level.

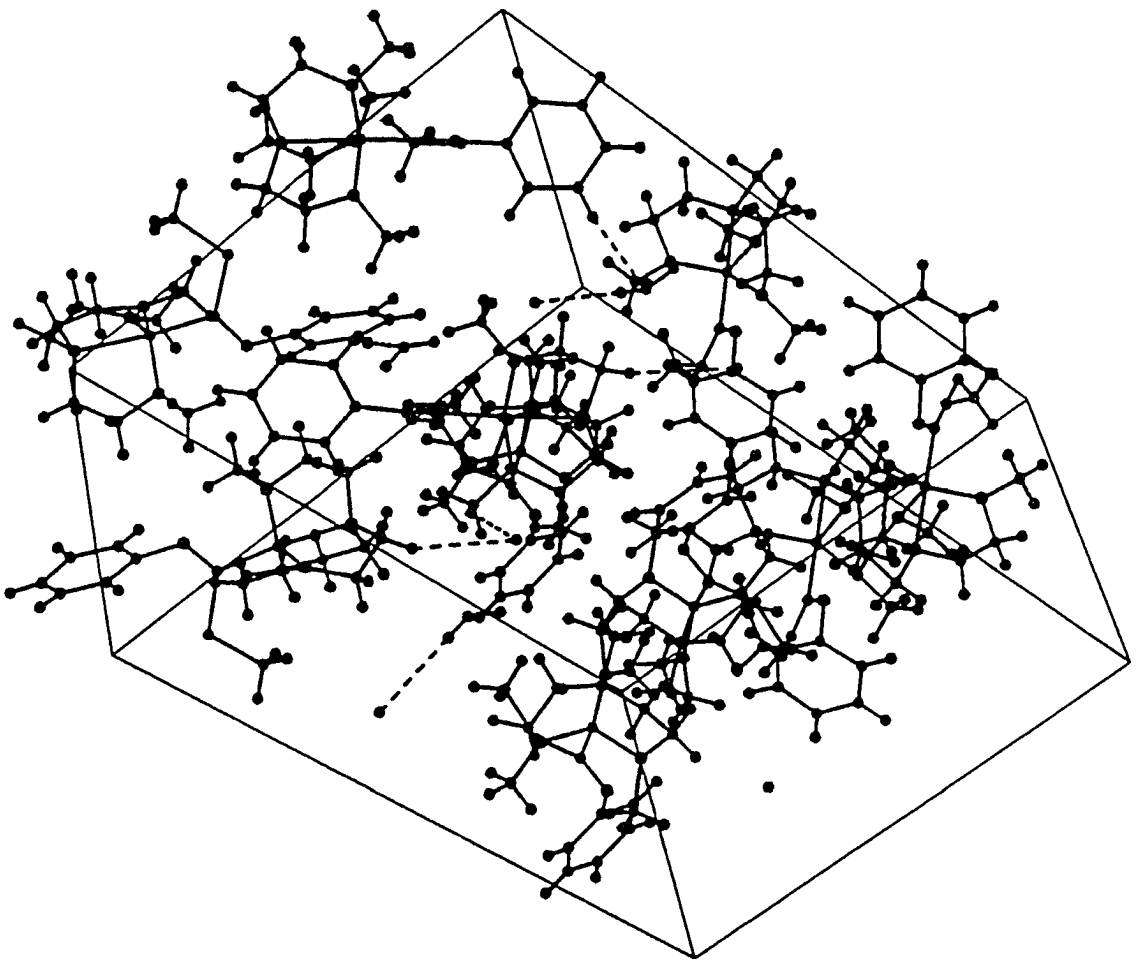

Figure 7. Unit cell projection for the X-ray crystallographic solution of **9**(I)

Table 3. X-Ray Crystallographic Data for **6** and **7**

	cis-$Re(CO)_4$(**1**)Br, **6**	$Hg(\mathbf{1})_2Cl_2$, **7**
Formula	$C_{10}H_{21}O_4N_4PBr$	$C_{18}H_{24}N_8Cl_2HgP_2$
Formula weight	597.22	704.03
Space group	Pbca	$Pca2_1$
a, Å	16.291(2)	15.557(6)
b, Å	15.269(5)	9.508(7)
c, Å	15.018(6)	18.218(6)
V, Å	3735.8(31)	2695(4)
Z	8	4
$d_{clcd.}$, g/cm^3	2.112	1.735
Crystal size, mm	0.50 x 0.45 x 0.35	0.40 x 0.30 x 0.30
$\mu(MoK_\alpha)$, cm^{-1}	90.0	60.49
Data collection instrument	Enraf-N0nius CAD4	Rigaku AFC6R
Radiation	$MoK_\alpha(\lambda = 0.71073$ Å)	$MoK_\alpha(\lambda = 0.71069)$
Orientation reflections,		
Number, range	25, 24.6 - 28.6	25, 12.3 - 15.1
Temperature, °C	-50 ± 1	25 ± 1
Scan method	θ – 2θ	θ – 2θ
Data collection range, 2θ, deg	4 - 50	1.10 - 50.1
Number of unique data	3694	2743

Table 3, Continued.

	cis-$Re(CO)_4$(**1**)Br, **6**	$Hg(\mathbf{1})_2Cl_2$, **7**
with $F_o^2 > 3\sigma(F_o^2)$	2416	1889
No. parameters refined	217	279
R[a]	0.028	0.028
R_w[b]	0.035	0.033
Quality-of-fit indicator[c]	0.87	1.28
Largest shift/esd., final cycle	0.00	0.09
Largest peak, e/Å^3	1.8(2)	1.09

[a] $R = \Sigma /\!/ F_o/ - /F_c /\!/ / \Sigma /F_o/$.

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

[c] Quality-of-fit = $[\ \Sigma_w(/F_o/)^2/(N_{obs} - N_{parameters})]^{1/2}$

Table 4. X-Ray Crystographic Data for **8**(I) and **9**(I)

	8(I)	**9**(I)
Formula	$C_{11}H_{24}IN_4PS_2$	$[C_{17}H_{29.80}IN_5O_{0.40}PS$
Formula weight	434.35	500.59
Space group	$P2_12_12_1$	$Pca2_1$
a, Å	9.975(5)	16.786(3)
b, Å	11.436(3)	10.756(2)
c, Å	14.722(5)	24.328(4)
V, Å^3	1679.1(18)	4392.4(13)
Z	4	8
$d_{clcd.}$, g/cm^3	1.718	1.514
Crystal size, mm	0.95 x 0.70 x 0.60	0.45 x 0.354 x 0.35
$\mu(MoK_\alpha)$, cm^{-1}	22.6	22.6
Data collection instrument	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Radiation	$MoK_\alpha(\lambda = 0.71073Å)$	$MoK_\alpha(\lambda = 0.71073Å)$
Orientation reflections,		
Number, range	25, $23.0 < \theta < 30.3$	25, $21.9 < \theta < 29.3$
Temperature, °C	-50(1)	20(1)
Scan method	$\theta - 2\theta$	$\omega - 2\theta$
Data collection range, 2θ, deg	4.0 - 50.0	4.50 - 49.92
Number of unique data	1924	7690
with $F_o^2 > 3\sigma(F_o^2)$	1629	6401 ($I \geq 2\sigma(I)$)
No. parameters refined	173	463

Table 4, Continued.

	8(I)	**9**(I)
R^a	0.034	0.0422 ($I \geq 2\sigma(I)$)
$R_w{}^b$	0.061	0.1135 ($I \geq 2\sigma(I)$)
Quality-of-fit indicator[c]	1.84	1.58
Largest shift / esd., final cycle	0.02	0.001, 0.000
Largest peak, e/Å^3	0.72	0.958

[a] $R = \Sigma /\!/ F_o / - / F_c /\!/ / \Sigma / F_o /$.

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

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

Table 5. Positional Parameters and Their Estimated Standard Deviations for *cis*-$(CO)_4Re[P(NMeCH_2CH_2)_3N]Br$, **6**

Atom	x	y	z	B(Å^2)
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(2)
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(4)	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)
C(12)	0.4296(3)	0.7542(4)	0.1037(5)	3.3(1)
C(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)

Table 5, Continued.

Atom	x	y	z	B(Å^2)
O(13)	0.4283(3)	0.9420(3)	-0.0437(3)	4.3(1)
C(14)	0.5534(4)	0.8700(4)	0.1396(4)	2.4(1)
C(14)	0.5624(3)	0.9187(3)	0.1967(3)	3.6(1)

Table 6. Positional Parameters and Their Standard Deviations for $Hg(\mathbf{1})_2Cl_2$, **7**

Atom	x	y	z	B(Å^2)
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(9)	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)	0.2321(1)	-0.284(1)	0.1754(7)	4.0(7)
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)

Table 6, Continued.

Atom	x	y	z	B(Å2)
C(10)	-0.0469(9)	0.558(1)	-0.117(1)	4.5(7)
C(11)	0.0341(1)	-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 7. Positional Parameters and Their Estimated Standard Deviations for **8**(I).

Atom	x	y	z	B(Å^2)
I	0.24477 (4)	0.00291 (3)	0.30542 (3)	3.230 (9)
P	-0.2392 (1)	-0.00544 (8)	0.58388 (9)	1.51 (2)
S(2)	-0.5158 (1)	0.0575 (1)	0.5222 (1)	2.99 (2)
S(1)	-0.4021 (2)	0.1719 (1)	0.6866 (1)	3.75 (3)
N(1)	-0.0142 (5)	-0.1446 (3)	0.5616 (2)	2.02 (7)
C(1)	-0.2791 (7)	-0.0202 (5)	0.4004 (3)	3.1 (1)
N(2)	-0.2612 (4)	-0.0779 (3)	0.4892 (3)	2.02 (7)
C(2)	-0.2155 (5)	-0.2005 (4)	0.4839 (3)	2.04 (8)
C(3)	-0.0638 (5)	-0.2056 (4)	0.4826 (3)	2.22 (8)
C(4)	-0.0751 (6)	0.1647 (4)	0.6494 (4)	2.8 (1)
N(3)	-0.1152 (4)	0.0853 (3)	0.5746 (2)	1.69 (7)
C(5)	0.0007 (4)	0.0566 (4)	0.5144 (3)	2.04 (8)
C(6)	0.0741 (4)	-0.0482 (4)	0.5477 (3)	1.69 (8)
C(7)	-0.3528 (5)	-0.1499 (4)	0.7063 (4)	2.36 (9)
N(4)	-0.2376 (4)	-0.0871 (3)	0.6736 (3)	1.86 (7)
C(8)	-0.1059 (5)	-0.1252 (4)	0.7128 (3)	1.95 (8)
C(9)	-0.0290 (5)	-0.2015 (4)	0.6491 (3)	1.98 (8)
C(10)	-0.3922 (5)	0.0836 (4)	0.6009 (3)	1.96 (8)
C(11)	-0.6479 (5)	0.1525 (6)	0.5566 (4)	3.3 (1)

Table 8. Positional Parameters and Equivalent Isotropic Displacement Parameters for **9**(I)

Atom	x	y	z	U(eq, Å^2)[a]
I(1)	0.3800(1)	0.0598(1)	0.1610(1)	0.056
I(2)	0.6272(1)	0.5069(1)	0.0615(1)	0.061(1)
S(1)	0.4398(4)	0.6131(2)	0.7844(1)	0.061(1)
P(1)	0.5845(1)	0.4305(1)	0.7534(1)	0.037(1)
N(1)	0.6806(4)	0.3868(6)	0.6945(2)	0.057(2)
N(2)	0.5274(4)	0.3851(6)	0.7016(2)	0.053(1)
N(3)	0.6256(3)	0.3184(5)	0.7914(2)	0.043(1)
N(4)	0.6337(3)	0.5643(5)	0.7555(3)	0.051(1)
N(5)	0.4958(3)	0.4314(5)	0.8467(2)	0.047(1)
C(1)	0.5615(7)	0.3256(12)	0.6527(4)	0.104(4)
C(2)	0.6427(7)	0.3629(13)	0.6428(4)	0.99(4)
C(3)	0. 7096(4)	0.2955(9)	0.7799(4)	0.069(2)
C(4)	0.7196(5)	0.2792(8)	0.7194(4)	0.072(2)
C(5)	0.6835(7)	0.6028(9)	0.7104(5)	0.094(3)
C(6)	0.7330(7)	0.4986(9)	0.6922(5)	0.103(4)
C(7)	0.4446(5)	0.3488(8)	0.7084(4)	0.071(2)
C(8)	0.5804(5)	0.2022(7)	0.7977(3)	0.061(2)
C(9)	0.6376(6)	0.6399(10)	0.8048(4)	0.86(3)
C(10)	0.5010(4)	0.4832(6)	0.8014(3)	0.041(1)

[a]Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 8, Continued.

Atom	x	y	z	U(eq, Å^2)[a]
C(11)	0.4654(5)	0.6691(8)	0.7167(3)	0.069(2)
C(12)	0.4388(4)	0.4689(6)	0.8870(3)	0.047(2)
C(13)	0.3585(5)	0.4506(8)	0.8797(4)	0.061(2)
C(14)	0.3068(6)	0.4806(8)	0.9214(5)	0.078(3)
C(15)	0.3326(6)	0.5317(8)	0.969094)	0.073(2)
C(16)	0.4127(6)	0.5464(8)	0.9770(4)	0.072(2)
C(17)	0.4656(5)	0.5172(7)	0.9354(4)	0.061(2)
S(1')	0.8037(1)	0.8655(2)	0.9371(1)	0.057(1)
P(1')	0.6539(1)	1.0326(1)	0.9748(1)	0.036(1)
N(1')	0.5608(3)	1.0581(5)	1.0346(2)	0.045(1)
N(2')	0.7125(3)	1.0749(5)	1.0268(2)	0.044(1)
N(3')	0.6091(3)	1.1459(5)	0.9397(2)	0.044(1)
N(4')	0.6092(3)	0.8958(5)	0.9681(3)	0.046(1)
N(5')	0.7432(3)	0.8958(5)	0.8806(2)	0.045(1)
C(1')	0.6791(5)	1.1183(9)	1.0787(3)	0.066(2)
C(2')	0.5985(5)	1.0839(14)	1.0860(3)	0.105(5)
C(3')	0.5269(5)	1.1619(11)	0.9531(4)	0.078(3)
C(4')	0.5144(6)	1.1619(11)	1.0127(4)	0.093(3)
C(5')	0.5556(6)	0.8477(7)	1.0127(4)	0.074(2)
C(6')	0.5128(7)	0.9464(8)	1.0353(6)	0.106(4)
C(7')	0.7952(4)	1.1167(8)	1.0209(3)	0.063(2)
C(8')	0.6548(5)	1.2659(6)	0.9363(3)	0.056(2)

Table 8, Continued.

Atom	x	y	z	U(eq, Å2)[a]
C(9')	0.6045(5)	0.8279(10)	0.9174(4)	0.077(3)
C(10')	0.7372(4)	0.9929(5)	0.9253(2)	0.038(1)
C(11')	0.7800(5)	0.7959(7)	1.0032(3)	0.062(2)
C(12')	0.8029(4)	1.0256(6)	0.8403(3)	0.045(2)
C(13')	0.8790(5)	1.0696(9)	0.8469(4)	0.063(2)
C(14')	0.9314(5)	1.0526(8)	0.8044(4)	0.070(2)
C(15')	0.9131(5)	0.9922(8)	0.7511(4)	0.064(2)
C(16')	0.8359(6)	0.9519(8)	0.7511(4)	0.074(2)
C(17')	0.7787(4)	0.9677(7)	0.7918(3)	0.056(20
O	0.8078(4)	0.7866(6)	0.6314(3)	0.073(3)

Table 9. Bond Distances (Å) for $(CO)_4Re[P(NMeCH_2CH_2)_3N]Br$, **6**

Atom 1	Atom 2	Distances[a]
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)
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)

[a]Numbers in parentheses are estimated standard deviations in the last significant digits.

Table 9, Continued.

Atom 1	Atom 2	Distances[a]
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)

Table 10. Bond distances (Å) for Hg (**1**) Cl_2, **7**

Atom 1	Atom 2	Distances[a]
Hg	Cl(1)	2.652(4)
Hg	Cl(2)	2.637(4)
Hg	P(1)	2.47093)
Hg	P(2)	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)
N(4)	C(9)	1.47(2)
N(5)	C(10)	1.44(2)

[a]Numbers in parentheses are estimated standard deviations in the last significant digits.

Table 10, Continued.

Atom 1	Atom 2	Distances[a]
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)

Table 11. Bond Distances (Å) for **8**(I)

Atom 1	Atom 2	Distances[a]
P	N(1)	2.771(4)
P	N(2)	1.636(3)
P	N(3)	1.620(3)
P	N(4)	1.618(3)
P	C(10)	1.852(4)
S(2)	C(10)	1.718(4)
S(2)	C(11)	1.782(5)
S(1)	C(10)	1.619(4)
N(1)	C(3)	1.444(5)
N(1)	C(6)	1.426(5)
N(1)	C(9)	1.451(5)
C(1)	N(2)	1.475(5)
N(2)	C(2)	1,477(5)
C(2)	C(3)	1.514(6)
C(4)	N(3)	1.484(5)
N(3)	C(5)	1.494(5)
C(5)	C(6)	1.487(6)
C(7)	N(4)	1.438(6)
N(4)	C(8)	1.500(5)
C(8)	C(9)	1.494(6)

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

Table 12. Bond Distances (Å) for **9**(I)

Atom 1	Atom 2	Distances[a]
P(1)	N(1)	2.209(6)
P(1)	N(2)	1.657(5)
P(1)	N(3)	1.669(5)
P(1)	N(4)	1.661(6)
S(1)	C(10)	1.790(6)
S(1)	C(11)	1.804(8)
P(1)	C(10)	1.687(9)
N(1)	C(2)	1.432(11)
N(1)	C(4)	1.461(10)
N(1)	C(6)	1.490(12)
N(2)	C(1)	1.454(10)
N(2)	C(7)	1.468(10)
N(3)	C(3)	1.458(8)
N(3)	C(8)	1.470(9)
N(4)	C(5)	1.440(11)
N(4)	C(9)	1.452(11)
N(5)	C(10)	1.241(8)
N(5)	N(12)	1.427(9)
C(1)	C(2)	1.44(2)
C(3)	C(4)	1.492(11)

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

Table 12, Continued.

Atom 1	Atom 2	Distances[a]
C(5)	C(6)	1.464(14)
C(12)	C(17)	1.364(11)
C(12)	C(13)	1.373(10)
C(13)	C(14)	1.375(12)
C(14)	C(15)	1.352(14)
C(15)	C(16)	1.368(14)
C(16)	C(17)	1.383(11)
S(1')	C(10')	1.790(6)
S(1')	C(11')	1.818(7)
P(1')	N(4')	1.659(5)
P(1')	N(2')	1.665(6)
P(1')	N(3')	1.667(5)
P(1')	N(1')	2.151(6)
N(1')	C(2')	1.428(10)
N(1')	C(6')	1.447(10)
N(1')	C(4')	1.462(10)
N(2')	C(1')	1.459(9)
N(2')	C(7')	1.466(8)
N(3')	C(3')	1.438(9)
N(3')	C(8')	1.509(9)
N(4')	C(9')	1.436(9)

Table 12, Continued.

Atom 1	Atom 2	Distances[a]
N(4')	N(5')	1.470(9)
N(5')	C(10')	1.260(8)
N(5')	C(12')	1.429(8)
C(1')	C(2')	1.415(12)
C(3')	C(4')	1.466(11)
C(5')	C(6')	1.412(12)
C(12')	C(13')	1.372(10)
C(12')	C(17')	1.393(10)
C(13')	C(14')	1.370(12)
C(14')	C(15')	1.371(13)
C(15')	C(16')	1371(14)
C(16')	C(17')	1.391(12)
O	H(10)	0.80
O	H(20)	0.98

Table 13. Bond Angles (deg) for *cis*-$(CO)_4$Re(**1**)Br, **6**

Atom 1	Atom 1	Atom 3	Angle[a]
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)	8.4(3)
Re	P	N(2)	112.6(2)
Re	P	N(3)	115.7(2)
Re	P	N(4)	112.1(2)
N(2)	P	N(3)	104.8(2)
N(2)	P	N(4)	104.9(2)

[a]Numbers in parentheses are estimated standard deviations in the last significant digits.

Table 13, Continued.

Atom 1	Atom 1	Atom 3	Angle[a]
N(3)	P	N(4)	105.9(3)
C(3)	N(1)	C(6)	117.0(6)
C(3)	N(1)	C(9)	120.995)
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(3)	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)	119.3(4)
P	N(4)	C(7)	119.3(4)
P	N(4)	C(7)	123.2(4)
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(12)	O(12)	174.6(6)
Re	C(13)	O(13)	179.5(6)

Table 13, Continued.

Atom 1	Atom 1	Atom 3	Angle[a]
Re	C(14)	O(14)	175.6(6)
Re	C(11)	O(11)	176.8(6)

Table 14. Bond Angles (deg) for $Hg(\mathbf{1})_2Cl_2$, **7**

Atom 1	Atom 1	Atom 3	Angle[a]
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)	P(2)	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)
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)
C(1)	N(1)	C(4)	121(1)
C(1)	N(1)	C(7)	120(1)
C(4)	N(1)	C(7)	119(1)

[a]Numbers in parentheses are estimated standard deviations in the last significant digits.

Table 14, Continued.

Atom 1	Atom 1	Atom 3	Angle[a]
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(6)	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)
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)

Table 14, Continued.

Atom 1	Atom 1	Atom 3	Angle[a]
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)
N(5)	C(16)	C(17)	115(1)
N(8)	C(17)	C(16)	113(1)

Table 15. Bond Angles (deg) for **8**(I)

Atom 1	Atom 1	Atom 3	Angle[a]
N(2)	P	N(3)	110.8(2)
N(2)	P	N(4)	113.9(2)
N(2)	P	C(10)	106.4(2)
N(3)	P	N(4)	115.5(2)
N(3)	P	C(10)	106.7(2)
N(4)	P	C(10)	102.4(2)
C(10)	S(2)	C(11)	103.5(2)
C(3)	N(1)	C(6)	118.0(3)
C(3)	N(1)	C(9)	117.6(3)
C(6)	N(1)	C(9)	122.5(3)
P	N(2)	C(1)	123.0(3)
P	N(2)	C(2)	119.0(3)
C(1)	N(2)	C(2)	114.5(3)
N(2)	C(2)	C(3)	110.2(3)
N(1)	C(3)	C(2)	108.3(3)
P	N(3)	C(4)	122.4(3)
P	N(3)	C(5)	120.0(2)
C(4)	N(3)	C(5)	111.5(3)
N(3)	C(5)	C(6)	111.3(3)
N(1)	C(6)	C(5)	111.5(3)

[a]Numbers in parentheses are estimated standard deviations in the last significant digits.

Table 15, Continued.

Atom 1	Atom 1	Atom 3	Angle[a]
P	N(4)	C(7)	123.6(3)
P	N(4)	C(8)	119.4(3)
C(7)	N(4)	C(8)	115.2(3)
N(4)	C(8)	C(9)	112.2(3)
N(1)	C(9)	C(8)	110.4(3)
P	C(10)	S(2)	113.9(2)
P	C(10)	S(1)	119.9(2)
S(2)	C(10)	S(1)	126.2(2)

Table 16. Bond Angles (deg) for **9**(I)

Atom 1	Atom 1	Atom 3	Angle[a]
H(10)	O	H(20)	134.5
C(10)	S(1)	C(11)	109.5(3)
N(2)	P(1)	N(4)	124.5(3)
N(2)	P(1)	N(3)	116.6(3)
N(4)	P(1)	N(3)	113.8(3)
N(2)	P(1)	C(10)	97.6(3)
N(4)	P(1)	C(10)	95.0(3)
N(3)	P(1)	C(10)	100.2(3)
N(2)	P(1)	N(1)	82.3(3)
N(4)	P(1)	N(1)	80.8(3)
N(3)	P(1)	N(1)	84.5(2)
C(10)	P(1)	N(1)	174.7(3)
C(2)	N(1)	C(4)	114.9(8)
C(2)	N(1)	C(6)	112.0(9)
C(4)	N(1)	C(6)	113.0(8)
C(2)	N(1)	P(1)	106.4(5)
C(4)	N(1)	P(1)	103.1(4)
C(6)	N(1)	P(1)	106.5(5)
C(7)	N(2)	C(1)	110.4(7)
C(7)	N(2)	P(1)	123.1(5)

[a]Numbers in parentheses are estimated standard deviations in the last significant digits.

Table 16, Continued.

Atom 1	Atom 1	Atom 3	Angle[a]
C(1)	N(2)	P(1)	121.3(6)
C(3)	N(3)	C(8)	112.1(6)
C(3)	N(3)	P(1)	114.6(5)
C(8)	N(3)	P(1)	117.2(4)
C(5)	N(4)	C(9)	116.3(7)
C(5)	N(4)	P(1)	121.0(6)
C(9)	N(4)	P(1)	122.2(5)
C(10)	N(5)	C(12)	122.5(5)
C(2)	C(1)	N(2)	112.5(8)
N(1)	C(2)	C(1)	108.9(7)
N(3)	C(3)	C(4)	108.5(6)
N(1)	C(4)	C(3)	105.4(6)
N(4)	C(5)	C(6)	109.8(8)
N(5)	C(6)	N(1)	105.8(8)
N(5)	C(10)	S(1)	120.6(5)
N(5)	C(10)	P(1)	118.1(5)
S(1)	C(10)	P(1)	121.1(4)
C(17)	C(12)	C(13)	119.4(7)
C(17)	C(12)	N(5)	118.6(6)
C(13)	C(12)	N(5)	121.9(7)
C(12)	C(13)	C(14)	119.4(5)
C(15)	C(14)	C(13)	121.7(9)

Table 16, Continued.

Atom 1	Atom 1	Atom 3	Angle[a]
C(14)	C(15)	C(16)	118.9(8)
C(15)	C(16)	C(17)	120.7(5)
C(12)	C(17)	C(16)	120.4(8)
C(10')	S(1')	C(11')	108.7(3)
N(4')	P(1')	N(2')	125.7(3)
N(4')	P(1')	N(3')	113.2(3)
N(2')	P(1')	N(3')	117.1(3)
N(4')	P(1')	C(10')	99.9(3)
N(2')	P(1')	C(10')	96.2(3)
N(3')	P(1')	C(10')	99.9(3)
N(4')	P(1')	N(1')	81.5(2)
N(2')	P(1')	N(1')	83.2(2)
N(3')	P(1')	N(1')	85.8(2)
C(10')	P(1')	N(1')	173.9(2)
C(2')	N(1')	C(6')	113.4(9)
C(2')	N(1')	C(4')	114.0(9)
C(6')	N(1')	C(4')	109.9(9)
C(2')	N(1')	P(1')	107.2(5)
C(6')	N(1')	P(1')	107.8(5)
C(4')	N(1')	P(1')	103.7(5)
C(1')	N(2')	C(7')	110.5(6)
C(1')	N(2')	P(1')	121.2(4)

Table 16, Continued.

Atom 1	Atom 1	Atom 3	Angle[a]
C(7')	N(2')	P(1')	124.7(5)
C(3')	N(3')	C(8')	111.8(5)
C(3')	N(3')	P(1')	115.8(5)
C(8')	N(3')	P(1')	116.6(4)
C(9')	N(4')	C(5')	113.3(6)
C(9')	N(4')	P(1')	124.1(6)
C(5')	N(4')	P(1')	121.3(5)
C(10')	N(5')	C(12')	123.5(5)
C(2')	C(1')	N(2')	113.1(7)
C(1')	C(2')	C(4')	111.3(6)
N(3')	C(3')	C(4')	110.7(6)
N(1')	C(4')	C(3')	108.5(7)
C(6')	C(5')	N(4)	110.1(7)
C(5')	C(6')	N(1')	109.7(8)
N(5')	C(10')	S(1')	118.1(4)
N(5')	C(10')	P(1')	119.7(4)
S(1')	C(10')	P(1')	122.1(3)
C(13')	C(12')	C(17')	121.7(7)
C(13')	C(12')	N(5')	120.3(7)
C(17')	C(12')	N(5')	117.6(6)
C(14')	C(13')	C(12')	117.5(9)
C(13')	C(14')	C(15')	124.2(8)

Table 16, Continued.

Atom 1	Atom 1	Atom 3	Angle[a]
C(14')	C(15')	C(16')	116.2(8)
C(15')	C(16')	C(17')	123.1(8)
C(16')	C(17')	C(12')	117.2(8)
H(10)	O	H(20)	134.5

PAPER 3. SYNTHESIS OF NEW EXCEEDINGLY STRONG NON-IONIC BASES: $R=P(MeNCH_2CH_2)_3N$

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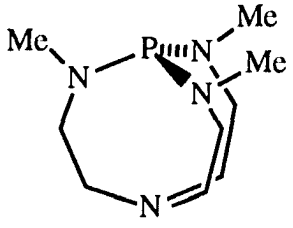
ABSTRACT

The syntheses of $MeN{=}P(MeNCH_2CH_2)_3N$ (**4**), $[HRNP(MeNCH_2CH_2)_3N](CF_3CO_2)$ (R = Ph, **5**(CF_3CO_2); R = Me, **6**(CF_3CO_2)), $[MePhNP(MeNCH_2CH_2)_3N]I$ (**7**(I)), the stable azide adduct $MeN_3P(MeNCH_2CH_2)_3N$ (**8**), $[HRNP(NMe_2)_3](CF_3CO_2)$ (R = Ph, **9**(CF_3CO_2); R = Me, **10**(CF_3CO_2)) are reported. Equilibria measured by ^{31}P NMR spectroscopy reveal the relative ordering of basicity: t-$BuN{=}P[N{=}P(NMe_2)_3]_3$ > $P(MeNCH_2CH_2)_3N$ (**1**) > $MeN{=}P(MeNCH_2CH_2)_3N$ (**4**) > $MeN{=}P(NMe_2)_3$ > DBU > $PhN{=}P(MeNCH_2CH_2)_3N$ (**3**) > $PhN{=}P(NMe_2)_3$ in CD_3CN. The unusually strong basicities of the polycyclic cage bases (e.g., those of **1** and **4** are *ca.* 17 and more than 3 pK_b units stronger than DBU, respectively) and the stability of adduct **8** is rationalized on the basis of partial transannulation from the bridgehead nitrogen to phosphorus which effectively delocalizes positive charge. The structure of **5**(CF_3CO_2) determined by X-ray means is also reported, revealing a transannular distance of 2.559 (4) Å which is facilitated by a widened average MeN-P-NMe bond angle of 114.9 (2)°.

INTRODUCTION

Strong non-ionic bases play an important role in organic synthesis because of the generally milder reaction conditions they generally permit,[1] the enhanced reactivity of the more naked anions in the poorly associating ion pairs formed upon substrate deprotonation by such bases (in contrast to ionic bases)[2] and the better solubility of non-ionic bases at room temperature and at the low temperatures required for some reactions.[3] Non-ionic bases are typically sterically hindered nitrogen compounds such as Proton Sponge,[4] DBU,[5] DBN[5a,6] and peralkylated guanidines.[7] P$_4$-*t*-Bu, (*t*-BuN=P[N=P(NMe$_2$)$_3$]$_3$) is a base whose conjugate acid (which is protonated on the *t*-BuN nitrogen) is about 18 pK_a units weaker than that of HDBU$^+$.[3] Recently reported from our laboratories was the unusual non-ionic base **1**[8] which is protonated at phosphorus (rather than at nitrogen) to give cation **2**, whose structure has been obtained by X-ray means.[8a] The pK_a of **2**, though surprisingly large in DMSO (with an



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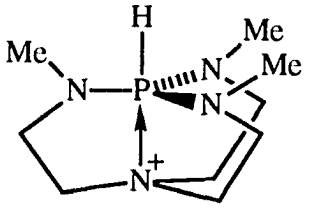

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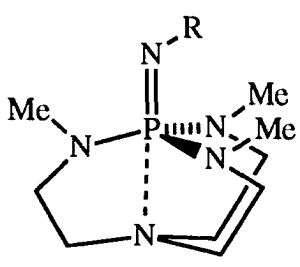
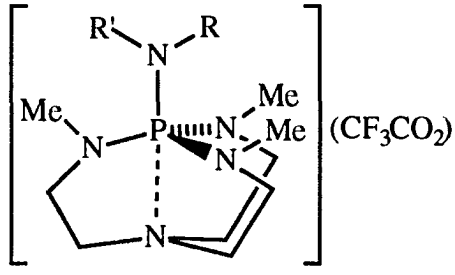
upper limit of 26.8[8c,d]), is not quite as large as that reported for the conjugate acid of P$_4$-*t*-Bu in THF (28.04). The use of base **1** in organic synthesis, however, would appear to have two main advantages over P$_4$-*t*-Bu: (1) **1** is easier and less expensive to synthesize (requiring three steps from commercially available starting materials) while P$_4$-*t*-Bu requires seven steps (one of them requiring six days),[3] and (2) salts of **2** formed in reactions utilizing **1** as a strong base are quite insoluble in common organic solvents, whereas this is not the case with salts of the conjugate acid of P$_4$-*t*-Bu. Thus the separation of the organic product from salts of **2** is not

only more facile, but the recovery of base **1** from such salts is easy, requiring only treatment with *t*-BuO$^-$. Base **1** is also a superior catalyst for the trimerization of aryl isocyanates to triisocyanurates.[9]

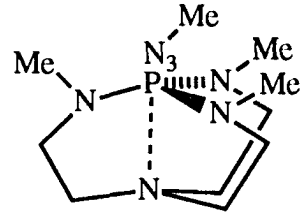
In view of the strong basicity of **1** that results from transannulation, it was of interest to determine how the basicity and transannulation capability of **1** changes when it is transformed into an imidophosphatranes such as **3**[10] and **4**, and how the basicities of the latter compounds compare with those of the analogous acyclic analogues $PhN{=}P(NMe_2)_3$ and $MeN{=}P(NMe_2)_3$, and with P_4-*t*-Bu. In this paper we report the synthesis and isolation of the new imidophosphatrane **4**; the conjugate acid cations of **3** and **4**, namely, **5** and **6**, respectively; the methylated cation of **3**, namely, **7**, the azide intermediate of **4**, namely, **8**; the conjugate acid



3, R = Ph
4, R = Me



5(CF_3CO_2), R = Ph, R' = H
6(CF_3CO_2), R = Me, R' = H
7(I), R = Ph, R' = Me



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cations of $PhN{=}P(NMe_2)_3$ and $MeN{=}P(NMe_2)_3$, namely, **9** and **10**, respectively; and the

$[HPhNP(NMe_2)_3](CF_3CO_2)$	$[HMeNP(NMe_2)_3](CF_3CO_2)$	$[HP_4$-*t*-$Bu](CF_3CO_2)$
9(CF_3CO_2)	**10**(CF_3CO_2)	**11**(CF_3CO_2)

conjugate acid of P_4-*t*-Bu, namely **11**. We also report the structure of **5**(CF_3CO_2) as determined by X-ray means and the relative basicities of **3**, **4** $PhN{=}P(NMe_2)_3$, $MeN{=}P(NMe_2)_3$, DBU, **1** and P_4-*t*-Bu.

EXPERIMENTAL SECTION

Acetonitrile and benzene were dried with CaH_2, and THF, toluene and pentane were dried with sodium. All solvents were freshly distilled and all reactions were done under argon. ^1H and ^{13}C NMR spectra were recorded on a Nicolet NT-300 and a Varian VXR-300 NMR spectrometer, respectively. ^{31}P NMR spectra were recorded on a Bruker WM-200 NMR spectrometer using 85% H_3PO_4 as the external standard. High resolution and FAB mass spectra were recorded on a KRATOS MS-50 spectrometer. Elemental analysis were performed by Desert Analytics.

Compounds **1** and **2**(Cl) were synthesized according to our previously published method.[8,10] Phenyl[11] and methyl[12] azides were synthesized following earlier reports.

WARNING. Azides can decompose explosively and should be handled with appropriate care.[11]

PhN=P(NMe$_2$)$_3$. Although this compound is known,[13] we found the following procedure convenient. To a solution of hexamethyl phosphorus triamide (5.0 g, 85%, 2.6 mmol) in benzene (15 mL) at 70 °C was added dropwise a solution of phenyl azide (3.182g, 2.674 mmol) in benzene (15 mL) over a period of 30 min. The mixture was refluxed for 10 h. and allowed to cool to room temperature. The solvent was removed in vacuo and the residue was distilled at 127 °C/0.4 torr (127 °C/0.4 torr[13]) to give a yellowish liquid (5.9 g, 90%; Lit.[13], 91%). ^{31}P NMR (CD_3CN): 20.66; ^1H (CD_3CN): 2.63 (d, 18H, NCH_3, $^3J_{PH}$ = 9.6 Hz); 6.50-7.01 (m, 5H, Ph); ^{13}C (CD_3CN): 37.69 (d, NCH_3, $^2J_{PC}$ = 3.2 Hz), 116.71, 123.38, 123.60 and 129.47 (d, $^2J_{PC}$ = 1.1 Hz, Ph); HRMS *m/z* calcd for $C_{12}H_{23}N_4P$: 254.16604. Found 254.16611 (33, M^+).

MeN=P(NMe$_2$)$_3$. Although this is a known compound,[14] we found the following procedure convenient. To a solution of $P(NMe_2)_3$ (5.0 g, 85%, 3.1 mmol) in toluene (50 mL) at 0-5 °C was added with a syringe precooled in a refrigerator, cold methyl azide (8.7 g, 15

mmol). The mixture (in a flask closed by a septum) was stirred at 0-5 °C for 1.5 h., then at room temperature for 1h. with the flask vented by a needle, and finally at 50-60 °C for 5h. The volatiles were removed in vacuo and the crude product was distilled in vacuo to give a colorless liquid (3.75 g, 63%, Lit.[14], 81%, 36-39 °C/~0.4 torr, 48-52 °C/vacuum[14]). ^{31}P (CD_3CN): 30.60; ^{1}H (CD_3CN): 2.56 (d, 18H, $N(CH_3)_2$, $^{3}J_{PH}$ = 9.3 Hz), 2.72 (d, 3H, NCH_3, $^{3}J_{PH}$ = 23.1 Hz). ^{13}C (CD_3CN): 31.73 (d, NCH_3, $^{2}J_{PC}$ = 4.3 Hz), 37.65 (d, $N(CH_3)_2$, $^{2}J_{PC}$ = 4.5 Hz); HRMS *m/z* calcd for $C_7H_{21}N_4P$: 192.15039. Found: 192.15012 (7, M^+).

PhN=P(MeNCH$_2$CH$_2$)$_3$N, 3. This compound was synthesized according to our previously reported method[10] with a minor modification. To a solution of **1** (2.192 g, 1.015 mmol) in benzene (60 mL) at 70 °C was added dropwise a solution of phenyl azide (1.227 g, 1.031 mmol) in benzene (50 mL) over a period of 45 min. The mixture was refluxed for 12 h. and allowed to cool to room temperature. The solution was concentrated to about 20 mL. Crystallization was induced by adding pentane and allowing the solution to remain in a freezer for 4 h. The supernatant liquid was removed with a syringe and the yellowish solid product was dried in vacuo to give ^{1}H NMR spectroscopically pure **3** (2.7 g, 88%; lit., 84%[10]). ^{31}P NMR (CD_3CN): 16.17; ^{1}H NMR (CD_3CN): consistent with that in the literature;[10] HRMS *m/z* calcd for $C_{15}H_{26}N_5P$: 307.19259. Found 307.19251 (31, M^+).

MeN=P(MeNCH$_2$CH$_2$)$_3$N, 4. *Method A.* A solution of 0.50 g (1.8 mmol) of **8** (see later) in benzene (20 mL) was refluxed for 10 h. The solution was concentrated in vacuo to about 2 mL. This concentrate was crystallized by adding pentane and allowing the solution to remain in a freezer overnight. The supernatant liquid was removed by syringe to give the yellowish solid **4** (0.42 g, 94%) after drying in vacuo. ^{31}P (CD_3CN): 26.65; ^{1}H (CD_3CN): 2.62 (d, 9H, $N_{eq}CH_3$, $^{3}J_{PH}$ = 7.8 Hz), 2.71 (t, 6 H, $N_{ax}CH_2$, $^{3}J_{HH}$ = 5.5 Hz), 2.79 (d, 3 H, $N_{exo}CH_3$, $^{3}J_{PH}$ = 22.2 Hz), 2.83 (dt, 6 H, $N_{eq}CH_2$, $^{3}J_{PH}$ = 12.3 Hz, $^{3}J_{HH}$ = 5.5 Hz); ^{13}C (CD_3CN): 31.42 (d, $N_{exo}CH_3$, $^{2}J_{PC}$ = 2.2 Hz), 34.44 (d, $N_{eq}CH_3$, $^{2}J_{PC}$ = 4.8 Hz), 49.16

(s, $N_{ax}CH_2$), 51.37 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 2.2 Hz); HRMS *m/z* calcd. for $C_{10}H_{24}N_5P$: 245.17694. Found 245.17679 (32, M^+).

Method B. To a solution of **1** (0.705 g, 3.26 mmol) in toluene (20 mL) at 0-5 °C was added by syringe cold methyl azide (3 mL). The mixture (in a flask closed by a septum) was stirred at 0-5 °C for 3 h., at room temperature for 0.5 h. with the flask vented by a needle and then at 80-90 °C for 10 h. The solution was concentrated in vacuo to about a 3 mL concentrate which was crystallized by adding pentane and allowing the solution to stand in a freezer overnight. The supernatant liquid was removed by syringe to give a yellowish solid (0.73 g, 91%) after drying in vacuo.

[HPhNP(MeNCH$_2$CH$_2$)$_3$N]CF$_3$CO$_2$, 5(CF$_3$CO$_2$). To a solution of **3** (0.193 g, 0.629 mmol) in CH_3CN (2 mL) was added by syringe trifluoroacetic acid (0.076 g, 0.67 mmol). The solution was stirred for 1 h. at room temperature and then evaporated in vacuo to remove the solvent. The residue was washed with ethyl acetate and dried in vacuo to give **5**(CF_3CO_2) as a ^1H NMR spectroscopically pure white solid (0.26 g, 97%). Colorless crystals were grown from THF/ethyl acetate in a freezer. ^{31}P (CD_3CN): 18.35; ^1H (CD_3CN): 2.74 (d, 9H, $N_{eq}CH_3$, $^3J_{PH}$ = 11.7 Hz), 2.82 (t, 6H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.4 Hz), 3.04 (dt, 6H, $N_{eq}CH_2$, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 5.4 Hz), 6.79 (bd, s, 1H, NHPh), 6.93-7.28 (m, 5H, Ph); ^{13}C (CD_3CN): 37.47 (d, $N_{eq}CH_3$, $^2J_{PC}$ = 4.3 Hz), 50.37 ($N_{ax}CH_2$), 50.38 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 7.0 Hz), 119.98, 120.06, 122.45 and 130.17 (Ph); (The CF_3CO_2 signals were weak and were not recorded); MS (FAB) *m/z*: 308.1 (100, [PhNHP(MeNCH$_2$CH$_2$)$_3$N]$^+$), 729.4 (0.1, [(PhNH(MeNCH$_2$CH$_2$)$_3$N)$_2$CF$_3$CO$_2$]$^+$); Elemental analysis calculated for $C_{17}H_{27}F_3N_5O_2P$: C, 48.43; H, 6.46; N, 16.62. Found: C, 48.34; H, 6.81; N, 15.94.

[HMeNP(MeNCH$_2$CH$_2$)$_3$N]CF$_3$CO$_2$, 6(CF$_3$CO$_2$): To a solution of **4** (0.366 g, 1.49 mmol) in CH_3CN (4 mL) was added by syringe trifluoroacetic acid (0.169 g, 1.49 mmol). The mixture was stirred for 1 h. and evaporated in vacuo to remove the solvent. The residue was recrystallized from ethyl acetate/pentane in a freezer overnight. The supernatant

liquid was removed by syringe to give a white solid (0.51 g, 96%) after drying in vacuo. ^{31}P (CD_3CN): 37.88; ^{1}H (CD_3CN): 2.65 ($N_{ax}CH_2$, overlapping with $N_{eq}CH_3$), 2.70 (d, $N_{exo}CH_3$, $^{3}J_{PH}$ = 10.2 Hz, partially overlapping with $N_{eq}CH_3$), 2.72 (d, $N_{eq}CH_3$, $^{3}J_{PH}$ = 9.6 Hz), 2.86 (dt, 6H, $N_{eq}CH_2$, $^{3}J_{PH}$ = 14.7, $^{3}J_{HH}$ = 4.8 Hz), 4.06 (bd s, 1H, $N_{exo}H$); ^{13}C (CD_3CN): 29.05 ($N_{exo}CH_3$), 35.50 (d, $N_{eq}CH_3$, $^{2}J_{PC}$ = 2.7 Hz), 50.03 (d, $N_{ax}CH_2$, $^{3}J_{PC}$ = 1.1 Hz), 51.43 (d, $N_{eq}CH_2$, $^{2}J_{PC}$ = 2.7 Hz); MS (FAB) *m/z*: 246.2 (100, $[MeNHP(MeNCH_2CH_2)_3N]^+$), 605.3 (0.7, $[(MeNHP(MeNCH_2CH_2)_3N)_2CF_3CO_2]^+$); Elemental analysis calculated for $C_{12}H_{25}F_3N_5O_2P$: C, 40.09; H, 7.01; N, 19.49. Found: C, 39.72; H, 7.20; N, 19.15.

[MePhNP(MeNCH$_2$CH$_2$)$_3$N]I, 7(I). To a solution of **3** (0.202 g, 0.658 mmol) in CH_3CN (2 mL) was added by syringe methyl iodide (0.104 g, 0.731 mmol). The mixture was stirred for 5 h. and evaporated in vacuo to remove volatiles. The residue (0.295 g, 100%) was ^{1}H NMR spectroscopically pure **15**(I). ^{31}P NMR (CD_3CN): 36.31; ^{1}H (CD_3CN): 2.55 (d, 9H, $N_{eq}CH_3$, $^{3}J_{HH}$ = 9.6 Hz), 2.76 (t, 6H, $N_{ax}CH_2$, $^{3}J_{HH}$ = 4.7 Hz), 2.89 (dt, 6H, $N_{eq}CH_2$, $^{3}J_{PH}$ = 15.0 Hz, $^{3}J_{HH}$ = 4.7 Hz), 3.19 (d, 3H, $N_{exo}CH_3$, $^{3}J_{PH}$ = 8.4 Hz), 7.36-7.48 (m, 5H, Ph); ^{13}C (CD_3CN): 35.95 (d, $N_{exo}CH_3$, $^{2}J_{PC}$ = 3.2 Hz), 43.62 (d, $N_{eq}CH_3$, $^{2}J_{PC}$ = 5.4 Hz), 49.92 (d, $N_{ax}CH_2$, $^{3}J_{PC}$ = 1.1 Hz), 52.28 (d, $N_{eq}CH_2$, $^{2}J_{PC}$ = 2.7 Hz), 128.64 (d, Ph, J_{PC} = 1.1 Hz), 130.50 (d, Ph, J_{PC} = 2.7 Hz), 130.88 (d, Ph, J_{PC} = 1.1 Hz), 144.11 (d, Ph, J_{PC} = 4.3 Hz); MS (FAB) *m/z*: 322.1 (100, $[MeNPhP(MeNCH_2CH_2)_3N]^+$), 771.3 (1.7, $[(MeNPhP(MeNCH_2CH_2)_3N)_2I]^+$); Elemental analysis calculated for $C_{16}H_{29}IN_5P$: C, 42.75; H, 6.51, N, 15.59. Found: C, 41.99; H, 6.64, N, 15.12.

MeN$_3$P(MeNCH$_2$CH$_2$)$_3$N, 8. To a solution of **1** (2.388 g, 1.165 mmol) in toluene (15 mL) at 0-5 °C was added by a precooled syringe cold methyl azide (3.1 g, 5.4 mmol). The mixture was stirred in a flask closed by a septum at 0-5 °C for 2h., then at room temperature for 0.5 h. with the flask vented by a needle, and finally at 50-60 °C for 2 h. The solution was concentrated to about 5 mL and pentane added, and then it was placed in a freezer for 5 h. The

parent liquid was removed by syringe and the solid product dried in vacuo to give 2.85 g (95%) of **8**. ^{1}H (CD_3CN): 2.67 (d, 9H, $N_{eq}CH_3$, $^{3}J_{PH}$ = 7.8 Hz), 2.78 (t, 6H, $N_{ax}CH_2$, $^{3}J_{HH}$ = 6.5 Hz), 2.90 (dt, 6H, $N_{eq}CH_2$, $^{3}J_{PH}$ = 17.1 Hz, $^{3}J_{HH}$ = 6.5 Hz), 3.25 (s, 3 H, N_3CH_3); ^{13}C (CD_3CN): 35.55 (d, $N_{eq}CH_3$, $^{2}J_{PC}$ = 2.7 Hz), 48.27 (s, N_3CH_3), 50.09 (s, $N_{ax}CH_2$), 52.11 (d, $N_{eq}CH_2$, $^{2}J_{PC}$ = 1.6 Hz); HRMS *m/z* calcd for $C_{10}H_{24}N_7P$: 273.18309. Found 273.18406 (1, M^+), 245.17652 (4, M^+-N_2).

[HPhNP(NMe$_2$)$_3$]CF$_3$CO$_2$, 9(CF$_3$CO$_2$). To a solution of PhN=P(NMe_2)$_3$ (1.50 g, 5.90 mmol) in CH_3CN (8 mL) was added by syringe trifluoroacetic acid (0.67 g, 5.9 mmol). The mixture was stirred for 1 h. and evaporated in vacuo to remove volatiles. The residue was washed with ethyl acetate and dried in vacuo to give white solid **9** (CF_3CO_2) (2.1 g, 95%). ^{31}P (CD_3CN): 36.62; ^{1}H (CD_3CN): 2.71 (d, 18H, NCH_3, $^{3}J_{PH}$ = 9.9 Hz), 7.06-7.34 (m, 5H, Ph), 8.95 (b, 1 H, NHPh); ^{13}C (CD_3CN): 37.48 (d, $N(CH_3)_2$, $^{2}J_{PC}$ = 4.8 Hz), 121.67 (d, Ph, $^{2}J_{PC}$ = 7.0 Hz), 124.35, 130.46 and 140.28 (Ph); (CF_3CO_2 signals were not recorded because of weakness); MS (FAB) *m/z*: 255.0 (100, $[(Me_2N)_3PNHPh]^+$), 622.9 (2.1, $[((Me_2N)_3PNHPh)_2CF_3CO_2]^+$).

HMeNP(NMe$_2$)$_3$, 10(CF$_3$CO$_2$). To a solution of MeN=P(NMe_2)$_3$ (0.765 g, 3.98 mmol) in acetonitrile (5 mL) was added by syringe trifluoroacetic acid (0.454 g, 3.98 mmol). The mixture was stirred for 1 h. and then evaporated under vacuum to remove the solvent. The residue was recrystallized from ethyl acetate/pentane at freezer temperature for 4h. The supernatant liquid was removed with a syringe and the crystalline product dried in vacuo to give **10**(CF_3CO_2) (1.1 g, 93%). ^{31}P (CD_3CN): 43.09; ^{1}H (CD_3CN): 2.59 (d, 3H, NCH_3, $^{3}J_{PH}$ = 12.6 Hz), 2.68 (d, 18H, $N(CH_3)_2$, $^{3}J_{PH}$ = 9.6 Hz), 5.41 (br, 1 H, N*H*CH_3); ^{13}C (CD_3CN): 27.58 (NCH_3), 37.06 (d, $N(CH_3)_2$, $^{2}J_{PC}$ = 4.8 Hz). MS (FAB) *m/z*: 193.1 (100, $[MeHNP(NMe_2)_3]^+$), 499.2 (2,4, $[(MeNHP(NMe_2)_3)_2CF_3CO]^+$).

[HP$_4$-*t*-Bu]CF$_3$CO$_2$, 11(CF$_3$CO$_2$): To a solution of P$_4$-*t*-Bu (0.347 g, 0.547 mmol) in THF (5 mL) was added by syringe trifluoroacetic acid (0.062 g, 0.547 mmol) and

the mixture was stirred for 2 h. The clear solution was evaporated in vacuo to give NMR spectroscopically pure **11**(CF_3CO_2) (0.4 g, 100%): ^{31}P (THF, CD_3CN external lock solvent): -22.90 (q, 1P, $^2J_{PP}$ = 50.5 Hz), 13.39 (d, 3P, $^2J_{PP}$ = 50.5 Hz); ^1H NMR (CD_3CN): 1.28 (s, 9H, *t*-Bu), 2.63 (d, 55 H, NMe_2, $^3J_{PH}$ = 9.9 Hz and HN^+(*t*-Bu)); MS (FAB) *m/z*: 634.4 (100, [P_4-*t*-Bu-H]$^+$); ^{31}P NMR of P_4-*t*-Bu, (THF, CD_3CN external lock solvent): -24.44 (q, 1P, $^2J_{PP}$ = 20.2 Hz), 5.73 (d, 3P, $^2J_{PP}$ = 20.2 Hz).

pK_a Value of 2. The pK_a of **2** was measured by ^{31}P NMR spectroscopy in an equilibration (equilibrium, see Disscusion). *Method A.* To an NMR tube containing the acid [HP_4-*t*-Bu]CF_3CO_2, **11**(CF_3CO_2), (0.0426 g, 0.0569 mmol) and 1.5 mol percent of $Cr(acac)_3$ as a relaxagent was added a solution of the base **1** (0.0123 g, 0.0569 mmol) in THF. The mixture was diluted to 1 mL with THF and shaken for 30 min. The ^{31}P NMR spectrum (CD_3CN as the external lock solvent) of the mixture showed signals of all four components (i.e. **1**, **2**, **11** and P_4-*t*-Bu) and their ratios did not change over 24 h. The pK_a value of **2** in THF was then calculated to be 26.7 from the integration ratios of the four components and the known pK_a value (28.0 in THF) of P_4-*t*-Bu.[3]

Method B. To an NMR tube containing (0.0273 g, 0.108 mmol) of acid **2**(Cl) and 1.5 mole percent of $Cr(acac)_3$ was added a solution of P_4-*t*-Bu (0.0808 g, 0.108 mmol) in THF. The mixture was diluted to 1 mL with THF. The pK_a value of **2** in THF calculated by the same method as in Method A is 26.5, giving an average value of 26.6 in THF.

Using the method of Schwesinger,[3] the pK_a value of cation **2** in MeCN (40.7) was obtained by interpolation from its pK_a value in THF (26.6) and the corresponding pK_a values of 28.0 in THF and 42.1 in MeCN of [HP_4-*t*-Bu]$^+$.

Equilibria 2-13. For each of these equilibria (see Discussion) the pairs of acid-base reactants and products in CD_3CN were run independently and the equilibrium composition for each reaction was measured by ^{31}P NMR spectroscopy. In each case only the two compounds on the right side (i.e., the products) of these equilibria could be observed in the ^{31}P NMR

spectra upon mixing the pairs of reactants or products. The formation of $[HDBU]^+$ in these equilibria was accomplished by mixing equimolar amounts of DBU and CF_3CO_2H in CD_3CN.

Crystal Structure Analysis of 5 (CF_3CO_2). A colorless crystal in the shape of an elongated cube was attached to the tip of a glass fiber. The cell constants for data collection were determined from reflections found by a rotation photograph. Pertinent data collection and reduction information are given in Table 1. Lorentz and polarization corrections, a correction based on decay in the standard reflections and an absorption correction was applied to the data. The agreement factor for the averaging of observed reflections was 2.1%. The space group $P2_12_12_1$ was chosen based on the systematic absences. This assumption proved to becorrectas shown by a successful direct-methods solution[16] and subsequent refinement. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms with the exception of H10A (bonded to N5) were modelled as riding atoms with a bond distance of 0.96 Å with refined isotropic thermal parameters. In the case of methyl groups, the three hydrogens were constrained to have a single thermal parameter. H10A was refined isotropically. The absolute configuration was determined to be the initial model. Refinement calculations were performed on a Digital Equipment Corp. MicroVAX 3100/76 computer using the SHELXTYL-Plus programs.[15]

Table 1. Summary of Crystallographic Data for **5**(CF_3CO_2).

	Data
crystal system	orthorhombic
space group	$P2_12_12_1$
formula	$C_{17}H_{27}F_3N_5O_2P$
formula wt, g mol^{-1}	421.4
a, Å	11.031 (4)
b, Å	11.788 (4)
c, Å	15.355 (5)
V, $Å^3$	1996.6 (12)
Z	4
r(calcd), g cm^{-3}	1.402
temp, °C	-50
abs coeff, mm^{-1}	0.188
crystal dimens, mm	0.5 x 0.45 x 0.40
trans. factors, max to min %	0.7789 - 0.6355
abs corr applied	semi-empirical
diffractometer	Siemens P4/RA
radiation	MoK_α (k = 0.71073 Å)
monochromator	highly oriented graphite crystal
method of structure soln	direct methods
refinement method	full matrix least squares
scan type	$2\theta-\theta$
scan range, deg	1.00 plus K_a-separation

Table 1, Continued.

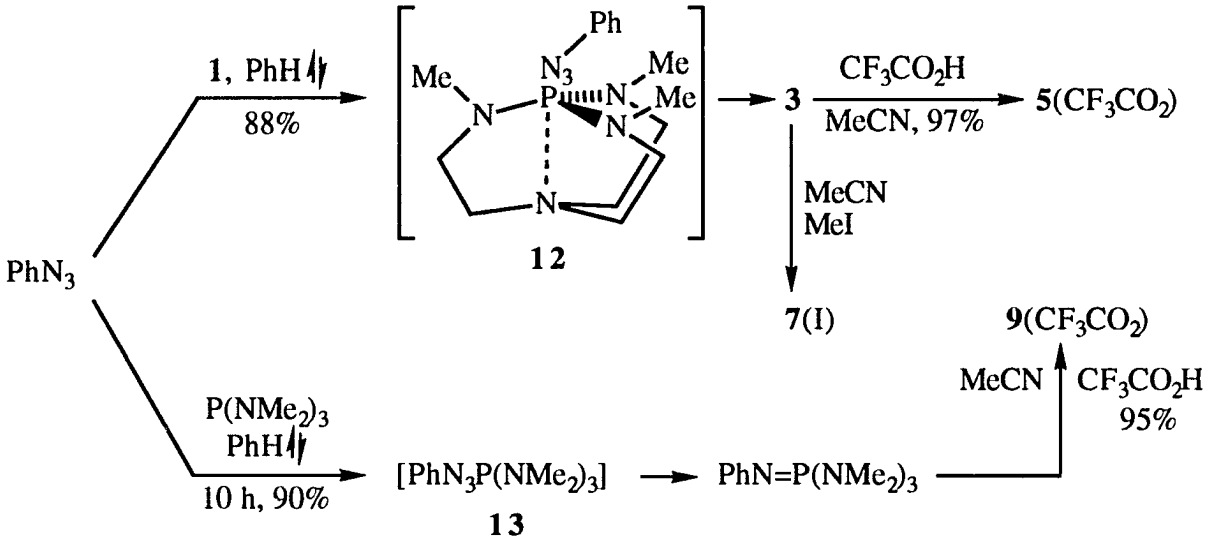
	Data
reflcns meas	6233
no. unique reflcns	5796
no. of reflcns used	2943
R	5.19
R_w	5.45
goodness-of-fit	1.77

DISCUSSION

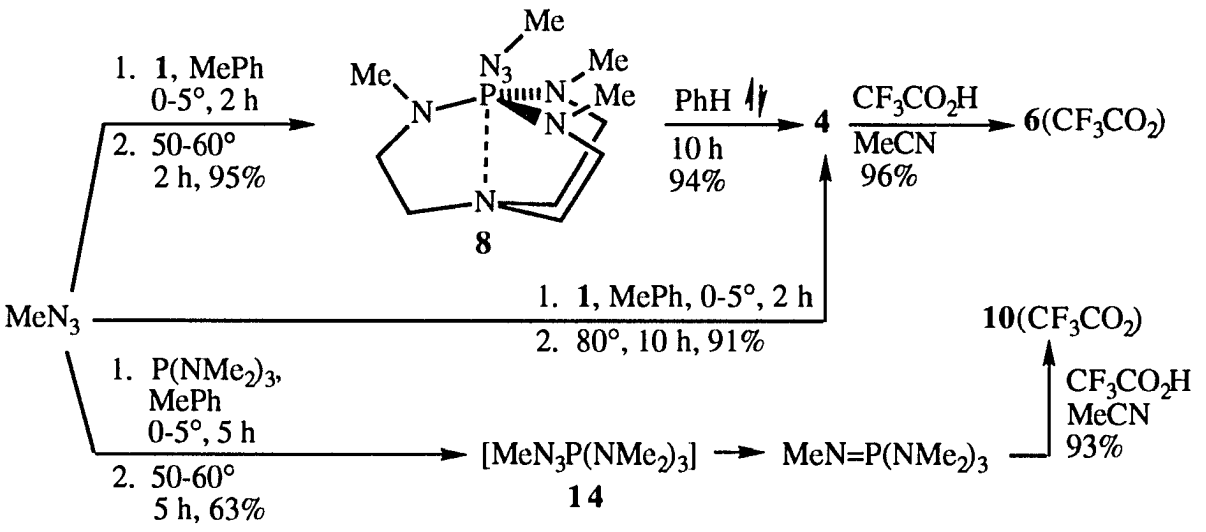
Syntheses. In Schemes 1 and 2 are summarized the syntheses of compounds **3-10**. Intermediate **12** in Scheme 1 was isolated earlier by us.[10] In contrast to intermediate **14** in Scheme 2, its polycyclic analogue **8** is isolatable after heating the initial reaction mixture at 50-60 °C for 2 h, and it requires harsher treatment than **14** to convert it to the corresponding imido derivative **4**. A rationale for this observation is put forth in the last section. Spectroscopically pure **11**(CF_3CO_2) formed in quantitative yield upon addition of one equivalent of CF_3CO_2H to P_4-*t*-Bu.

Basicity measurements. Equilibria 1-13 were established by mixing pairs of reactants and also by mixing pairs of products. Reactants and products could be detected by ^{31}P NMR spectroscopy in the case of equilibrium 1 in THF, therefore allowing the determination of an average pK_a for cation **2** of 26.6. The analogous equilibrium in MeCN

Scheme 1



Scheme 2



could not be established owing to the instability of this solvent with respect to polymerization in the presence of P_4-*t*-Bu.[3] The pK_a value of cation **2** in MeCN was obtained by interpolation (see Experimental) to be 41.2, thus rendering it stronger than $HDBU^+$ by a factor of $\sim 10^{17}$. Because equilibria 2-13 are strongly shifted to the right, only the phosphorus-containing products could be detected by ^{31}P NMR spectroscopy, and therefore only a relative ordering of

$$\mathbf{1} + \mathbf{11} \underset{}{\overset{\text{THF}}{\rightleftharpoons}} \mathbf{2} + P_4\text{-}t\text{-Bu} \quad (1)$$

$$\mathbf{1} + \mathbf{6} \overset{\text{MeCN}}{\rightleftharpoons} \mathbf{2} + \mathbf{4} \quad (2)$$

$$\mathbf{1} + \mathbf{10} \overset{\text{MeCN}}{\rightleftharpoons} \mathbf{2} + MeN{=}P(NMe_2)_3 \quad (3)$$

$$\mathbf{1} + [HDBU]^+ \overset{\text{MeCN}}{\rightleftharpoons} \mathbf{2} + DBU \quad (4)$$

$$\mathbf{1} + \mathbf{5} \overset{\text{MeCN}}{\rightleftharpoons} \mathbf{2} + \mathbf{3} \quad (5)$$

$$\mathbf{4} + \mathbf{10} \overset{\text{MeCN}}{\rightleftharpoons} \mathbf{6} + MeN{=}P(NMe_2)_3 \quad (6)$$

$$\mathbf{4} + [HDBU]^+ \overset{\text{MeCN}}{\rightleftharpoons} \mathbf{6} + DBU \quad (7)$$

$$MeN{=}P(NMe_2)_3 + [HDBU]^+ \overset{\text{MeCN}}{\rightleftharpoons} \mathbf{10} + DBU \quad (8)$$

$$\mathbf{3} + \mathbf{9} \underset{}{\overset{\text{MeCN}}{\rightleftharpoons}} \mathbf{5} + \text{PhN=P(NMe}_2)_3 \quad (9)$$

$$\text{DBU} + \mathbf{5} \underset{}{\overset{\text{MeCN}}{\rightleftharpoons}} [\text{HDBU}]^+ + \mathbf{3} \quad (10)$$

$$\text{DBU} + \mathbf{9} \underset{}{\overset{\text{MeCN}}{\rightleftharpoons}} [\text{HDBU}]^+ + \text{PhN=P(NMe}_2)_3 \quad (11)$$

$$\mathbf{4} + \mathbf{5} \underset{}{\overset{\text{MeCN}}{\rightleftharpoons}} \mathbf{6} + \mathbf{3} \quad (12)$$

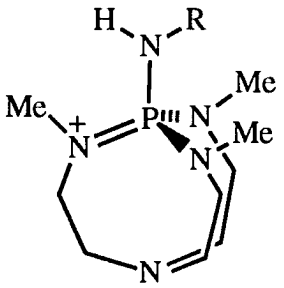
$$\text{MeN=P(NMe}_2)_3 + \mathbf{9} \underset{}{\overset{\text{MeCN}}{\rightleftharpoons}} \mathbf{10} + \text{PhN=P(NMe}_2)_3 \quad (13)$$

the basicities could be obtained in CD_3CN:

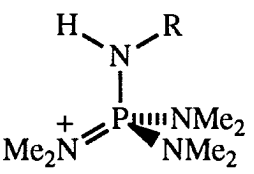
$$P_4\text{-}t\text{-Bu} > \mathbf{1} > \mathbf{4} > \text{MeN=P(NMe}_2)_3 > \text{DBU} > \mathbf{3} > \text{PhN=P(NMe}_2)_3$$

From this order it can be deduced that **4** is more than 1500 times a stronger base than DBU in MeCN since **4** is stronger than $MeN=P(NMe_2)_3$, which in turn was determined earlier to be 1500 times stronger than DBU.[1]

Structural considerations. A striking feature of this series of basicities in CD_3CN is that **1** is quite comparable to P_4-*t*-Bu in basicity since the pK_a values of the corresponding conjugate acids in this solvent are 40.7 and 42.1,[3] respectively. This is especially interesting in view of the different protonation sites in these bases and the different sources of stability of the conjugate acids (i.e., extensive resonance stabilization in the case of cation **11** and a robust chelated structure in the case of cation **2**). A second striking feature of the above basicity sequence is that **4** and **3** are more basic than their corresponding acyclic analogues $MeN=P(NMe_2)_3$ and $PhN=P(NMe_2)_3$, respectively. It could be argued that resonance structures of type **15** may be favored over those of type **16**. Another possibility is that transannulation from the bridgehead nitrogen in cations **5** and **6** inductively enhances the basicity of the imido nitrogen and delocalizes the positive charge as in **17**. We do not believe resonance structures such as **15** are primarily responsible for the stronger basicity of **3** and **4**



15



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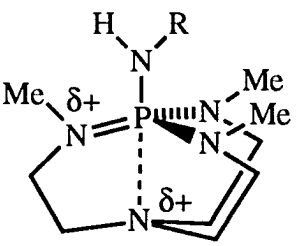


17

over their acyclic counterparts. First of all **16** would have more structural flexibility than **15**, and might therefore be expected to adopt a less strained configuration to accommodate the delocalized pi bonds inherent in the resonance structures. Secondly, any greater delocalization of positive charge out to the Me_2N nitrogens of **15** than in **16** might be expected to cause the CH_3 carbon and hydrogens in **15** to appear at lower field than in **16**. An examination of the NMR data for these atoms in **5**, **6**, **9** and **10**, however, (see Experimental) reveals no consistent trends.

If resonance structures of type **15** for **5** and **6** were enhanced by some degree of transannulation as shown in **17**, the positive charge could be predominantly delocalized to the bridgehead nitrogen (N_{ax}). The most convincing evidence for such transannulation is found in the structure of **5**(CF_3CO_2) shown in Figure 1 which we have determined by X-ray means. Here the P-N_{ax} distance of 2.551 (3) Å is 23% shorter than the sum of the van der Waals radii (3.35 Å).[17] To accommodate transannulation, the average MeN-P-NMe angle in **5**(CF_3CO_2) (115.1 (2)°) is considerably larger than tetrahedral. In an earlier publication[16a] we described a series of eight structures determined by X-ray means in which the MeN-P-NMe angle opened from 104.5° to 119.6° while the transannular distance closed from 3.33 Å to 1.967 Å. This plot is shown in Figure 2 with the insertion of these data for **5**(CF_3CO_2). The linearity of the plot prior to inclusion of this compound ($r^2 = 0.98$) is essentially preserved when the data for

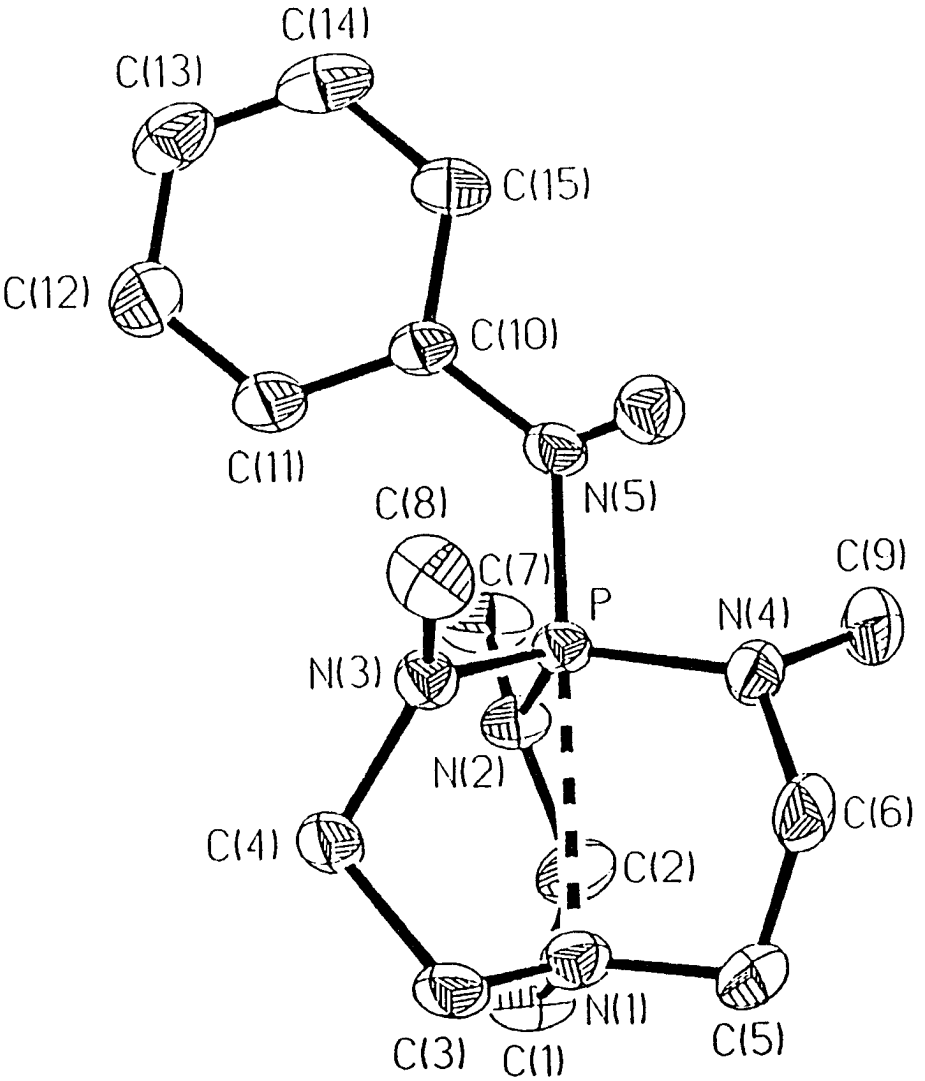


Figure 1. ORTEP drawing of **5** with ellipsoids drawn at the 50% level.

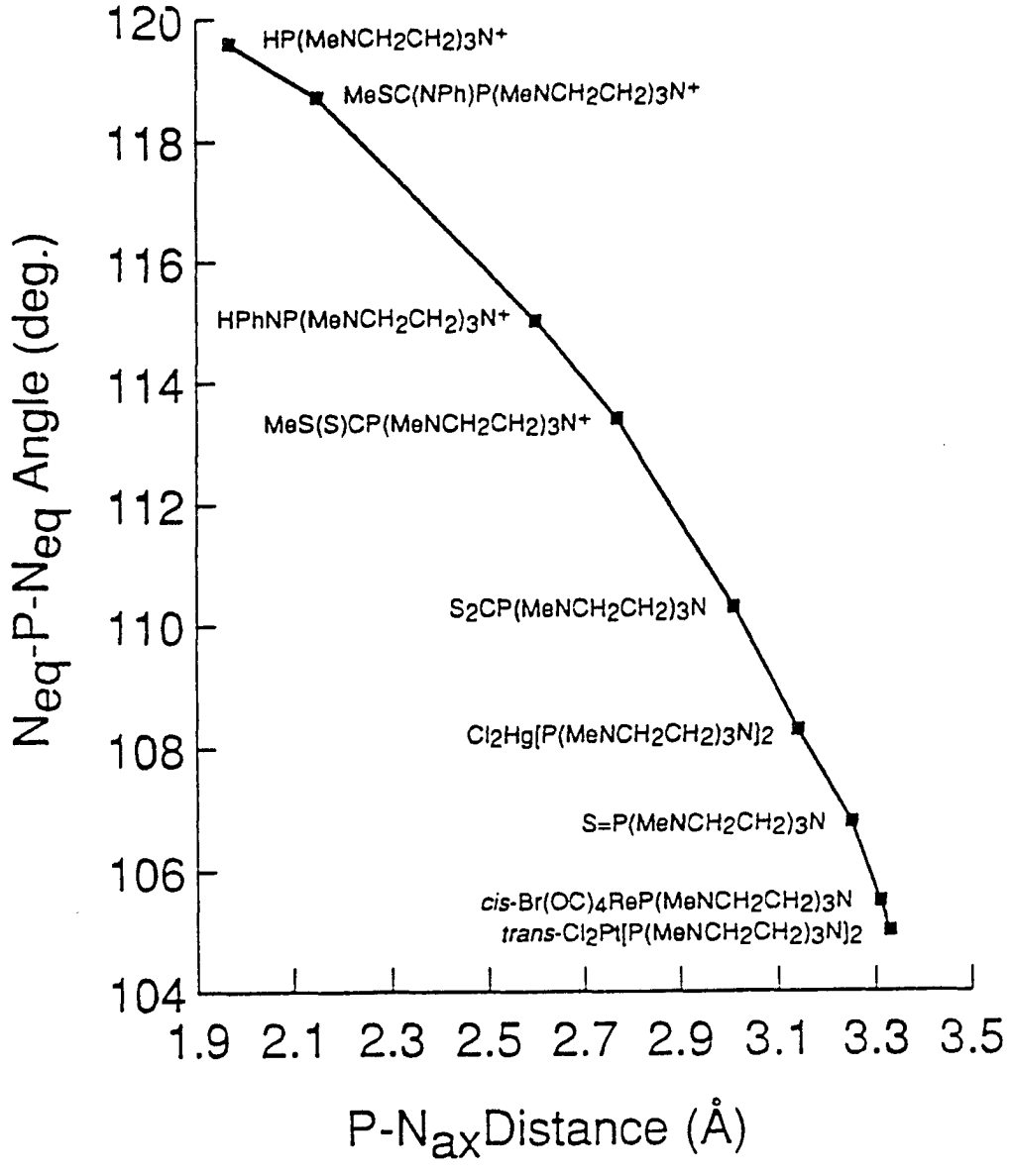
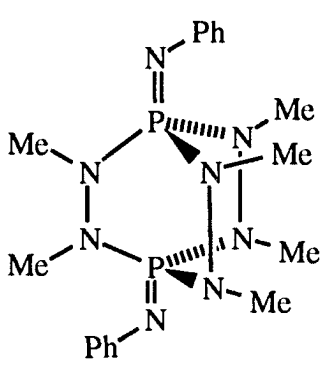


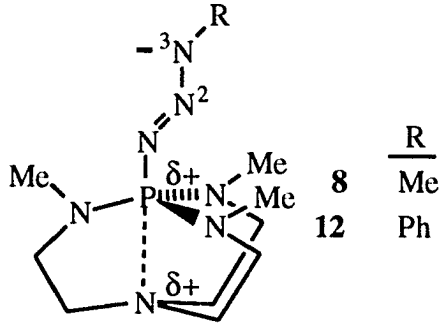
Figure 2. Plot of P-N_{ax} distances against MeN-P-NMe angles in ZP(MeNCH$_2$CH$_2$)$_3$N compounds.

cation **5** are added ($r^2 = 0.97$). It is interesting to note from Figure 2 how protonation at or near the bridgehead of **1** affects its structure. Protonation of the phosphorus of **1** to give cation **2** results in a 1.4 Å reduction in P-N_{ax} distance if it is assumed[18] that the structural metrics of **1** are similar to those of its platinum complex[19] in Figure 2. As might be expected, protonation of the imido nitrogen adjacent to phosphorus in **3** to give cation **5** gives rise to a smaller decrease (0.7 Å) in the P-N_{ax} distance, if it can be assumed that the transannular distance in **3** is at least as long as that in $S{=}P(MeNCH_2CH_2)_3N$[19] in Figure 2, which contains the less electronegative sulfur substituent. Interestingly, methylation[16] of a sulfur in $S_2CP(MeNCH_2CH_2)_3N$,[16,19] which is two atoms removed from the phosphorus, results in a larger decrease P-N_{ax} distance (0.8 Å) than the aforementioned protonation of the adjacent imido nitrogen.

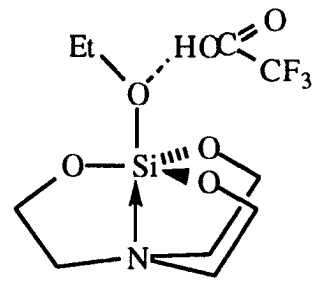
Although the protonating proton in **5**(CF_3CO_2) was located in the crystal structure determination (H-N = 0.895 (43) Å), its position on the imido nitrogen is further ascertained from the lengthening of the P=NPh multiple bond in the structurally related compound **18** (1.52 (1) Å)[20] to **5**(CF_3CO_2) (1.644 (4) Å). The latter distance is comparable to that of the



18



	R
8	Me
12	Ph



19

MeN-P single bonds in **5**(CF_3CO_2) (avg. 1.636 (4) and in **18** (1.66(8) Å). The expected compression of the PhNP bond angle from **18**(134.3 (7)°[20]) to that in **5**(CF_3CO_2) (130.7 (4)°)

owing to protonation of the imido nitrogen is obscured if one invokes three times the esd values as the margin of error. That protonation has not occurred on the bridgehead nitrogen (N_{ax}) of **5**(CF_3CO_2) is evident from the protrusion of this nitrogen above the plane of its substituent carbons. It is also unlikely that a CH_3N nitrogen is protonated since the sum of the angles around each of these nitrogens is very similar (N2, 352.8°; N3, 355.8°; N4, 353.3°) as are the CH_3N-P bond lengths (P-N(2), 1.636 (4); P-N(3), 1.633 (3); P-N(4), 1.638 (4) Å). It is interesting to note that the proton on the imido nitrogen is hydrogen bound to an oxygen of the $CF_3CO_2^-$ ion (H---O, 2.059 (50) Å). This interaction is reminiscent of that in **19** for which we determined from the structural metrics that in contrast to **5**($CFCO_2$), the proton of CF_3CO_2H hydrogen bonds to the atrane, rather than protonating it.[21]

As a consequence of imido-nitrogen protonation in **5**(CF_3CO_2) and **6**(CF_3CO_2), the CH_3N=P proton and carbon resonances of **4** move upfield upon protonation (0.1 and 2.3 ppm, respectively). This result is made reasonable by considering that the imido double bond has been converted to an amino single bond and that the positive charge has been delocalized onto the cage nitrogens. This reasoning is also consistent with the concommitant decrease in $^2J_{PC}$ (from 2.2 Hz to undetectable) and $^3J_{PH}$ (from 22.2 to 10.2 Hz) in the CH_3 group of this substituent, reflecting a decrease in *s*-character in the N-C linkage. These effects are also seen in comparing the ^1H and ^{13}C NMR spectra of $MeN{=}P(NMe_2)_3$ and **10**(CF_3CO_2).

A rationale is now put forth for the comparative stability to N_2 elimination of **8** and **12**[11] with their respective acyclic counterparts $MeN_3P(NMe_2)_3$ and $PhN_3P(NMe_2)_3$. Structure determinations carried out by X-ray means of such intermediates reveals a nearly planar PN_3C chain and an E configuration around N^1-N^2 which has partial double bond character; the E configuration of P=N-N=NR being a second resonance form.[20] Clearly, partial transannulation (as shown in the proposed structures for **8** and **12**) would delocalize the phosphonium positive charge, thereby stabilizing these intermediates by strengthening the

$N^1=N^2$ double bond and making rotation around N^1-N^2 (a proposed requirement for N_2 elimination[22]) more difficult.

CONCLUDING REMARKS

Nitrogen-to-phosphorus transannulation plays a surprisingly large role in conferring exceedingly strong basicities on the systems studied herein. While **1** (pK_a of **2**, 26.6) is not quite as strong a base as P_4-*t*-Bu (pK_a of $[HP_4$-*t*-$Bu]^+$, 28.0) in THF, it is possible that derivatives of **1** may even more closely rival P_4-*t*-Bu in basicity. Thus, for example, the pK_a of $P(HNCH_2CH_2)_3N$ (29.6) in DMSO is significantly higher in this solvent than the upper limit measured for **1** (26.8).[9c,d] Also included in studies underway is an examination of the potential advantages of non-nucleophilic non-ionic bases of the type studied here in organic reactions requiring this type of base, e.g., DBU and DBN.

ACKNOWLEDGMENT

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18. This assumption is made reasonable by the observation that the P---N_{ax} distance in the Pt complex[20] (Figure 2) is near the van der Waals sum of 3.35 Å. The platinum moiety is bulky and Pt(II) is electron rich (d^8), and can engage in retrodative pi bonding. Thus no large shift of phosphorus lone pair density to Pt is expected and hence no transannulation is seen. The presence of only a phosphorus lone pair as the fourth phosphorus substitutent in **1** is therefore not expected to favor transannulation.

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SUPPLEMENTARY MATERIALS

Table 2. Positional Parameters and Equivalent Isotropic Displacement Coefficients for **5**(CF_3CO_2)

Atom	x	y	z	U(eq)[a]
p	0.4452(1)	0.0286(1)	0.0325(1)	0.038(1)
N(1)	0.3464(3)	0.0094(3)	0.1820(2)	0.052(1)
C(1)	0.2281(4)	-0.0316(5)	0.1578(2)	0.063(2)
C(2)	0.2422(4)	-0.0917(4)	0.0715(3)	0.066(2)
N(2)	0.3090(3)	-0.0185(3)	0.0094(2)	0.047(1)
C(3)	0.3525(4)	0.1251(4)	0.2120(3)	0.056(2)
C(4)	0.3541(4)	0.1977(4)	0.1314(2)	0.049(1)
N(3)	0.4496(3)	0.1564(2)	0.0718(2)	0.041(1)
C(5)	0.4312(4)	-0.0720(4)	0.2206(3)	0.062(2)
C(6)	0.5514(4)	-0.0545(4)	0.1758(2)	0.058(2)
N(4)	0.5351(3)	-0.0625(3)	0.0812(2)	0.048(1)
C(7)	0.2716(4)	-0.0423(5)	-0.0814(3)	0.079(2)
C(8)	0.5650(4)	-0.2175(4)	0.0749(3)	0.066(2)
C(9)	0.5506(5)	-0.1763(3)	0.0430(3)	0.070(2)
N(5)	0.5153(3)	0.0428(3)	-0.0625(2)	0.047(1)
C(10)	0.4992(4)	0.1252(4)	-0.1283(2)	0.047(1)
C(11)	0.4104(4)	0.2068(4)	-0.1258(3)	0.070(2)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 2, Continued.

Atom	x	y	z	U(eq)[a]
C(12)	0.3997(5)	0.2867(5)	-0.1912(3)	0.081(2)
C(13)	0.4771(5)	0.2849(5)	-0.2616(3)	0.076(2)
C(14)	0.5641(6)	0.2025(5)	-0.2654(3)	0.073(2)
C(15)	0.5771(4)	0.1228(4)	-0.1980(2)	0.056(2)
C(1')	-0.1684(5)	-0.0774(5)	-0.1031(4)	0.084(2)
O(1')	-0.0866(4)	-0.1128(5)	-0.1498(3)	0.143(2)
O(2')	-0.2761(4)	-0.0856(4)	-0.1121(3)	0.107(2)
C(2')	-0.2761(4)	-0.0244(5)	-0.0174(4)	0.082(2)
F(1')	-0.1434(6)	-0.0922(5)	0.0459(3)	0.194(3)
F(2')	-0.0180(3)	0.0111(4)	-0.0114(4)	0.179(3)
F(3')	-0.1929(3)	0.0668(4)	0.0011(3)	0.145(2)

Table 3. Bond Distances for **5**(CF_3CO_2)

Atom 1	Atom 2	Distances(Å)[a]
P	N(1)	2.551(3)
P	N(3)	1.623(3)
N(1)	C(1)	1.441(6)
N(1)	C(5)	1.466(6)
C(2)	N(2)	1.482(6)
C(3)	C(4)	1.505(6)
N(3)	C(8)	1.468(5)
C(6)	N(4)	1.467(5)
N(5)	C(10)	1.413(5)
C(10)	C(15)	1.373(5)
C(12)	C(13)	1.378(7)
C(14)	C(15)	1.406(6)
C(1')	O(2')	1.201(7)
C(2')	F(1')	1.267(8)
C(2')	F(3')	1.307(7)
N(5)	H	0.895(43)
P	N(2)	1.641(3)
P	N(4)	1.642(3)
P	N(5)	1.659(3)
N(1)	C(3)	1.440(6)

[a] Numbers in parentheses are estimated standard deviations in the last significant digits.

Table 3, Continued.

Atom 1	Atom 2	Distance(Å)[a]
C(1)	C(2)	1.510(6)
N(2)	C(7)	1.481(5)
C(4)	N(3)	1.478(5)
C(5)	C(6)	1.507(6)
N(4)	C(9)	1.473(5)
C(10)	C(11)	1.373(7)
C(13)	C(14)	1.367(8)
C(1')	O(1')	1.225(8)
C(1')	C(2')	1.516(9)
C(2')	F(2')	1.312(6)
C(11)	C(12)	1.382(7)

Table 4. Bond Angles for **5**(CF_3CO_2)

Atom 1	Atom 2	Atom 3	Angles(°)[a]
N(1)	P	N(2)	76.9(1)
N(2)	P	N(3)	114.9(2)
N(2)	P	N(4)	115.4(2)
N(1)	P	N(5)	177.4(1)
N(3)	P	N(5)	102.7(2)
P	N(1)	C(3)	100.6(2)
P	N(1)	C(5)	98.6(2)
C(3)	N(1)	C(5)	117.4(3)
C(1)	C(2)	N(2)	110.0(4)
P	N(2)	C(7)	121.5(3)
N(1)	C(3)	C(4)	106.0(3)
P	N(3)	C(4)	121.0(3)
C(4)	N(3)	C(8)	116.0(3)
C(5)	C(6)	N(4)	109.6(4)
P	N(4)	C(9)	119.0(3)
N(5)	C(10)	C(11)	123.5(4)
C(11)	C(10)	C(15)	118.9(4)
C(11)	C(12)	C(13)	120.4(5)
C(13)	C(14)	C(15)	121.1(5)
O(1')	C(1')	O(2')	129.3(6)

[a]Numbers in parentheses are estimaed standard deviations in the last sinificant digits.

Table 4, Continued.

Atom 1	Atom 2	Atom 3	Angles[a]
O(2')	C(1')	C(2')	114.0(5)
C(1')	C(2')	F(2')	116.9(5)
C(1')	C(2')	F(3')	112.4(5)
F(2')	C(2')	F(3')	102.8(5)
N(1)	P	N(3)	76.2(1)
N(1)	P	N(4)	77.9(1)
N(3)	P	N(4)	114.9(2)
N(2)	P	N(5)	105.7(2)
N(4)	P	N(5)	100.6(2)
P	N(1)	C(1)	100.7(2)
C(1)	N(1)	C(3)	116.3(4)
C(1)	N(1)	C(5)	117.5(4)
N(1)	C(1)	C(2)	106.9(3)
P	N(2)	C(2)	120.9(3)
C(2)	N(2)	C(7)	111.0(3)
C(3)	C(4)	N(3)	109.3(3)
P	N(3)	C(8)	119.6(3)
N(1)	C(5)	C(6)	106.7(3)
P	N(4)	C(6)	118.8(3)
C(6)	N(4)	C(9)	116.0(3)
P	N(5)	C(10)	129.7(3)
N(5)	C(10)	C(15)	117.7(4)

Table 4, Continued.

Atom 1	Atom 2	Atom 3	Angles[a]
C(10)	C(11)	C(12)	121.2(4)
C(12)	C(13)	C(14)	118.6(5)
C(10)	C(15)	C(14)	119.7(4)
O(1')	C(1')	C(2')	116.5(5)
C(1')	C(2')	F(1')	112.0(5)
F(1')	C(2')	F(2')	104.8(6)
F(1')	C(2')	F(3')	107.0(5)

PAPER 4. SYNTHESIS AND REACTIVITY PATTERNS OF NEW PRO-AND QUASI-AZAPHOSPHATRANES $ZP(MeNCH_2CH_2)_3N$

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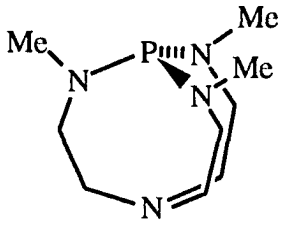
ABSTRACT

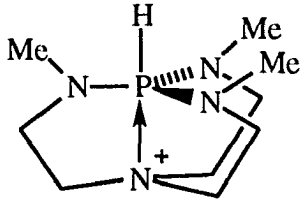
Partial bridgehead-bridgehead P-N transannulation in $^{-}S_2C[P(MeNCH_2CH_2)_3N]^+$ (**4**) stabilizes this unusual CS_2 adduct, facilitating the synthesis of a series of $RS(S)C[P(MeNCH_2CH_2)_3N]^+$ cations from the reaction of **4** with RX (**5**, R = Me; **6**, R = CH_2=$CHCH_2$; **7**, R = Et; **8**, R = *n*-Pr; **9**, R = *n*-Bu; **10**, R = *i*-Pr). The relative rates of formation of **5**-**10** are in accord with S_N2 attack of sulfur on the alpha carbon of RX. The structure determination of **5**(I) by X-ray means revealed that formation of cation **5** from **4** is accompanied by shortening of the transannular interaction from 3.008 Å to 2.771 Å. We also report the synthesis of a series of regio-isomeric products of the reaction of S=P(MeNCH2CH2)3N (**11**) with RX, namely, $RS[P(MeNCH_2CH_2)_3N]^+$ (R = Me, Et, *n*-Bu) and $S=P(MeNCH_2CH_2)_3NR^+$ (R = Me, Et). The slow decomposition of **4** to **11** in solution is also described.

INTRODUCTION

The bicyclic pro-azaphosphatrane **1** has been shown to be a remarkably strong base, reacting with a proton to give the stable azaphosphatrane **2**.[1-3] Cation **2** features a Å



1



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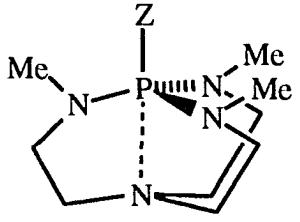
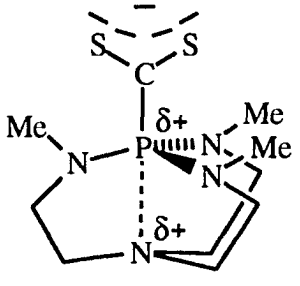


3

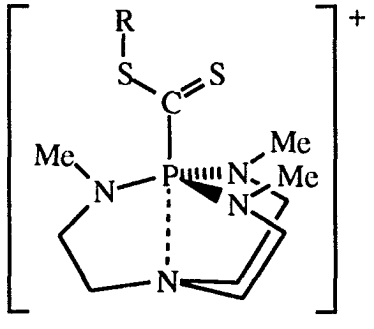
transannular P←N covalent bond that forms via inversion of the bridgehead nitrogen.[1-3] We have also recently demonstrated that **1** forms quasi-azaphosphatranes **3** in which the P-N_{ax} bond distance is intermediate between the sum of the P and N van der Waals radii (3.35 Å) and the covalent transannular bond distance in **2**, depending on the nature of Z.[4]

As part of our continuing exploration of the chemical consequence of partial transannulation in these systems, we report herein the synthesis of a series of quasi-azaphosphatrane cations **5-10** and rationalize the relative rates with which these products are

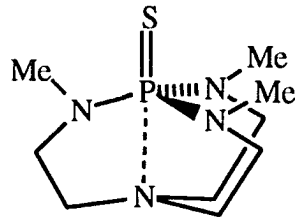


4

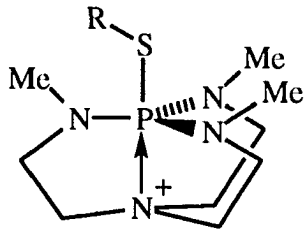
	R		R
5	Me	**9**	*n*-Bu
6	allyl	**10**	*i*-Pr
7	Et		
8	*n*-Pr		



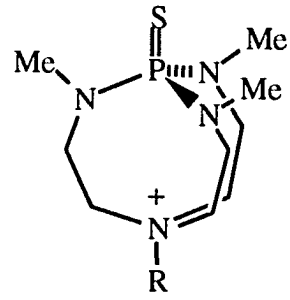
formed from **4** and the RX reagents. We also report that pro-azaphosphatrane **11**[2,5] reacts with MeI to give the regioisomers **12a**(I) and **12b**(I) whereas **4** in the presence of MeI forms only **5**(I) whose crystal structure was communicated earlier.[4] Although the analogous regioisomers are formed from **11** in the presence of EtI (**13a,b**), only **14a** is realized with *n*-BuI, and no reaction is observed using *i*-PrI. The decomposition of **4** to **11** is also described.



11



12a, R = Me
13a, R = Et
14a, R = *n*-Bu



12b, R = Me
13b, R = Et

DISCUSSION

Synthesis and reactions. Although we reported the synthesis of adduct **4** earlier,[4] its stability relative to rearrangement 1 characteristic of the acyclic analogues is worthy of

$$\underset{\textbf{15}}{(R_2N)_3\overset{+}{P}C(S)S^-} \longrightarrow \underset{\textbf{16}}{(R_2N)_2PS(S)CNR_2} \qquad (1)$$

comment. Thus $(R_2N)_3P$ in the presence of CS_2 provides spectroscopic evidence for **15** at -20°, but this zwitterion rapidly rearranges at room temperature to give **16**.[6] In the presence of additional CS_2, up to two more dithiocarbamate linkages can be formed.[6] The relative stability of **4** is attributed to increased stability of the P→C donor bond by partial transannular N→P bonding which shortens the latter distance by 10.2% from the sum of the P and N van der Waals radii (3.35 Å)[7] to 3.008 Å.[2] Transannular bonding permits delocalization of the N_{ax} lone pair and the P→C bond pair over a three-center four-electron MO system that also delocalizes the positive charge as shown in **4**. The stabilization of adduct **4** by the enhanced basicity of phosphorus is consistent with the known stability of $(n\text{-}Bu)_3P^+C(S)S^-$, for example,[8] and this stability facilitates the synthesis of the alkylated derivatives **5**-**10**.

The red solids **5**(I) and **6**(I) are formed rapidly (< five minutes) and quantitatively (**5**(I) with some exothermicity) by adding MeI and $CH_2{=}CHCH_2I$, respectively, to **4** at room temperature. Although high resolution EI mass spectroscopy failed to detect a parent cation for **5**(I), low resolution FAB spectra revealed peaks for the parent cations of both **5**(I) and **6**(I), and curiously an M_2I^+ peak for **5**(I) for reasons that are not clear.

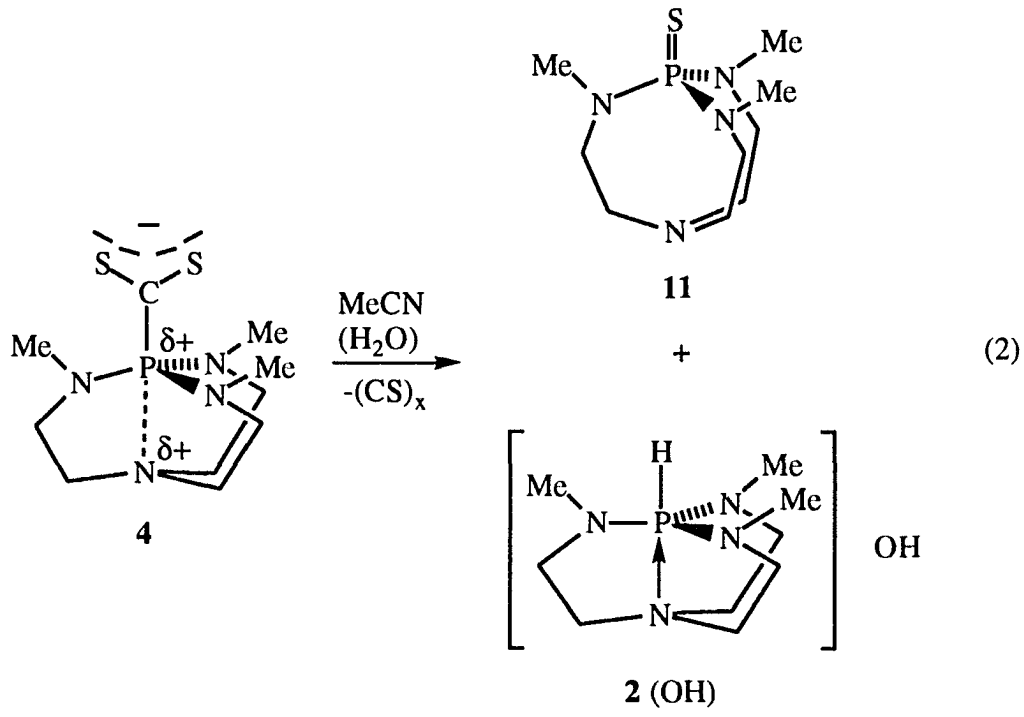
Addition of EtI to **4** failed to produce even a color change after three minutes. Adding MeCN to dissolve **4** caused the solution to turn violet after five minutes of stirring at room temperature. Monitoring by ^{31}P NMR spectroscopy, however, revealed that twenty minutes

was required to complete the reaction. Evaporation of the volatiles under vacuum gave pure **7**(I) in quantitative yield. As in the case of **5**(I), the FAB mass spectrum of **7**(I) featured M^+ and M_2I^+ peaks. Analogous reactions of *n*-PrI, *n*-BuI and *i*-PrI with **4** in MeCN at room temperature required 35 min., 55 min. and > 6 hours, respectively, for quantitative formation (as monitored by ^{31}P NMR spectroscopy) of **8**(I), **9**(I) and **10**(I). The relative reaction rates in MeCN of RX with **4**, namely, MeI ≅ CH_2=$CHCH_2I$ > EtI > *n*-PrI >> *i*-PrI are consistent with S_N2 attack by the negatively charged sulfur in **4** on the alpha carbon of RX. This conclusion is supported by the relative reaction rates of *n*-PrI and *n*-PrBr (35 min and > 6 hours, respectively) with **4** to give **8**(I) and **8**(Br), and the failure of compounds possessing still poorer leaving halides such as CD_2Cl_2, $CDCl_3$, $ClCO_2Et$, $ClSiMe_3$, PhC(O)Cl and $CF_3CO_2SiMe_3$ to react with **4** in MeCN.

Both **5**(I) and **11** could conceivably undergo alkylation of the bridgehead nitrogen with MeI. Whereas this reaction in MeCN was not realized in the case of **5**(I), **11** gave rise to regio-isomers in which the sulfur atom was alkylated (**12a**) as well as the bridgehead nitrogen (**12b**) in a 1.4 to 1.0 ratio as monitored by ^{31}P NMR spectroscopy. Compound **11** in the presence of EtI formed **13a**, **13b** (8.2:1) whereas with *n*-BuI only **14a** was detected. With *i*-PrI, no reaction was indicated by ^{31}P NMR spectroscopy. These results accord with the ideas that (a) the bridgehead nitrogen in **5** is less nucleophilic than in **11** (a point we justify on structural grounds later) and (b) the bridgehead nitrogen in **11** is more sensitive to bulk of the alkylating group than the sulfur. That the ratios of the regio-isomers formed are kinetically rather than thermodynamically established was shown by isolating them in the case of **12a** and **12b** and demonstrating that neither interconverted to the other upon heating in MeCN at 40-45° for 10 h.

As stated earlier, **4** is very stable with respect to the rearrangement observed for acyclic analogues (reaction 1). Indeed **4** is stable for months in the solid state in an inert atmosphere. Over a period of weeks in MeCN solution at room temperature, however, monitoring by ^{31}P

NMR spectroscopy showed that **4** decomposes to **11**, varying amounts of **2**(OH) (depending upon the moisture content of the solvent) and presumably $(CS)_x$. This reaction is accelerated to



(2)

completion in about 30 min. in boiling MeCN. The proportion of the ^{31}P NMR peaks for **11**and **2**(OH) ranged from 3:1 for CD_3CN dried only with molecular sieves to 20:1 for CD_3CN dried with molecular sieves followed by refluxing over and distillation from CaH_2. It is plausible to suggest that the equilibrium (reaction 3) observed for acyclic analogues[6] of **4** lies further to the left in the case of **4**, owing to the greater basicity of phosphorus in **4** as

$$(R_3N)_3\overset{+}{P}C(S)S^- \rightleftharpoons (R_3N)_3P + CS_2 \qquad (3)$$

suggested earlier. However, to the extent that **4** does dissociate to CS_2 and **1**, protonation and sulfuration of the latter compound to **2** and **11**, respectively, are apparently competing processes in reaction 2. The sulfuration of **1** by CS_2 in reaction 2 is related to reaction 4 which was reported earlier.[9]

$$Et_3P + RN{=}C{=}S \longrightarrow Et_3P{=}S + RN{\equiv}C \quad (4)$$

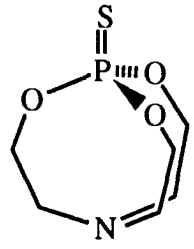
By contrast, the quasi-azaphosphatrane cations **5-10** are very stable in solution as well as in the solid state. Thus **5**(I) is stable at room temperature in the solid state for at least eight months or in moist MeCN for at least two months. Even heating the solution at 45° for 10 hours produced no changes detectable by ^{31}P NMR spectroscopy.

Structural considerations. The ORTEP drawing of **5**(I) in Figure 1 features a P-N_{ax} distance of 2.771 Å (which is 17% shorter than the sum of the P and N van der Waals radii) and an upwardly protruding N_{ax} atom suggestive of partial transannulation. The N_{eq}-P-N_{eq} angles (av. 113.4°) are substantially larger than those (av. 105°) in *trans*-$Cl_2Pt(\mathbf{1})_2$,[2] in which transannulation is absent (P-N_{ax} = 3.33 Å). This angle difference also reflects the existence of partial transannulation in **5**(I). Of the three quasi-azaphosphatrane structures known (i.e., **4**, **5**(I) and **11**), that of **5**(I) is closest to adopting the trigonal bipyramidal stereochemistry of **2**. Interestingly, the shortening of the P-N_{ax} distance from 3.008 Å in **4**[2] to 2.771 Å in **5**(I) does not result in an upfield ^{31}P chemical shift as is usually associated with an increase in phosphorus coordination in phosphatranes.[1,3,4,10-12] Indeed δ ^{31}P moves somewhat to lower field, progressing from 21.8 ppm in **4** to 24.1 ppm in **5** and remaining near this value for **6-10** (see Experimental). Phosphorus-31 coupling to the $N(CH_2)_3$ protons and carbons has been observed in fully transannulated cations such as **2**.[1,10] However, in none of the compounds **4-14** are such couplings observed, therefore precluding the non-detection of this coupling as a criterion for the total absence of transannulation.

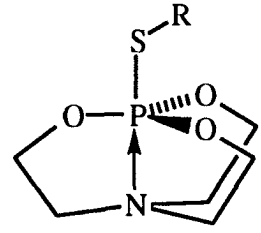
The greater stability in solution of **5**(I) relative to **4** is rationalized on the basis of the overall positive charge on cation **5** which would tend to strengthen its bonds. The greater hydrolytic stability of **5** (compared with **4**) may arise from the greater delocalization of the positive charge of **5** in the axial bonding system, which would render the phosphorus and its ligated carbon less electrophilic.

It should be noted that the decrease in the P-N_{ax} distance from **11** (3.25 Å^2) to **4** (3.008 Å^2) to **5** (2.771 Å) with concomitant opening of the N_{eq}-P-N_{eq} bond angles (106.8°, 110.3° and 113.4°, respectively) is not determined by the bulk of exocyclic phosphorus substituent. Because the size of this group actually increases from S to CS_2 to $SCSMe^+$ in this series (i.e., **11** to **4** to **5**), it is clear that increasing electron withdrawing effects prevail.

Binding an alkyl cation to a sulfur of **4** clearly enhances the polarization of the P lone pair toward the C. The shorter P←N_{ax} distance in cation **5** and its higher positive charge compared with **11** also renders the bridgehead nitrogen of cation **5** less nucleophilic toward RX. Whether the regio-isomers **12a**, **13a** and **14a** derived from alkylation of the sulfur of **11** possess the azaphosphatrane structure as shown (i.e., containing a normal five-coordinate phosphorus) is not certain in the current absence of suitable crystals for X-ray analysis. While the upfield ^{31}P chemical shift from **11** to the cations **12a**, **13a** and **14a** is substantial (*ca.* 25 ppm) it is not as strong as that observed earlier in going from **17** to the cations **18a**, **18b** (*ca.* 55 ppm).[13] The fully transannulated structure for **18b** was confirmed earlier by X-ray means.[14] Alkylation of the bridgehead nitrogen of **11** to give the regio-isomers **12b** and **13b**



17



18a, R = Me

18b, R = Et

leads to only a very small change (*ca.* 0.2 ppm) in the ^{31}P chemical shift. This suggests that any stereoelectronic changes in the phosphorus environment caused by conversion of the nearly planar nitrogen in **11**[2] to a presumably nearly tetrahedral geometry are not registered in the ^{31}P chemical shift. By contrast, the ^{29}Si chemical shift in **19** moves 15.3 ppm downfield

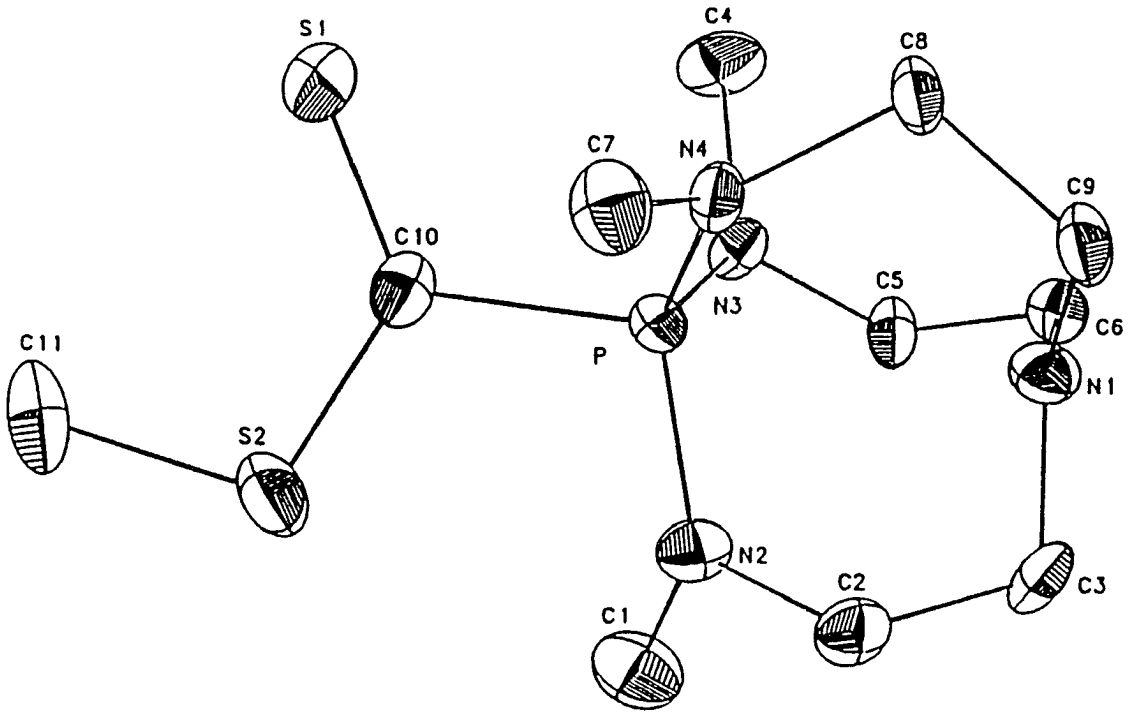
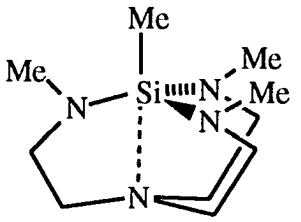
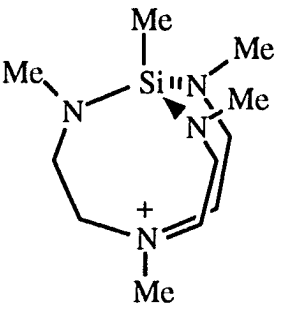


Figure 1. ORTEP drawing of **5** with thermal ellipsoids at the 50% probability level.

upon quaternization of the bridgehead nitrogen to give **20**.[15] The increased sensitivity of the ^{29}Si chemical shift to the stereochemical change induced by quaternization can be attributed in part to the fact that the transannular distance in **19** is 24% shorter than the sum of the van der Waals radii[2] while in **11** it is only 3% shorter.[2]



19



20

EXPERIMENTAL SECTION

All procedures were carried out in an atmosphere of argon using solvents dried by standard means. NMR spectrometers employed were a Nicolet NT-300 or a Varian VXR-300 for ^{1}H spectra (except in the case of **5**(I) for which a Unity-500 was used), a Bruker WM-200 for ^{31}P spectra, a Bruker MSL-300 for solid state ^{31}P spectra and a Varian VXR-300 for ^{13}C spectra. Infrared spectra were recorded with a Bruker IFS-113 V spectrometer. Fast atom bombardment spectra were recorded with KRATOS MS-50 spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc. 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. Micro VAX II computer using the CAD4-SDP programs.

Starting material **4** was prepared by our previously published method.[1,5]

$[CH_3SC(S)P(NMeCH_2CH_2)_3N]I$, 5(I). MeI (1.88 g, 13.2 mmol) was syringed into a 10 mL flask containing 0.12 g (0.41 mmol) of brown solid **4**. An exothermic reaction was observed and a red solid was formed immediately. Acetonitrile was added to the reaction mixture until all of the red solid was dissolved. The red solution was stirred for 1-2 minutes and the volatiles were removed in vacuo to afford spectroscopically pure red solid **5**(I) (0.178 g, quantitative) according to its ^{31}P, ^{1}H and ^{13}C NMR spectra. The red solid (0.178 g) was redissolved in 3 mL of dry acetonitrile. The solution was cooled in a freezer (about -25 °C) overnight to grow large crystals. The red solution was removed carefully with a syringe and the crystals were dried in vacuo giving 0.079 g of crystals suitable for X-ray analysis. ^{31}P NMR (CD_3CN): 24.10; ^{1}H NMR (CD_3CN): 2.72 (s, 3H, SCH_3), 2.85 (t, 6H, $N_{ax}CH_2$, $^{3}J_{HH}$ = 5.7 Hz), 2.86 (d, 9H, $N_{eq}CH_3$, $^{3}J_{PH}$ = 11.1 Hz), 3.01 (td, 6H, $N_{eq}CH_2$, $^{3}J_{PH}$ = 15.6 Hz, $^{3}J_{HH}$ = 5.7 Hz); ^{13}C NMR (CD_3CN): 21.25 (d, SCH_3, $^{3}P_{PC}$ = 0.1 Hz), 38.08 (d, $N_{eq}CH_3$, $^{2}J_{PC}$ = 2.0 Hz), 50.39 (d, $N_{eq}CH_2$, $^{2}J_{PC}$ = 3.5 Hz), 51.77 ($N_{ax}C$), 232.50 (d, PC,

$^1J_{PC}$ = 154.9 Hz); IR (KBr pellet): 640(s), 887(s), 1009(s), 1041(s), 1074(s), 1101(s), 1203(s), 1222.5(s), 1323(s), 1381(s), 1405(s), 1460(s), 2856(m), 2951(m); MS (FAB) *m/z*: 307.1(100, $[MeSC(S)P(NMeCH_2CH_2)_3N]^+$), 741.2 (1.0, $[MeSC(S)P(NMeCH_2CH_2)_3N)_2I]^+$); elemental analysis: Calcd. for $C_{11}H_{24}IN_4PS_2$: C, 30.43; H, 5.58; N, 12.91. Found: C, 30.45; H, 5.26; N, 12.72.

$[CH_2=CHCH_2SC(S)P(NMeCH_2CH_2)_3N]I$, 6(I). Excess allyl iodide (0.5 mL) was placed in a 5 mL flask containing 0.050 g (0.17 mmol) of **4** and 3 mL of CD_3CN. A red solution was formed immediately after stirring for 5 min., the volatiles were removed in vacuo to give a quantitative yield of product (0.078 g). ^{31}P NMR (CD_3CN): 23.50; ^1H NMR (CD_3CN): 2.84 (t, 6H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.7 Hz), 2.86 (d, 9H, $N_{eq}CH_3$, $^3J_{PH}$ = 11.1 Hz), 3.01 (td, 6H, $N_{eq}CH_2$, $^3J_{PH}$ = 15.6 Hz, $^3J_{HH}$ = 5.4 Hz), 3.98 (d, 2H, SCH_2, $^3J_{HH}$ = 6.9 Hz), 5.25 (dd, 1H, H_b of $-CH_c=CH_aH_b$, $^2J_{H_aH_b}$ = 1.2 Hz; $^3J_{H_bH_c}$ (*cis*) = 10.8 Hz), 5.40 (dd, 1H, H_a, $^2J_{H_aH_b}$ = 1.2 Hz, $^3J_{H_aH_c}$ (*trans*) = 17.4 Hz), 5.88 (m, 1H, H_c); ^{13}C NMR (CD_3CN): 38.29 (d, $N_{eq}CH_3$, $^2J_{PC}$ = 1.4 Hz), 40.22 (d, SC, $^3J_{PC}$ = 1.4 Hz), 50.49 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 3.7 Hz), 51.82 ($N_{ax}C$), 121.75, 130.30, 231.07 (d, PC, $^1J_{PC}$ = 153.2 Hz); MS (FAB) *m/z*: 333.1(100, $[CH_2=CHS(S)P(NMeCH_2CH_2)_3N]^+$).

$[EtSC(S)P(NMeCH_2CH_2)_3N]I$, 7(I). EtI (1.35 g, 8.6 mmol) was syringed into a 10 mL flask containing 0.080 g (0.27 mmol) of brown solid **4**. No heat evolution or color change was observed within 3 minutes. Acetonitrile (8 mL) was added with a syringe and after stirring for 5 min., a violet solution was formed, although the ^{31}P NMR spectrum showed that the reaction was incomplete. After the solution was stirred for another 14 min., the reaction was complete and the volatiles were removed in vacuo to give a quantitative yield (0.12 g) of NMR spectroscopically pure orange solid **7**(I). ^{31}P NMR (CD_3CN): 23.62; ^1H NMR (CD_3CN): 1.32 (t, 3H, $^3J_{HH}$ = 7.8 Hz), 2.82 (t, 6H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.7 Hz), 2.86 (d, 9H, $N_{ax}CH_3$, $^3J_{PH}$ = 10.8 Hz), 2.99 (td, 6H, $N_{eq}CH_2$, $^3J_{PH}$ = 15.6 Hz, $^3J_{HH}$ = 5.7 Hz), 3.31(q,2H, SCH_2, $^3J_{PH}$ = 7.8 Hz); ^{13}C NMR (CD_3CN): 11.27 (SC*C*), 32.15 (d, S*C*, $^3J_{PC}$

= 1.1 Hz), 38.10 ($N_{eq}CH_3$, $^2J_{PC}$ = 1.9 Hz), 50.38 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 3.4 Hz), 51.79($N_{ax}C$); MS (FAB) *m/z*: 21.1 (100, [EtSC(S)P($NMeCH_2CH_2$)$_3$N]$^+$).

[*n*-PrSC(S)P($NMeCH_2CH_2$)$_3$N]I, 8(I). *n*-PrI (1.19 g, 7.0 mmol) was added *via* syringe to **4** (0.10 g, 0.34 mmol). No color change was observed in 8 min. and so 10 mL of acetonitrile was added. The mixture was stirred for 1.5 h and evaporated in vacuo to give a quantitative yield (0.157 g) of NMR spectroscopically pure red solid **8**. ^{31}P NMR (CD_3CN): 23.82; ^{1}H NMR (CD_3CN): 1.02 (t, 3H, $SCCCH_3$, $^3J_{HH}$ = 7.2 Hz), 1.73 (m, 2H, $SCCH_2$), 2.83 (t, 6H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.7 Hz), 2.86 (d, 9H, $N_{eq}CH_3$, $^3J_{PH}$ = 11.1 Hz), 3.00 (td, 6H, $N_{eq}CH_2$, $^3J_{PH}$ = 15.6 Hz, $^3J_{HH}$ = 5.7 Hz), 3.31 (t, 2H, SCH_2, $^3J_{HH}$ = 7.5 Hz); ^{13}C NMR (CD_3CN): 13.76 (SCC*C*), 20.48 (SC*C*), 39.43 (SC), 38.03 (d, $N_{eq}CH_3$, $^2J_{PC}$ = 1.8 Hz), 50.37 (d, $N_{eq}CH_2$), $^2J_{PC}$ = 3.2 Hz), 51.82 ($N_{ax}CH_2$), 231.68 (d, PC, $^1J_{PC}$ = 153.7 Hz); (FAB) *m/z*: 335.0 (100, [*n*-PrSC(S)P($NMeCH_2CH_2$)$_3$N]$^+$), 796.9 (0.4, [(*n*-PrSC(S)P($NMeCH_2CH_2$)$_3$N)$_2$I]$^+$).

[*n*-BuSC(S)P($NMeCH_2CH_2$)$_3$N]I, 9(I). Excess *n*-butyl iodide (0.5 mL) was placed in an NMR tube containing 0.018 g (0.061 mmol) of **4** and 0.5 mL of CD_3CN. After 15 minutes of shaking, the ^{31}P NMR spectrum of the pink solution showed a new peak at 24.4 ppm of ~0.1 the intensity of the starting material. After standing overnight, the pink solution was evaporated under vacuum to give a quantitative yield (0.028 g) of NMR spectroscopically pure red solid **9**(I). ^{31}P NMR (CD_3CN): 24.04; ^{1}H NMR (CD_3CN): 0.93 (t, 3H, $SCCCCH_3$, $^3J_{HH}$ = 7.5 Hz), 1.73 (m, 2H, $SCCCH_2$), 1.68 (m, 2H, $SCCH_2$), 2.83 (t, 6H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.7 Hz), 2.86 (d, 9H, $N_{eq}CH_3$, $^3J_{PH}$ = 10.8 Hz), 2.99 (td, 6H, $N_{eq}CH_2$, $^3J_{PH}$ = 15.6 Hz, $^3J_{HH}$ = 5.7 Hz), 3.33 (t, 2H, SCH_2, $^3J_{HH}$ = 7.5 Hz); ^{13}C NMR (CD_3CN): 13.38 (SCCC*C*), 22.49 (SCC*C*), 28.44 (SC*C*), 37.01 (d, SC, $^3J_{PC}$ = 0.9 Hz), 37.69 (d, $N_{ax}CH_3$, $^2J_{PC}$ = 1.8 Hz), 49.98 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 3.2 Hz), 51.44 ($N_{ax}C$), 231.05 (d, PC, $^1J_{PC}$ = 154.1 Hz). MS (FAB) *m/z*: 349.1 (100, [*n*-BuSC(S)P($NMeCH_2CH_2$)$_3$N]$^+$), 825.1 (0.3, [(*n*-BuSC(S)P($NMeCH_2CH_2$)$_3$N)$_2$I]$^+$).

[*i*-PrSC(S)P(NMeCH$_2$CH$_2$)$_3$N]I, 10(I). *i*-PrI (0.31 g, 1.8 mmol) was added to an NMR tube containing 0.020 g (0.092 mmol) of **4** and 0.8 mL of MeCN. After 5 h, ^{31}P NMR spectroscopy revealed an incomplete reaction. The mixture was allowed to stand for an additional 43 h at which point the ^{31}P NMR spectrum showed that the reaction was complete. The solvent was removed in vacuo to give a quantitative yield (0.031 g) of NMR spectroscopically pure blue-violet solid **10**. ^{31}P NMR (CD_3CN): 23.82; ^{1}H NMR (CD_3CN): 1.39 (d, 6H, $SCCH_3$, $^3J_{HH}$ = 6.9 Hz), 2.82 (t, 6H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.7 Hz), 2.86 (d, 9H, $N_{eq}CH_3$, $^3J_{PH}$ = 11.1 Hz), 2.99 (td, 6H, $N_{eq}CH_2$, $^3J_{PH}$ = 15.6 Hz, $^3J_{HH}$ = 5.7 Hz), 4.06 (septet, 1H, SCH, $^3J_{HH}$ = 6.9 Hz); ^{13}C NMR (CD_3CN): 20.53 (SC*C*), 38.11 (d, $N_{ax}CH_3$, $^2J_{PC}$ = 1.7 Hz), 42.45 (d, SC, $^3J_{PC}$ = 0.9 Hz), 50.39 (d, $N_{eq}CCH_2$), $^2J_{PC}$ = 2.9 Hz), 51.87 ($N_{ax}C$), 231.67(d, PC, $^1J_{PC}$ = 154.2Hz); MS(FAB) *m/z* 335.0(100,[*i*-PrSC(S)P(NMeCH$_2$CH$_2$)$_3$N]$^+$), 796.9 (0.2, [(*i*-PrSC(S)P(NMeCH$_2$CH$_2$)$_3$N)$_2$I]$^+$).

[*n*-PrSC(S)P(NMeCH$_2$CH$_2$)$_3$N]Br, 8(Br). Excess *n*-PrI (0.70 g, 4.1 mmol) was added to an NMR tube containing 0.0375 g (0.128 mmol) of **4**. No heat evolution or color change could be observed in 8 minutes. At this point 0.5 mL of CD_3CN was added and the mixture was shaken for 1/2 h. The ^{31}P NMR spectrum showed a new peak at 24.22 ppm with ~5% of the intensity of the starting compound. Upon standing overnight the mixture gave a violet solution with a single peak at 24.22 ppm in the ^{31}P NMR spectrum. The volatiles were removed in vacuo to afford a quantitative yield (0.059 g) of NMR spectroscopically pure pink solid **8**(Br). ^{31}P NMR (CD_3CN): 24.22; ^{1}H NMR (CD_3CN): 1.02 (t, 3H, $SCCCH_2$, $^3J_{HH}$ = 7.5 Hz), 1.73 (m, 2H, $SCCH_2$), 2.83 (t, 6H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.7 Hz), 2.86 (d, $N_{eq}CH_3$, $^3J_{PH}$ = 11.1 Hz), 3.00 (td, 6H, $^3J_{PH}$ = 15.6 Hz, $^3J_{HH}$ = 5.7 Hz), 3.30 (t, 2H, SCH_2, $^3J_{HH}$ = 7.5 Hz); ^{13}C NMR (CD_3CN): 13.75 (SCC*C*), 20.49 (SC*C*), 38.04 ($N_{eq}CH_3$, $^2J_{PC}$ = 1.8 Hz), 39.42 (SC), 50.36 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 3.2 Hz), 51.81 ($N_{ax}C$), 231.68 (d, PC, $^1J_{PC}$ = 153.16 Hz); MS (FAB) *m/z*: 335.0 (100, [*n*-PrSC(S)P(NMeCH$_2$CH$_2$)$_3$N]$^+$) 756.0 (0.5, [(*n*-PrSC(S)P(NMeCH$_2$CH$_2$)$_3$N)$_2$Br]$^+$).

Reaction of 11 with MeI. Excess MeI (0.50 mL) was added to a solution of **11** (0.048 g, 0.19 mmol) in acetonitrile (5 mL). The solution was stirred at 40 °C for 10 h after which the solvent was removed in vacuo to give a quantitative yield of a white solid. ^{31}P NMR spectroscopy in DMSO showed two signals (49.42 and 75.77 ppm, respectively) in the ratio of 1.4 to 1.0. The white solid was stirred with 5 mL of acetonitrile for 3 h., filtered in vacuo and washed with 4 mL of acetonitrile to give 0.03 g (40%) of white solid compound **12b** according its ^{31}P and ^{1}H NMR spectra. ^{31}P NMR (DMSO-d_6): 75.97; ^{1}H NMR (DMSO-d_6): 2.70 (d, 9H, $N_{eq}CH_3$, $^{3}J_{PH}$ = 9.3 Hz), 3.12 (s, 3H, $N_{ax}CH_3$), 3.19 (m, 6H, $N_{ax}CH_2$), 3.85 (m, $N_{eq}CH_2$). The filtrate was evaporated in vacuo to give 0.038 g (51%) of white solid **12a** according to its ^{31}P, ^{1}H and ^{13}C NMR spectra. ^{31}P NMR (DMSO-d_6): 49.42; ^{1}H NMR (DMSO-d_6): 2.42 (d, 3H, SCH_2, $^{3}J_{PH}$ = 13.5 Hz), 2.78 (t, 6H, $N_{ax}CH_2$, $^{3}J_{HH}$ = 5.4 Hz), 2.82 (d, $N_{eq}CH_3$, 9H, $^{3}J_{PH}$ = 12.6 Hz), 3.01 (td, 6H, $N_{eq}CH_2$, $^{3}J_{PH}$ = 15.6 Hz, $^{3}J_{HH}$ = 5.4 Hz); ^{13}C NMR (CD_3CN): 15.20 (d, SC, $^{2}J_{PC}$ = 5.1 Hz), 36.38 (d, $N_{eq}CCH_3$), $^{2}J_{PC}$ = 4.6 Hz), 50.57 (d, $N_{eq}CH_2$, $^{2}J_{PC}$ = 2.8 Hz), 51.38 ($N_{ax}C$); MS (FAB) *m/z* for **12a**: 263.1(100, $[MeS\text{-}P(NMeCH_2CH_2)_3N]^+$), 653.0 (0.2, $[(MeS\text{-}P(NMeCH_2CH_2)_3N)_2I]^+$; *m/z* for **12b**: 263.1 (100, $[S{=}P(NMeCH_2CH_2)_3NMe]^+$), 653.1 (1.3, $[(S{=}P(NMeCH_2CH_2)_3NMe)_2I]^+$).

Compound **12a** (10 mg) in CH_3CN (5 mL) was heated at 40-45 °C for 10 h. The solvent was removed in vacuo to give a white solid whose ^{31}P NMR (DMSO-d_6) spectrum showed a single peak at 49.42 ppm characteristic of **12a**. Similarly 8 mg of **12b** in CH_3CN (5 mL) was heated at 40-45 °C for 10 h. The solvent was removed in vacuo to give a white solid whose ^{31}P NMR (DMSO-d_6) showed a single peak at 75.77 ppm characteristic of **12b**.

Reaction of 11 with EtI. Ethyl iodide (1.0 mL) was added to a solution of **11** (0.051 g, 0.21 mmol) in acetonitrile (7 mL). The solution was heated at 55 °C for 43 h. to give a clear solution. The solvent was removed in vacuo to give a quantitative yield (0.090 g) of white solid mixture of **13a, 13b.** A ^{31}P NMR spectrum of the mixture in DMSO-d_6 solution

showed peaks at 50.42 (**13a**) and 75.91 ppm (**13b**) in the ratio of 8.2 to 1.0, respectively. Because **13b** was not soluble in acetonitrile, ^{1}H and ^{13}C NMR spectra of the mixture only showed signals for compound **13a**. ^{31}P NMR (DMSO-d_6) for **13a**: 50.42; ^{1}H NMR (DMSO-d_6) for **13a**: 1.30 (dt, 3H, $SCCH_3$, $^{4}J_{PH}$ = 2.7 Hz, $^{3}J_{HH}$ = 7.5 Hz), 2.75 (t, 6H, $N_{ax}CH_2$, $^{3}J_{HH}$ 5.1 Hz), 2.79 (d, 9H, $N_{eq}CH_3$, $^{3}J_{PH}$ = 12.6 Hz), 2.98 (td, partially overlapping with SCH_2 signal, $N_{eq}CH_2$, $^{3}J_{PH}$ = 14.7 Hz, $^{3}J_{HH}$ = 5.1 Hz), 2.98 (SCH_2, overlapping with $N_{eq}CH_2$ signal); ^{13}C NMR (CD_3CN) for **13a**: 15.82 (d, SC*C*, $^{3}J_{PC}$ = 6.0 Hz), 27.95 (d, S*C*, $^{2}J_{PC}$ = 5.0 Hz), 36.36 (d, $N_{eq}CCH_3$, $^{2}J_{PC}$ = 4.3 Hz), 50.64 (d, $N_{eq}CH_2$, $^{2}J_{PC}$ = 2.4 Hz), 51.53 ($N_{ax}C$). However, a ^{1}H NMR spectrum of the mixture in DMSO-d_6 solution clearly showed not only the signals of **13a** but also the characteristic multiplet for the $N_{eq}CH_2$ protons of **13b** (similar to those in **12b**) at 3.56 to 4.01 ppm. Other peaks of **13b** were not resolved because of low intensity and/or overlap with peaks belonging to **13a**. ^{31}P NMR (DMSO-d_6 for **13b**): 75.91; MS (FAB) *m/z* for the mixture: 277 (100, [EtS-$P(NMeCH_2CH_2)_3N]^+$ and $[S{=}P(NMeCH_2CH_2)_3NEt]^+$), 681.3 (0.4, [(EtS-$P(NMeCH_2CH_2)_3N]_2I]^+$ and $[(S{=}P(NMeCH_2CH_2)_3NEt)_2]^+$).

Reaction of 11 with *n*-BuI. To a solution of **11** (0.11 g, 0.45 mmol) in acetonitrile (4 mL) was added 3 mL of *n*-butyl iodide. The solution was stirred at 50-55 °C for 4 d. and then evaporated in vacuo to give a quantitative yield (0.19 g) of white solid **14a**. ^{31}P NMR (DMSO-d_6): 51.50; ^{1}H NMR (DMSO-d_6): 0.88 (t, 3H, $SCCCCH_3$, $^{3}J_{HH}$ = 7.4 Hz), 1.39 (m, 2H, $SCCCH_2$), 1.62 (m, 2H, $SCCH_2$), 2.74 (t, 6H, $N_{ax}CH_2$, $^{3}J_{HH}$ = 5.1 Hz), 2.79 (d, 9H, $N_{eq}CH_3$, $^{3}J_{PH}$ = 12.6 Hz), 2.98 (td, 6H, $N_{eq}CH_2$, $^{3}J_{PH}$ = 17.1 Hz, $^{3}J_{HH}$ = 5.1 Hz), ~3.0 (SCH_2, overlapping with $N_{eq}CH_2$); ^{13}C NMR (CD_3CN): 13.80 (SCCC*C*), 22.59 (SCC*C*), 33.19 (SC*C*), 33.33 (d, S*C*, $^{2}J_{PC}$ = 3.4 Hz), 36.40 (d, $N_{eq}CH_3$, $^{2}J_{PC}$ = 5.0 Hz), 50.61 (d, $N_{eq}CH_2$, $^{2}J_{PC}$ = 2.9 Hz), 51.58 ($N_{ax}C$); MS (FAB) *m/z*: 305.2 (100, [*n*-$BuSP(NMeCH_2CH_2)_3N]^+$), 737.3 (1.5, $[(n\text{-}BuSP(NMeCH_2CH_2)_3N)_2I]^+$).

Reaction of 11 with *i*-PrI. To a solution of **11** (0.050 g, 0.20 mmol) in acetonitrile (5 mL) was added *i*-PrI (0.5 mL). The solution was stirred at 50 °C for 84 h and evaporated in vacuo to give only the starting material **11** as shown by ^{1}H NMR spectroscopy.

Measurement of reaction rates of 4 with RX. To an NMR tube containing **4** (0.063 mmol) and CD_3CN (0.7 mL) was added RX (0.063 mmol). ^{31}P NMR spectra of the reaction mixture were recorded every 5 min. The reaction times for reaction completion were < 5 min. for MeI and CH_2=$CHCH_2I$, 20 min. for *n*-EtI, 35 min. for *n*-PrI, 55 min. for *n*-BuI, > 6 h. for *i*-PrI and > 6 h. for *n*-PrBr.

Crystal Structure Analysis of 5(I). A colorless crystal of the title compound was attached to the tip of a glass fiber and mounted on the diffractometer for data collection at -5 °C ± 1°C. The cell constants for data collection were determined from a list of reflections found by an automated search routine.

Lorentz and polarization corrections were applied. A correction based on a decay in the standard reflections of 2.0% was applied to the data. An absorption correction based on a series of Y-scans was applied. The agreement factor for the averaging of the observed reflections was 1.8% (based on F).

The acentric space group $P2_12_12_1$ was indicated initially by systematic absences and intensity statistics.[15] The positions of the atoms were determined by direct methods.[15] All nonhydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were found by the difference Fourie technique 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 were not refined. Selected bond distances and angles are given Table 1.

Table 1. Selected Bond Distances and Angles in **5**(I).

	Bond Distances (Å)		
P-N1	2.771 (4)	P-N3	1.620 (3)
P-N2	1.636 (3)	P-N4	1.618 (3)
	Bond Angles (°)		
N2-P-N3	110.8 (2)	C3-N1-C6	118.0 (3)
N2-P-N4	113.9 (2)	C3-N1-C9	117.6 (3)
N3-P-N4	115.5 (2)	C6-N1-C9	122.5 (3)

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PAPER 5. $P(MeNCH_2CH_2)_3N$ AS A SUPERIOR CATALYST FOR THE CONVERSION OF ISOCYANATES TO ISOCYANURATES

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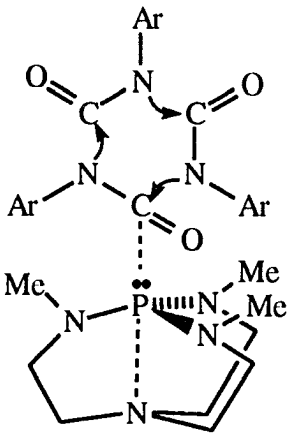
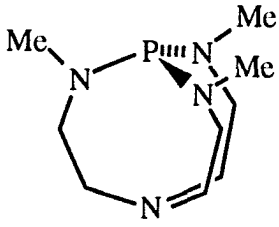
SUMMARY/JUSTIFICATION

The superior action of $P(MeNCH_2CH_2)_3N$ as a catalyst in the conversion of isocyanates to industrially relevant isocyanurates is attributed to the unusually large Lewis basicity of the phosphorus in this catalyst and its ability to form P-N transannular interactions of substantially varying strength. Thus the title reactions in benzene at room temperature afforded a 97% yield of triphenyl isocyanurate in 3 min. and a 99% yield of tri-*para*-methoxyphenyl isocyanurate in 8 min. Both products were isolated in tlc purity. These results should be of broad interest to industrial as well as academic organic and inorganic main-group element chemists.

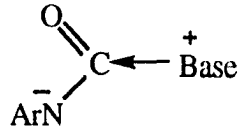


COMMUNICATION

Triaryl isocyanurates are useful as activators for the continuous anionic polymerization and post-polymerization of ε-caprolactam to nylon-6 possessing a low unreacted monomer content and a highly stable melt viscosity.[1] Recently the superior thermal properties and hydrolytic stability of isocyanurate-based foams and plastics have generated considerable interest in the development of efficient isocyanate trimerization catalysts.[2] A wide variety of catalysts for the trimerization of aryl isocyanates to triaryl isocyanurates has been reported.[1,3] Because impure triaryl isocyanurates impair the quality of nylon-6, much attention has been given to achieving high purity of such activators.[1a] However, purification methods are attended by substantial lowering of product yield, and attempts to increase the yield of trimer frequently involve large amounts of catalyst under vigorous conditions for long periods. Here we report on the superior properties of **1** as a unique catalyst for the trimerization of aryl isocyanates, and we present evidence for the catalytic pathway.



1



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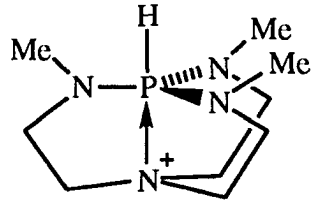
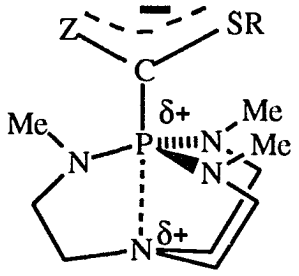


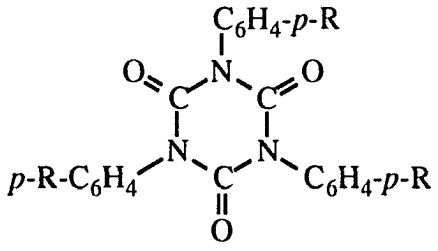
3

Because reported catalysts for the trimerization of isocyanates are typically Lewis bases, it has been proposed that their activity depends upon their basicity[4] and/or upon the stability of zwitterionic intermediates such as **2**.[3c,d] This suggests that a strong base capable of forming a stable zwitterionic intermediate could function as an efficient catalyst for the trimerization of aryl isocyanates. Recently we reported that **1** is an exceptionally strong base

whose conjugate acid **3** has a pK_a of about 27 in DMSO[5,6] and that zwitterionic adducts such as **4** and **5** can be isolated.[7] The partial transannulation indicated for **4** was verified by



	Z	R
4	S	nothing
5	PhN	nothing
6	S	Me^+
7	PhN	Me^+



	R
8	H
9	OMe

a structure determination by X-ray means in which it was shown that the bridgehead-bridgehead distance in **4** (3.008 *Å*[7]) is intermediate between that presumed in **1** (ca. 3.35 *Å*[8]) and that measured for cation **3** (1.967 *Å*[7]). This distance in **4** is about 0.3 *Å* longer than in its methylated derivative **6** (2.771 *Å*[7]), suggesting that the corresponding distance in **7** (2.190 *Å*[7]) probably lengthens to ca. 2.5 *Å* in **5** (for which suitable crystals for X-ray cyrstallography could not be grown).

Here we demonstrate that trimers **8** and **9** can be synthesized in tlc purity in 97 and 99% yield, respectively, in one step in 3 and 8 min, respectively, at room *T* via trimerization of the corresponding aryl isocyanates, using only 0.33 mole % of **1** as the catalyst. By contrast, $P(NMe_2)_3$, (an acyclic analogue of **1**) produces only a small yield of the cyclic dimer of phenyl isocyanate, even over an extended period of time. Catalyst **1** is also superior in comparison with the other catalysts previously described. Thus, for example, Et_3N while reported to give

a 100% conversion of phenyl isocyanate at 100 °C, requires 10% catalyst and a pressure of 800 *MPa* for 20 h,[3a,b] and $AsBu_3$ provides an 18-99% yield over 12-34 min periods, but the reaction is very sensitive to *T*.[3f] Moreover, criteria of purity were not addressed. While **1** is very soluble in organic solvents, benzene is best if a solvent is used for the reaction because solubilities of the reactants are high and product stability is low. Thus simple washing of the product with benzene provides tlc pure **8** or **9** in nearly quantitative yield.

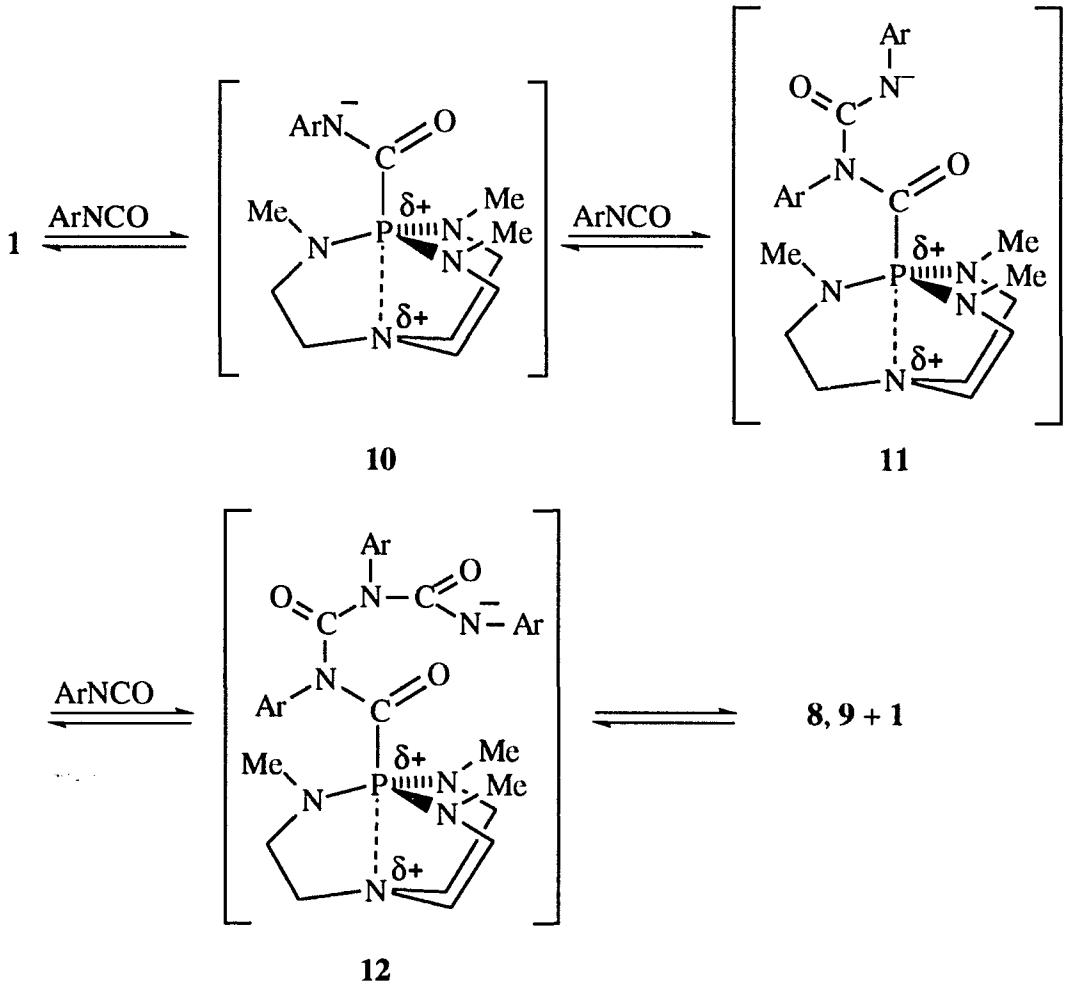
An electron donating group on the aromatic ring of aryl isocyanates renders the carbonyl carbon less electrophilic, and hence more difficult to trimerize, as has been shown to be the case for *p*-MeC_6H_4NCO.[3c,d] With **1** as the catalyst, we find that even a *para*-methoxy substituent on the aryl ring leads to a 99% yield of trimer upon extension of the reaction time to 8 min.

The pathway shown in Scheme 1 is analogous to those proposed earlier[3c,d,h] for other catalysts, although none of the zwitterionic catalyst-arylisocyanate adduct intermediates were detected previously. In our reaction with PhNCO, however, we observe a transient peak in the ^{31}P NMR spectrum at 29.46 ppm in C_6D_6 and an *m/z* peak (FAB) at 336.1 (*M* + H) for an isolated solid apparently containing an intermediate. With *p*-$MeOC_6H_4NCO$ a corresponding ^{31}P NMR peak is seen at 29.23 ppm in C_6D_6. It is therefore tempting to attribute these data to the presence of the corresponding intermediates **10** in both cases. The stability of adduct **5** (the thio analogue of **10**) to further reaction with PhNCS[7] can be ascribed to the diminished nucleophilicity and electrophilicity of the PhN nitrogen and PhNC carbon, respectively, induced by the less electronegative sulfur.

It has been reported that the cyclodimerization of PhNCO is an equilibrium reaction disfavored by increasing temperature,[9] and that trimer formation is thermodynamically allowed from 0-850K.[10] Thus the dimer/trimer ratio decreases with increasing temperature in the presence of the (weak) catalyst $P(NMe_2)_3$.[11] The much stronger catalytic action of **1** may be attributed to its substantial stabilizing influence on adducts **10** and **11** in Scheme 1, and

particularly on **11** in order to enable it to nucleophilically attack a third ArNCO molecule. The basicity of the nucleophilic nitrogen in **11** is undoubtedly enhanced by electron induction from the bridgehead nitrogen in the quasi transannular bond which has been shown to exist in **4**, **6** and **7**, for example.[7] It is reasonable to suppose that as intermediate **12** undergoes closure of

Scheme 1



the six-membered ring, the resultant increase in electron density on the P-C carbon weakens the transannular bond, thereby facilitating departure of trimer and regeneration of the catalyst **1**, in which the transannular interaction is weakest.[7,8] Strong support for the postulated flexibility of the transannular interaction in **1** (depending upon the nature of the phosphorus substituent)

is the stepwise closure of this distance over a series of eight compounds from 3.33 *Å* (which is essentially the sum of the P and N covalent radii) to 1.967 *Å*.[7]

Experimental Procedure. To a one-necked round bottomed flask (250 mL, filled with N_2 and closed with a septum) containing a solution of **1** (0.11 *g*, 0.50 mmol) in dry benzene (10 mL) was added by syringe, phenyl isocyanate (18.0 *g*, 99% pure, 150 mmol, Aldrich). After the mixture was stirred at room *T* for 3 min, the white precipitate which had very rapidly formed, solidified into a mass in a few s. The solid was cooled to room *T*, dried under vacuum, ground to powder, stirred with 30 mL of dry benzene for 2 h, filtered in vacuo, further washed with 15 mL of dry benzene and finally dried in vacuo to give 17.2 *g* (96.6%) of ^{1}H NMR spectroscopically and tlc (silica gel, using hexane:ether = 2:1, or $CHCl_3$, or $CHCl_3$:acetone = 50:1 as eluents) pure **8**. M.p. (uncorrected): 279.0-279.5 °C (lit. 281-281.5 °C[1b]); ^{1}H NMR ($CDCl_3$): δ 7.35-7.51 (m, C_6H_5); ^{13}C NMR (CD_3CN): δ 128.21, 128.74, 129.16, 133.39, 148.46; HRMS (*m/z*): calcd and found for $C_{21}H_{15}N_3O_3$ 357.11134 (54, M^+); Elemental Analysis calcd (found): C, 70.57 (69.80) H, 4.23 (4.36 N, 11.76 (11.62). The analogous reaction with *p*-$MeOC_6H_4NCO$ carried out over 8 min gave a 98.7% yield of ^{1}H NMR spectroscopically and tlc (silica gel, same solvent systems as used for **8**) pure **9** after washing with benzene (80 mL) and drying in vacuo at 50 °C. M.p. (uncorrected): 261.0-261.5 °C (lit. 261-2 °C[1b]); ^{1}H NMR ($CDCl_3$): δ 3.81 (s, 9H, OCH_3), 6.96 (d, 4H, C_6H_4) $^3J_{HH}$ = 8.7 Hz), 6.27 (d, 4H, C_6H_4; $^3J_{HH}$ = 8.7 Hz); HRMS (*m/z*): calcd for $C_{24}H_{21}N_3O_6$, 447.14304. Found, 447.14358 (50, M^+). Following these reactions by ^{31}P NMR for the detection of intermediates was carried out in 0.8 mL of C_6D_6 containing 0.037 *g* (0.17 mmol) of **1** and 0.062 *g* (0.52 mmol) of PhNCO, and in 0.7 mL of C_6D_6 containing 0.057 *g* (0.26 mmol) of **1** and 0.094 *g* (0.79 mmol) of *p*-$MeOC_6H_4NCO$. When 0.08 *g* (0.7 mmol) of PhNCO was added by syringe to a solution of 0.1 g (0.5 mmol) of **1** in ether (10 mL), a colorless solid precipitated which was dried in vacuo to give 0.14 g of a colorless solid. ^{31}P

NMR (CD_3CN): δ 31.11, -9.35; MS (*m/z*, FAB): 336.1 (*M*+H, for **10**, 52) and 217.1 (*M*+H for **1**, 100). The analogous reaction with $P(NMe_2)_3$ (0.17 *g*, 1.0 mmol) was carried out in 45 mL of dry benzene with 11.9 *g* (0.10 mol) of PhNCO. After reaction for five *d* at 60-70 °C and upon standing for 10 h at room *T*, a small amount of white precipitate appeared. The volatiles were removed under vacuum, the residue was stirred with 5 mL of benzene and then the suspension was filtered washed with acetonitrile (5 x 2 mL) and dried, giving 0.48 *g* (4%) of cyclic dimer. M.p., 182-183 °C (Lit. 175°[10]); ^1H NMR (CD_3CN): δ 7.4-7.5 (m); HRMS (*m/z*): Calcd for $C_{14}H_{10}N_2O_2$, 238.07423. Found, 238.07428 (3.5, M^+).

ACKNOWLEDGMENTS

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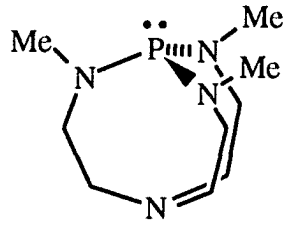
PAPER 6. SELECTIVE AND EFFICIENT SYNTHESIS OF PERHYDRO-1,3,5-TRIAZINE-2,4,6-TRIONES AND CARBODIIMIDES FROM ISOCYANATES USING $ZP(MECH_2CH_2)_3N$ CATALYSTS

ABSTRACT

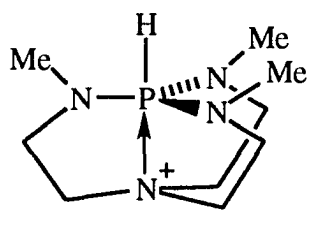
With concentrations as low as 0.0033 mole percent $ZP(MeNCH_2CH_2)_3N$ (Z = lone pair, **1**) isocyanates are catalytically trimerized to perhydro-1,3,5-triazine-2,4,6-triones (isocyanurates) at room temperature. This reaction proceeds readily in the presence or absence of solvent and the catalyst can be recycled at least six times without detectable degradation. Though not as potent a catalyst as **1**, the molecule in which Z = NPh (**3**) also facilitates this reaction and evidence is adduced that the catalytically active species is the adduct **3**•ArNCO (**6**). In contrast, $Ch=P(MeNCH_2CH_2)_3N$ (Ch = O, **4**; Ch = S, **5**) selectively catalyze the transformation of isocyanates to carbodiimides and do so more efficiently than their acyclic analogues $O=P(NMe_2)_3$ and $(MeO)_2P(S)Ph$, respectively. The crystal structure of **4** is reported for the first time and details of the crystal structure of $[PhN=C(SMe)P(MeNCH_2CH_2)_3N]I$ reported earlier by us in preliminary form are presented. Both structures support the hypothesis that $P\text{-}N_{ax}$ transannulation plays a lead role in the catalytic activities of **1** and **3-5**.

INTRODUCTION

In the course of our synthetic and structural investigations of pro-azaphosphatrane **1**, its azaphosphatranium derivative **2** and quasi-azaphosphatrane derivatives such as **3**-**5**,[1-6] we have discovered that **1** is a non-ionic superbase[5] useful in organic synthesis as a deprotonation



1



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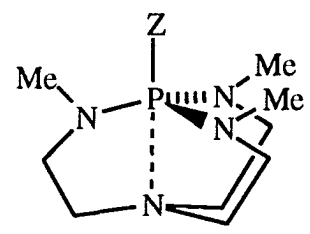
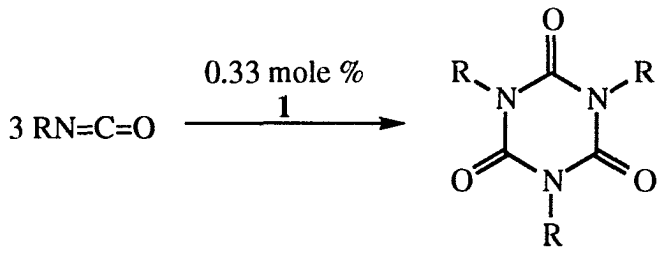


Z	
3	NPh
4	O
5	S

agent and that it functions as a superior catalyst for the rapid and clean conversion of aryl isocyanates to perhydro-1,3,5-triazine-2,4,6-triones (isocyanurates):[7]



(1)

Isocyanurates, which in some cases are stable to 400 °C,[8] enhance the dimensional and hydrolytic stability of urethane polymer networks and also impart low combustibility.[9] Hence the efficient trimerization of isocyanates is currently of considerable commercial importance, especially in the production of rigid urethane-modified isocyanurate foams.[10] Triaryl isocyanurates are also useful as activators for the continuous anionic polymerization and post-polymerization of ε-caprolactam to nylon-6 possessing a low monomer content and a highly stable melt viscosity.[11] Triallyl isocyanurate is used to make polymers for the preparation of flame-retardant laminating materials for electrical devices.[12a] It is also utilized as a cross-

linking agent for plastics[12b] and as a monomer in making copolymer resins that are water-resistant, transparent and impact-resistant.[12c-f]

As part of our continuing exploration of the catalytic properties of **1**, we report here: 1) the extension of our catalysis studies to the trimerization of alkyl isocyanates, 2) an investigation of the lifetime of catalyst **1** in trimerization reactions, and 3) how far the catalyst concentration can be reduced without seriously impairing the rate of trimerization. We also report on the catalytic activity and selectivity of **3** in converting isocyanates to isocyanurates,

$$2RNCO \xrightarrow{\textbf{4 or 5}} RN{=}C{=}NR + CO_2 \qquad (2)$$

and on the greater catalytic activity of **4** and **5** in catalytically transforming isocyanates to carbodiimides compared with their acyclic analogues $O{=}P(NMe_2)_3$ and $(MeO)_2P(S)Ph$, respectively. The effect of partial transannulation in **3-5** on their catalytic activities will be discussed.

RESULTS AND DISCUSSION

Isocyanurate formation catalyzed by 1. In the following paragraphs the three major advantages of **1** over a wide variety of other catalysts for the trimerization of isocyanates will be discussed.[13]

First, a substantial variety of isocyanates can be used as substrates for catalyst **1**. Compound **1** catalyzes the trimerization of phenyl isocyanate quantitatively and in GC purity within a few minutes (entry 1, Table 1). The IR spectrum of the reaction mixture reveals no band characteristic of the N=C=O at 2260 cm^{-1}. An electron-donating group on the aromatic ring of an aryl isocyanate renders the carbonyl less electrophilic, and hence more difficult to

Table 1. Synthesis of Isocyanurates Catalyzed by **1**.[a]

entry	RNCO		T	reaction	reaction	isolated
	R	mmol	(°C)	solvent (mL)	time	yield (%)
1	Ph	150	25	PhH (5)	3 min.	97
2	Ph	150	25	none	2 min.	94
3	Ph	150	65	PhH (80)	40 hr.	96
4	*p*-$MeOC_6H_4$	75	25	PhH (5)	8 min.	99
5	*p*-$MeOC_6H_4$	75	25	none	5 min.	94
6	*p*-$MeOC_6H_4$	150	65	PhH (80)	72 hr.	95
7	Et	25	25	THF (1)	5 min.	82[b]
8	CH_2=$CHCH_2$	23	25	THF (1)	3 dy	75

[a]Using 0.33 mole % **1**. Conversion was 100% according to the IR and ^1H NMR spectra of the crude product. [b]The yield upon distillation of a small scale reaction.

trimerize, as has been shown to be the case for *p*-MeC_6H_4NCO, which other catalysts fail to trimerize.[14] Using **1** as the catalyst, we find that even the much stronger electron-donating *p*-$MeOC_6H_4$ moiety leads to a 99% isolated yield of trimer on extension of the reaction time to eight minutes (entry 4 in Table 1).

Few catalysts have been reported to trimerize alkyl isocyanates. In the presence of Et_3N, for example, ethyl isocyanate trimerizes in 65% yield after 20 hours at 70 °C and 800 MPa.[15] In contrast, **1** readily catalyzes this transformation with 100% conversion and in 82% isolated yield in five minutes at room temperature (Table 1, entry 7). An earlier preparation of triallyl isocyanurate involves the reaction of allyl chloride and highly toxic potassium cyanate at 150 °C and gives a poor (ca. 30%) yield.[16a] Although improvements in the yield were reported later, the purification procedures were complicated.[16b-f] A two-step synthesis for triallyl isocyanurate includes the initial formation of triallyl cyanurate via the reaction of cyanuric chloride with allyl alcohol followed by thermal rearrangement to the corresponding isocyanurate in toluene containing Cu and $FeCl_2/SnCl_4$[16g] or a salt of Cu[16h], or by employing DMF as a solvent containing a methyl silicate drying agent.[16i] In the present work, **1** quantitatively trimerizes allyl isocyanate (entry 8, Table 1) as shown by the lack of detectable N=C=O band in the IR spectrum of the reaction mixture. Moreover, the spectrum was identical with that of pure triallyl isocyanurate obtained in 75% yield by distillation of the product.

Secondly, **1** can be used in relatively small quantities for rapid and efficient isocyanate trimerization. Normally, substantial amounts of other catalysts are required to achieve reasonable yields of isocyanurates. For example, triphenyl isocyanurate was obtained in 63% yield in an overnight reaction catalyzed by $Si(OCH_2CH_2NMe_2)_4$.[17] Triphenyl and tri(*p*-chlorophenyl) isocyanurate was obtained in 66 and 80% yields, respectively, in 24 hours using 5% alkoxy alkenes as catalysts.[14] It is noteworthy that such catalysts fail to trimerize the less reactive *p*-MeC_6H_4NCO or alkyl isocyanates. Triaryl and trialkyl isocyanates were obtained in

22-100% yield after 20 hours at 100 °C and 800 MPa in the presence of 10% Et_3N.[15] According to Table 1, however, such catalyses can be accomplished in quite short time periods under very mild conditions with a small amount of **1**.

We were interested to determine how far the catalyst concentration could be reduced while maintaining reasonable catalytic efficiency. As is seen in Table 2, when the concentration of **1** is 0.083 mole % (a four-fold reduction from entries **1** and **2** in Table 1) the trimerization of phenyl isocyanate reaches completion in 15 minutes giving the corresponding isocyanurate in 93% isolated yield. Step-wise reduction of this catalyst ratio to 0.0033 mole % (i.e., ~0.3 mg of **1**) a reasonable yield (76%) of the trimer could still be isolated after stirring the reaction mixture for 24 hours.

Thirdly, the catalyst survives repeated use. For the first cycle of the catalyst **1** (0.33 mole %) was dissolved in THF (5 mL) and phenyl isocyanate (5.48 g) added to the catalyst

Table 2. Room Temperature Synthesis of Triphenyl Isocyanurate with Varying Catalyst (**1**) Concentration.[a]

	mole %	PhNCO	reaction	product yield[b]	
entry	of **1**	(g)	time	g	%
1	0.083	4.38	15 min.	4.90	92.8
2	0.033	5.48	38 min.	6.01	91.3
3	0.0066	5.48	15 hr.	5.97	90.6
4	0.0033	5.48	24 hr.	5.00	75.9

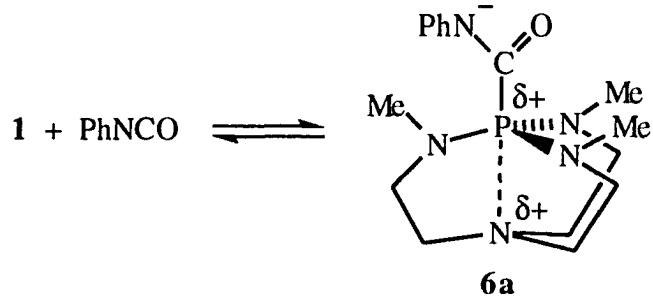
[a]One mL of THF was used to dissolve the catalyst **1**. [b]The product crystallizes with one mole of THF as was shown by integration of its ^1H NMR spectrum. THF was removed *in vacuo* at 40-50 °C.

solution. After stirring for five minutes at room temperature, the solid trimer was filtered in vacuo, washed within the filter with pentane (3 x 3 mL) and dried in vacuo to give the corresponding 1:1 isocyanurate•THF complex (as indicated by ^{1}H NMR spectroscopy). The filtrate and washings were combined, concentrated to ~5 mL and then re-used for the second cycle. This procedure was repeated for all six cycles. The yield of product ranged from 82.4% in the first run to 108.0% in the sixth run (the latter owing to incomplete precipitation in the previous run) with an average isolated yield of 97.8%.

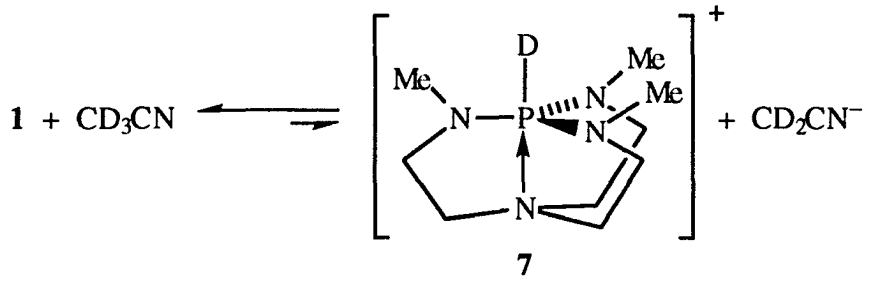
A variety of organic solvents lend themselves to these catalytic trimerization reactions, including benzene, THF, toluene and DMF. In these solvents, catalyst **1** is very soluble whereas the solid trimers are less so, facilitating easy separation by filtration and recycling of the filtrate containing the catalyst. As can be seen from Table 1, large ratios of solvent to substrate lengthen reaction times in part because the reaction is exothermic. Thus the temperature rise accelerates the reaction when small amounts of solvent are used.

Acetonitrile is not recommended for these trimerizations owing to an interesting side reaction. Compound **1** appears to be stable in CD_3CN for days and at least for 12 hours at 50° according to ^{31}P NMR spectra for these solutions, which exhibit only a peak for **1** at 119.95 ppm. However, 15 minutes after adding PhNCO to such a solution at room temperature, a peak at 30.03 ppm has grown to 20 times the intensity of the peak at 119.95 ppm. We tentatively assign the peak at 30.03 ppm to intermediate **6a** in reaction 3 (*vide infra*). With the passage of time, this peak decreases as a 1:1:1 triplet at -9.98 ppm ($^{1}J_{PD}$ = 736 Hz) and the 119.95 ppm peak grow. After 30 hours, the peak at 30.03 ppm has disappeared and those at -9.98 and 119.95 ppm remain for weeks in the ratio 1:4.3. Simultaneous with the disappearance of the peak at 30.03 ppm, crystals appeared which upon ^{1}H NMR, ^{13}C NMR, HRMS and MP analysis were shown to be triphenyl isocyanurate. The 1:1:1 triplet at -9.98 ppm is undoubtedly due to the deuterium analogue of **2** ($d^{31}P$ -10.6 ppm, $^{1}J_{PH}$ = 491 Hz[1a]).

The observation that it appears only after PhNCO is added, suggests that equilibrium 4, though small, may be driven to the right by reaction 5. Apparently the latter reaction can compete with



6a (3)



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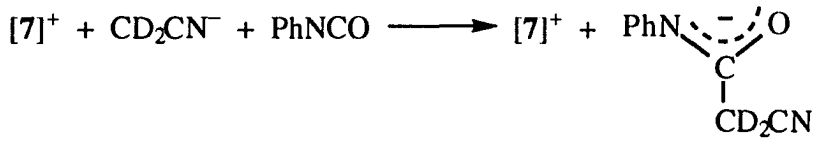
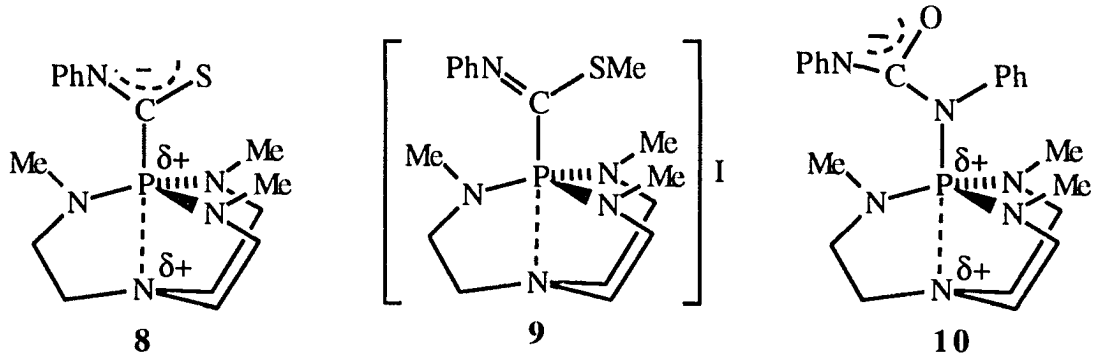


(5)

the catalytic trimerization reaction for PhNCO. Attempts to isolate **7**(PhNC(O)CD_2CN) failed as did addition of MeI or Me_3OBF_4 for the purpose of isolating the alkylated anion.

Additional evidence for intermediate **6a** in the trimerization of PhNCO has been gathered. Fifteen minutes after three equivalents of PhNCO were added to a solution of **1** in C_6D_6, ^{31}P NMR peaks at 120.3 ppm (**1**) and 29.46 ppm (presumably **6a**) were observed in a ratio of 1:1.5. After about seven hours, only the downfield peak remained and triphenyl isocyanurate precipitated. Although the ^1H spectrum of the reaction mixture after 15 minutes was complex, the ^{13}C NMR spectrum revealed non-benzenoid chemical shifts consistent only with the presence of **1**, trimer and **6a**. Moreover, the doublet at 161.08 ppm ($^1J_{PC}$ = 201.6 Hz)

assigned to the carbonyl carbon of **6a**, is in the region of the thiocarbonyl carbon of **8** (178.41 ppm, $^{1}J_{PC}$ = 187.8 Hz) which was isolated and structurally characterized by X-ray means as

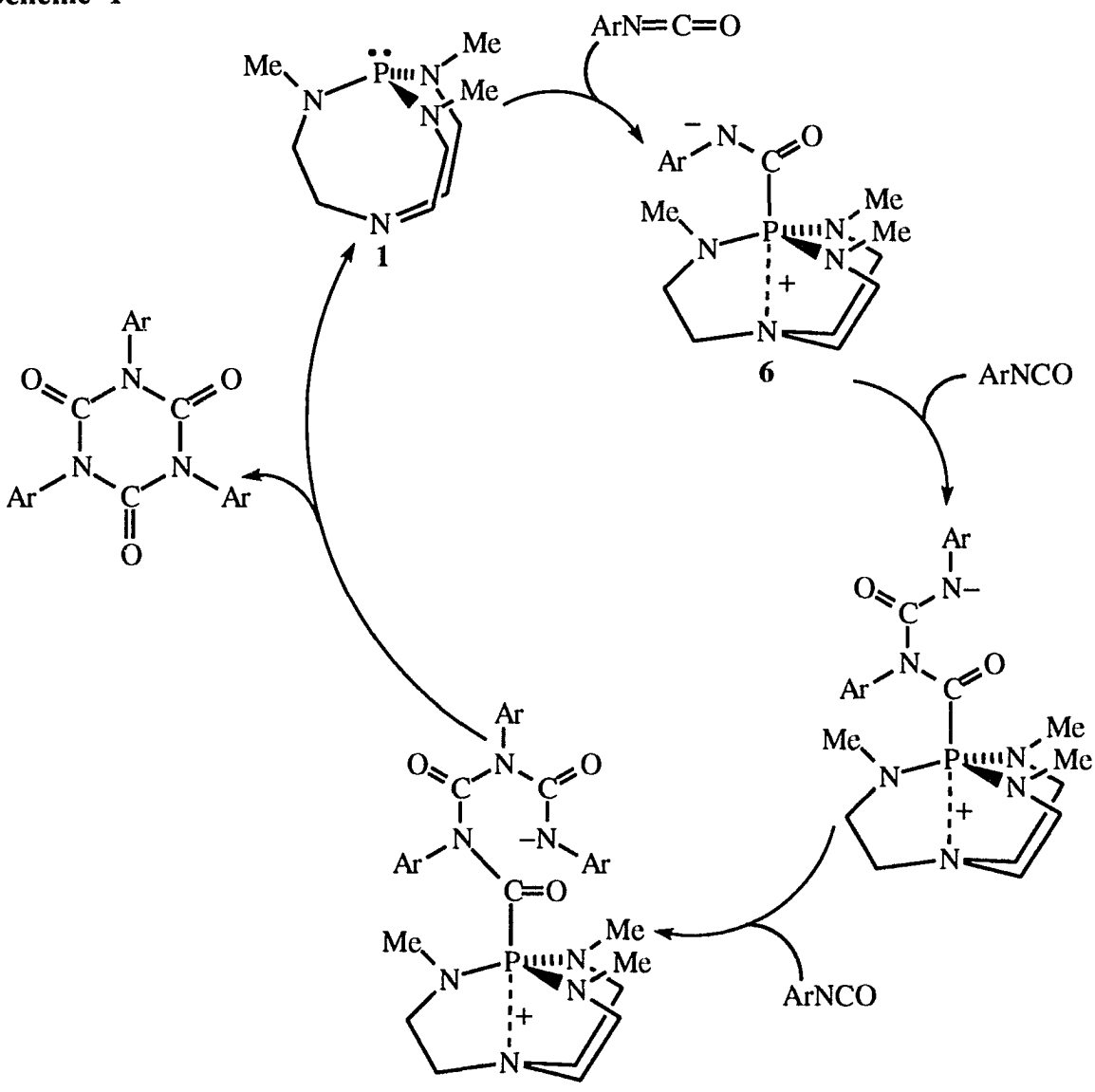


8 **9** **10**

its derivative **9**(I).[6] The ^{31}P chemical shift of **6a** (29.46 ppm) is close to that of its analogue **8** (29.60 ppm). An attempt to isolate **6a** from a 1:1 equimolar mixture of **1** and phenyl isocyanate in Et_2O resulted in a precipitate which upon filtration gave a powder whose FAB mass spectrum revealed a strong peak for **6a** at 336.1 daltons $(M+H)^+$ (with no detectable peaks of higher mass) and a base peak for **1** at 217.1 daltons $(M+H)^+$. Because FAB/MS gave $(M+H)^+$ peaks for analogous species such as zwitterionic **8** and cationic **9**,[4,5] it is likely that **6a** is an intermediate that exists in detectable concentration in this catalytic reaction depicted in Scheme 1. Attempts to purify the precipitate or to trap **6a** as an alkylated cation by adding MeI to the reaction mixture failed. ^{31}P NMR spectroscopy also revealed a peak at 29.23 ppm assigned to the intermediate *p*-$MeOC_6H_4NCO$•**1** (**6b**) in the trimerization of *p*-$MeOC_6H_4NCO$ catalyzed by **1**.

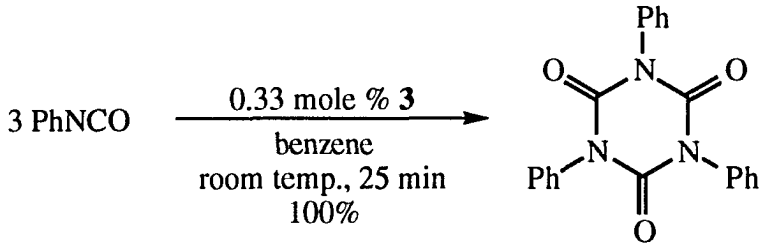
The importance of transannulation in the intermediates shown in Scheme 1 can be inferred from the structure of **9**(I) shown in Fig. 1. Cation **9** can be viewed as a methylated derivative of this analogue of **6a**. The transannular distance in cation **9** is 2.209(6) Å which is 34% shorter than the sum of the P and N van der Waals radii of 3.34 Å. Further evidence for transannulation is the average of the N_{eq}-P-N_{eq} bond angles (118.3(3)°) which is very close to the 120° expected for trigonal bipyramidal phosphorus. While the cationic charge on **9** could

Scheme 1



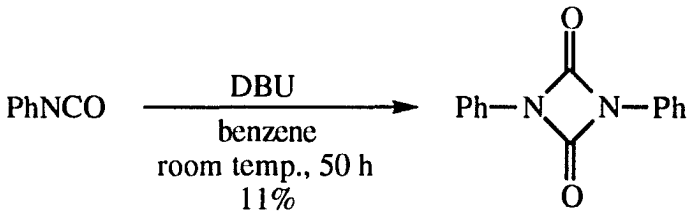
be expected to accentuate transannulation over a zwitterionic species such as **6a**, the zwitterionic CS_2 adduct of **1** (i.e., $^{-}S_2CP^{+}(MeNCH_2CH_2)_3N$) is also partially transannulated, featuring a P-N_{ax} distance of 3.008 Å[6] which is 10% shorter than the sum of the van der Waals radii.

Isocyanurate formation catalyzed by 3. Like **1**, **3** is also a strong catalyst for trimerizing phenyl isocyanate:



(6)

Quantitative isolation of the trimer followed washing and drying of the precipitated product. By contrast, we found that DBU, though a stronger base than **3**[5], is a much weaker catalyst, leading to dimeric rather than trimeric product:



(7)

Earlier[7] we suggested that the much stronger catalytic activity of **1** than its acyclic analog $P(NMe_2)_3$ arises from the stabilization of intermediate **6** by transannular interaction. It could be expected that intermediate **10**, arising from **3**, is similarly stabilized, and indeed this seems to be the case. The ^{31}P NMR spectrum taken ten minutes after a 1:3 solution of **3** and phenyl isocyanate in C_6D_6 had been made revealed peaks at 21.91 and 13.35 ppm in a ratio of about 1:50. The downfield peak, tentatively assigned to **10**, grows while the upfield resonance due to **3** decreases over time. By the next morning, the peak corresponding to **3** disappeared and only the peak at 21.91 ppm remained. In addition, the ^{13}C NMR spectrum of the reaction mixture displayed a new peak at 154.00 ppm tentatively regarded as stemming from the carbonyl carbon of **10**. After crystals of trimer were isolated from this solution, the solution was added to 2.5 g of phenyl isocyanate. After one day at room temperature, an 85% yield of product was isolated. Since **1** was not regenerated in this reaction and **10** is the only detectable

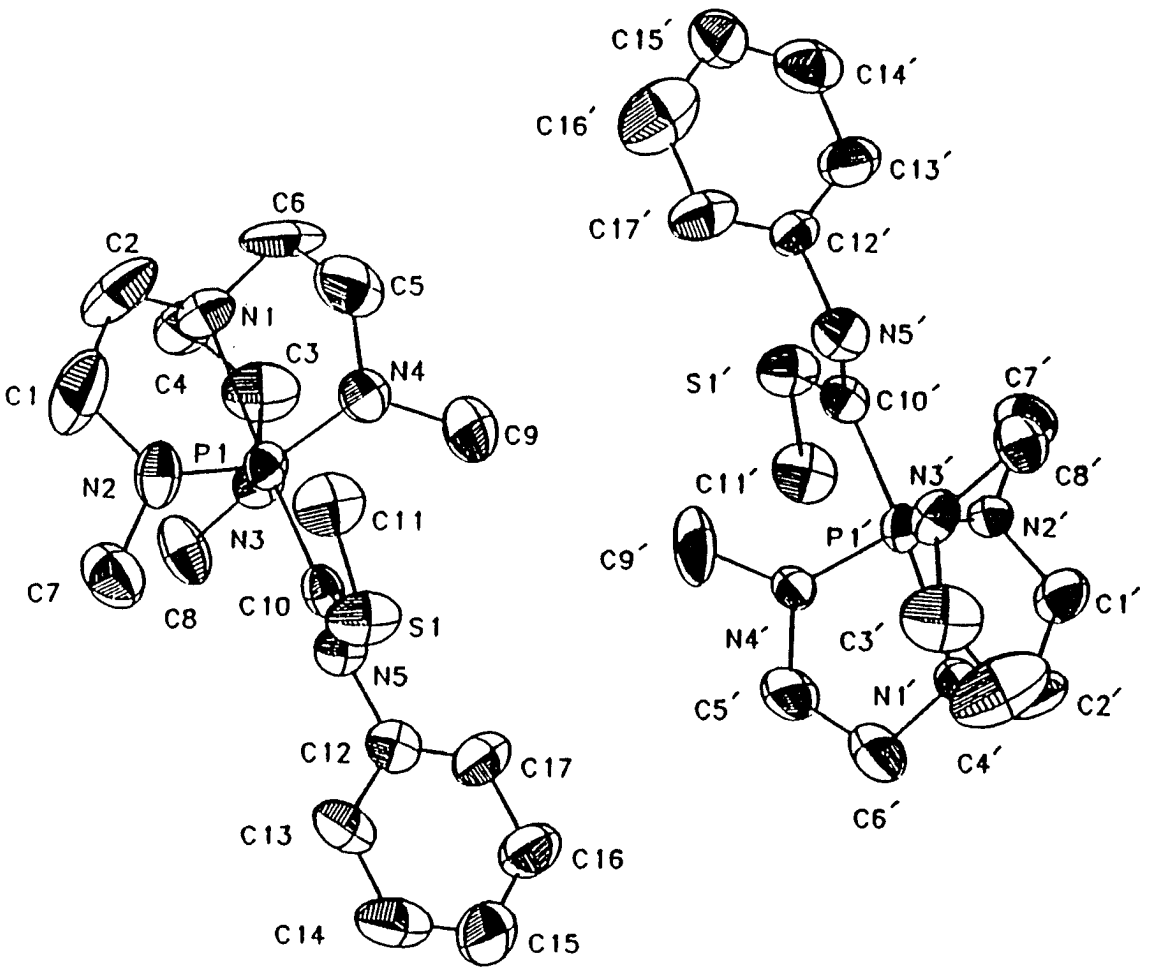
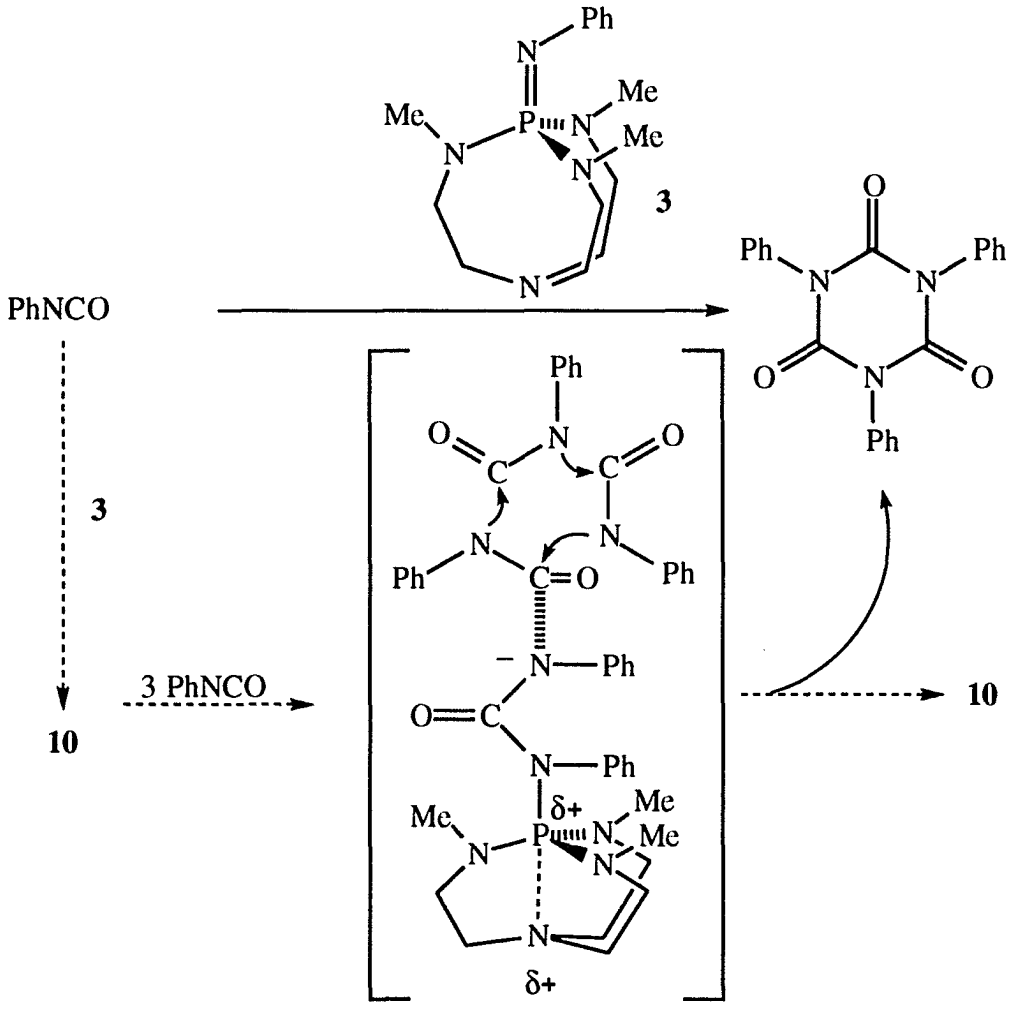


Fig. 1. ORTEP drawing of **9**. Ellipsoids are drawn at the 50% probability level.

species at the end of the reaction, it is not unreasonable to suggest that adduct **10** is the catalytically active species as depicted in Scheme 2.

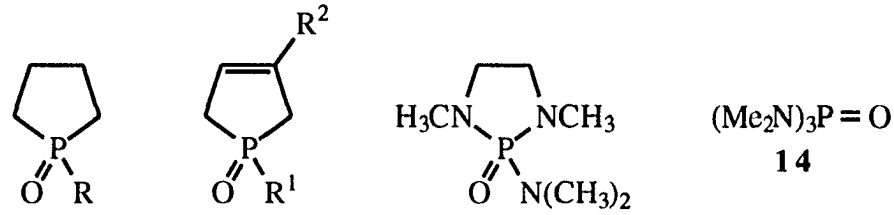
Scheme 2



Carbodiimide formation catalyzed by 4 and 5. As a consequence of both their intrinsic interest and their great importance as versatile reagents in organic synthesis, carbodiimides rank as one of the most important classes of compounds in organic chemistry.[18] Of particular significance is their use as condensing agents in the synthesis of peptides and nucleotides. More recently, carbodiimides have been shown to provide an efficient annulation

route to highly substituted indoles, quinindolines and isoquinolines which are pharmacologically active compounds, displaying strong cytostatic antitumor activity.[19]

The synthesis of diaryl carbodiimides from aryl isocyanates, using cyclic phospholanes **11**[20a] and phospholenes **12**[20b] as catalysts, represents a decided improvement in view of their ease of preparation in high yield and purity by this route over other methods.[18] These preparations are carried out over a range of temperatures (room temperature to 194 °C).



11 **12** **13** **14**

R^1 = Et, Ar

R^2 = H, CH_3

Catalyst **12** where R^1 = Ph, R^2 = Me, is most widely used because of its facile synthesis.[20c,d] The stronger catalytic activity of **12** than **11** in these reactions may be associated with some donation of pi-electron density from the ring carbons to the P=O moiety. However, these catalysts produce only moderate yields of dialkyl carbodiimides from alkyl isocyanates and they do not catalyze the conversion of strongly sterically hindered isocyanates such as Ph_2CHNCO into carbodiimides.[20a]

It is well known that the catalytic activity of phosphoryl compounds increases with P=O bond nucleophilicity.[18b] Electron-withdrawing groups bound to the phosphorus atom decrease this nucleophilicity and thus decrease the catalytic activity in the order: $R_3P{=}O > R_2(RO)P{=}O > R(RO)_2P{=}O > (R_2N)_3P{=}O \geq (RO)_3P{=}O$,[21a] while electron-donating groups increase P=O nucleophilicity and increase the catalytic activity. Thus in **12** ($R^2 = CH_3$, $R^1 = p\text{-}R^3C_6H_4$), the increasing catalysis order for R^3 is H < Me < NEt_2.[21b] We have mentioned earlier in this paper that bridgehead P-N transannulation is an important factor in rendering **1** the most

effective catalyst thus far discovered for the conversion of isocyanates into isocyanurates. By analogy, we thought that **4**[1b] might be a stronger catalyst for the conversion of isocyanates to carbodiimides than its analog **13** (which is also an analgoue of **11**) and its analogue **14** (which lacks the opportunity for transannular bonding). Such enhanced P=O bond nucleophilicity in **4** expected from electron donation of the bridgehead nitrogen lone pair via partial bridgehead P-N transannulation, is substantiated by the P-N_{ax} distance (3.137 (3) Å) obtained by means of an X-ray diffraction study (Fig. 2). This transannular distance is 6% shorter than the sum of the van der Waals radii of the P and N atoms (3.34 Å). Indeed **4** catalyzes the condensation of both aryl and alkyl isocyanates **15** to their corresponding carbodiimides **16** in high yield (reaction 8, Table 3). Although **4** is not as strong a catalyst as

$$\underset{\textbf{15}}{2\ RN{=}C{=}O} \xrightarrow{\text{catalyst}} \underset{\textbf{16}}{RN{=}C{=}NR} \qquad (8)$$

11 or **12** it is interesting that **4** is a much stronger catalyst than its analogues **13** and **14** in which no opportunity for transannulation exists to augment their P=O bond nucleophilicity. The stronger catalytic activity of **4** over **13** and **14** can be seen from comparison experiments (entry 3 versus entries 7 and 8 in Table 3), in which **4** requires a much shorter time than **13** or **14** for the complete conversion of *o*-tolyl isocyanate to di(tolyl) carbodiimide at reflux temperature.

Compound **5**, described earlier by us,[1b] is also a more effective catalyst than the acyclic sulfide $(CH_3O)_2P(S)Ph$ which at 0.9 mole % provides only a 20% yield of **16a** after 16.5 hr at 162 °C. It is no surprise that **5** is nearly as catalytically active as **4** because **5** also exhibits a partial P-N_{ax} transannular bond (although it is only 3% shorter than the sum of van der Waals radii[2]) and **5** may share the same reaction pathway with **4** as shown in Scheme 3. Unlike the pathway for other O=P compounds,[23] the phosphorimide **18** is not expected as an intermediate in our systems because if it were formed, it would catalyze the trimerization of isocyanates to

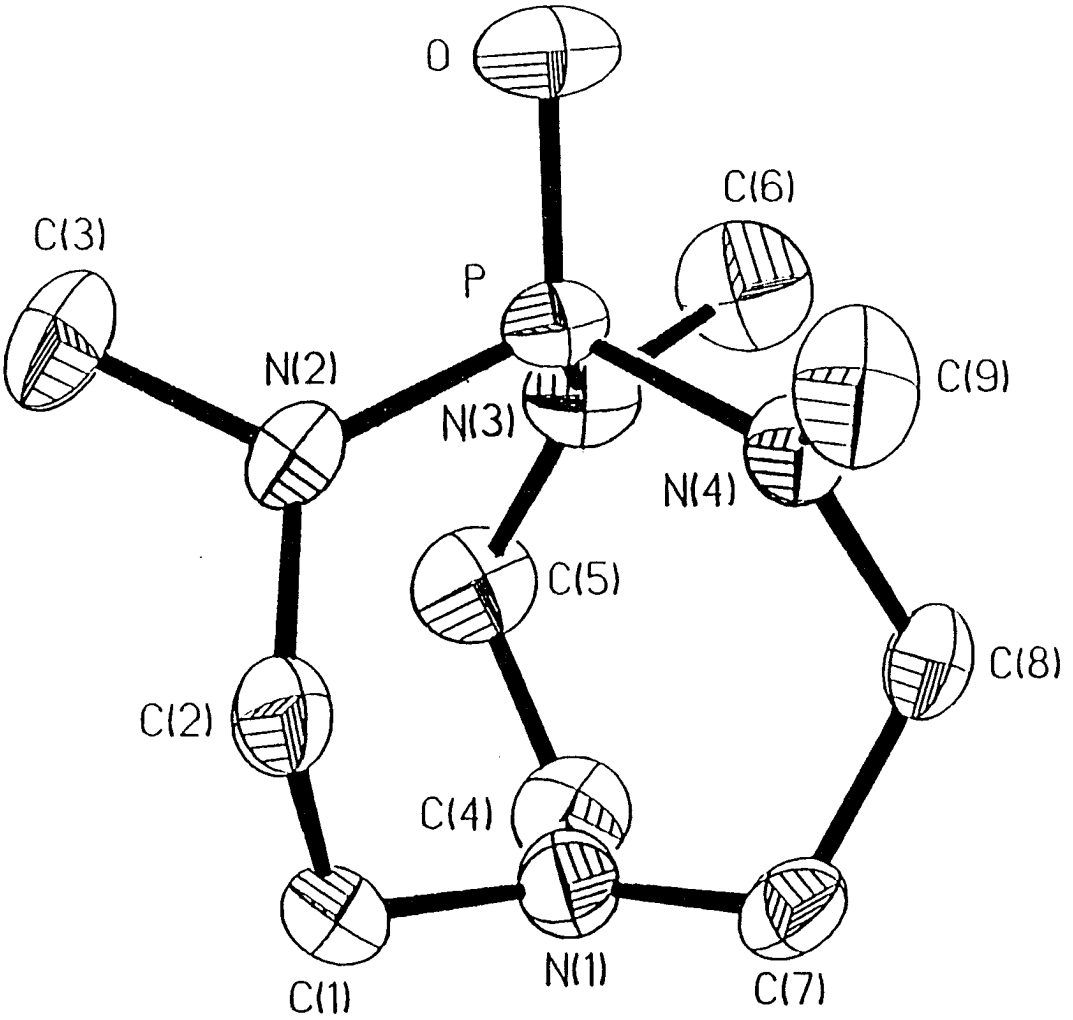


Fig. 2. ORTEP drawing of **4**. Ellipsoids are drawn at the 50% probability level.

Table 3. Catalytic Synthesis of Carbodiimides

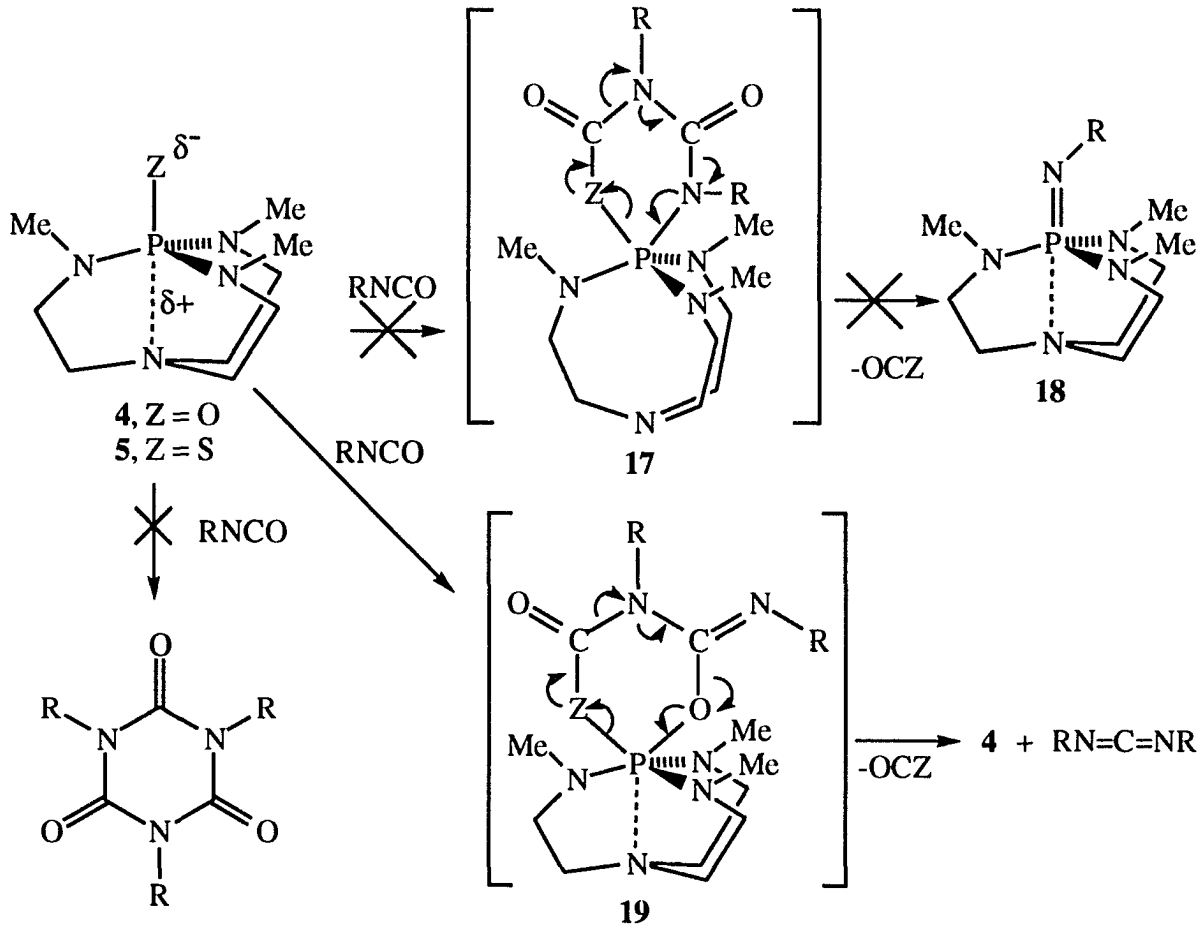
entry	R of **15, 16**	catalyst	temperature	time (h)	isolated yield of **16**
1	Ph	**4**	180-210 °C	5.5	84%[a] (**16a**)
2	3-ClC_6H_4	**4**	145-180 °C	6.5	98%[b] (**16b**)
3	2-MeC_6H_4	**4**	180-250 °C	12	80% (**16c**)
4	*c*-C_6H_{11}	**4**	200-230 °C	91	92% (**16d**)
5	*n*-$C_{18}H_{37}$	**4**	160-230 °C	96	90%[b] (**16e**)
6	Ph	**5**	180-210 °C	5.5	81%[a] (**16a**)
7	2-MeC_6H_4	**13**	180-250 °C	29	-[c] (**16c**)
8	2-MeC_6H_4	**14**	180-250 °C	30	-[d] (**16c**)

[a]Distillation gave 65% of monomeric **16a** (R = Ph). The solid residue of the remainder of the yield was dimeric $(PhNC{=}NPh)_2$ (see Experimental). [b]The crude product had a very high boiling point and was not purified. [c]100% Conversion as shown by lack of a detectable N=C=O absorption in the IR. [d]After 30 h at 180-250 °C, conversion was not complete according to the IR spectrum and persistent CO_2 evolution.

isocyanurates as discussed earlier. No isocyanurate was detected in the HRMS and IR spectra of the residues obtained upon distillation of the carbodiimides, however. The failure of **18** to form in Scheme 3 can be attributed to the preferential formation of intermediate **19** over **17** owing to greater stability of the P-O bond compared with P-N, and less steric encumbrance of the R group proximal to the methyl groups in **19**. The observed reaction is also driven by the evolution of CO_2 (and OCS) which is also favored by **19** since breakage of an P-Z bond is compensated by P=O formation.

Regardless of whether **4** or **5** was used as the catalyst, only **4** was present after reaction completion, as was shown, by ^{31}P NMR spectroscopy. Although the evolution of CO_2 was easily demonstrated by the formation of a white precipitate in a solution of $Ca(OH)_2$, no attempt was made to separate and identify the small amount of OCS that probably formed when **5** was used as the catalyst.

Scheme 3



EXPERIMENTAL SECTION

General. All procedures were carried out in an atmosphere of argon or nitrogen. Et_2O, THF and pentane were dried by refluxing with sodium and were distilled under nitrogen. CD_3CN, CH_3CN, C_6D_6 and benzene were dried with CaH_2 and distilled under argon. NMR spectrometers employed were a Nicolet NT-300 for ^1H spectra, a Bruker WM-200 for ^{31}P spectra and a Varian VXR-300 for ^{13}C spectra. Standards for the NMR spectra were TMS (^1H, internal), 85% H_3PO_4 (^{31}P, external), and the δ 118.20 peak of the solvent CD_3CN or the δ 128.00 peak of the solvent C_6D_6 (^{13}C, internal). Infrared spectra were recorded with a Bruker/FS-113 V spectrometer. High-resolution and FAB mass spectra were recorded on a KRATOS MS-50 spectrometer. A solution molecular weight of compound $(PhNC{=}NPH)_2$ in chloroform and elemental analyses were performed by Desert Analytics. X-ray data collections and structure solutions were carried out at the Iowa State University Molecular Structure Laboratory. The catalysts **1** and **3-5** were synthesized by our previously published methods.[1] All melting points are uncorrected.

Triphenyl isocyanurate. *Method A*: To a one-necked round bottomed flask (250 mL, filled with N_2 and closed with a septum) containing a solution of **1** (0.11 g, 0.50 mmol) in dry benzene (10 mL) was added by syringe, phenyl isocyanate (18.0 g, 99% pure, 150 mmol, Aldrich). After the mixture was stirred at room temperature for 3 min, the white precipitate which had very rapidly formed, transformed the reaction mixture into a solid mass in a few seconds. The solid was cooled to room temperature, stirred with 30 mL of dry benzene for 2 h, filtered in vacuo, further washed with 15 mL of dry benzene and finally dried in vacuo to give 17.2 g (96.6%) of pure product as shown by ^1H NMR spectroscopic, TLC (silica gel using hexane:ether = 2:1, or $CHCl_3$, or $CHCl_3$:acetone = 50:1 as eluents) and GC (in $CHCl_3$) > 99.9% pure product. Mp: 279.0-279.5 °C (lit. 281-281.5 °C[11b]); IR (KBr pellet): 1726 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): 7.35-7.51 (m, C_6H_5); ^{13}C NMR (CD_3CN):

128.21, 128.74, 129.16, 133.39, 148.46; HRMS (*m/z*): calcd and found for $C_{21}H_{15}N_3O_3$ 357.11134 (54, M^+).

Method B: To 0.11 g (0.50 mmol) of **1** under argon was added by syringe phenyl isocyanate (18.0 g, 99% pure, 150 mmol, Aldrich). The mixture was stirred at room temperature. A white precipitate formed rapidly after 2 min of stirring and a solid mass appeared in a few seconds thereafter. The solid mass was cooled, ground to powder and then stirred with 30 mL of dry benzene, filtered *in vacuo*, further washed with 10 mL of dry benzene and finally dried at 40-50 °C to give 10.7 g (94.4%) of tlc-pure triphenyl isocyanurate. M.p. 279.0-279.5 °C. IR (KBr pellet): 1726 cm^{-1} (C=O).

Method C: To a solution of **1** (0.11 g, 0.50 mmol) under argon in dry benzene (80 mL) was added by syringe, phenyl isocyanate (18.0 g, 99% pure, 150 mmol, Aldrich). The mixture was stirred and heated at 60-70 °C for 40 h and then allowed to stand at room temperature for 10 h. The white precipitate was filtered and dried *in vacuo* to give 16.8 g (94%) of GC-pure triphenyl isocyanurate. M.p. 279.0-279.5 °C. The mother liquor was concentrated to about 50 mL, filtered and washed with dry benzene (2 x 5 mL) to give 0.41 g of triphenyl isocyanurate which was also GC pure. The total yield was 96%.

Tri(*p*-methoxy)phenyl isocyanurate. *Method A*: To a solution of **1** (0.06 g, 0.3 mmol) in dry benzene (5 mL) under argon was added by syringe *p*-methoxyphenyl isocyanate (11.3 g, 99% pure, 75 mmol, Aldrich). After about 3 minutes of stirring at room temperature, a white precipitate formed gradually and within another 5 min the mixture solidified. The solid was cooled to room temperature and evacuated to remove solvent. The residue was ground to powder, stirred with 50 mL of dry benzene, filtered *in vacuo*, further washed with 30 mL of dry benzene and finally dried *in vacuo* at 50 °C to give 11.1 g (99%) of TLC and GC-99.9% pure tri(*p*-methoxy)phenyl isocyanurate. M.p. 261.0-261.5 °C (lit. 261-262 °C[11b]); IR (KBr pellet): 1697 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): 3.81 (s, 9 H, OCH_3), 6.96 (d, 4 H, C_6H_4,

$^3J_{HH}$ = 8.7 Hz), 6.27 (d, 4 H, C_6H_4, $^3J_{HH}$ = 8.7 Hz); HRMS (*m/z*): calcd for $C_{24}H_{21}N_3O_6$, 447.14304. Found: 447.14358 (M^+, 50).

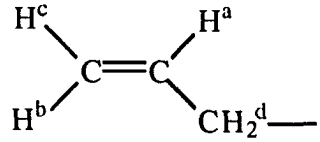
Method B: To 0.06 g (0.3 mmol) of **1** under argon was added by syringe *p*-methoxy phenyl isocyanate (11.3 g, 99% pure, 75.0 mmol, Aldrich). The mixture was stirred at room temperature. After 5 minutes of stirring, a white precipitate formed very rapidly and the mixture solidified in a few seconds. The solid was cooled to room temperature, ground to powder, stirred with 50 mL of dry benzene, filtered *in vacuo*, further washed with 30 mL of dry benzene within the filter and finally dried *in vacuo* at 50 °C to give 10.5 g (94%) of TLC and GC-99.9% pure tri(*p*-methoxylphenyl isocyanurate. M.p. 261.0-261.5 °C. IR (KBr pellet): 1697 cm^{-1} (C=O).

Method C: To a solution of **1** (0.11 g, 0.50 mmol) in dry benzene (80 mL) under argon was added by syringe *p*-methoxyphenyl isocyanate (22.6 g, 99% pure, 150 mmol, Aldrich). The mixture was stirred and heated at 60-70 °C for 72 h and allowed to stand at room temperature for 10 h. The precipitate was filtered *in vacuo*, washed with dry benzene (2 x 15 mL) and dried *in vacuo* at 50 °C to give 21.5 g (95%) of TLC and GC-99.9% pure tri(*p*-methoxy)phenyl isocyanurate. M.p. 261.0-261.5 °C. IR (KBr pellet): 1697 cm^{-1} (C=O).

Triethyl isocyanurate. To a solution of **1** (0.018 g, 0.89 mmol) in pentane (1 mL) under argon was added by syringe EtNCO (1.79 g, 25.3 mmol) at room temperature. The reaction mixture became warm and a colorless crystalline precipitate formed immediately. After about 5 min., the reaction temperature began to fall and the solid was filtered and dried *in vacuo* to give triethyl isocyanurate (1.46 g, 81.7%). M.p. 93-94 °C (lit.[24] 95 °C); IR (Nujol mull): 1693 cm^{-1} (C=O); ^1H NMR ($CDCl_3$), 1.21 (t, 9 H, $^3J_{HH}$ = 6.9 Hz, CH_3), 3.91 (q, 6 H, $^3J_{HH}$ = 6.9 Hz, CH_2). ^{13}C NMR ($CDCl_3$): 13.03 (CH_3), 38.07 (CH_2), 148.57 (C=O). HRMS (*m/z*): calcd for $C_9H_{15}N_3O_5$: 213.11030. Found: 213.11169 (M^+, 100).

Triallyl isocyanurate. To a stirred solution of **1** (0.016 g, 0.074 mmol) in dry THF (1 mL) under argon was added by syringe allyl isocyanate (1.88 g, 22.6 mmol). There was no

obvious change of the reaction mixture after 3 days of stirring at room temperature. The solvent was removed *in vacuo* and the residue was vacuum distilled to give 1.4 g (75%) of pure triallylisocyanurate. Mp 23-24 °C (lit.[16b] 25-26 °C). IR (neat), 1686 cm^{-1} (C=O). ^1H NMR ($CDCl_3$):



4.45 (ddd, 2 H, H^d, $^3J_H{}^aH^d$ = 6.0 Hz, $^4J_H{}^bH^d$ = $^4J_H{}^cH^d$ = 1.2 Hz); 5.20 (tdd, 1 H, H^c, $^3J_H{}^cH^a$ = 11.1 Hz, $^2J_H{}^cH^b$ = 1.5 Hz, $^4J_H{}^cH^d$ = 1.2 Hz), 5.26 (tdd, 1 H H^b, $^3J_H{}^bH^a$ = 16.2 Hz, $^2J_H{}^cH^b$ = 1.5 Hz, $J_H{}^bH^d$ = 1.2 Hz), 5.80 (tdd, 1 H, H^a, $^3J_H{}^aH^b$ = 16.2 Hz, $J_H{}^aH^c$ = 11.1 Hz, $^3J_H{}^aH^d$ = 6.0 Hz). ^{13}C NMR ($CDCl_3$): 44.88 (CH_2), 118.85 (C=), 130.74 (C=), 148.39 (C=O). MS (*m/z*, EI) 249.1 (6). The IR spectrum of the crude reaction mixture showed complete absence of the band at 2260 cm^{-1} characteristic of N=C=O in the starting material and is identical with the pure trimer obtained upon distillation. Hence the catalytic trimerization was quantitative.

A general procedure for trimerization of PhNCO in the presence of varying concentrations of 1. To a stirred solution of **1** in THF (1 mL) was added by syringe PhNCO. Upon completion of the trimerization (i.e., when cooling of the exothermic reaction occurred), dry pentane (5 mL) was added to precipitate $(PhNCO)_3$ remaining in solution. The solid was filtered and dried *in vacuo* at room temperature to give $(PhNCO)_3$•THF as confirmed by ^1H NMR spectroscopy. ($CDCl_3$): 1.82 (t, 4 H, $^3J_{HH}$ = 6.9 Hz, THF), 3.72 (t, 4 H, $^3J_{HH}$ = 6.9 Hz, THF), 7.36-7.60 (m, 15 H, 3 C_6H_5). The relevant data are summarized in Table 2.

A general procedure for recycling catalyst 1 in the trimerization of PhNCO. To a stirred solution of **1** (0.033 g, 0.15 mmol) in THF (5 mL) under argon was added by syringe PhNCO (5.48 g, 99%, 46.4 mmol) at room temperature. A colorless

crystalline solid began to separate within 30 seconds along with evolution of heat which ceased after about 5 minutes. The solid was then filtered washed with pentane (3 x 3 mL) within the filter and dried *in vacuo* at room temperature. The solid was identified as $(PhNCO)_3$•THF by ^1H NMR spectroscopy (see above paragraph). The combined filtrate and washings were concentrated to about 5 mL and re-used as the catalyst solution for the second cycle. This procedure was repeated five times.

Detection of the intermediates 6a and 6b. To a solution of **1** (0.037 g, 0.17 mmol) in C_6D_6 (0.8mL) in an NMR tube was added PhNCO (0.062 g, 0.52 mmol). The mixture was briefly shaken. Fifteen minutes after the addition of PhNCO to the solution of **1**, the ^{31}P NMR spectrum was recorded showing peaks at 29.46 (**6a**) and 120.31 ($\mathbf{1}^{1b}$) ppm, respectively, in the ratio of 1:1.5. The intensity of the peak at 120.3 ppm increased while that at 29.46 ppm decreased with time as indicated by ^{31}P NMR spectra taken every 15 minutes. After about 7 hours, the peak at 24.46 ppm disappeared completely and only the one at 120.31 ppm remained.

In a separate experiment, a reaction mixture was monitored by ^1H NMR spectroscopy.15 minutes after the addition of three equivalents of PhNCO to a solution of **1** in C_6D_6 in an NMR tube. The ^1H NMR spectrum showed two sets of signals, namely, those of **1** and those assigned to the NCH_2 and NCH_3 protons of **6a**. The phenyl proton region consisted of overlapping proton signals.

In another experiment, a reaction mixture was monitored by ^{13}C NMR spectroscopy about 10 minutes after addition of three equivalents of PhNCO to a solution of **1** in C_6D_6 in an NMR tube. The first spectrum showed a new peak (doublet) at 161.1 ppm ($^1J_{PC}$ = 201.6 Hz) not assignable to carbons in PhNCO, triphenyl isocyanurate or **1** recorded in the same solvent. This peak disappeared after about 7 hours when the reaction was complete and was assigned the chemical shift of the C=O carbon of **6a**.

In another experiment, one equivalent of PhNCO (0.08 g, 0.7 mmol) was added by syringe to a dilute solution of **1** (0.1 g, 0.5 mmol) in dry diethyl ether (5 mL) under argon to give an immediate colorless precipitate. The precipitate was filtered *in vacuo* about 1 min after the addition of PhNCO, washed with dry ether (2 mL) within the filter and dried *in vacuo*. The mass spectrum (FAB, CH_3CN as solvent, 3-nitrobenzyl alcohol as matrix) of the solids showed a peak at 217.1 (M+H; for **1**, 100) and a peak at 336.1 (M+H, for **6a**, 50) and no peak higher than mass 336.1. The ^{31}P NMR spectrum (C_6D_6) of this solid showed a peak at 29.46 ppm (**6a**) which disappeared slowly as the peak at 120.31 ppm (**1**) increased.

For the detection of **6b**, 0.094 g (0.79 mmol) of *p*-$MeOC_6H_4NCO$ was added by syringe to a solution of **1** (0.0.57 g, 0.26 mmol) in C_6D_6 (0.7 mL). The ^{31}P NMR spectrum recorded about 15 min after the addition of *p*-$MeOC_6H_5NCO$ showed peaks at 29.21 ppm (**6b**) and 120.31 ppm in the ratio of 3:10. The peak at 29.21 ppm disappeared overnight while the peak at 120.31 ppm remained.

Reaction of PhNCO with 1 in CD_3CN. To **1** (0.020 g, 0.093 mmol) in an NMR tube under N_2 were added CD_3CN (0.6 mL) and PhNCO (0.033 g, 0.28 mmol). The ^{31}P NMR spectrum recorded 15 min. later indicated peaks at 30.01 (**6a**) and 119.95 ppm (**1**) in the ratio of 100:5. The peak at 30.01 ppm decreased as peaks at -9.98 (t, $^1J_{PD}$ = 750 Hz, **7**) and at 119.95 ppm (**1**) increased. After 8.7 hours, the peak at 30.01 ppm disappeared completely and the peaks at -9.98 and 119.95 ppm remained for weeks in the ratio of 1:4.3. After the peak at 30.01 ppm had disappeared, colorless crystals had formed and so the solution was transferred by syringe to another NMR tube for the additional monitoring. These crystals (10 mg) were dried *in vacuo* and identified by ^1H NMR, ^{13}C NMR and HRMS as triphenyl isocyanurate.

The zwitterionic adduct $PhN(CS)P(MeNCH_2CH_2)_3N$, 8. To a solution of **1** (0.14 g, 0.60 mmol) in dry diethylether (3 mL) under N_2 was added by syringe PhNCS (0.081 g, 0.60 mmol). The mixture was stirred for 5 min. and the greenish yellowish solid

which had formed was collected by vacuum filtration, washed with dry ether (5 mL) and dried *in vacuo* to give **8** (0.22 g, 100%). ^{31}P NMR (CD_3CN): 29.60 ppm. ^{1}H NMR (CD_3CN): 2.83 (m, 2 H, CH_2), 2.94 (m, 2 H, CH_2), 3.00 (d, 9 H, NCH_3, $^{3}J_{PH}$ = 9.0 Hz), 6.89-7.27 (m, 5 H, Ph). ^{13}C NMR (CD_3CN): 37.30 (d, $^{2}J_{PC}$ = 3.2 Hz, NCH_3), 50.14 (s, $N_{eq}CH_2$) 52.48 (s, $N_{ax}CH_2$), 122.36 (d, C(2) of Ph, $^{4}J_{PC}$ = 1.4 Hz), 122.80 (s, C(3) or C(4) of Ph), 120.95 (s, C(4) or C(3) of Ph), 154.59 (d, $^{3}J_{PC}$ = 37.1 Hz, C(1) of Ph), 178.40 (d, $^{1}J_{PC}$ = 187.8 Hz, NCS). MS (*m/z*, FAB, CH_3CN as solvent, 3-nitrobenzyl alcohol as matrix); 352.2 (M+H, base peak).

[PhN=C(SMe)P(MeNCH$_2$CH$_2$)$_3$N]I, 9(I). To **8** (0.073 g, 0.20 mmol) in CH_3CN (1 mL) was added by syringe MeI (0.5 g, 3.5 mmol). The exothermic reaction mixture was stirred for 30 min. to give a slightly yellowish solution. Volatiles were removed *in vacuo* to give a light yellowish solid (0.14 g, 100%). ^{31}P (CD_3CN): 14.45. ^{1}H NMR (CD_3CN), 2.18 (d, 3 H, SCH_3, $^{4}J_{PH}$ = 0.6 Hz), 2.90 (t, $N_{ax}CH_2$, $^{3}J_{PH}$ = 5.1 Hz), 2.94 (d, 9 H, NCH_3, $^{3}J_{PH}$ = 11.4 Hz), 3.08 (td, 6 H, $N_{eq}CH_2$, $^{3}J_{PH}$ = 15.3 Hz, $^{3}J_{HH}$ = 7.3 Hz), 6.89-7.40 (m, 5 H, Ph). ^{13}C NMR (CD_3N): 16.90 (d, SC, $^{3}J_{PC}$ = 2.3 Hz), 38.23 (d, NCH_3, $^{2}J_{PC}$ = 3.3 Hz), 49.69 ($N_{ax}CH_2$), 50.67 (d, $N_{eq}CH_2$, $^{2}J_{PC}$ = 6.0 Hz), 119.0 (d, $^{4}J_{PC}$ = 1.4 Hz, C(2) of Ph), 125.69 (C(3) or C(4) of Ph), 130.19 (C(4) or C(3) of Ph), 149.96 (d, $^{3}J_{PC}$ = 22.5 Hz, C(1) of Ph), 167.30 (d, $^{1}J_{PC}$ = 186.9 Hz, NCS); MS (*m/z*, base peak): 366.3 (M^+). For elemental and crystal structural analysis, the crude product was dissolved in CH_3CN (0.8mL). The small flask that contained the above solution was placed in a Dewar flask which was placed in a freezer at about -20°C. After several days, large colorless crystals were formed. The supernatant was removed by syringe and the cystals were dried in vacuo. Melt point 148-149°C; Elemental analysis: calcd (found) for $C_{17}H_{29}N_5PSI$: C, 41.35 (40.82); H, 5.93 (5.88); N, 14.19 (13.78).

General procedure for the synthesis of carbodiimides from isocyanates using catalysts 4 or 5. A single-neck round bottom flask containing an isocyanate and a

catalyst (0.56 mole % for entries 1, 2, 5-6 and 0.37 mole % for entries 3, 7 and 8 in Table 3) was equipped with a condenser. The top of the condenser was closed with a septum through which cannulas were inserted for an argon inlet and a gas outlet. The gas outlet was passed through a saturated $Ca(OH)_2$ solution. The mixture in the flask was heated in an oil bath until no more $CaCO_3$ was precipitated from a fresh saturated $Ca(OH)_2$ solution. At this point an IR spectrum of the reaction mixture was recorded which revealed the complete absence of the characteristic N=C=O band of the starting material. The crude product was then distilled at reduced pressure. The reaction temperatures, times for completing the reactions and the yields of isolated carbodiimides are summarized in Table 3.

Diphenyl carbodiimide **16a** (R = Ph)[20b]: Bp: 104-5 °C/0.2 Torr. IR (neat): 2135 cm^{-1} (N=C=N). HRMS (*m/z*): calcd. for $C_{13}H_{10}N_2$: 194.08440. Found 194.08476.

Di(3-chloro)phenyl carbodiimide **16b** (R = 3-ClC_6H_4):[20b] IR (neat): 2143 cm^{-1} (N=C=N). HRMS (*m/z*): calcd. for $C_{13}H_8Cl_2N_2$: 262.00645. Found 262.00662.

Di(2-methyl)phenyl carbodiimide **16c** (R = 2-MeC_6H_4):[20a] Bp: 132-134 °C/0.72 Torr. IR (neat): 2138 cm^{-1} (N=C=N). MS (*m/z*): calcd. for $C_{15}H_{14}N_2$: 222.11570. Found 222.11544.

Dicyclohexyl carbodiimide **16d**: Bp: 120-122 °C/0.48 Torr. IR (neat), 2117 cm^{-1} (N=C=N). HRMS (*m/z*): calcd. for $C_{13}N_2H_{22}$: 206.17830. Found 206.17807. IR spectrum was identical with that of an authentic sample (Aldrich).

Dioctadecyl carbodiimide **16e**:[22] IR (neat): 2137 cm^{-1} (N=C=N). HRMS (*m/z*): calcd. for $C_{37}H_{23}N_2$: 545.57737. Found 545.57670.

Dimer of diphenyl carbodiimide, (PhNC=NPh)$_2$. Diphenyl carbodiimide subjected to thermal treatment had been suggested[20b] to trimerize and polymerize. In our experiments the residue obtained after distillation of the diphenyl carbodiimide **16a** was shown to be the title dimer which formed in 19% yield. Mp: 163-164 °C. ^1H NMR ($CDCl_3$): 6.86 (m, 10 H, 2 C_6H_5), 7.01 (m, 10 H, 2 C_6H_5). HRMS (*m/z*): calcd. for $C_{26}H_{20}N_4$:

388.16880. Found 388.16918. MS (CI, NH_3, *m/z*): 389.1 $(M+H)^+$. Solution molecular weight (osmometry, $CHCl_3$): 414.

Detection of catalysts. (A) A mixture of PhNCO (0.78 g, 6.6 mmol) and $O=P(MeNCH_2CH_2)_3N$ (**4**, 0.26 g, 1.1 mmol) was heated at 200-210 °C until evolution of CO_2 ceased (*ca.* 0.5 hr). The ^{31}P NMR ($CDCl_3$) spectrum of the reaction mixture showed a peak at 19.8 ppm corresponding to the catalyst **4**.

(B) A mixture of PhNCO (0.49 g, 4.1 mmol) and $S=P(MeNCH_2CH_2)_3N$ (**5**, 0.17 g, 0.68 mmol) was heated at 200-210 °C until evolution of CO_2 (and presumably OCS) ceased (*ca.* 40 min). The ^{31}P NMR spectrum ($CDCl_3$) of the reaction mixture showed a peak at 19.8 ppm corresponding to catalyst **4**.

PhNCS in the presence of catalyst 4. A mixture of PhNCS (27.0 g, 0.20 mol) and **4** (0.26 g, 0.011 mmol) was heated at 160 °C to 200 °C for 11.5 h following the aforementioned general procedure. The mixture was cooled to room temperature and then subjected to distillation at 25-40 °C/0.14 torr to give 26.5 g of starting material PhNCS.

Molecular structures of 4 and 9(I). A colorless crystal of **4**, obtained from a benzene/pentane solution cooled in a freezer, was mounted in a glass capillary tube on the CAD4 diffractometer for a data collection at -50 ± 1 °C graphite monochromated MoK_α radiation (0.71073 Å). Lorentz and polarization corrections were applied. A correction based on a nonlinear decay in the standard reflections was applied to the data. An absorption correction based on a series of y-scans was applied. The agreement factor for the averaging of observed reflections was 2.3% (based on F). Axial photographs indicated that the lattice was monoclinic. The space group $P2_1/c$ was chosen based on the systematic absences. The crystal structure was solved by direct methods using the SHELXTL-Plus package (Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990). Refinement calculations were performed on a Digital Equipment Corp. Vax Station 3100 computer using the same program package. All non-hydrogen atoms were placed directly from the E-map and were refined anisotropically. All

methylene hydrogens were generated with ideal positions with C-H distances equal to 0.96 Å and were refined with isotropic thermal parameters as riding atoms. The methyl hydrogens were refined as rigid bodies initially and in the final cycles of least-squares were converted to riding atoms with isotropic thermal parameters. Crystal and structure refinement data are as follows: $C_9H_{21}N_4OP$, 0.40 x 0.40 x 0.35 mm, monoclinic, $P2_1/c$, a = 7.187(2), b = 14.190(4) Å, c = 12.161(3) Å, β = 105.31(2)°, V = 1197.1(5) $Å^3$, Z = 4, F(000) = 504, d(calcd) = 1.289 g/cm^3, omega scans, $2\theta-\theta$, 1656 observed data ($F \geq 6.0$ s (F)), 145 parameters, R = 0.0351, R_w = 0.0598.

A colorless crystal of **9**(I), grown from a saturated CH_3CN solution cooled slowly by placing it in a Dewar flask and then storing the Dewar flask in the freezer for several days, was attached to the tip of a glass fiber and mounted on the CAD4 diffractometer for a data collection at 20 ± 1 °C. The cell constants for data collection were determined from a list of reflections found by an automated search routine. Lorentz and polarization corrections were applied. A correction based on a decay in the standard reflections was required for this data set. An absorption correction based on a series of ψ-scans was applied. The agreement factor for the averaging of observed reflections was 2.6% (based on F). The acentric space group $Pca2_1$ was indicated initially by systematic absences and intensity statistics using the SHELX-86 package (G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Göttingen, F. R. G.). Using the same program package, positions of all the atoms were determined by a Patterson interpretation program. All nonhydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed at idealized positions as riding atoms with isotropic temperature factors set equal to 1.2 times the isotropic equivalent of that atom. The $Pca2_1$ space group requires two independent molecules per asymmetric unit. The cations are nearly centrosymmetric, however the iodine anions are clearly noncentrosymmetric. Attempts to refine this structure in Pbcm failed. The initial refinement in SDP (Enraf-Nonius Structure Determination Package; Enraf-Nonius: Delft, Holland) was converted to SHELXL-

93 (G. M. Sheldrick, *J. Appl. Cryst.* **1993**, in preparation) to test for racemic twinning. A twinned crystal was confirmed and refined as such. Difference Fourier maps of the residual peaks revealed the presence of one molecule of H_2O which was added to the refinement. Refinement calculations were performed on a Digital Equipment Corp. MicroVAX II computer using the CAD4-SDP program. 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. Thermal ellipsoid illustrations were drawn using SHELXTYL-Plus (Siemens Industrial Automation, Inc., Madison, WI). Crystal and structure refinement data are as follows: $C_{17}H_{29}IN_5P \cdot H_2O$, 0.45 x 0.35 x 0.35 mm, $Pca2_1$, a = 16.786(3) Å, b = 10.756(2) Å, c = 24.328(4) Å, $\alpha = \beta = \gamma = 90.0°$, V = 4392.4(13) $Å^3$, Z = 8, F(000) = 2032 d(calcd) = 1.51 g/cm^3, omega scans, w-2q, 6401 observed data ($I \geq 2$ s (I), 463 parameters, R = 0.042, R_w = 0.113.

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SUPPLEMENTARY MATERIALS

Data Collection for $O=P(MeCH_2CH_2)_3N$, 4. A clear crystal of the title compound was mounted in a glass capillary tube on the CAD4 diffractometer for a data collection at -50±1°C. Pertinent data collection and reduction information is given in Table 4. Lorentz and polarization corrections were applied. A correction based on a nonlinaer decay in the standard reflections was applied to the data. An absorbtion correction based on a series of y-scans was applied. The agreement factor for the averaging of observed reflactions was 2.3%(based on F).

Structure Solution and Refinement For $O=P(MeCH_2Ch_2)_3N$, 4. Axial photographs indicated that the lattice was monoclinic. The space group $P2_1/c$ was chosen based on the systematic absences. The crystal structure was solved by the direct methods.[1] All non- hydrogen atoms were placed directly from the E-map and were refined anisotropically. All methylene hydrogens were generated with ideal posions with C-H distances equal to 0.96Å and were refined with isotropical thermal parameters as riding atoms. The methyl hydrogens were refined as rigid bodies initially and in the final cycles of least-squares were converted to riding atoms with isotropic thermal parameters.

The P-N(1) interatomic distance is 3.137Å. The structure is found to be stabilized by an intermolecular hydrogen bond from O to H2B(C7) equal to 2.343Å. The average N-P-N bond angles is 107.6 degree.

X-ray data collection and structure solution were carried out at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital equipment Corp. VaxStation 3100 computer using the SHELXTL-Plus programs.

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Table 4. X-Ray Crystallographic Data for $O=P(MeCH_2CH_2)_3N$, **4**

	Crystal Data
Formula	$C_9H_{21}N_4OP$
Formula weight, g/mol^{-1}	232.3
Space group	$P2_1/c$
a, Å	7.187(2)
b, Å	14.190(4)
c, Å	12.161(3)
b, deg	105.31(2)
V, Å^3	1197.1(5)
Z	4
$d_{calc.}$, g/cm^3	1.289
Crystal size, mm	0.40 x 0.40 x 0.35
m(MoK_α), cm^{-1}	47.0
Data collection instrument	Enraf-Nonius CAD4
Radiation	$MoK_\alpha(\lambda = 0.71073Å)$
Orientation reflection, number, range(2θ)	25, 4.0-50.0
Temperature, deg	-50
Scan Method	2θ–θ
Data collection range(2θ), deg	4.0-50.0
Number of data collected	4401
Number of unique data	2110
with $F_o^2>3\sigma(F_o^2)$	1656

Table 4, Continued.

	Crystal data
Number of parameters refined	145
Min./max. transmission	0.8512/0.8942
R^a	0.0351
$R_w{}^b$	5.98
Quality-of-fit indicator	1.05
Largest shift/esd, final cycle	
Largest peak, e/Å^3	0.30

[a] $R = \Sigma /\!/ F_o / - / F_c /\!/ / \Sigma / F_o /$

[b] $R_w = [\Sigma_w (/ F_o / - / F_c /)^2 / \Sigma_w / F_o /^2]$; $w = 1/\sigma^2 (/ F_o /)$

[c] Quality-of-fit = $[\Sigma_w (/ F_o /)^2 / (N_{obs} - N_{parameters})]^{1/2}$

Table 5. Positional Parameters and Equivalent Isotropic Displacement Coefficients(Å) for **4**

Atom	x	y	z	U_{eq}[a]
P	0.64379(1)	0.6671(1)	0.1760(1)	0.031(1)
O	0.6676(3)	0.7218(1)	0.0777(1)	0.052(1)
N(1)	0.5932(3)	0.5476(1)	0.3832(1)	0.039(1)
C(1)	0.4147(3)	0.5981(2)	0.3751(2)	0.046(1)
C(2)	0.4109(3)	0.6931(2)	0.3195(2)	0.041(1)
N(2)	0.4369(2)	0.6909(1)	0.2038(2)	0.035(1)
C(3)	0.2623(3)	0.6993(2)	0.1102(2)	0.051(1)
C(4)	0.5929(4)	0.4645(2)	0.3173(2)	0.048(1)
C(5)	0.5312(4)	0.4835(2)	0.1901(2)	0.048(1)
N(3)	0.6501(3)	0.5528(1)	0.1516(2)	0.039(1)
C(6)	0.8040(4)	0.5160(2)	0.1064(3)	0.061(1)
C(7)	0.7708(3)	0.5875(2)	0.4503(2)	0.035(1)
C(8)	0.9010(3)	0.6195(1)	0.3789(2)	0.032(1)
N(4)	0.8168(2)	0.6901(1)	0.2919(2)	0.030(1)
C(9)	0.8600(3)	0.7882(2)	0.3256(2)	0.046(1)

[a]equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 6. Bond Distances(Å) $O{=}P(MeCH_2CH_2)_3N$, **4**

Atom 1	Atom 2	Distances[a]
P	O	1.473(2)
P	N(3)	1.652(2)
N(1)	C(1)	1.450(3)
N(1)	C(7)	1.437(3)
C(2)	N(2)	1.467(3)
C(4)	C(5)	1.517(4)
N(3)	C(6)	1.456(4)
C(8)	N(3)	1.459(3)
P	N(2)	1.645(2)
P	N(4)	1.648(2)
N(1)	C(4)	1.425(3)
C(1)	C(2)	1.504(4)
N(2)	C(3)	1.460(3)
C(5)	N(3)	1.459(3)
C(7)	C(8)	1.513(3)
N(4)	C(9)	1.461(3)

[a]Numbers in parentheses are estimated standard deviations in the last significant digits.

Table 7. Bond Angles(deg) for $O=P(MeCH_2CH_2)_3N$, **4**

Atom 1	Atom 2	Atom 3	Angles[a]
O	P	N(2)	111.4(1)
N(2)	P	N(3)	107.9(1)
N(2)	P	N(4)	107.6(1)
C(1)	N(1)	C(4)	120.0(2)
C(4)	N(1)	C(7)	120.9(2)
C(1)	C(2)	N(2)	114.8(2)
P	N(2)	C(3)	119.6(2)
N(1)	C(4)	C(5)	112.5(2)
P	N(3)	C(5)	123.9(2)
C(5)	N(3)	C(6)	116.5(2)
C(7)	C(8)	N(4)	114.8(2)
P	N(4)	C(9)	119.0(1)
O	P	N(3)	110.9(1)
O	P	N(4)	111.5(1)
N(3)	P	N(4)	107.3(1)
C(1)	N(1)	C(7)	118.8(2)
N(1)	C(1)	C(2)	112.6(2)
P	N(2)	C(2)	123.5(1)
C(2)	N(2)	C(3)	116.5(2)
C(4)	C(5)	N(3)	114.1(2)

[a]Numbers in parentheses are estimated standard deviations in the last significant digits.

Table 7, Continued.

Atom 1	Atom 2	Atom 3	Angles[a]
P	N(3)	C(6)	118.7(2)
N(1)	C(7)	C(8)	123.4(1)
P	N(4)	C(8)	123.7(1)
C(8)	N(4)	C(9)	115.9(2)

PAPER 7. NON-IONIC SUPERBASE-PROMOTED SYNTHESIS OF PYRROLS AND OXAZOLES: FACILE SYNTHESIS OF PORPHYRINS AND α-C-ACYLAMINO ACID ESTERS

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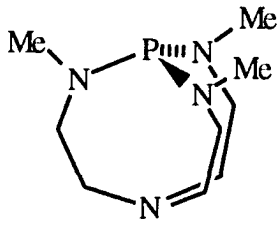
ABSTRACT

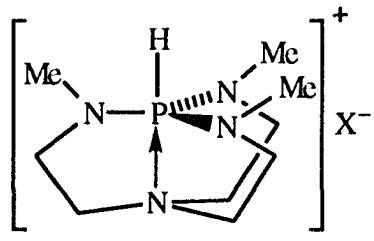
The reaction of acyl chlorides or acid anhydrides with isocyanoacetates in the presence of the superior strong non-ionic base $P(MeNCH_2CH_2)_3N$ **1** gave oxazoles in 98-99% yield. Treatment of the oxazoles with HCl-MeOH gave α-C-acylamino acid esters in 81-82% yield. The reaction of β-acetoxy-α-nitroalkanes or nitroalkenes with isocyanoacetates in the presence of **1** gave pyrrols in 100% yield. The conjugate acid of **1** can be treated with K-O-*t*-Bu to regenerate **1**. Treatment of the pyrrols with $LiAlH_4$, followed by PTSA-$CH_2(OMe)_2$ and oxidation gave porphyrins in 65-69% yield. LiCl, which functions both as a strong nucleophile in the S_N2 demethylation of the 5,5'-bis(methoxycarbonyl)-3,3',4,4'-tetramethyl dipyrromethane **22a** and as a Lewis acid in the electrophilic substitution cyclization of paraformaldehyde at dipyrromethane, facilitates the combination of four reactions into a one-pot synthesis of OEP in 67% yield from **22a**.

INTRODUCTION

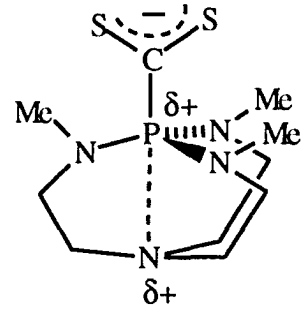
We have found that the bridgehead P-N transannulation in **2**[1,2] and partial transannulation in **3**[3] and **4-6**[4] greatly enhances the thermal stability of these adducts or reaction intermediates. This effect renders **1** a very useful synthetic reagent as, for example, an extremely strong non-ionic base[5,6] and as a superior catalyst for the conversion of isocyanates to isocyanurates in Scheme 1, in which evidence for intermediate **4** has been put forth.[4]



1



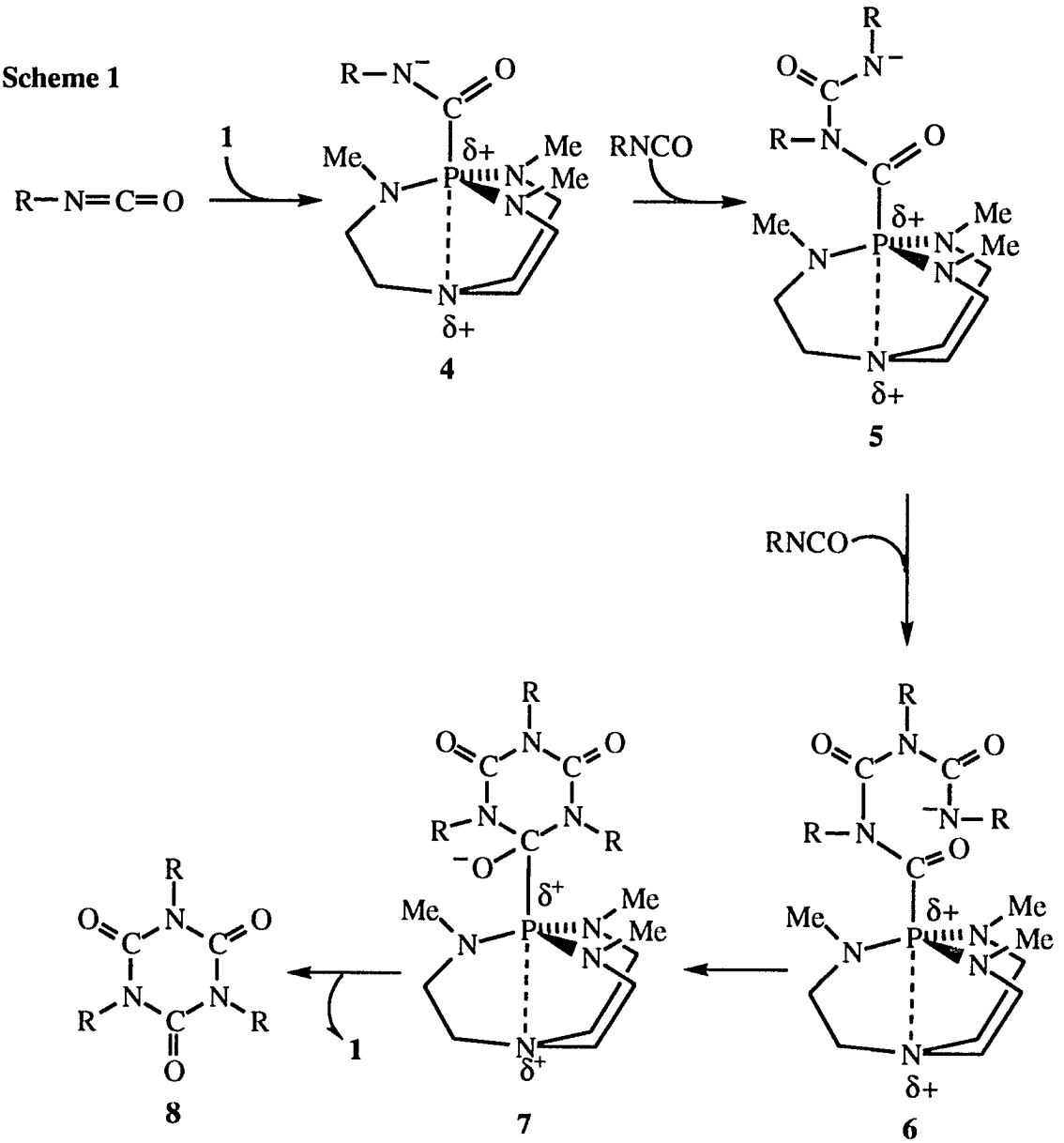
2



3

In connection with the potentially wide utility of **1** in organic synthesis, we were attracted to the powerful deprotonation capability of **1** whose basicity is about 10^{17} times stronger than DBU. While the latter base has been widely used in organic synthesis[7] because of its advantages over ionic bases, it is often inefficient or fails in reactions involving deprotonation. In the present paper, we report the application of **1** as a much stronger deprotonation agent than DBU in the improved synthesis of oxazoles and pyrrols which are utilized in the syntheses of α-C-acylamino acid esters and porphyrins, respectively. We also report the importance of LiX in the facile synthesis of porphyrins from pyrrols.

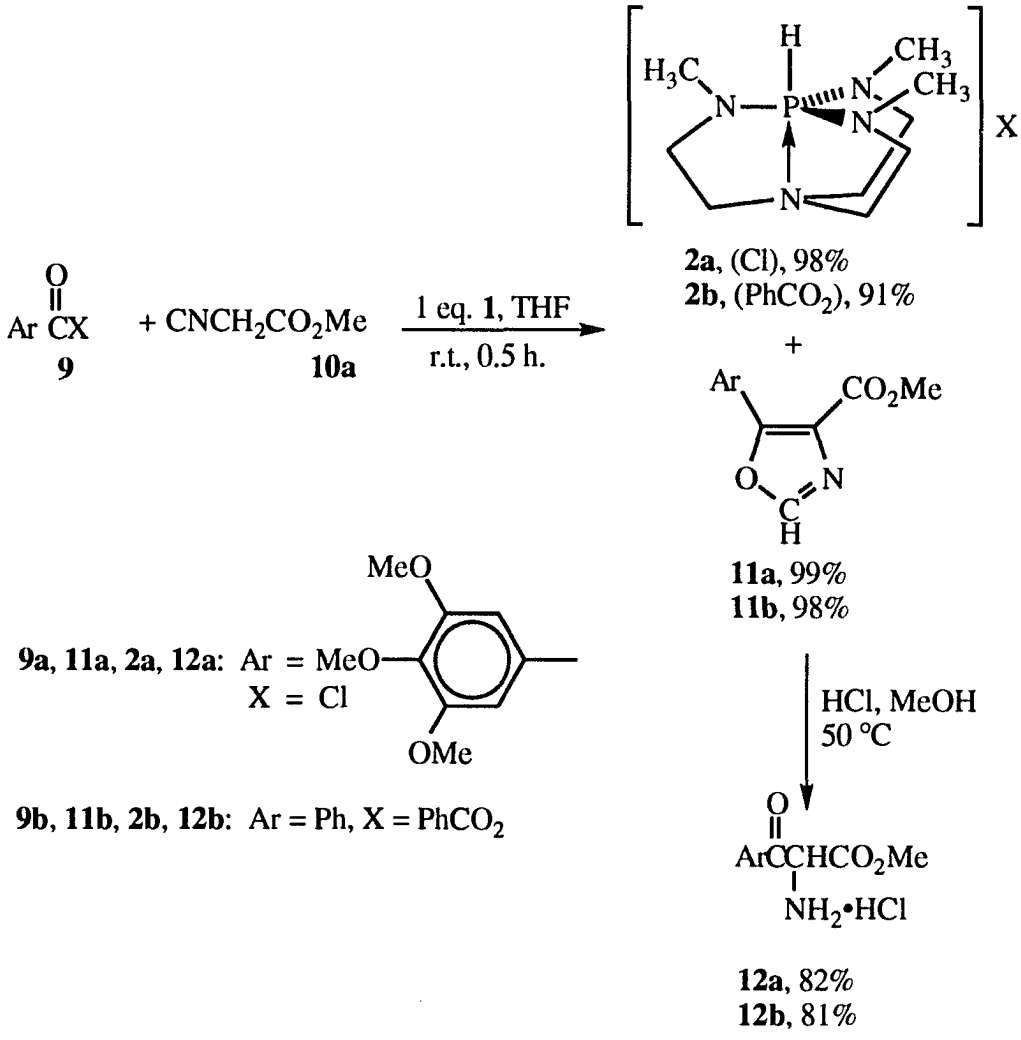
Scheme 1



RESULTS AND DISCUSSION

Synthesis of Oxazoles and α-C-Acylamino Acid Esters. Oxazoles are intermediates to pharmaceutically interesting α-C-acylamino acids which in turn are useful intermediates in the synthesis of β-hydroxyamino acids, especially β-aryl serines and amino

Scheme 2



alcohols including sympathomimetic agents such as ephedrine and epinephrine.[7] To obtain reasonable yields of oxazoles, reactions of isocyanoacetates with acyl chlorides or acid

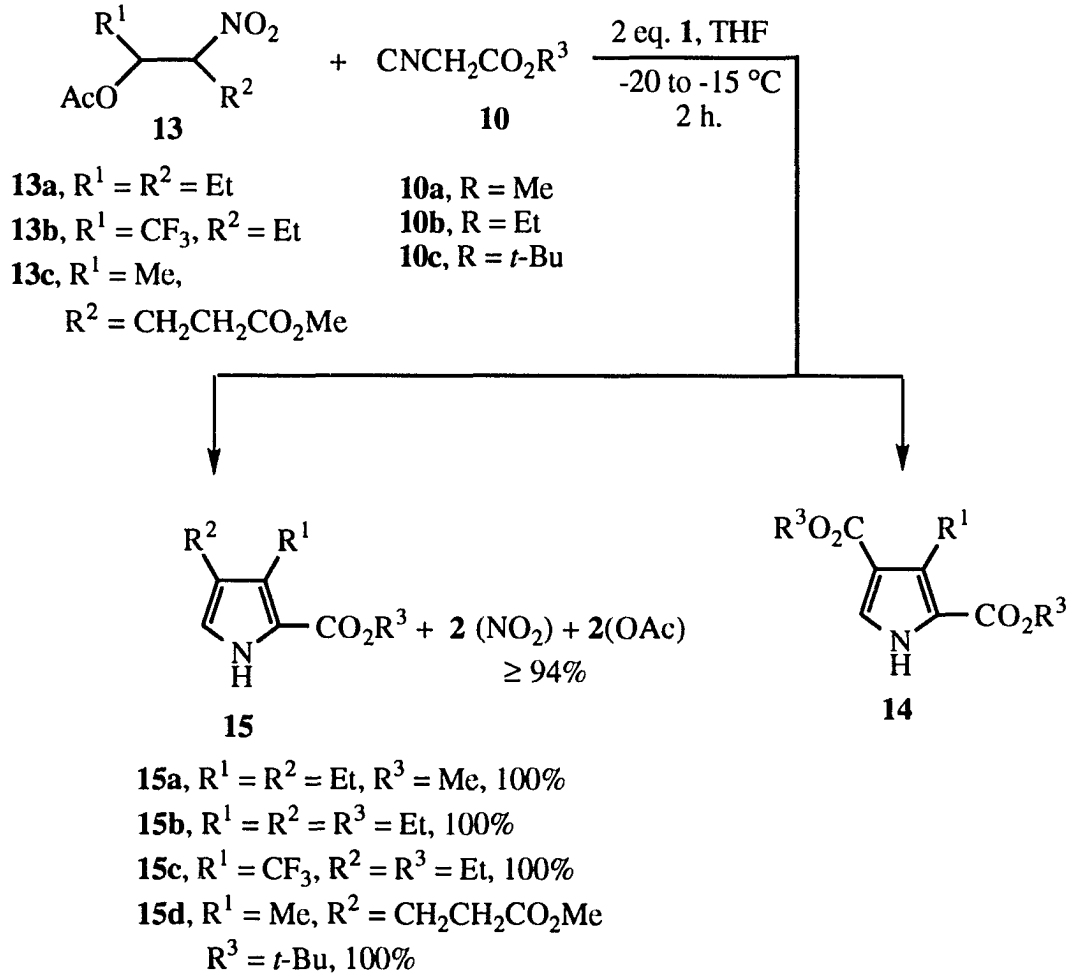
anhydrides in the presence of a large excess of triethylamine or DBU are quite lengthy (typically 48 h).[8a,b] We repeated the reaction of **9a** with **10a** in Scheme 2 in the presence of one equivalent of DBU and found that the reaction mixture obtained after stirring for two hours at room temperature gave a very complicated ^{1}H NMR spectrum, and the GC of this mixture showed that only about 8% of **11a** had formed. On the other hand, in the presence of one equivalent of **1**, the same reaction conditions gave ^{1}H NMR spectroscopically pure product **11a** and **2**(Cl) in 99 and 98% yields, respectively, within one-half hour. Similarly, the reaction of **9b** and **10a** in the presence of one equivalent of **1** (Scheme 2) also went to completion within one-half hour, giving ^{1}H NMR spectroscopically pure products **11b** and **2**($PhCO_2$) in 100% and 91% yields, respectively. Products **11a** and **11b** were sufficiently pure that losses from recrystallization or chromatography could be avoided, allowing them to be directly reacted with HCl-MeOH to give pure **12a** and **12b** in 82 and 81% yields, respectively, after recrystallization.

Another advantage of **1** over DBU is that crystalline **2**(Cl) and **2**($PhCO_2$) can be easily separated from **11a** or **11b** in high yield simply by filtration, since these salts are quite insoluble in non polar or weakly polar solvents. This also allows **1** to be regenerated by treating **2** with KO-*t*-Bu.[9]

Synthesis of α-AlkoxycarbonylPyrrol and Dipyrromethane Derivatives. Pyrrol derivatives are important intermediates in the synthesis of bioactive porphyrins. Octaethylporphyrin (OEP) for example, is widely used for biological modeling studies because of its high symmetry, relatively good solubility and its stability. Pyrrol derivatives are also important intermediates for the synthesis of bile pigments, drugs and agrochemicals.[10,11] Most methods[12] for the synthesis of OEP begin from 2-ethoxycarbonyl-3,4-diethyl-5-methylpyrrol, prepared by the Knorr reaction of ethyl propionylacetate with 2,4-pentanedione. These methods are inconvenient owing to difficulties in preparing the starting materials and in appropriately transforming the 5-methyl group in the pyrrol ring system for further reaction.

The methods developed recently by Barton et al.,[13] Ono et al.,[14] and Sessler et al.[15] for the synthesis of 3,4-disubstituted pyrrol-2-esters as key intermediates to porphyrins (starting from b-acetoxy-α-nitroalkenes (or α-nitroalkenes) and isocyanoacetates in the presence of a non-ionic base such as DBU or guanidine) is very advantagious in view of its brevity, its use of easily accessible starting materials and its flexibility for the synthesis of variously functionalized porphyrins, compared with the traditional Knorr approach. However, the preparation of OEP and other porphyrins is still problematic, particularly whenever more than

Scheme 3



one gram is required, because of the accompanying formation of undesired 2,4-di(alkoxycarbonyl)pyrrol **14**[14b] in Scheme 3, which lowers the yield of the desired α-alkoxycarbonylpyrrol **15**, requiring the latter to be isolated chromatographically on a small scale.

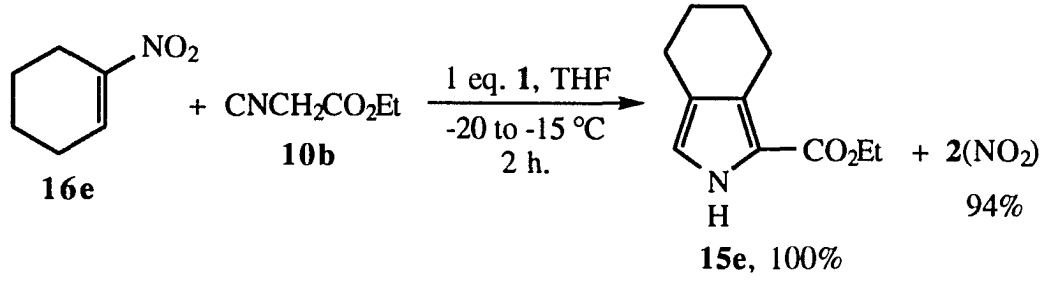
We tried to suppress the side reaction leading to **14** by reducing the reaction temperature. But at -20 to -15 °C, DBU failed to promote the formation of either **14** or **15** at an appreciable rate. For example, treatment of β-acetoxy-α-nitrohexane **13a** and ethyl isocyanoacetate **10b** in THF with two equivalents of DBU at -20 to -15.°C for 2 h produced nearly undetectable amounts of **15** and no detectable quantity of **14** by ^{1}H NMR spectroscopy. On the other hand, treatment of **13** and **10** in THF with two equivalents of **1** at -20 to -15 °C for 2 h afforded ^{1}H NMR spectroscopically pure pyrrols **15a-d** in quantitative yield with no detectable by-product **14** (Scheme 3). Moreover, the protonated base was separated from **15** as a mixture of **2**(NO_2) and **2**(OAc) in high yield and purity by filtration. The high yield and purity of the crude products **15a-d** permitted the avoidance of chromatographic purification processes and the accompanying product losses, allowing these compounds to be directly used in the synthesis of porphyrins.

Superbase **1** has good solubility both in non-polar solvents (e.g., benzene, pentane, hexane) and in polar solvents (e.g., THF, diethyl ether, acetonitrile, pyridine and DMF). The corresponding crystalline protonated superbase salts **2**(NO_2) and **2**(OAc) are virtually insoluble in non-polar and weakly polar solvents such as pentane, hexane, diethyl ether, ethylacetate and DMF but are very soluble in water. On the other hand, the pyrrol derivatives **15a-d** are very soluble in non-polar and weakly polar solvents such as hexane, diethyl ether and THF. The large difference in solubility between the salts **2**(NO_2) or **2** OAc) and **15** allows the former to be removed by filtration, while **15** remains in solution. The salts can be subsequently deprotonated with *t*-BuOK in high yield, allowing **1** to be recycled for greater economy. To our knowledge, no isolation process of protonated DBU or any other protonated non-ionic

base followed by regeneration of the non-ionic base has been established, mainly because protonated DBU, for example, is quite soluble both in non-polar and polar solvents, making its recycling difficult.

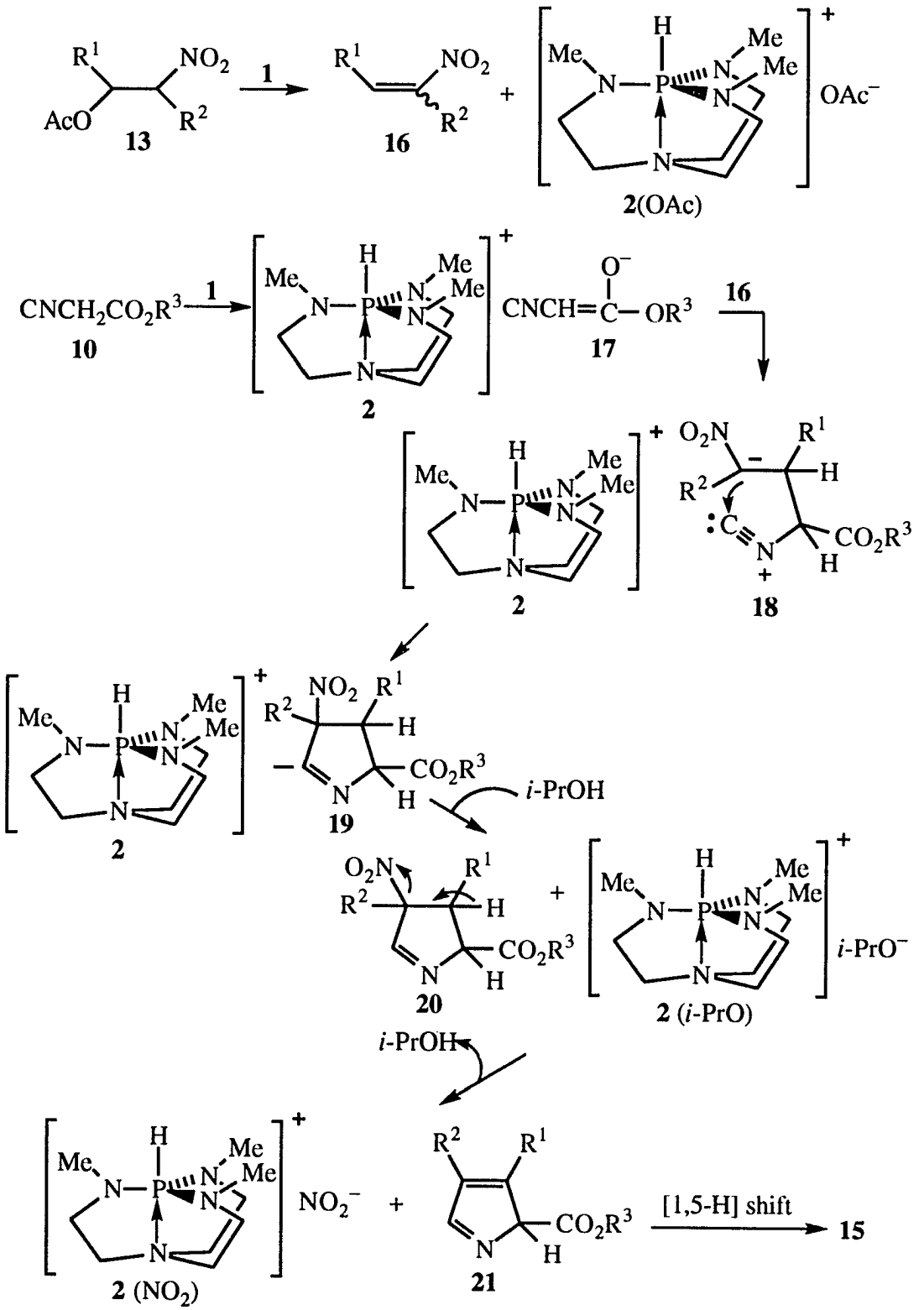
According to the reaction pathway in Scheme 4, which is similar to that proposed by Barton and coworkers,[13] it is believed that the strong basicity of **1** allows the rapid and complete elimination of HOAc from **13** to give **16**, and the rapid conversion of **10** to **17**. This is followed by Michael addition of the isocyanoacetate anion **17** to α-nitro-olefin, even at low temperature. It has been reported[16] that the carbanion obtained by deprotonation of substrates with P_4-*t*-Bu are more nucleophilic than when obtained with lithium di-isopropylamide. Anion **17** obtained by the action of **1** may also be more nucleophilic compared with similar anions obtained by deprotonation of isocyanoacetate with ionic bases or non-ionic bases such as DBU and guanidine. In our process, cation **2** is charge-delocalized from the bridgehead P atom to three equatorial N atoms and to the transannulated bridgehead N atom which is located on the opposite end of the cage. This large cation may be only weakly attracted to anion **17**, allowing **17** to be relatively unencumbered by the cation and hence more nucleophilic. Thus, the stronger basicity of **1** and the enhanced nucleophilicity of **17** allow the reaction to proceed at low temperature to afford compound **15** as the only pyrrol product.

Similarly, treatment of commercially available α-nitrocyclohexene and ethyl isocyanoacetate in THF at -20 to -15 °C with one equivalent of the superbase **1** rapidly affords 2-ethoxycarbonyl-3,4-butylenepyrrol **15e** in quantitative yield (reaction 1).



(1)

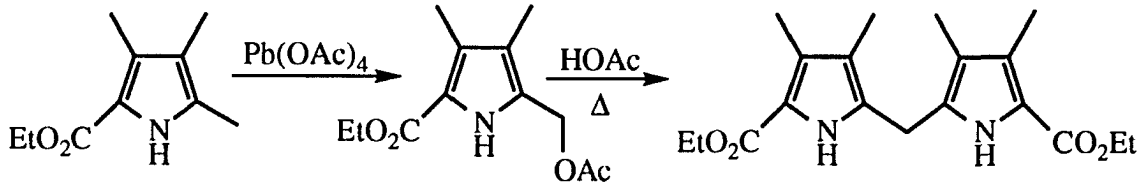
Scheme 4



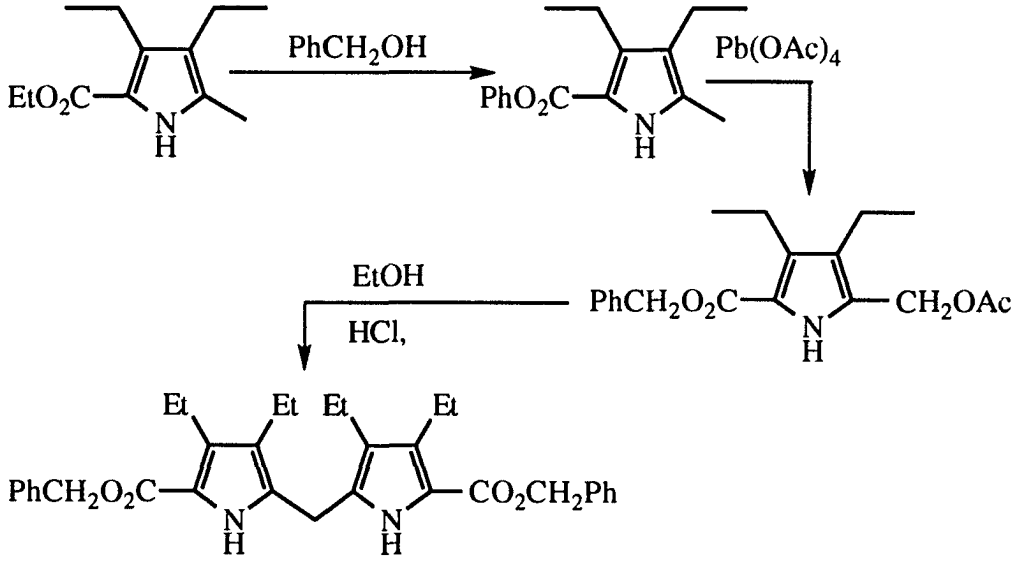
Dipyrromethane derivatives are precursors to important types of sterically blocked *meso*-diarylporphyrin compounds. Precursors such as 5,5'-bis(ethoxycarbonyl)-3,3',4,4'-tetramethyldipyrromethane[17] and 5,5'-bis(ethoxycarbonyl)-3,3'-diethyl-4,4'-dimethyl dipyrromethane[18] have been synthesized using comparatively tedious procedures. A more recent revised procedure[19] for 5,5'-bis(ethoxycarbonyl)-3,3',4,4'-tetramethyl-di-pyrromethane consists of a two-step reaction sequence from 2-ethoxy-carbonyl-3,4,5-trimethylpyrrol shown in Scheme 5. A similar synthesis was described for 5,5-bis(benzyloxycarbonyl)-3,3',4,4'-tetraethyldipyrromethane[20] (Scheme 6).

In the present work, 5,5'-bis(methoxy)carbonyl-3,3',4,4'-tetraethyldipyrromethane **22a** was synthesized in one step in 88% yield directly from **15a** as shown in Scheme 7. The

Scheme 5

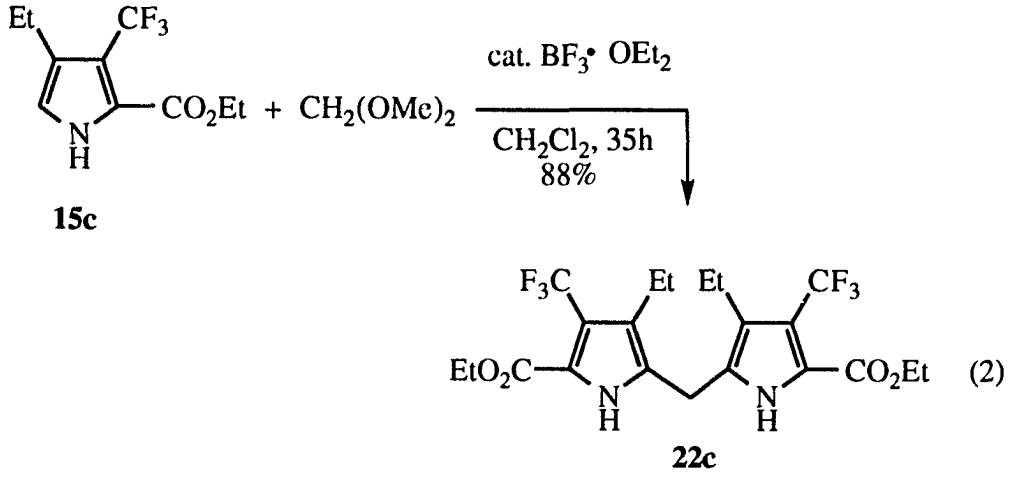


Scheme 6



reaction was complete in about 30 minutes in refluxing ethanol in the presence of a catalytic amount of hydrochloric acid. Compound **22a** changes from colorless to red upon exposure to air, but it is stable under N_2 or in the refrigerator for at least six months. Ono and coworkers reported that electron-deficient trifluoromethyl substituted pyrrols reacted with $CH_2(OMe)_2$ in the presence of the catalyst PTSA very slowly, taking 7 days for completion of the reaction. This is also true for pyrrol **15c**. Thus, PTSA-catalyzed electrophilic substitution of the pyrrol **15c** with $CH_2(OMe)_2$ took 10 days for completion as monitored by TLC. Hydrochloric acid is not a suitable catalyst because no apparent product **22c** (see reaction 2) was formed (as monitored by TLC) when **15c** and $(CH_2O)_n$ in EtOH in the presence of a catalytic amount of hydrochloric acid was refluxed for 40 min. The proton of PTSA or HCl may be hydrogen-bound to either the F or the pyrrol ring nitrogen, rendering the pyrrol ring more electron-

Scheme 7

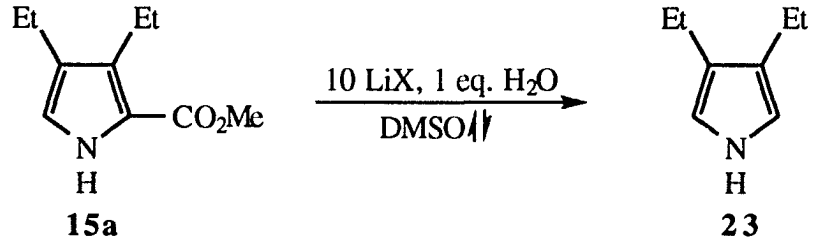


deficient, and thus decreasing electrophilic substitution. However, when BF_3•OEt_2 was used as a Lewis acid catalyst (reaction 2) the conversion of **15c** with $CH_2(OMe)_2$ to **22c** was complete within 35 hours at room temperature. Similarly, the conversion of **15a** and *para*-trifluorotolylaldehyde to the dipyrromethane derivative **22b** (Scheme 7) was complete

within 10 hours at room temperature using the same catalyst. Products **22b** and **22c** were isolated by flash chromatography in 91 and 88% yields, respectively.

Preparation of α-Unsubstituted Pyrrol Derivative 23. The cleavage of esters to furnish a carboxylic acid is a common organic transformation that is usually carried out in a routine manner by acidic or basic hydrolysis. However, pyrrol derivatives are sensitive to acidic conditions and so the *alpha*-ester group is generally removed by saponification and subsequent thermal decarboxylation. Although this method provides a means of preparing 3,4-dialkylated pyrrols, the yield is very low (38-40%) and the product is not pure, thus requiring a purification by subsequent vacuum distillation.[15]

A new method reported here for removing the *alpha*-ester group in pyrrol rings involves an S_N2 demethylation with lithium halides and subsequent thermal decarboxylation in DMSO (reaction 3). The advantages of this approach are: (1) The S_N2 dealkylation with LiX in DMSO is very fast and 100% complete in 1.5-3.0 hours at reflux temperature. The intermediate *alpha*-lithium carboxylate is quickly decarboxylated to 3,4-diethylpyrrol **23** without isolation, in contrast to the traditional saponification and subsequent decarboxylation



15a **23** (3)

which is completed in less than 50% yield in 6-10 hours.[22] The reaction rates for lithium halides in our process decrease in the order: LiCl (1-5 h) > LiBr (2.0 h) > LiI (3.0 h) with the commercially least expensive halide being the fastest in reaction 3. When **15a** in DMSO was refluxed with 10 equivalents of NaCl, no product **23** was detected by TLC after 3 hours. Apparently Li^+ is a better carboxy oxygen complexing metal than Na^+, making the carboxy group a better S_N2 leaving group when Cl^- attacks the methyl of the ester group in an S_N2

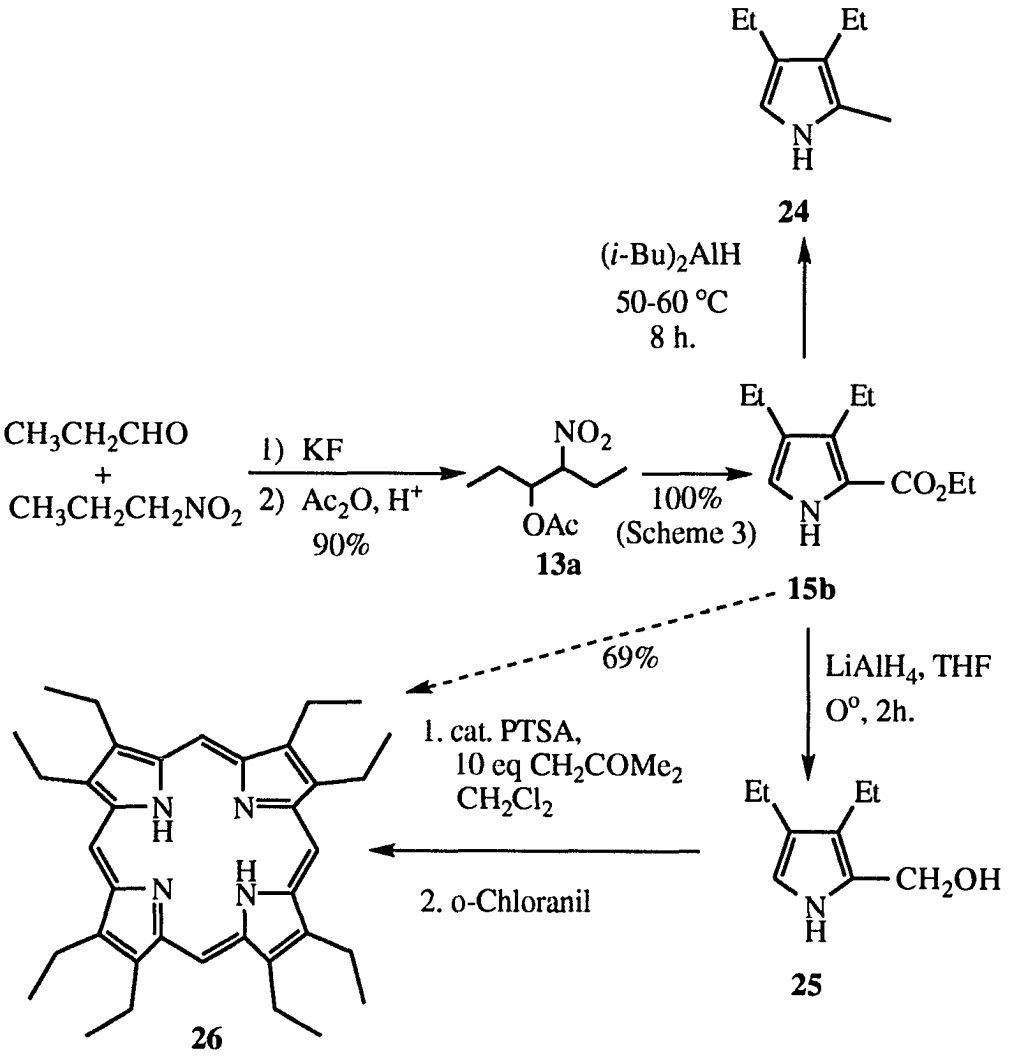
fashion. (2) The decarboxylation produces α-unsubstituted pyrrols in high yield in a one-pot reaction, thus saving labor and energy. (3) The demethylation and subsequent decarboxylation process can potentially be carried out on a large scale. (4) One of the great values of pyrrol ester cleavage by S_N2 dealkylation is that the reaction can be selective. Biomolecular nucleophilic substitutions are well known to be quite sterically sensitive and thus only the esters of unhindered alcohols undergo cleavage (methyl works best) if there are two or more different ester groups in the same pyrrol ring.

Synthesis of Porphyrins. It is well known that $(i\text{-Bu})_2AlH$ is a milder and more selective reducing agent than $LiAlH_4$, normally reducing esters to alcohols when two equivalents are used.[23] However, when a solution of **15a** and two equivalents of $(i\text{-Bu})_2AlH$ were stirred at room temperature for 1 hour and at 50-65 °C for 2.6 hours, no reduction occurred. On the other hand, at 50-60 °C for 8 hours, **15b** was reduced to 3,4-diethyl-2-methylpyrrol **24** (Scheme 8) which was isolated by distillation. Ono et al.[14]reported that under controlled reaction conditions, $LiAlH_4$ selectively reduces **15b** to α-hydroxymethyl-3,4-diethylpyrrol **25** which was converted to OEP **26** in two steps in trace to 55% yield under various conditions. These authors proposed that the catalyst PTSA first converted α-hydroxymethyl-3,4-diethylpyrrol to formaldehyde and 3,4-diethylpyrrol, which was subsequently cyclized to OEP **26**. They also found that $CH_2(OMe)_2$ as an additional source of formaldehyde increased the yield of OEP **26** from 23% to 55%.

In this report, the crude product **15b** prepared in 100% yield as mentioned earlier, was reduced to α-hydroxymethyl-3,4-diethylpyrrol **25** (Scheme 8) which was then converted to OEP **26** in various yields under different conditions (see Table 1 in Experimental Section). In summary we found that **25** was not stable and changed its color from nearly colorless to red even upon storage in a refrigerator. If the crude product was stored or dried with anhydrous $MgSO_4$ overnight, the yield of OEP was only 21%. If the crude product **25** was not stored or

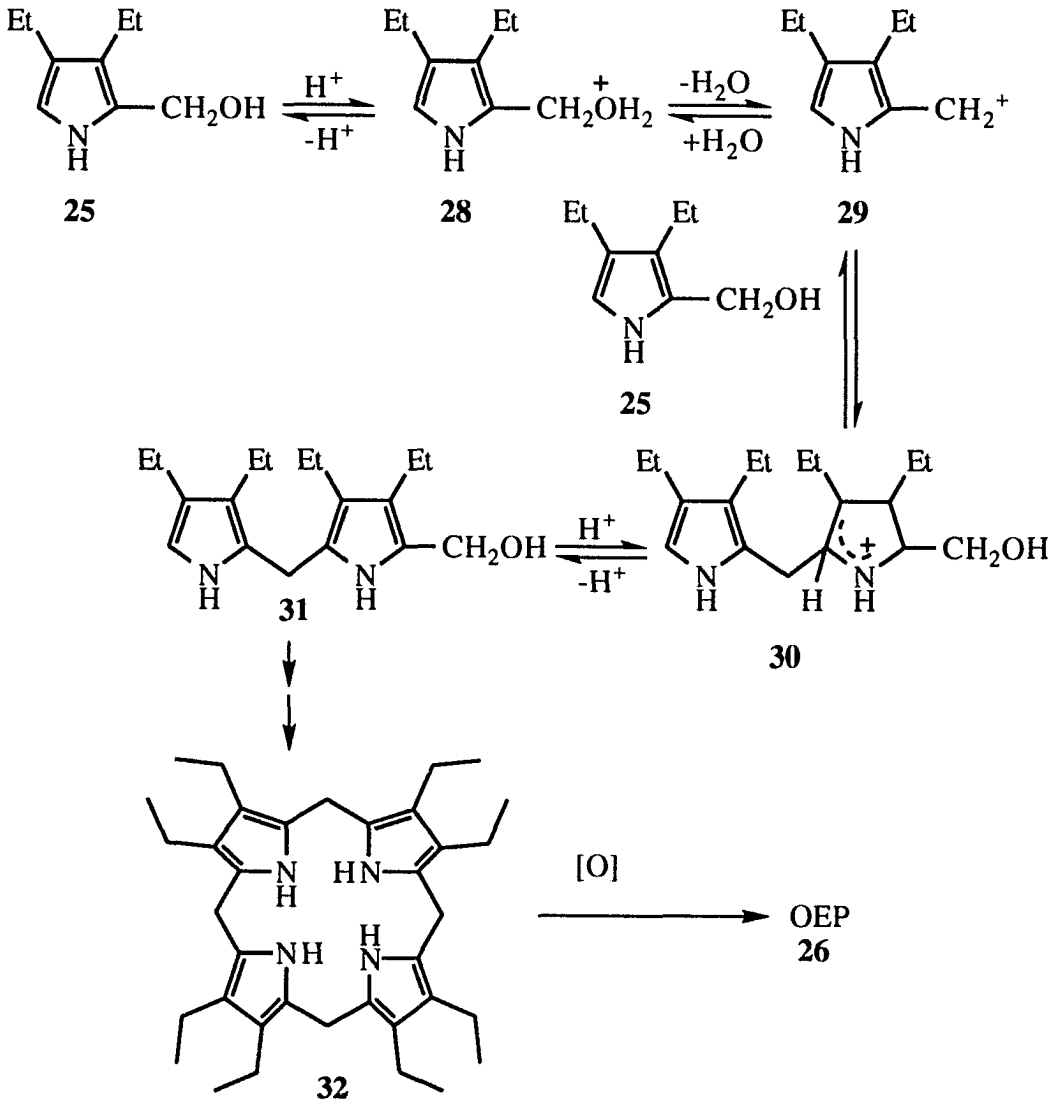
dried but immediately reacted in the presence of the catalyst PTSA in CH_2Cl_2, the OEP yield increased to 53%. If the crude product was immediately reacted in the presence of the catalyst PTSA and ten equivalents of $CH_2(OMe)_2$ as a dehydrating agent, the OEP yield was increased to 69% (Scheme 8). However, the OEP yield was decreased to 23% when ten equivalents of $(CH_2O)_n$ replaced $CH_2(OMe)_2$. From these observations, we propose the possible reaction

Scheme 8

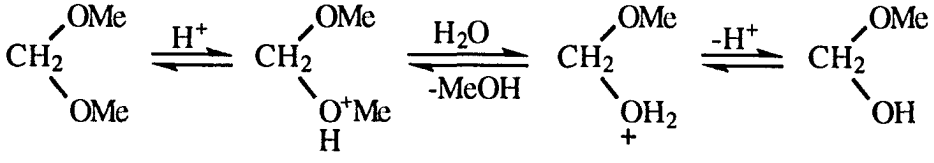


pathway shown in Scheme 9. Under acid conditions, α-hydroxymethyl-3,4-diethylpyrrol **25** reversibly eliminates a molecule of H_2O and generates 3,4-diethylpyrrol-α-methyl cation **29**, which then electrophilically reacts with another molecule of α-hydroxymethyl-3,4--diethylpyrrol **25** to afford the intermediate **30**. Species **30** eliminates H^+ to give the intermediate **31**. This process is repeated, finally affording octa-ethylporphyrinogen **32** which

Scheme 9

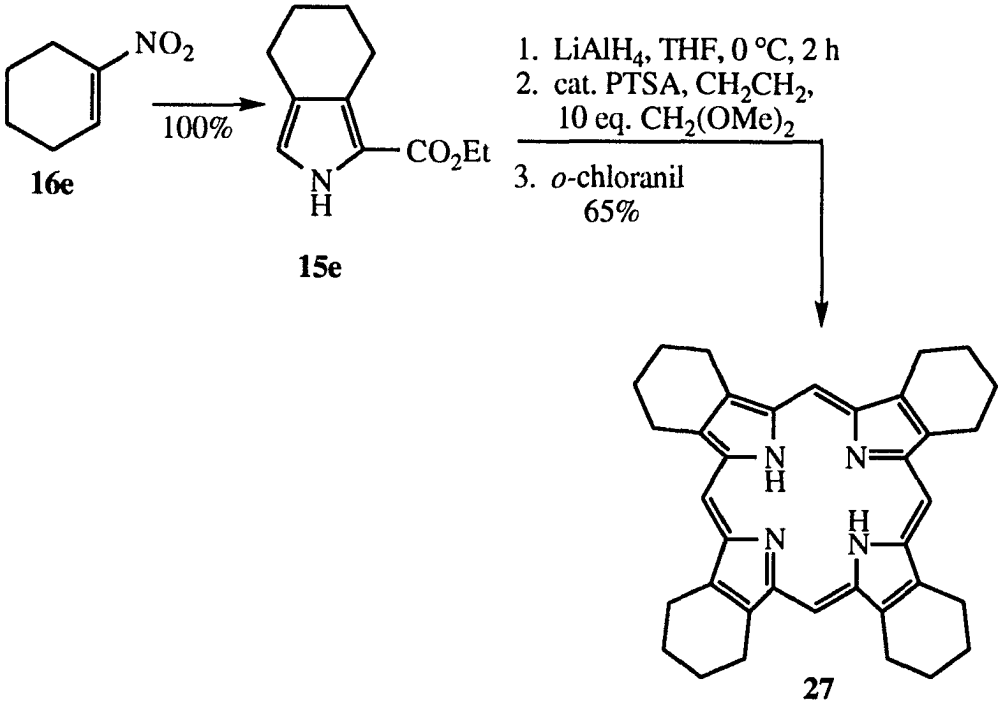


is subsequently oxidized to OEP. Since elimination and addition of H_2O is reversible, removal of H_2O would shift the equilibrium toward porphyrinogen **32**, thus increasing the yield of OEP. $CH_2(OMe)_2$ may be similar to $(CH_3)_2C(OMe)_2$, which is also a dehydrating agent,[24] converting H_2O to hemiacetal in the presence of an acid catalyst (reaction 4). Addition of $(CH_2O)_n$ decreases the OEP yield because $(CH_2O)_n$ competitively attacks the 5-position of the pyrrol ring **25** to form 2,5-dihydroxymethyl-3,4-diethylpyrrol consequently interrupting the tetramerization leading to the porphyrinogen **32**. Here the yield of OEP was increased to 69% from **15b** and the overall yield of OEP was as high as 62% based on the commercially available starting materials CH_3CH_2CHO or $CH_3CH_2CH_2NO_2$.



(4)

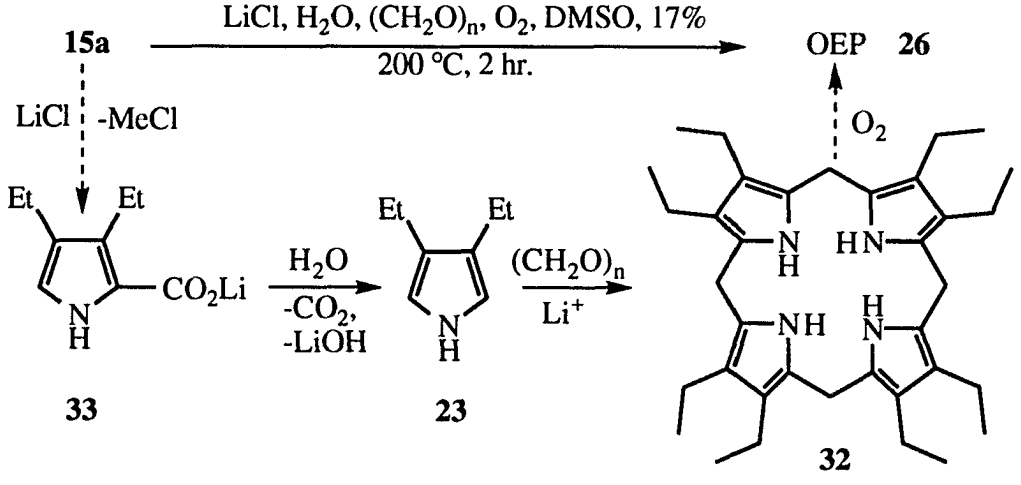
Scheme 10



In a similar manner, porphyrin **27** was synthesized in 65% overall yield based on the commercially available starting material α-nitrocyclohexene when ten equivalents of the dehydrating agent $CH_2(OMe)_2$ were used (Scheme 10).

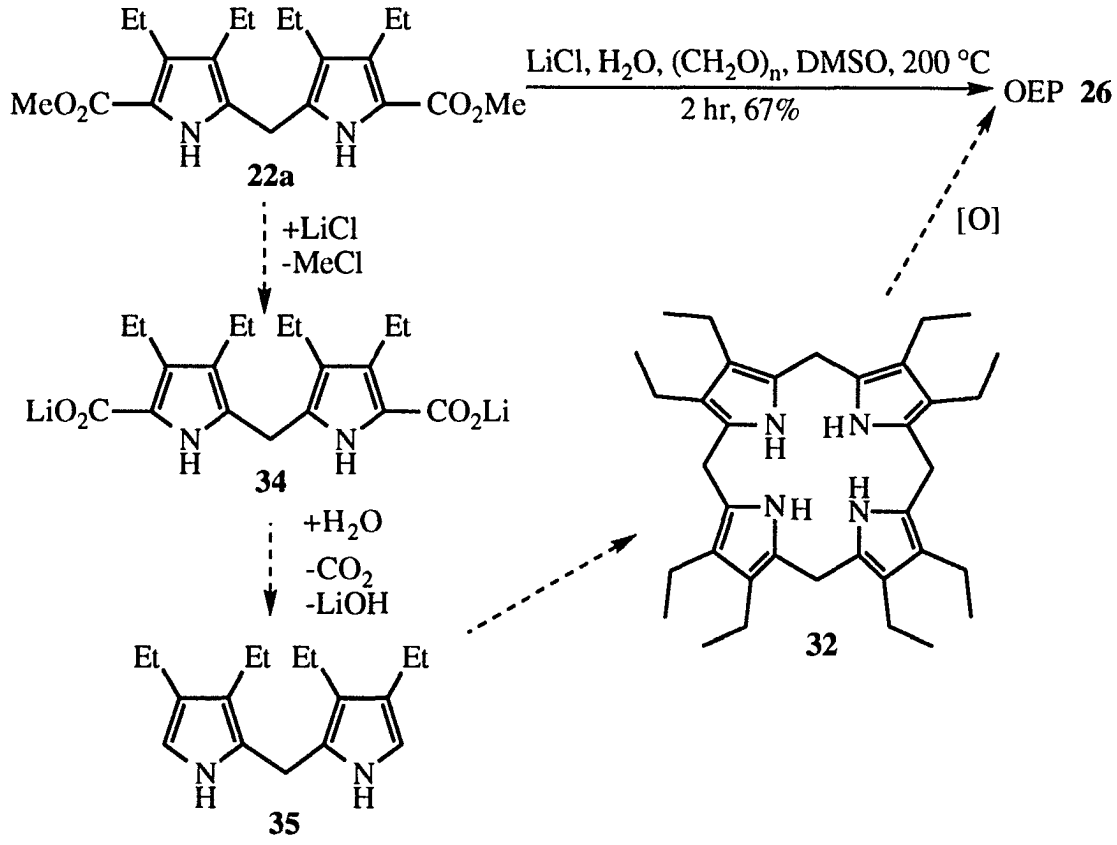
As reported earlier by others,[14] we also find that the PTSA-catalyzed condensation cyclization of pyrrol **23** with formaldehyde, followed by oxidation gives a very low yield (16%) of OEP **26**. This may be a consequence of the instability of the pyrrol **23**, or because of entropy-favored linear polymerization of the pyrrol **23** with formaldehyde. We therefore designed a one-pot reaction procedure involving four reactions (Scheme 11) in which the pyrrol **23**, generated *in situ* by fast demethylation with LiCl and subsequent thermal decarboxylation, cyclized with paraformaldehyde by the catalysis of the Lewis acidic Li^+ cation to give the porphyrinogen **32** which was quickly oxidized by O_2 to afford OEP **26** in 17% overall yield. Here we find that LiCl functions both as a strong nucleophile (Cl^- anion) in the demethylation of **15a** and as a Lewis acid (Li^+) in the cyclization of **23** with paraformaldehyde. This experiment essentially restricted the instability effect of **23** on the low yield of OEP since **23** was generated *in situ*. The linear polymerization or oligomerization of **23** with formaldehyde could account for the low yield of OEP, and thus the pre-formation of

Scheme 11



the dipyrromethane **35** (Scheme 12) at least partially circumvents the entropy-unfavored tetramerization in Scheme 11. Indeed, as shown in Scheme 12, OEP was isolated in 67% yield in a one-pot synthesis from **22a** which was prepared by the HCl-catalyzed electrophilic substitution of $(CH_2O)_n$ at **15a** and isolated in 88% yield.

Scheme 12



Bases of type **1** are potentially useful as stoichiometric deprotonating agents in a variety of synthetic applications wherein weaker bases such as DBU are inadequate. Sterically hindered **1** and its analogues may also be useful in generating kinetic enolates, in catalyzing acylation and anionic polymerization reactions, and in serving as an electronically flexible

ligand in palladium-catalyzed syntheses. Investigations of these and other applications of compound of type **1** are currently underway.

CONCLUSIONS

Compound **1** is a highly efficient non-ionic deprotonating agent for the high yield syntheses of α-C-acylamino acid esters from oxazoles and porphyrins from pyrrols or dipyrromethanes. Because of the extremely strong basicity of **1**, deprotonations are more complete and faster than with typical non-ionic bases such as Et_3N, DBU, or Proton Sponge. Other advantages of **1** demonstrated here are that deprotonations with this compound can be carried out at relatively low temperatures (thus minimizing side reactions), its protonated product **2**(X) can be easily separated from the reaction mixture by filtration, and **1** can be recovered in one step from **2**(X) for recycling. Halogenated solvents such as CH_2Cl_2, $CHCl_3$ and CCl_4 should be avoided, however, owing to their interesting reactivities with **1** to be reported later. Other useful synthetic improvements in the syntheses described here are: (1) the use of $BF_3{\bullet}OEt_2$ as a better catalyst than a protic acid for the electrophilic substitution of fluorosubstituted pyrrols with $CH_2(OMe)_2$, (2) the utilization of $CH_2(OMe)_2$ as a dehydrating agent to improve the OEP yield, and (3) our discovery of the effectiveness of LiCl as both a nucleophile for dealkylation of the dicarboxylate **34** and as a Lewis acid catalyst in the electrophilic cyclization of dipyrromethane **35** with $(CH_2O)_n$ to give porphyrinogen **32** in our one-pot synthesis of OEP in 67% overall yield.

EXPERIMENTAL SECTION

General. THF, toluene and pentane were refluxed with sodium in the presence of benzophenone and freshly distilled. Benzene and acetonitrile were refluxed with CaH_2 and freshly distilled. Compound **1** was prepared as described previously.[1,2a] NMR spectrometers employed included a Nicolet NT-300 or a Varian VXR-300 for ^1H spectra, a Bruker WM-200 for ^{31}P spectra, and a Varian VXR-300 for ^{13}C spectra. Standards for the NMR spectra were TMS (^1H, internal), 85% H_3PO_4 (^{31}P, external) and the δ 118.20 peak of the solvent CD_3CN or the δ 77.0 peak of the solvent $CDCl_3$ (^{13}C, internal). Infrared spectra were recorded with a Bruker IFS-113V spectrometer. UV spectra were recorded with an HP8452A spectrophotometer. HRMS and fast atom bombardment (FAB) mass spectra were recorded with a KRATOS MS-50 spectrometer. The solvent and the matrix employed were CH_3CN and 3-nitrobenzyl alcohol, respectively, for FAB mass spectra of **12a** and **12b**. Elemental analyses were performed by Desert Analytics.

4-Methoxycarbonyl-5-(3,4,5-trimethoxyphenyl)oxazole 11a (Ar = 3,4,5-trimethoxyphenyl)[8a,b] using the superbase 1. To a magnetically stirred solution of the superbase (0.47 g, 2.1 mmol) in dry THF (5 mL) at 5 °C was added in one portion methyl isocyanoacetate **10a** (0.23 g, 2.1 mmol, 95%). The solution was stirred for 15 min. To this stirred solution was added dropwise a solution of 3,4,5-trimethoxy benzoylchloride **9a** (0.50 g, 2.1 mmol, 98%) in THF (5 mL) at 5 °C. The reaction mixture was then stirred at room temperature for 30 min. to form a solid-liquid biphasic system lacking an isocyanoacetate odor when the flask was opened. The biphasic mixture was diluted with ethyl acetate (40 mL) and filtered in vacuo. The solid was washed with ethyl acetate (2 x 10 mL) within the filter and dried in vacuo to give ^{31}P NMR and ^1H NMR spectroscopically pure **2(Cl)** (0.52 g, 98%). ^{31}P NMR (CD_3CN): -9.40. ^1H NMR (CD_3CN): 2.60 (d, 9 H, NCH_3, $^3J_{PH}$ = 17.4 Hz), 2.98 (dt, 6 H, $N_{eq}CH_2$, $^3J_{PH}$ = 11.1 Hz, $^3J_{HH}$ = 6.0 Hz), 3.12 (dt,

6 H, $N_{ax}CH_2$, $^3J_{PH}$ = 5.7 Hz, $^3J_{HH}$ = 6.0 Hz), 5.28 (d, 1 H, PH, $^1J_{PH}$ = 493.8 Hz). The combined filtrate and washings were washed with water (5 mL). The organic phase was separated and the aqueous phase was extracted with ethyl acetate (15 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and rotary-evaporated to give ^1H NMR spectroscopically pure **18a** (0.61 g, 99%). ^1H NMR (CD_3CN): 3.78 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 3.85 (s, 6 H, OCH_3), 7.37 (s, 2 H, NH-H), 8.06 (s, 1 H, C_2H). HRMS: calcd 293.08994 for $C_{14}H_{15}NO_6$, measured 293.08940.

4-Methoxycarbonyl-5-(3,4,5-trimethoxyphenyl)oxazole 11a (Ar = 3,4,5-tri-methoxyphenyl) using DBU. To a stirred solution of methyl isocyanoacetate **10a** (0.44 g, 4.2 mmol, 95%) in dry THF (5 mL) at 5 °C was added DBU (0.63 g, 4.2 mmol). After the solution was stirred for 45 min, a solution of 3,4,5-trimethoxybenzoyl chloride (0.99 g, 4.2 mmol) in THF (10 mL) was added dropwise at 5 °C. The mixture was then further stirred at room temperature for 2 h. to give a brown solution with a heavy isocyanoacetate odor when the flask was opened. The solution was rotary evaporated, washed with water (10 mL) and extracted with ethyl acetate (2 x 35 mL). The combined organic extracts were rotary evaporated in vacuo to give a brown oil (0.68 g). The ^1H NMR spectrum showed that this brown oil contained mainly unreacted methyl isocyanoacetate and trimethoxybenzoic acid arising from the aqueous workup, with a small amount of the desired 4-methoxycarbonyl-5-(3,4,5-trimethoxyphenyl)oxazole **11a**. Gas chromatography of this mixture showed that only ~8% of **11a** had formed.

4-Methoxycarboyl-5-phenyloxazole 11b (Ar = Ph)[8a,b] using the superbase 1. To a solution of the base **1** (0.91 g, 4.2 mmol) in dry THF (5 mL) at 5 °C was added by syringe methyl isocyanoacetate **10a** (0.44 g, 4.2 mmol, 95%). After the solution was stirred at 5 °C for 15 min., a solution of benzoic anhydride (0.97 g, 4.2 mmol) in dry THF (5 mL) was added at 5 °C. The mixture was then stirred at room temperature for 30 min. to form a solid-liquid biphasic system without the odor of the isocyanoacetate when the flask was

opened. The biphasic mixture was rotary-evaporated in vacuo and the residue was treated with diethyl ether (30 mL) followed by filtration in vacuo. The solid was washed within the filter with ether (3 x 10 mL) and dried in vacuo to give **2**($PhCO_2$) (1.30 g, 91%). ^{31}P NMR (CD_3CN): -9.52. ^1H NMR (CD_3CN): 2.58 (d, 9 H, NCH_3, $^3J_{PH}$ = 17.4 Hz), 2.96 (dt, 6 H, $N_{eq}CH_2$, $^3J_{PH}$ = 11.4 Hz, $^3J_{HH}$ = 6.0 Hz), 3.10 (dt, 6 H, $N_{ax}CH_2$, $^3J_{PH}$ = 7.2 Hz, $^3J_{HH}$ = 6.0 Hz), 5.28 (d, 1 H, PH, $^1J_{PH}$ = 493.8 Hz), 7.23 and 7.89 (two m, 5 H, C_6H_5). The filtrate and the washings were combined and washed with water (10 mL). The organic phase was separated and the aqueous phase was extracted with ethyl acetate (20 mL). The combined organic phases were rotary evaporated in vacuo to give ^1H NMR spectroscopically pure **11b** (0.85 g, 100%). ^1H NMR (CD_3CN): 3.83 (s, 3 H, OCH_3), 7.49 and 7.96 (two m, 5 H, C_6H_5), 8.03 (s, 1 H, C_2H). HRMS: calcd 203.05824 for $C_{11}H_{19}NO_3$, measured 203.05833.

α-(3,4,5-Trimethoxyphenyl)acylamino acid methyl ester hydrochloride 12a (Ar = 3,4,5-tri-methoxyphenyl).[8a,b] The crude oxazole prepared using **1** (0.61 g, 2.1 mmol) was dissolved in a mixture of methanol (15 mL) and concentrated hydrochloric acid (5 mL). The solution was stirred at 50°C for 6 h. The literature work up[8b] gave pure **12a** (0.55 g, 82%, lit.[8b] 80%), m.p. 175-176 °C (lit.[8b] 174-175 °C). ^1H NMR (DMSO-d_6): 3.71 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 3.87 (s, 6 H, OCH_3), 6.34 (s, 1 H, CH), 7.47 (s, 2 H, C_6H_2), 9.11 (br, 3 H, NH_3^+). Mass spectrum (FAB): 284 $(M-Cl)^+$, required for $(M-Cl)^+$ 284.

α-Phenylacylamino acid methyl ester hydrochloride 12b (Ar = Ph).[8a,b] Crude 4-methoxycarbonyl-5-phenyloxazole **11b** (0.83 g, 4.1 mmol) prepared above using **1** was dissolved in a mixture of methanol (6 mL) and concentrated hydrochloric acid (2.5 mL) which was stirred at 50 °C for 6 h. The work-up[8b] used for **12a** gave pure **12b** (0.76 g, 81%, lit.[8b] 84%). m.p. 186-187 °C (lit.[8b] 185-186 °C), ^1H NMR (DMSO-d_6): 3.88 (s, 3 H,

OCH_3), 6.25 (s, 1 H, CH), 7.61 (m, 2 H, Ar-H_2), 7.76 (m, 1 H, Ar-H), and 8.15 (d, 2 H, $^3J_{HH}$ = 7.5 Hz, Ar-H_2), 9.20 (br, 3 H, CH_3). Mass spectrum (FAB): 194 $(M-Cl)^+$, required for $(M-Cl)^+$ 194.

2-Ethoxycarbonyl-3,4-diethylpyrrol 15b[14a] using the superbase 1. To a magnetically stirred solution of 4-acetoxy-3-nitrohexane **13a** (0.68 g, 3.6 mmol), ethyl isocyanoacetate **10b** (0.43 g, 3.6 mmol, 95%) and *iso*-propanol (0.8 mL) in dry THF (5 mL) at -20 °C was added dropwise a solution of **1** (1.6 g, 7.2 mmol) in dry THF (5 mL). The addition funnel was rinsed with 2 mL of dry THF and the rinsing solution was added dropwise to the reaction mixture. The mixture was stirred at -20 °C to -15 °C for 2 h. to form a solid **2**(Y)/liquid biphasic system which gave no isocyanoacetate odor when the flask was opened. The solvent was rotary-evaporated in vacuo and the residue was extracted with hexane (20 mL). The precipitate was filtered in vacuo, washed within the filter with diethyl ether (2 x 10 mL) and dried in vacuo to give ^{31}P and ^1H NMR spectroscopically pure solid product **2**(Y) (Y = OAc, NO_2, mixture, 1.86 g, 96%). ^{31}P NMR (CD_3CN), -9.27 (Y = NO_2) and -9.47 (Y = AcO). ^1H NMR spectrum ($CDCl_3$) of the mixture of **2**(NO_2) and **2**(OAc): 1.98 (s, 3 H, $CH_3CO_2^-$), 2.60 (d, 9 H, NCH_3, $^3J_{PH}$ = 17.4 Hz), 2.98 (dt, 6 H, $N_{eq}CH_2$, $^3J_{PH}$ = 11.1 Hz, $^3J_{HH}$ = 6.3 Hz), 3.11 (dt, 6 H, $N_{ax}CH_2$, $^3J_{PH}$ = 10.8 Hz, $^3J_{HH}$ = 6.0 Hz), 5.27 (d, 1 H, PH, $^1J_{PH}$ = 494.1 Hz). The combined filtrate and washings were washed with water (15 mL). The organic phase was separated and the aqueous phase was extracted with ethyl acetate (2 x 25 mL). The combined organic phases were dried with anhydrous $MgSO_4$ and rotary-evaporated in vacuo to give **15b** as a ^1H NMR spectroscopically pure orange oil (0.70 g, 100%). ^1H NMR ($CDCl_3$): 1.14 (t, 3 H, CH_3, $^3J_{HH}$ = 7.5 Hz), 1.17 (t, partially overlapped with the peak at 1.14, 3 H, CH_3, $^3J_{HH}$ = 7.5 Hz), 1.35 (t, 3 H, CH_3, $^3J_{HH}$ = 7.5 Hz), 2.45 (q, 2 H, CH_2, $^3J_{HH}$ = 7.5 Hz), 2.75 (2 H, CH_2, $^3J_{HH}$ = 7.5 Hz), 4.31 (q, 2 H, OCH_2, $^3J_{HH}$

= 7.5 Hz), 6.67 (d, 1 H, C(5)H, $^3J_{HH}$ = 2.7 Hz), 8.76 (br, 1 H, NH). HRMS 195.12593 calcd for $C_{11}H_{17}NO_2$, measured 195.12556.

Salt **2**(Y) can be washed away with water if recovery of **1** is not desired. Thus, the solid-liquid biphasic mixture obtained in the aforementioned procedure was rotary-evaporated in vacuo. The residue was mixed with water (15 mL) and the mixture extracted with ethyl acetate (3 x 25 mL). The extract was dried with anhydrous $MgSO_4$, and rotary-evaporated in vacuo to give **15b** as a ^1H NMR spectroscopically pure orange oil (0.70 g, 100%).

Recycling superbase 1. To a magnetically stirred suspension of potassium *t*-butoxide (1.2 g, 0.011 mol) in dry CH_3CN (20 mL) was added dropwise a solution of **2**(Y) (Y = NO_2, OAc, a mixture, separated as aforementeioned, 1.85 g, 6.9 mmol) in dry CH_3CN (20 mL) by syringe. The mixture was stirred at room temperature for 1 hour and evaporated in vacuo (oil pump). By cannula, 200 mL of dry pentane was added to the residue which was then stirred overnight. The pentane solution was transferred by cannula to another dry flask (500 mL), from whence it was evaporated in vacuo to give a white solid which was sublimed at 50 °C/0.02 torr to give pure **1** (1.22 g, 82%).

2-Ethoxycarbonyl-3,4-diethylpyrrol 15b using DBU. Method A: To a magnetically stirred solution of 4-acetoxy-3-nitrohexane **13a** (0.68 g, 3.6 mmol), ethyl isocyanoacetate **10b** (0.43 g, 3.6 mmol, 95%) and *iso*-propanol (0.8 mL) in dry THF (5 mL), was added dropwise a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.12 g, 7.37 mmol) in dry THF (5 mL) at 0-35 °C. The addition funnel was rinsed with THF (2 mL) and the rinsing solution was added to the reaction mixture. After stirring at room temperature for 15 h, the mixture was poured into water (15 mL), extracted with ethyl acetate (2 x 25 mL) and dried with anhydrous $MgSO_4$. The solvent was removed in vacuo to give a mixture of **15b** and **14b** (0.65 g) in the ratio of 9:1 (as shown by ^1H NMR integration for the C(5)H). ^1H NMR ($CDCl_3$) of **14b**: 7.43 (d, $^2J_{HH}$ = 2.6 Hz), other peaks were overlapped with the peaks

of **15b**. HRMS of the mixture of **14b** and **15b**: **15b** calcd 195.12593 for $C_{11}H_{17}NO_2$, measured 195.12546; **14b** calcd 239.13270 for $C_{12}H_{17}NO_4$, measured 239.13213. **Method B:** The same reaction was conducted at -20 to -15 °C for 2 h. The reaction mixture was then poured into water (15 mL) and rotary evaporated in vacuo to remove THF. The residue was diluted with water (5 mL) and extracted with ethyl acetate (2 x 25 mL). The extracts were dried with anhydrous $MgSO_4$ overnight, and rotary evaporated in vacuo to give 0.68 g of a brown liquid with a heavy isocyanoacetate odor. The brown oil displayed a complicated ^1H NMR spectrum consistent with the presence of mainly starting material **13a** and **10b** with nearly no detectable **15b**.

2-Methoxycarbonyl-3,4-diethylpyrrol 15a using the superbase 1. To a magnetically stirred solution of 4-acetoxy-3-nitrohexane (4.80 g, 25.0 mmol) **13a**, methyl isocyanoacetate **10a** (2.64 g, 25.0 mmol, 95%) and *iso*-propanol (6.5 mL) in dry THF (15 mL) at -20 °C was added dropwise a solution of **1** (10.95 g, 50.69 mmol) in dry THF (15 mL). The mixture was stirred at -20 to -15 °C for 2 h to form a solid-liquid biphasic system which was rotary evaporated to dryness. The residue was stirred with hexane (80 mL) for 30 min. The precipitate was filtered in vacuo, washed with ether (2 x 30 mL) and dried in vacuo to give ^{31}P and ^1H NMR spectroscopically pure **2**(Y) (Y = NO_2, OAc mixture, 12.8 g, 95%). The combined filtrate and washings were washed with water (20 mL) and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (2 x 50 mL), the combined organic phases were dried with anhydrous $MgSO_4$ and rotary evaporated in vacuo to give **15a** as a ^1H NMR spectroscopically pure orange oil (4.57 g, 100%) which solidified upon standing. ^1H NMR ($CDCl_3$): 1.13 (t, 3 H, CH_3, $^3J_{HH}$ = 7.5 Hz), 1.89 (t, 3 H, CH_3, $^3J_{HH}$ = 7.5 Hz), 2.46 (q, 2 H, CH_2, $^3J_{HH}$ = 7.4 Hz), 2.75 (q, 2 H, CH_2, $^3J_{HH}$ = 7.5 Hz), 3.84 (s, 3 H, OCH_3), 6.67 (d, 1 H, C(5)H, $^2J_{HH}$ = 2.7 Hz), 8.77 (br, 1 H, NH). For elemental analysis, a small amount of sample was recrystallized from hexane in a freezer. The supernatant was removed by syringe to give light yellowish crystals which were dried in

vacuo. IR (KBr pellet), 601, 737, 776, 812, 929, 975, 993, 1089, 1140, 1277, 1399, 1438, 1508, 1568, 1676, 2872, 2967, 3027, 3316 cm^{-1}. HRMS: calcd 181.11028 for $C_{10}H_{15}NO_2$, measured 181.11008. Elemental analysis: calcd C, 66.26; H, 8.35; N, 7.33, Found C, 66.03; H, 8.25; N, 7.98.

2-Ethoxycarbonyl-3,4-butylene pyrrol 15e using the superbase 1. To a solution of 1-nitrocyclohexene **16e** (0.66 g, 5.2 mmol) and ethyl isocyanoacetate **10b** (0.62 g, 5.2 mmol, 95%) in dry THF (5 mL) at -20 °C was added dropwise a solution of **1** (1.12 g, 5.23 mmol) in THF (5 mL). The addition funnel was rinsed with 2 mL of dry THF which was then added dropwise to the reaction mixture. The mixture was stirred at -20 to -15 °C for 2 h and evaporated in vacuo to dryness. The residue was stirred with hexane (25 mL) for 30 min and filtered in vacuo. The solid was washed with ether (2 x 10 mL) and dried in vacuo to give **2**(NO_2) (1.28 g, 94%). ^{31}P NMR (CD_3CN) of **2**(NO_2): -9.27. The combined filtrate and washings were washed with water (10 mL) and then the organic layer was separated. The aqueous layer was extracted with ethyl acetate (2 x 30 mL) and the combined organic layers were then dried with anhydrous $MgSO_4$ overnight and evaporated in vacuo to give **15e** (1.0 g, 100%) as a ^1H NMR spectroscopically pure solid. ^1H NMR ($CDCl_3$): 1.32 (t, 3 H, CH_3, $^3J_{HH}$ = 6.9 Hz), 1.72 (m, 4 H, CH_2), 2.52 (t, 2 H, CH_2, $^3J_{HH}$ = 5.7 Hz), 2.79 (t, 2 H, CH_2, $^3J_{HH}$ = 4.2 Hz), 4.27 (q, 2 H, OCH_2, $^3J_{HH}$ = 6.9 Hz), 6.62 (d, 1 H, C(5)H, $^3J_{HH}$ = 2.4 Hz), 8.87 (br, 1 H, NH). HRMS: calcd 193.11028 for $C_{11}H_{15}NO_2$, measured 193.11045.

2-Ethoxycarbonyl-3-trifluoromethyl-4-ethylpyrrol 15c[21] using the superbase 1. To a magnetically stirred solution of 2-acetoxy-3-nitro-1,1,1-trifluoropentane **13b** (1.99 g, 9.25 mmol), ethyl isocyanoacetate **10b** (1.10 g, 9.25 mmol, 95%) and *iso*-propanol (2.5 mL) in dry THF (5 mL) at -20 °C to -15 °C was added dropwise a solution of **1** (4.0 g, 18.5 mmol) in THF (5 mL). The addition funnel was rinsed with 2 mL of dry THF and the rinsing solution was added to the reaction mixture. The mixture was stirred at -20 °C to -15 °C for 2 h to form a solid **2**(Y)/liquid biphasic system which gave no isocyanoacetate odor

when the flask was opened. The solvent was removed and the residue was mixed with water (20 mL) and extracted with hexane (3 x 50 mL). The combined extracts were dried with $MgSO_4$ and rotary evaporated to give **15c** as a ^1H NMR spectroscopically pure oil (2.16 g, 100%) ^1H NMR ($CDCl_3$): 1.20 (s, 3 H, CH_3, $^3J_{HH}$ = 7.5 Hz), 1.36 (s, 3 H, CH_3, $^3J_{HH}$ = 7.5 Hz), 2.62 (q, 2 H, CH_2, $^3J_{HH}$ = 7.5 Hz), 4.38 (q, 2 H, CH_2, $^3J_{HH}$ = 7.5 Hz), 6.73 (d, 1 H, C(5)H, $^3J_{HH}$ = 1.8 Hz), 9.51 (br, 1 H, NH); HRMS 235.08201 calcd from $C_{10}H_{12}F_3NO_2$, measured 235.08222.

2-*t*-Butoxycarbonyl-4-methoxycarbonylethyl-3-methylpyrrol 15d[13] using superbase 1. To a magnetically stirred solution of 5-acetoxy-4-nitro-hexanoate **13c**[13] (0.83 g, 3.5 mmol), *t*-butyl isocyanoacetate (0.53 g, 3.5 mmol, 95%) and *iso*-propanol (0.5 mL) in dry THF (5 mL) at -20 °C to -15 °C was added dropwise a solution of **1** (1.548 g, 7.167 mmol) in THF (5 mL). The addition funnel was rinsed and the rinsing solution was added to the reaction mixture. The mixture was stirred at -20 to -15 °C for 2.0 hours to form a solid **2**(Y)/liquid biphasic system which gave no isocyanoacetate odor when the flask was opened. The solvent was rotary evaporated in vacuo. The residue was mixed with water (20 mL) and extracted with hexane (3 x 50 mL). The extracts were dried with $MgSO_4$ and then rotary evaporated to give a ^1H NMR spectroscopically pure oil **15d** (0.94 g, 100%). ^1H NMR ($CDCl_3$): 1.56 (s, 9 H, $C(CH_3)_3$), 2.26 (s, 3 H, $C(4)CH_3$), 2.53 (t, 2 H, CH_2, $^3J_{HH}$ = 7.5 Hz), 2.75 (t, 2 H, CH_2, $^3J_{HH}$ = 7.5 Hz), 3.67 (s, 3 H, OCH_3), 6.65 (d, 1 H, C(5)H, $^3J_{HH}$ = 3.4 Hz), 8.86 (br, 1 H, NH); HRMS 267.16706 for $C_{14}H_{21}NO_4$, measured 267.16735.

Bis-2-(5-methoxycarbonyl-3,4-diethylpyrro)methane 22a. A mixture of 2-methoxycarbonyl-3,4-diethylpyrrol **15a** (0.40 g, 2.2 mmol), paraformaldehyde (0.26 g, 8.6 mmol), ethanol (2.5 mL) and concentrated hydrochloric acid (0.05 mL) was refluxed for 30 min under argon, cooled to room temperature and then kept in a freezer overnight at about -20 °C. The resulting crystals were filtered in vacuo to give a white solid (0.36 g, 87.5%), m.p.

130-131 °C. ^{1}H NMR ($CDCl_3$): 1.06 (t, 6 H, CH_3, $^3J_{HH}$ = 7.5 Hz), 1.15 (t, 6 H, CH_3, $^3J_{HH}$ = 7.5 Hz), 2.42 (q, 4 H, CH_2, $^3J_{HH}$ = 7.5 Hz), 2.72 (q, 4 H, CH_2, $^3J_{HH}$ = 7.5 Hz), 3.80 (s, 6 H, OCH_3), 3.87 (s, 2 H, CH_2), 8.63 (br, 2 H, NH). ^{13}C NMR (CD_3CN): 16.30, 17.56, 18.79, 23.40, 51.24, 117.33, 124.00, 134.46, 162.05. IR (KBr pellet): 723, 779, 1010, 1140, 1256, 1281, 1448, 1494, 1619, 1695, 2870, 2932, 2966, 3320, 3368. HRMS: calcd 374.22056 for $C_{21}H_{30}N_2O_4$, measured 374.22025. Elemental analysis: calcd C, 67.34, H, 8.08, N, 7.48. Found C, 67.37, H, 8.00, N, 6.87.

Bis (5-methoxycarbonyl-3,4-diethylpyrro)-*p*-(1,1,1-trifluorotolyl) methane 22b. A solution of **15a** (1.0 g, 5.5 mmol) in CH_2Cl_2 (15 mL) was de-aerated with argon for 5 min. α,α,α-Trifluoro-*p*-tolualdehyde (1.1 g, 6.3 mmol) and BF_3•OEt_3 (0.31 g, 2.2 mmol) were added by syringe. After the mixture was stirred at room temperature for 10 h, TLC showed that **15a** disappeared and a new component **22b** appeared (R_f = 0.23, $CHCl_3$:hexane = 1:1). The volatiles were removed in vacuo at room temperature. The residue was dissolved in ethyl acetate (40 mL) and washed with sodium bicarbonate (50 mL, 5%). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (40 mL). The combined organic phases were concentrated in vacuo. Flash chromatography on silica gel (140 x 45 mm, $CHCl_3$:hexane = 1:1) gave the orange solid product **22b** (1.30 g, 90.9%). ^{1}H NMR ($CDCl_3$): 0.92 (t, 6 H, CH_3, $^3J_{HH}$ = 7.5 Hz), 1.14 (t, 6 H, CH_3, $^3J_{HH}$ = 7.5 Hz), 2.33 (q, 4 H, CH_2, $^3J_{HH}$ = 7.5 Hz), 2.71 (q, 4 H, CH_2, $^3J_{HH}$ = 7.5 Hz), 3.72 (s, 6 H, OCH_3), 5.63 (s, 1 H, CH), 7.18 (d, 2 H, $CF_3C_6H_4$, $^3J_{HH}$ = 7.5 Hz), 7.76 (d, 2 H, $CF_3C_6H_4$, $^3J_{HH}$ = 8.1 Hz), 8.57 (b, NH, 2 H). ^{13}C NMR ($CDCl_3$): 15.72 (CH_3), 15.78 (CH_3), 17.12 (CH_2), 18.32 (CH_2), 22.00 (CH), 51.05 (OCH_3), 117.73, 124.23, 125.82 (q, $^3J_{CF}$ = 3.1 Hz), 127.50 (q, CF_3, $^1J_{CF}$ = 266.8 Hz), 129.27 (q, $^2J_{CF}$ = 32.3 Hz), 128.57, 130.73, 134.16, 144.09, 161.79 (C=O). IR (KBr pellet): 594, 778, 1013, 1067, 1091, 1258, 1327, 1410, 1463, 1499, 1654, 1711, 2872, 2933, 2966, 3339 (NH) cm^{-1}. HRMS:

calcd. 518.23924 for $C_{28}H_{33}F_3N_2O_4$, found 518.23978. Elemental analysis: calcd. C, 64.85, H, 6.41, N, 5.40, found C, 64.65, H, 6.20, N, 5.51.

Bis-2-(5-ethoxycarbonyl-3-trifluoromethyl-4-ethylpyrro)methane 22c. A solution of 2-ethoxycarbonyl-3-trifluoromethyl-4-ethylpyrrol **15c** (0.25 g, 1.1 mmol), $CH_2(OMe)_2$ (0.41 g, 5.4 mmol) and $BF_3{\bullet}OEt_2$ (0.1 g, 0.7 mmol) in dry CH_2Cl_2 (10 mL) under argon was stirred at room temperature for 35 h. TLC showed complete conversion of **15c** to **22c** (R_f = 0.31 for **22c** and R_f = 0.42 for **15c**, hexane:ethylacetate = 4:1). The solvent was removed under vacuum and the residue was washed with 10% sodium bicarbonate (40 mL) and extracted with ethyl acetate (3 x 50 mL). The extracts were dried with sodium sulfate and rotary evaporated to give a white solid which was purified by flash chromatography on silica gel using CH_2Cl_2 as eluting solvent to give pure **22c** (0.23 g, 88.5%). ^1H ($CDCl_3$): 0.89 (t, 6 H, CH_3, $^3J_{HH}$ = 7.5 Hz), 1.29 (t, 3 H, CH_3, $^3J_{HH}$ = 7.5 Hz), 2.48 (q, 4 H, CH_2, $^3J_{HH}$ = 7.5 Hz), 4.25 (q, 4 H, CH_2, $^3J_{HH}$ = 7.5 Hz), 3.97 (s, 2 H, CH_2), 10.23 (br, 2 H, NH); ^{13}C NMR (CD_2Cl_2): 14.00 (s, CH_3), 16.03 (s, CH_3), 18.48 (q, CH_2, $^4J_{PC}$ = 2.1 Hz), 22.26 (s, C(2)CH_2), 61.9 (s, OCH_2), 116.86 (q, C(3), $^2J_{CF}$ = 38.1 Hz), 120.26 (q, C(4), $^3J_{PC}$ = 3.8 Hz), 123.94 (q, CF_3, $^1J_{PC}$ = 268.9 Hz), 125.15 (q, cd, J_{PC} = 1.6 Hz), 129.05 (s, C(5)), 160.44 (s, C=O); IR (KBr pellet): 779, 811, 1033, 1130, 1264, 1300, 1375, 1443, 1505, 1560, 1693, 1735, 2871, 2934, 2981, 3388 cm^{-1}; HRMS 482.16403 calcd for $C_{21}H_{24}F_6N_2O_4$, measured 482.16389. Elemental analysis: calcd C, 52.26, H, 5.02, N, 5.81, found C, 52.22, H, 4.84, N, 5.82.

PTSA was also used as an acid catalyst but the reaction was much slower and needed 10 days to reach completion.

3,4-Diethylpyrrol 23[15] using LiX. A mixture of 2-methoxycarbonyl-3,4-diethylpyrrol **15a** (1.0 g, 55 mmol), lithium chloride (2.4 g, 0.055 mol) and water (0.1 g, 6 mmol) in DMSO (25 mL) was de-aerated with argon for 10 min. and then refluxed for 1.5 h. TLC (silica gel plate, hexane:diethyl ether = 5:1) showed that all of the starting material **15a**

(R_f = 0.55) had disappeared and that a new composition **23** (R_f = 0.35) was formed. The mixture was poured into 100 g of ice-H_2O and extracted with diethyl ether (3 x 50 mL). The combined organic layers were washed with saturated sodium chloride (15 mL) and rotary evaporated in vacuo to give **23** (0.68 g, 100%) as a ^1H NMR spectroscopically pure oil. ^1H NMR ($CDCl_3$): 1.20 (t, 6 H, CH_3, $^3J_{HH}$ = 7.5 Hz), 2.46 (q, 4 H, CH_2, $^3J_{HH}$ = 7.5 Hz), 6.52 (d, 2 H, C(2)H and C(5)H; $^3J_{HH}$ = 2.4 Hz), 7.81 (br, 1 H, NH). HRMS: calcd 122.10480 for $C_8H_{13}N$, measured 123.10483.

The same reaction was conducted with LiBr (10 equivalents) and LiI (10 equivalents). The time needed for complete conversion of **15a** into **23** was 2.0 h for LiBr and 3.0 h for LiI. The yield of **23** in both cases was 100%. When the reaction was conducted with NaCl, however, no product **23** was formed after 3 h refluxing as shown by TLC.

3,4-Diethylpyrrol 23 using NaOH. Method A: To a solution of **15a** (1.0 g, 5.1 mmol) in 95% ethanol (5 mL) was added in one portion a sodium hydroxide (0.32 g, 8.2 mmol) solution in water (0.7 mL). The solution was de-aerated with argon for 10 min and then refluxed for 2 h. Following this, 5 mL of ethanol was distilled out at an oil bath temperature of 110 °C. The residue was mixed with water (3.5 mL) and refluxed under argon for 6.5 h, cooled to r.t. and extracted with diethylether (3 x 20 mL). The solvent was removed in vacuo to give a red-brown liquid **23** (0.31 g, 49%) which was contaminated with unreacted **15a** as shown by ^1H NMR spectroscopy. The aqueous layer was diluted with water (10 mL), neutralized with dilute hydrochloric acid and extracted with ether (2 x 20 mL). The aqueous layer was washed with 10% $NaHCO_3$ solution (10 mL) and extracted again with diethyl ether (2 x 20 mL). The combined ether phases were washed with 10% $NaHCO_3$ (5 mL) and evaporated in vacuo to give the sodium salt of 3,4-diethylpyrrol-2-carboxylate as a grey solid (0.48 g, 50%). ^1H NMR ($CDCl_3$: 1.16 (t, 3 H, CH, $^3J_{HH}$ = 7.5 Hz), 1.20 (t, 3 H, CH_3, $^3J_{HH}$ = 7.5 Hz), 2.46 (t, 2 H, CH_2, $^3J_{HH}$ = 7.5 Hz), 2.78 (t, 2 H, CH_2, $^3J_{HH}$ = 7.5 Hz),

6.74 (d, 1 H, C_5H, $^3J_{HH}$ = 2.7 Hz), 8.92 (br, 1 H, NH). **Method B**: To a solution of **15a** (1.0 g, 5.1 mmol) in 95% ethanol (5 mL) was added in one portion a sodium hydroxide (0.32 g, 8.2 mmol) solution in water (0.7 mL). The solution was de-aerated with argon and then refluxed for 6.5 h. Ethanol was distilled out at an oil bath temperature of 110 °C. After cooling to r.t., the residue was dissolved in a mixture of ethanol (1 mL) and water (3.5 mL). The resulting solution was refluxed for 19 h under argon and extracted with diethyl ether (3 x 40 mL) to give 0.17 g of an unidentified solid.

Reduction of 15b to 24 with (*i*-Bu)$_2$AlH. A solution of **15b** (1.01 g, 5.18 mmol) in benzene (20 mL) was de-aerated with dry argon. (*i*-Bu)$_2$AlH (3.7 mL, 2.9 g, 0.021 mol) was added by syringe over 10-15 min at 35-40 °C. The solution was heated at 50-60 °C for 8.0 h and then quenched with MeOH (15 mL) and H_2O (15 mL) at 20 °C. The solid was filtered off in vacuo and washed with boiling MeOH (3 x 25 mL). The combined filtrate and washings were concentrated in vacuo. The residue was mixed with hexane (30 mL) and filtered to remove solids. The filtrate was concentrated in vacuo to give 0.42 g of oil which was distilled to give **24** (70 mg, 9.9%, 43-50 °C/0.4 to 0.5 torr) as a light yellow liquid. ^{1}H NMR ($CDCl_3$): 1.08 (t, 3 H, $^3J_{HH}$ = 7.0 Hz), 1.18 (t, 3 H, $^3J_{HH}$ = 7.5 Hz), 2.16 (s, 3 H, C(2)Me), 2.35-2.47 (m, 4 H, CH_2), 6.38 (d, 1 H, C(5)H, $^3J_{HH}$ = 1.2 Hz), 7.54 (br, 1 H, NH). HRMS: calcd. for $C_9H_{15}N$ 137.12045, found 137.12054.

1,2,3,4,5,6,7,8-Octaethylporphyrin 26. To a stirred suspension of $LiAlH_4$ (0.41 g, 0.011 mol) in dry THF (15 mL) at 0 °C to 3 °C was added dropwise a solution of crude **15b** (0.70 g, 3.6 mmol) in THF (15 mL). The addition funnel was rinsed with THF (2 mL) and the rinsing solution was added dropwise to the reaction mixture. The mixture was stirred at 0-3 °C for 2 h and then 5 mL of ethyl acetate was added followed by 30 mL of saturated ammonium chloride to destroy excess $LiAlH_4$. The solid was filtered off and washed with ethyl acetate (40 mL). The organic phase was separated and the aqueous phase was extracted with ethyl acetate (2 x 30 mL). The combined organic phases were rotary evaporated

in vacuo at room temperature (using ice-H_2O as a recycling coolant to accelerate evaporation of solvent) to give a light-yellow oil **25**. To a solution of the crude, undried **25** and dimethoxymethane (2.7 g, 0.036 mol) in CH_2Cl_2 (15 mL, dried with P_4O_{10}) was added PTSA•H_2O (0.11 g, 0.59 mmol). The mixture, which was contained in an aluminum-foil-wrapped flask, was stirred at room temperature for 24 h. *o*-Chloranil (1.0 g, 4.1 mmol) in CH_2Cl_2 (10 mL) was added in one portion to the red reaction mixture, which was then stirred at room temperature for another 24 h. Finally, the mixture was washed with 1N NaOH (50 mL) and extracted with $CHCl_3$ (3 x 100 mL). The combined organic phases were rotary-evaporated and chromatographed on aluminum oxide (basic, activated, Brochman I, 2.5 x 17 cm) using CH_2Cl_2 as eluent. After evaporation of the eluent, the product was recrystallized from $CHCl_3$-MeOH to give pure OEP **26** (0.33 g, 69%). ^1H NMR ($CDCl_3$): -3.75 (br, 2 H, NH), 1.92 (t, 24 H, CH_3, $^3J_{HH}$ = 7.5 Hz), 4.10 (q, 16 H, CH_2, $^3J_{HH}$ = 7.5 Hz), 10.10 (s, 4 H, *meso*-H). UV-vis ($CHCl_3$): l_{max} 398, 498, 534, 566, 620 which was identical to that of an authentic sample from Aldrich. HRMS: calcd 534.37225 for $C_{36}H_{46}N_4$, measured 534.37072.

It was found (Table 1) that the combined organic phases containing crude 2-hydroxymethyl-3,4-diethylpyrrol **25** obtained from the $LiAlH_4$ reduction reaction, should not be stored or dried if a high yield of OEP **26** was desired, because **25** is not stable. Dimethoxymethane used as a dehydration agent to remove water formed from the acid-catalyzed condensation reaction of **25** increases the yield of **26**.

Method B: A solution of 3,4-diethylpyrrol prepared from 2-methoxycar-bonyl-3,4-diethylpyrrol (0.68 g, 5.4 mmol) and $(CH_2O)_n$ (0.165 g, 5.50 mmol) in benzene (200 mL) was de-aerated with argon for 15 min. PTSA•H_2O (0.02 g, 0.1 mmol) was added and the flask was wrapped with aluminum foil. The solution was heated at 55 °C for 15 h and then it was allowed to cool to room temperature. Oxygen was bubbled through the solution with a fritted

glass aerator until dryness. The residue was dissolved in $CHCl_3$ (25 mL), washed with 1N NaOH solution (25 mL) and water (2 x 20 mL). The organic layer was concentrated to 3-4 mL, layered with methanol (45 mL) for 24 h and filtered to give a violet powder (0.12 g, 16%). ^1H NMR and UV spectra of the product **26** were identical with an authentic sample.

Table 1. Preparation of OEP 26 from 15b

expt.	treatment of crude **25**	condensation reaction conditions	yield of OEP **26** (%)
1	not dried but immediately used	CH_2Cl_2, PTSA•H_2O $CH_2(OMe)_2$ (10 eq)	69
2	dried with $MgSO_4$ for 12 h	CH_2Cl_2, PTSA•H_2O $CH_2(OMe)_2$ (10 eq)	21
3	not dried but immediately used	CH_2Cl_2, PTSA•H_2O	53
4	not dried but immediately used	CH_2Cl_2, PTSA•H_2O $(CH_2O)_n$ (10 eq)	23

[a] In all four experiments, *o*-chloranil was used as the oxidant, basic aluminum oxide was used as the chromatography packing material and CH_2Cl_2 was employed as the eluting solvent.

Method C: To a solution of 2-methoxy-3,4-diethylpyrrol (1.33 g, 7.52 mmol) in DMSO (35 mL) was added LiCl (9.7 g, 0.225 mol), $(CH_2O)_n$ (0.26 g, 7.5 mmol) and H_2O (0.13 g, 7.5 mmol). The mixture was heated at 190-200 °C for 4 h while O_2 was bubbled in, and then it was poured into ice-H_2O (200 mL). The solid was separated by filtration and purified by chromatography (aluminum oxide, basic, activated Brochman I, 45 x 15 mm, CH_2Cl_2) and finally recrystallized from $CHCl_3$-MeOH ($CHCl_3$, 3 mL; MeOH, 60 mL) to give

the pure violet powdery product (0.17 g, 17%) which had ^{1}H NMR and UV spectra identical to that of an authentic sample of **26**.

Method D: A mixture of **22a** (1.05 g, 2.81 mmol) prepared from **15a** and $(CH_2O)_n$, LiCl (7.2 g, 0.17 mol), and water (0.10 g, 5.6 mmol) in DMSO (40 mL) was heated at 200-210 °C for 2 h with a small flow of air and then poured into ice-cooled phosphate buffer (100 mL). The solid was collected by filtration in vacuo. Residual solid adhering to the wall of the filter was collected by dissolving it in $CHCl_3$. The solid and $CHCl_3$ solution were combined and evaporated. The solid residue was chromatographed (Al_2O_3, basic, activated Brochman I, CH_2Cl_2) to give a violet powder which was recrystallized from $CHCl_3$ (3 mL) and methanol (70 mL) to give pure violet **26** (0.49 g, 67%) which possessed ^{1}H NMR and UV spectra identical to that of an authentic sample.

1,2-3,4-5,6-7,8-Tetrabutylenylporphyrin 27. To a suspension of $LiAlH_4$ (0.65 g, 0.016 mmol) in dry THF (20 mL) was added dropwise at 0-3 °C a solution of crude **15e** (1.0 g, 5.2 mmol) in dry THF (15 mL). The addition funnel was rinsed with dry THF (2 mL) and the rinsing solution was added dropwise to the reaction mixture. After the reaction mixture was stirred at 0-3 °C for 2 h, 5 mL of ethyl acetate and 40 mL of saturated ammonium chloride were added to destroy excess $LiAlH_4$. The solid was filtered off in vacuo and washed with ethyl acetate (50 mL). The organic phase was separated and the aqueous phase was extracted with ethyl acetate (2 x 40 mL), washed with saturated sodium chloride and rotary evaporated in vacuo at room temperature (using ice-H_2O as a recycling coolant). To the residue was added dry CH_2Cl_2 (20 mL), dimethoxymethane (3.4 g, 0.052 mol) and PTSA•H_2O (0.21 g, 1.1 mmol). The mixture, which was contained in an aluminum-foil-wrapped flask, was stirred at room temperature for 24 h. *o*-Choranil (1.53 g, 6.22 mmol) in CH_2Cl_2 (10 mL) was added to the reaction mixture, which was then stirred for another 24 h. Finally, the reaction mixture was washed with 1N NaOH solution, extracted with $CHCl_3$ (3 x 100 mL) and chromatographed on aluminum oxide (basic, activated Brochman I, 2.5 x 15 cm,

CH_2Cl_2). The product obtained upon evaporation was recrystallized from $CHCl_3$-MeOH to give pure **27** (0.44 g, 65%). ^1H NMR ($CDCl_3$: -3.84 (br, 2 H, NH), 2.49 (br, 16 H), 4.11 (br, 16 H), 9.88 (5, 4 H). UV-vis ($CHCl_3$): l_{max} 398, 498, 534, 566, 618. HRMS: calcd 526.30966 for $C_{36}H_{38}N_4$, measured 526.30885.

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GENERAL CONCLUSIONS

Summary. In this research, we have improved the synthesis of the non-ionic phosphorus superbase $P(MeNCH_2CH_2)_3N$ by using much cheaper starting materials, and easier and more economical processes.

We have synthesized pro-imidophosphatranes $RN=P(MeNCH_2CH_2)_3N$ (R = Me and Ph) and shown from equilibrium measurements that $MeN=P(MeNCH_2CH_2)_3N$ and $PhN=P(MeNCH_2CH_2)_3N$ are also strong non-ionic bases. The basicity order of P_4-*t*-Bu > $P(MeNCH_2CH_2)_3N$ > $MeN=P(MeNCH_2CH_2)_3N$ > $MeN=P(NMe_2)_3$ > DBU > $PhN=P(MeNCH_2CH_2)_3N$ > $PhN=P(NMe_2)_3$ shows that $P(MeNCH_2CH_2)_3N$ (pK_a of its conjugate acid = 40.7 in CH_3CN) rivals the basicity of P_4-*t*-Bu (i.e. *t*-$BuN=P[N=P(NMe_2)_3]_3$, pK_a of its conjugate acid = 42.1 in CH_3CN) and is the strongest phosphorus base known to date. This is especially interesting in view of the different protonation sites in these two bases and the different sources of stabilization of the conjugate acids (i.e. extensive resonance stabilization in the case of the protonated P_4-*t*-Bu and a robust chelated structure in the case of the protonated $P(MeNCH_2CH_2)_3N$). A second striking feature of the above basicity order sequence is that $MeN=P(MeNCH_2CH_2)_3N$ and $PhN=P(MeNCH_2CH_2)_3N$ are more basic than their corresponding acyclic analogues $MeN=P(NMe_2)_3$ and $PhN=P(NMe_2)_3$, respectively. The third feature is that pro-azaphosphatrane $P(MeNCH_2CH_2)_3N$ and pro-imidoazaphosphatrane $MeN=P(MeNCH_2CH_2)_3N$ are ca 10^{17} and at least 10^3 times stronger bases, respectively, than DBU which is a medium strong non-ionic base widely used in modern synthetic organic chemistry. The augmented basicity of $MeN=P(MeNCH_2CH_2)_3N$ and $PhN=P(MeNCH_2CH_2)_3N$ over their acyclic analogues is attributed to partial bridgehead P-N_{ax} transannulation which has been demonstrated in the conjugated acid $[PhNHP(MeNCH_2CH_2)_3N]CF_3CO_2$ by X-ray crystallography.

The full transannulation process that accompanies protonation of $P(MeNCH_2CH_2)_3N$ to give $H[P(MeNCH_2CH_2)_3N]^+$ cation is a model of S_N2 formation of a five-coordinate species, with the unusual feature that the nucleophilic nitrogen atom is forced to invert by virtue of its bridgehead position in the bicyclic structure $P(MeNCH_2CH_2)_3N$. However, we also observed a stepwise progression of intermediate P-N_{ax} distances and N_{eq}-P-N_{eq} angles (determined by X-ray means) in $ZP(MeNCH_2CH_2)_3N$ systems (Z = H^+, $PhN(MeS)C^+$, $PhHN^+$, $MeS(S)C^+$, Me^+, S_2C, $1/2Cl_2Hg$, O, S, $Br(CO)_4Re$, $1/2Cl_2Pt$), suggesting a stepwise partial S_N2 process that is a function of the Lewis acidity of the Z substituent. A nearly linear relationship (r = 0.98) between the P-N_{ax} distance and the average N_{eq}-P-N_{eq} angle in the above systems was seen. This flexibility of the bridgehead P-N_{ax} bond distance (or bond strength) is essential in rendering $P(MeNCH_2CH_2)_3N$ as a superior catalyst in the conversion of isocyanates to isocyanurates and to isocyanurate-based polymers.

Partial bridgehead transannulation also allows $PhN{=}P(MeNCH_2CH_2)_3N$ to be a strong catalyst in the conversion of isocyanates to isocyanurates, and $O{=}P(MeNCH_2CH_2)_3N$ and $S{=}P(MeNCH_2CH_2)_3N$ to be much stronger catalysts than their acyclic analogues in the selective conversion of isocyanates to carbodiimides. Partial bridgehead transannulation also stabilizes many adducts such as $RN_3P(MeNCH_2CH_2)_3N$, $S_2CP(MeNCH_2CH_2)_3N$ and $PhN{=}C(S)P(MeNCH_2CH_2)_3N$ so that they can be isolated in high yields. The relative rates of formation of $RSC(S)P(MeNCH_2CH_2)_3N$ are in accord with S_N2 attack of sulfur of the adduct $S_2CP(MeNCH_2CH_2)_3N$ on the α-carbon of RX.

The potent deprotonation capability of the superbase $P(MeNCH_2CH_2)_3N$ has been demonstrated in the base-promoted high yield synthesis of pyrrols from the reaction of β-acetoxy-α-nitroalkanes with isocyaoacetates, in which an E1cb acetic acid elimination and an enolate ring annulation reaction are involved. This potent deprotonation power of our superbase is further demonstrated in the fast and high-yield formation of oxazoles from the reaction of isocyanoacetates with acyl chlorides or acyl anhydrides, in which an enolate ring

reaction of isocyanoacetates with acyl chlorides or acyl anhydrides, in which an enolate ring annulation is involved. With the use of the superbase $P(MeNCH_2CH_2)_3N$, the overall yield of octaethylporphyrin has been improved to 62% from previously reported values of 5-25%. Because of the extremely strong basicity of the superbase, deprotonation is more complete and much faster than with traditional non-ionic bases such Et_3N, DBN, DBU, guanidines or Proton Sponge. Other advantages of our superbase demonstrated here are that deprotonation with this compound can be carried out both at room temperature and at low temperature. In addition, the advantages of our superbase over both DBN and DBU are nicely demonstrated in a total synthesis[1] of Vitamin A. The advantages of our superbase $P(MeNCH_2CH_2)_3N$ over P_4-*t*-Bu are: $P(MeNCH_2CH_2)_3N$ is cheaper and easier to synthesize, the conjugate acid of $P(MeNCH_2CH_2)_3N$ can be easily separated from organic products and the superbase can be recovered. It is highly likely that $P(MeNCH_2CH_2)_3N$ will be widely used in the future as non-ionic superbases and catalysts in synthetic organic chemistry, in pharmaceutical chemistry and in polymer chemistry.

Suggestions for Additional Research. In view of the structural features of the $ZP(RNCH_2CH_2)_3N$ systems, many other synthetic applications are proposed and a few examples are described below:

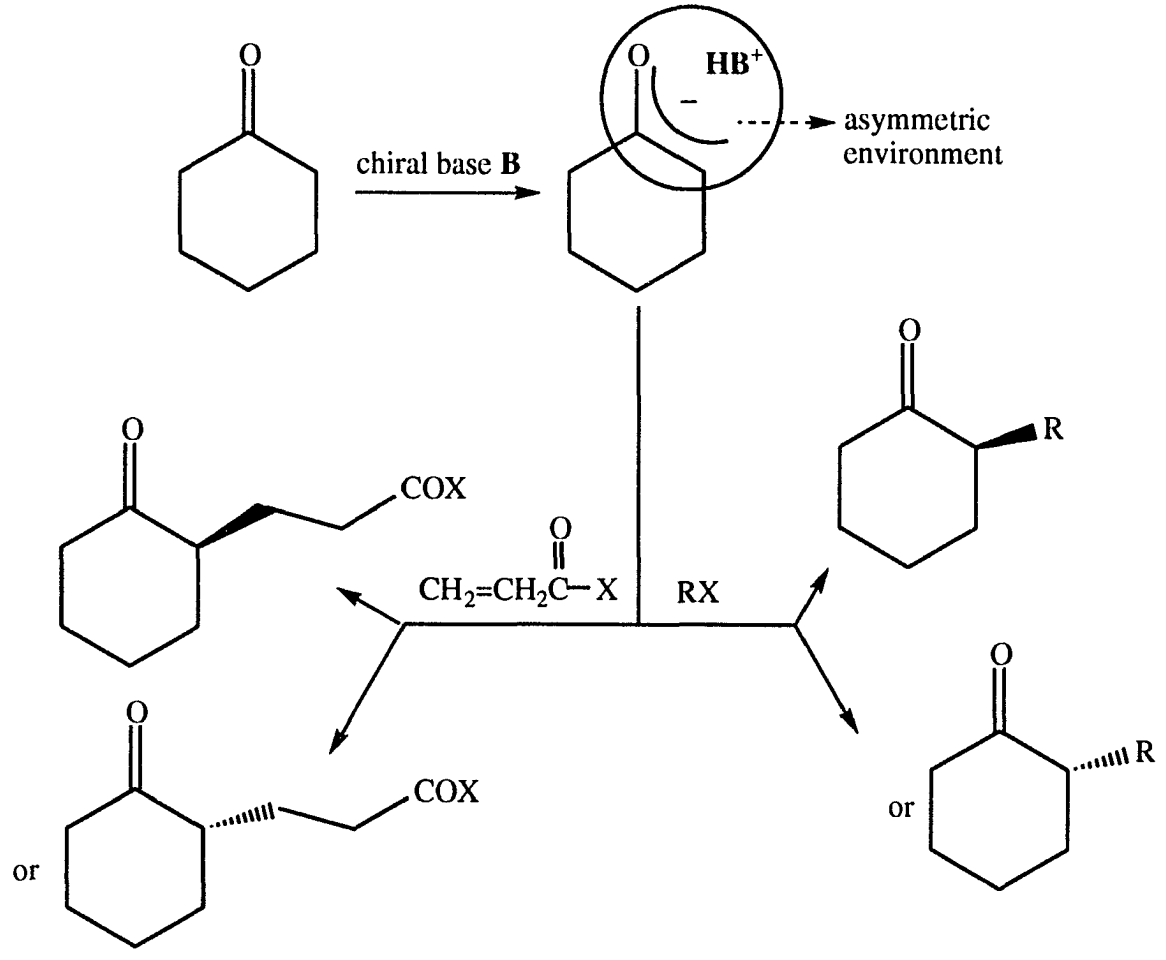
(a) $P(MeNCH_2CH_2)_3N$ may be a better ligand than PPh_3 in certain Pd(0) catalyzed reactions[2] which are extremely powerful tools in organic synthesis. Oxidative addition of $Pd(0)L_x$ to, for instance, aryl (or vinyl) halides or triflates requires electron-rich metal ligands so that the oxidation will be favorable, but the reductive elimination requires electron-poor metal ligands. It is therefore likely that the best ligands in certain palladium catalyzed reactions would be of intermediate electron-donicity, allowing a compromise among the diverse electronic requirements of each intermediate step. $P(MeNCH_2CH_2)_3N$ might be such a ligand because of its electron-donicity flexibility in the oxidative addition and reductive elimination

steps, based on the flexible transannulation we observed in a number of adducts, which depends in turn on the Lewis acidity of the exocyclic phosphorus substituent.

(b) $P(RNCH_2CH_2)_3N$ might exclusively produce kinetic enolates in view of its steric hindrance, and its observed rapid and quantitative deprotonation observed owing to its strong basicity. Selective formation of enolates is important for regioselective alkylation and enolate annulation.[3]

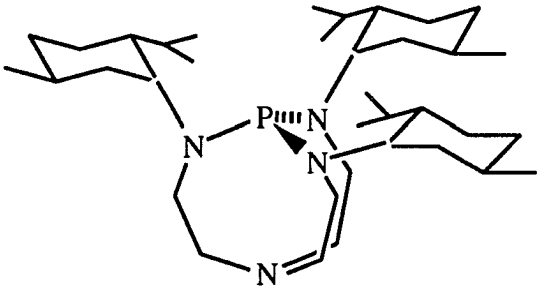
(c) Asymmetric protonation of enolate by using chiral proton sources for

Scheme 1



X = H, R, OR, NR_2, CN, NO_2, etc

enantioselectively producing chiral amides, esters has received considerable interest, and excellent results have recently achieved.[4] Although asymmetric alkylation and many other reactions of enolates generated by " asymmetric deprotonation" with a chiral base as shown in scheme 1 are synthetically important, no attention has been paid to them, probably due to the lack of strong chiral bases. **1** and **2** may be such chiral bases for achieving the above goals. **1**



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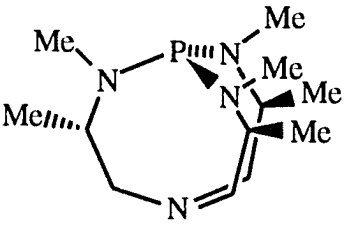
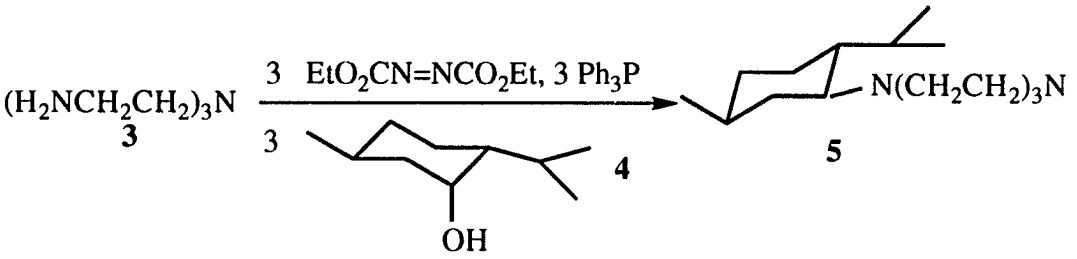
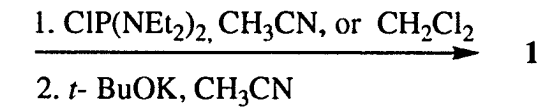
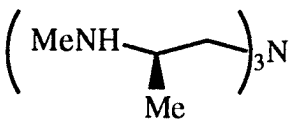


2

Scheme 2



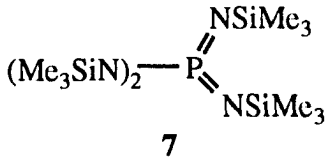




6

may be synthesized with the method as shown in scheme 2. The Mitsunobu reaction[5] of commercial available materials **3** and **4** would give **5** which gives **1** upon sequent treatments with $ClP(NEt_2)_2$ and *t*-BuOK, respectively. **2** may be similarly synthesized from **6**.

(d) If flexible transannulation occurs in compound **9**, $Ni(0)(\mathbf{9})_x$ may be a stronger catalyst than $Ni(0)(\mathbf{7})_x$[6] in the polymerization of olefins and may perhaps increase the molecular weight of polyolefins **8** which are attractive industrial materials.[7] Here the catalysis also involves oxidative addition and reductive elimination of the $Ni(0)L_x$, but the rate -determining step in the formation of the polymerization-active species is the release of the ligand from $Ni(0)L_y$ (e.g. $Ni(0)L_y$ = bis(1,5-cyclooctadiene)nickel or (cyclooctatetraene)nickel).[3] Ligand **9** might be synthesized by the method shown in scheme 3.



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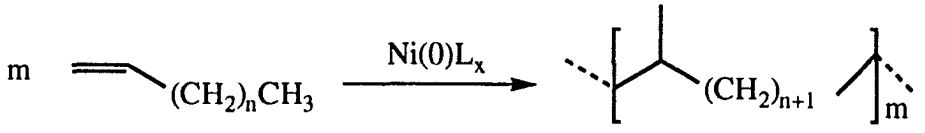

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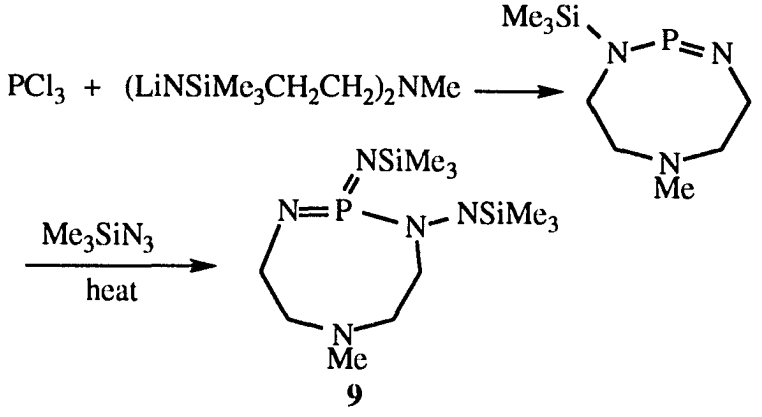
Scheme 3



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